the effect of diesel fuel properties on exhaust emissions from oxidation catalyst equipped diesel passenger vehicles

part 2

Prepared for the CONCAWE Automotive Emissions Management Group and based on work carried out by the Special Task Force on Diesel Fuel Emissions, (AE/STF-7).

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ABSTRACT

This report further evaluates the study reported in CONCAWE Report No. 94/55 and documents the ability of oxidation catalyst technology to reduce the influence of diesel fuel properties on exhaust emissions performance. The relationship between fuel properties and exhaust emissions was very vehicle dependent. Particulate emissions were found to correlate best with fuel density but no correlation was identified with total aromatics. Oxidation catalysts reduce particulate emissions by oxidizing hydrocarbons and are generally tolerant to fuel sulphur.

KEYWORDS

Diesel fuel, diesel fuel properties, oxidation catalyst, regulated emissions, particulate analysis.

CONTENTS

SUMMARY

Following the introduction of the harmonized European specification for diesel fuel (EN 590) and the introduction of oxidation catalysts for diesel passenger vehicles, CONCAWE conducted a programme to investigate the influence of future European commercial diesel fuels on the emissions performance of diesel vehicles fitted with the new catalyst technology.

The investigation was conducted using the European ECE 15+EUDC test procedure and steady-state driving with seven fuels having key properties in the range of 48 to 54 for cetane number, 0.834 to 0.850 kg/l for density and 337 to 367°C for the 95% point. Total aromatics content ranged from 16 to 26% volume. Six of the seven fuels were adjusted to a constant sulphur level of 0.05% mass, one fuel was doped to a 0.20% mass sulphur level. Six modern diesel passenger vehicles equipped with oxidation catalysts were included in the programme.

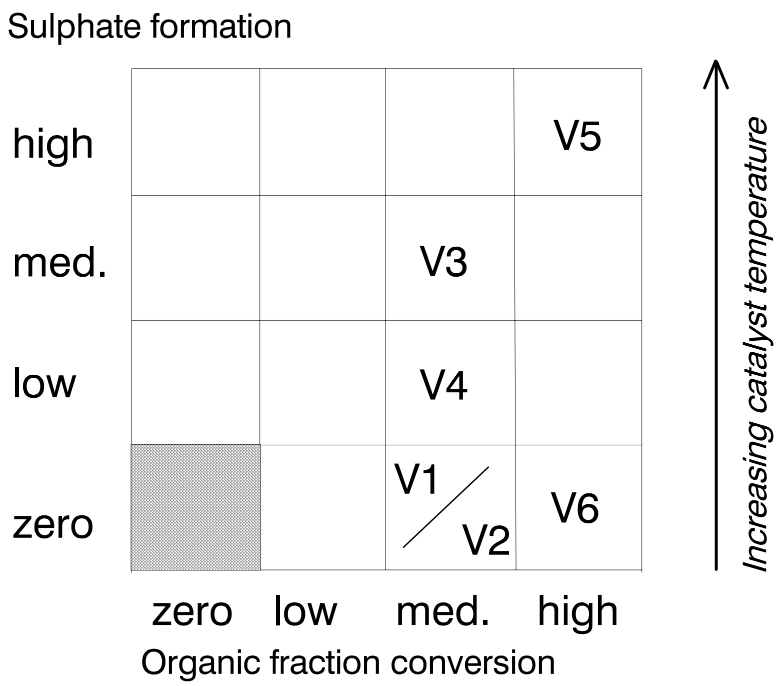
The first report on this study (CONCAWE Report No. 94/55) covered the emissions performance of the tested fuel set with and without the oxidation catalyst in place. This second report concentrates on fuel properties and particulate composition.

The study found that the influence of fuel properties on exhaust emissions is reduced in catalyst equipped vehicles and is very vehicle dependent. The fuel property which correlated best with particulates was density. Cetane number correlated with hydrocarbons and to some extent with carbon monoxide. No relationship was found between particulates and total aromatics.

Particulate compositional analysis shows that oxidation catalysts reduce particulate emissions by oxidizing unburnt hydrocarbons. Two out of the six vehicles exhibited increased sulphate formation which is counterproductive to particulate reduction. This was because of high catalyst temperatures and catalyst activity. Generally, catalysts are tolerant to fuel sulphur and this investigation showed that efficient conversion of hydrocarbons can be achieved without excessive sulphate formation with well balanced engine/vehicle/catalyst design (e.g. vehicles V1, V2, V6).

The range of modern, catalyst equipped diesel passenger cars used for this work indicates that vehicle/engine technology developments continue to have a major impact on emissions. By contrast, changing diesel fuel quality offers limited potential for emissions reduction.

Sulphate formation versus organic fraction conversion in catalyst equipped vehicles (V1 to V6)



1. INTRODUCTION

CONCAWE's Special Task Force on Diesel Fuel Emissions (AE/STF-7) has carried out a programme to investigate the influence of diesel fuel properties and the new oxidation catalyst technology on emissions performance. Oxidation catalyst technology has been introduced for European diesel passenger cars to further reduce exhaust emissions and , in particular, particulate emissions.[1, 2, 3] The objective of this programme was to study gaseous and particulate emissions (both engine out and after catalyst) from a range of light duty diesel vehicles.

Three major aspects were considered:

- The range of emissions for the fuel set both at engine out and after catalyst conditions.
- The influence of fuel properties on emissions at these conditions.
- The effect of fuel sulphur on particulate emissions with the catalyst in operation.

An earlier CONCAWE Report (94/55) discussed the emissions performance of a range of light duty diesel vehicles equipped with oxidation catalysts when tested on the fuel matrix described in **Section 3**. In addition, the effect of fuel sulphur on particulate emissions performance was also described. The current report documents the findings on the influence of specific fuel properties on emissions as well as the composition of the particulates.

The work was carried out in the laboratories of four CONCAWE member companies. Additional analytical studies were subcontracted to Ricardo Consulting Engineers as an integral part of the programme. Every attempt was made to standardize test and analytical procedures throughout the programme, so that a consistent body of data was made available.

Note: The following terminology is used throughout the report:

- "Engine-out" - exhaust emissions measured with the catalyst replaced with the conventional exhaust system.

- "After catalyst" - exhaust emissions measured with the catalyst fitted.

2. CHOICE OF DIESEL VEHICLES FOR THE PROGRAMME

The programme covered a range of European oxidation catalyst equipped diesel passenger vehicles including naturally aspirated (NA), turbocharged (TC), turbo-charged and inter-cooled (TC/IC), indirect injection (IDI) and direct injection (DI) types.

The characteristics of the passenger diesel vehicles employed in the programme are as follows:

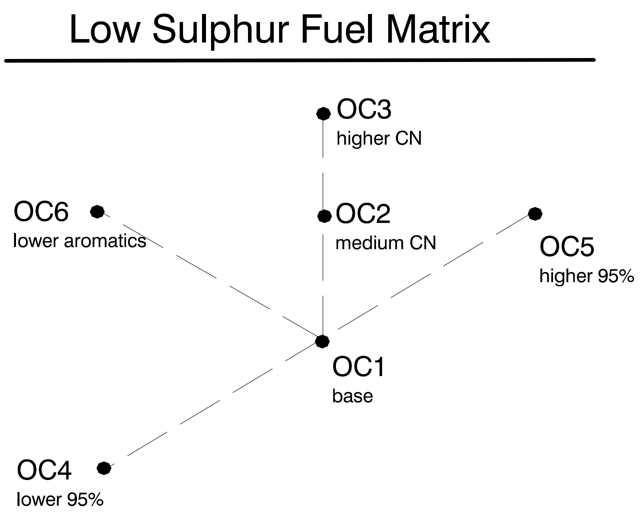
Vehicle No 1	1.9 litre	TC / IDI
Vehicle No 2	2.5 litre	TC / IC/ DI
Vehicle No 3	1.8 litre	NA / IDI
Vehicle No 4	2.5 litre	TC / IC / IDI
Vehicle No 5	2.5 litre	NA / IDI*
Vehicle No 6	1.8 litre	TC / IC / IDI*

* very low emissions model, meeting German traffic regulations STVZO annex XXIII.

3. TEST FUELS

In this report, all the low sulphur fuels discussed in the first part of the study are evaluated to establish the influence of their properties on exhaust emissions. These fuels form a matrix providing variation in cetane number, total aromatics content, density and 95% point (**Figure 1**). The research blends are considered to be typical of fuels that will be commercially available in the future in Europe. Fuel properties range as follows, cetane number from 48 to 54, density from 0.834 to 0.850 kg/l, 95% distillation point from 337 to 367°C and total aromatics from 15.6 to 25.7%vol (HPLC). The sulphur content of these fuels was adjusted to a constant sulphur level (0.05%m) by doping with tertiary butyl disulphide. This ensured that the influence of sulphur content on particulate emissions remained constant. It has been documented [4] that particulate emissions from fuels containing similar levels of sulphur, originating from either natural or doped sources, are identical. The basic fuel (OC1) was treated with 2-ethylhexyl nitrate ignition improver additive to provide a variation in the cetane (OC2, OC3) without altering any of the other fuel properties. For the evaluation of particulate composition, the higher sulphur containing fuel OC7 (**Table 1**) which was investigated in the earlier work was included in this report.

Figure 1



This range was considered to reflect a spread of typical European commercial diesel fuels and to be sufficiently wide to enable the influence of key fuel properties on emissions performance with oxidation catalyst equipped passenger vehicles to be determined.

Analytical data on the six fuels used in the programme are given in **Table 1**. These data are mean values calculated from multiple tests obtained in the laboratories of the CONCAWE member companies involved in the programme.

Attempts were made to minimize the intercorrelation between the key fuel properties of the six fuel matrix. However, high intercorrelation resulted between density and the 95% distillation point, see **Table 2**. Since fuels OC1, OC4 and OC5 were blended to solely vary with respect to the 95% point, cetane number and aromatics content were kept as constant as possible. However, density could not be kept constant for these three fuels and changed in the same direction as the 95% point, thus leading to intercorrelation between these two properties in the final matrix.

4. LUBRICATING OIL

In order to eliminate any influence of lubricating oil quality on the amount or nature of particulates generated in this programme, a commercial lubricating oil was chosen which satisfied the short-term test requirements of each engine employed in the programme. This oil, which was of SAE 15W/40 quality meeting API SF and DB 227.1 requirements, was used in all cars throughout the test programme. Inspection data on the unused oil are given in **Table 3**.

5. VEHICLE TEST PROCEDURES

The procedures used in the basic programme were those adopted for EU legislation covering emissions from diesel vehicles. Thus, the ECE-15 test cycle was used followed by the EUDC (extra urban driving cycle). In addition steady state emission testing at 120 km/h was carried out mainly to determine particulate emissions performance. ECE-15 and EUDC cycle testing was conducted with the oxidation catalyst fitted and in a second test set with the catalyst replaced by an ordinary exhaust pipe system.

Vehicle tests were conducted in four CONCAWE member companies' laboratories. All tests were carried out in duplicate, using a random order of fuel testing in each laboratory.

Details of the vehicle test procedures used are described in CONCAWE Report No. 94/55.

5.1. COLLECTION OF PARTICULATE

Particulate samples were collected separately from each vehicle over both ECE 15 and EUDC cycles. Samples were taken with and without the catalyst in place (Conditions A and C respectively as detailed in CONCAWE Report No. 94/55). Particulate samples were also generated from steady-state testing at 120 km/h (Condition B as also detailed in Report No. 94/55). Filters were generated from all tests and overall emissions data generated from averages, however only single filters from each combination of fuel/vehicle/condition/cycle were submitted for analysis.

All samples were collected using glass fibre papers (Whatman GF/A). Loaded papers were stored by wrapping tightly in aluminium foil and then heat sealed in a small plastic bag prior to being despatched for analysis. Filters generated from the steady-state testing were not analysed at this stage.

6. REGULATED EMISSIONS DATA

The gaseous and particulate emissions data from duplicate runs are shown in the form of mean values for each vehicle/fuel combination as total emissions (in g/km) over the combined ECE 15 + EUDC cycles in **Tables 4** to **7**.

These tables give gaseous and particulate emissions data (in g/km) for both engine out and after catalyst operation. For "engine out operation" the catalyst was replaced by an ordinary exhaust pipe. For "after catalyst operation" the catalyst was in place.

7. PARTICULATE ANALYSIS AND DATA

All particulate analysis was undertaken by Ricardo Consulting Engineers Ltd. on behalf of CONCAWE AE/STF-7.

For each fuel/vehicle/condition combination two filters were submitted for analysis; one each for the ECE15 and EUDC cycles. Each filter was analysed individually for total hydrocarbons and this was subsequently split into fuel and lubricant boiling range hydrocarbons. The pair of filters was then combined for sulphate and carbon determination over the combined cycle.

Ricardo uses a thermal desorption technique for hydrocarbon determination and is thus measuring *volatile* organic fraction (VOF) rather than the traditional soluble organic fraction (SOF).

Total particulate masses (g/test) for those filters which were analysed are shown in **Table 8**. It should be noted that the analysis data and interpretation relates to a *single* data point and not the mean of analyses as reported previously.

Compositional data are shown in **Tables 9 to 13**.

8. EVALUATION OF REGULATED EMISSIONS

Effects of fuel properties were evaluated at engine out conditions and with the catalyst in place. When fuel effects were observed they were strongly reduced with the catalyst in place.

In general fuel effects were found to be consistent across both ECE and EUDC cycles and therefore data analysis concentrated on the combined cycle results.

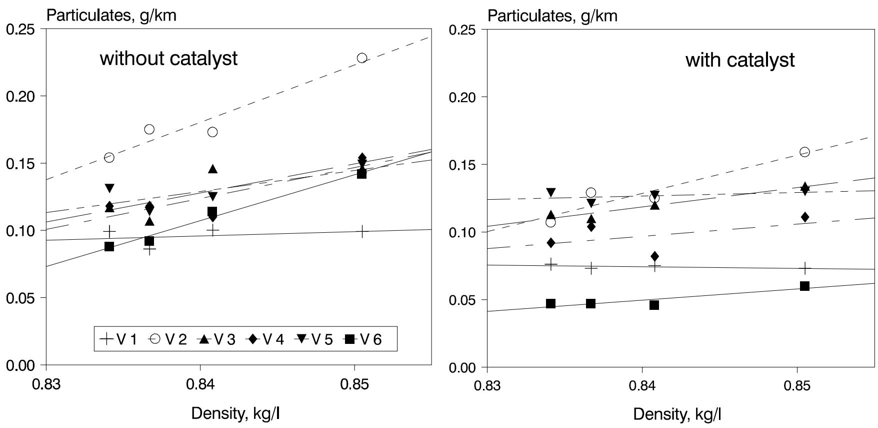
8.1. FUEL EFFECTS ON PARTICULATE EMISSIONS

Density

Without a catalyst in place five out of the six vehicles show an increase in particulate emissions as the density increases. Only vehicle V1 showed no effect. With the catalyst in place the influence of density was greatly reduced and two vehicles , V1 and V5, showed no effect (**Figure 2**).

Figure 2

Influence of Density on Particulates

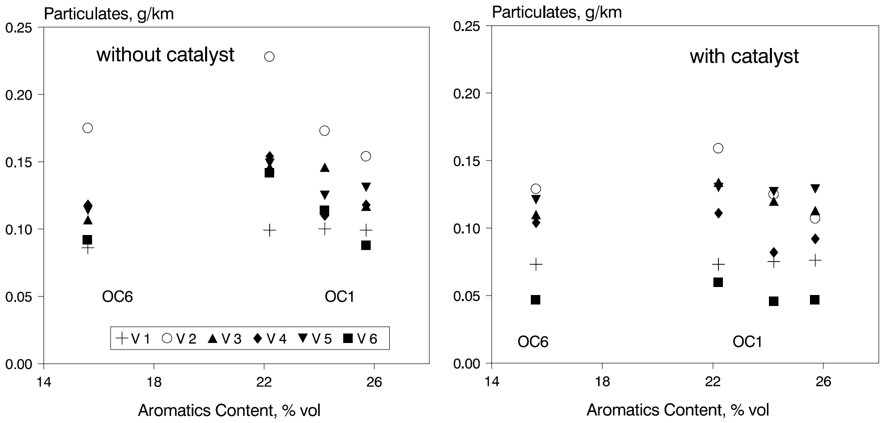


Total Aromatics Content

There was no effect of total aromatic content on particulate emissions either at engine out condition or with the catalyst fitted (**Figure 3**). There is no significant difference between particulate emissions from fuels OC6 (15.6% aromatics) and OC1 (24.2% aromatics).

Figure 3

Aromatics Content has <u>NO</u> Influence on Particulates



Poly-Aromatics Content

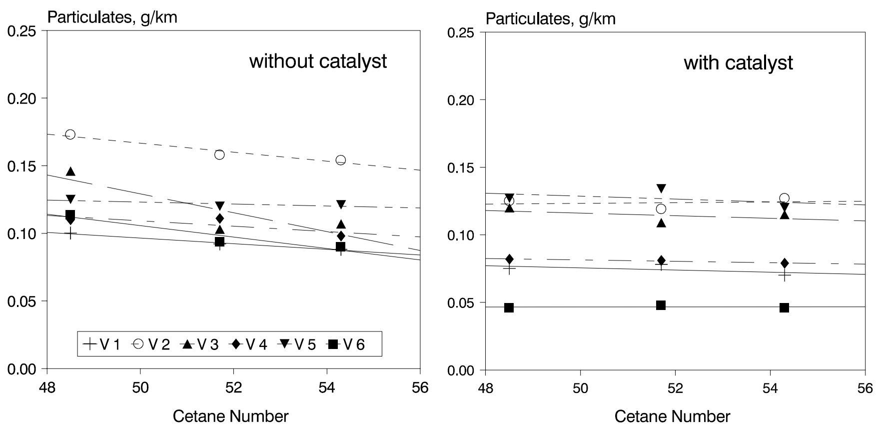
Polyaromatics content was a variable in the experimental design and is highly correlated with density in the test fuels used in this programme. Hence the possibility can not be excluded that part of the effect attributed to density may be due to polyaromatics. The separate influence of polyaromatics and density is being studied in the EPEFE programme.

Cetane Number

Fuels OC2 and OC3 are cetane improved versions of OC1. Without the catalyst in place increasing the cetane number decreased the particulate emissions with three vehicles (V2, V3 and V6) over the combined cycle. With the catalyst in place the effect of cetane number was negligible (**Figure 4**).

Figure 4

Influence of Cetane Number on Particulates

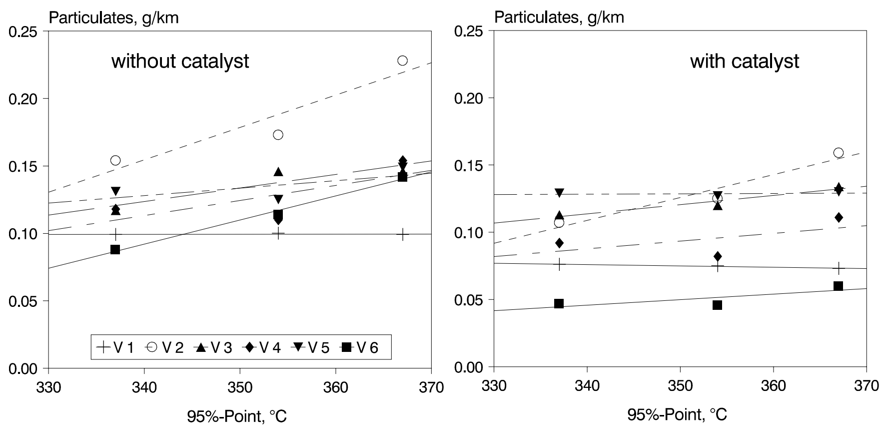


95% Distillation Point

Particulate emissions show an apparent relationship with T95 (**Figure 5**). This relationship is very similar to that obtained when evaluating the influence of density (**Figure 2**). Analysis of the fuel properties in the test fuel matrix shows that there is a high correlation between density and T95 (**Table 2**). Regression analysis however, shows a stronger correlation of particulate emissions with density rather than with T95 (**Section 8.1.1**). This finding is supported by a number of studies in which the inter-correlation between density and back-end volatility was successfully broken. [4, 5, 6, 7, 8]

Figure 5

Apparent Influence of 95% Point on Particulates



8.1.1. Regression analysis for fuel properties and particulates

Multiple regression analysis was conducted for each vehicle to determine the significance of fuel properties (CN, density, aromatics, 95% point) on particulate emissions performance at engine out condition and with the catalyst in place.

This stepwise analysis shows the following.

- Without the catalyst in place five vehicles showed significant fuel effects on particulate emissions. Density and/or cetane number were found to be the most important factors (see **Table** below).
- With the catalyst in place only three vehicles (V2, V3, V6) showed significant fuel effects on particulate emissions. In those cases density was the most important factor (see **Table** below).

Table with results from Multiple Regression Analysis (all fuels included)

		F-value				
Vehicle	Catalyst	Density	95%-Pt	CN	Aromatics	R-Sq.(adj.)
1	y	-	-	-	-	-
2	y	65.7	-	-	10	0.935
3	y	9.0	-	2.2	-	0.740
4	y	-	-	2.5	4.6	0.414
5	y	-	-	2.3	-	0.205
6	y	10.6	-	-	-	0.66
1	n	-	-	154	25.1	0.980
2	n	8.9	-	-	-	0.613
3	n	-	-	10.3	-	0.65
4	n	3.1	-	-	-	0.29
5	n	2.8	-	3.1	-	0.58
6	n	76.6	-	33.1	5.6	0.97

8.2. FUEL EFFECTS ON GASEOUS EMISSIONS

Hydrocarbon and carbon monoxide emissions were similarly influenced by the same fuel properties i.e. cetane number and density. The catalyst reduced these effects.

Without the catalyst in place increasing cetane number reduced both hydrocarbon and carbon monoxide emissions for most vehicles (**Figures 6** and **7**). This effect was reduced with the catalyst in place. Vehicles V1 and V5 were almost insensitive to changes of cetane number with or without the catalyst in place. Vehicle V3 is insensitive to cetane number changes with the catalyst in place.

Figure 6

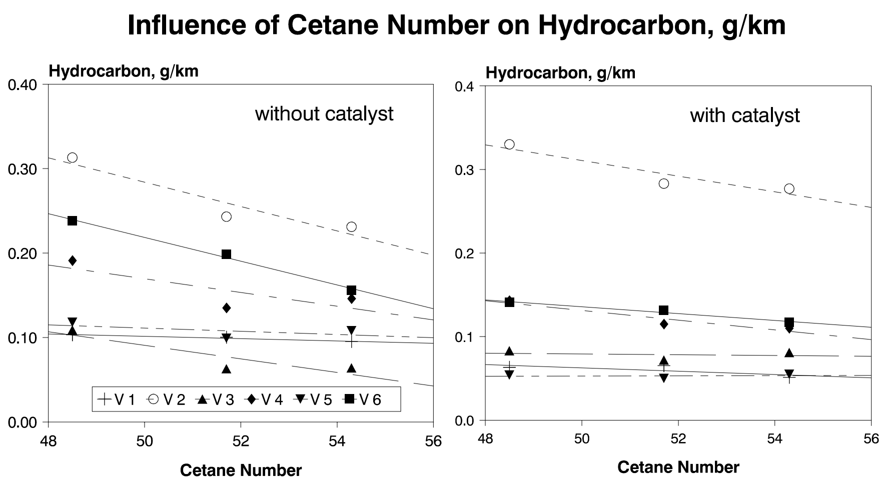
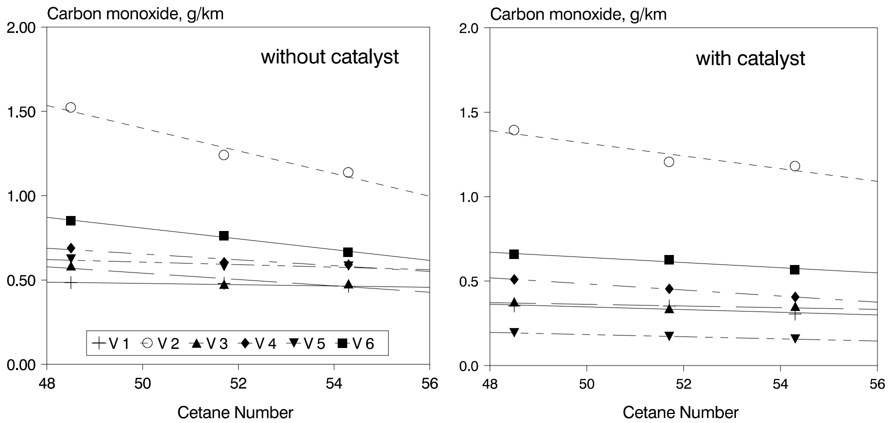


Figure 7

Influence of Cetane Number on Carbon Monoxide Emissions



Increasing density increased both hydrocarbons and carbon monoxide from most vehicles, with or without the catalyst in place.

Effects of cetane number and density were more pronounced for hydrocarbons than for carbon monoxide.

Nitrogen oxides were not significantly affected by fuel properties. This was observed both with and without the catalyst in place.

8.3. VEHICLE TECHNOLOGY EFFECTS ON EMISSIONS

The results obtained for this selection of modern, catalyst equipped diesel passenger cars demonstrates the impact that modern engine/vehicle technology development continues to have on emissions. The study shows that the range of emission levels between individual vehicles is much higher than the range resulting from changes in fuel properties. The spread between individual vehicle's emissions levels can be even higher with the catalyst in place than at engine out conditions. However, the absolute emissions levels are lower when the catalyst is in place. The sensitivity to fuel changes varies between the vehicles from negligible to very significant but is reduced with the catalyst in place.

9. EVALUATION OF PARTICULATE COMPOSITION.

Results of the compositional analysis are given as bar charts in **Figures 16 to 21** showing the data (mg/test) for the combined cycle analysis. Results for all fuel/vehicle combinations both with and without catalyst are provided.

These figures show the composition of the particulate with respect to fuel hydrocarbons, lubricant hydrocarbons, sulphate (plus bound water), carbon and also the fraction of particulate unaccounted for after analysis. For one vehicle (V4 with catalyst) the 'unaccounted' fraction appears to be very high. In this particular instance this was due to problems measuring the carbon fraction.

Low analytical recoveries were reported for vehicle V6, the reason for this is unknown. Negative values on the bar charts indicate where the analysis gave greater than 100% recovery. This is most noticeable for vehicle V5 and is thought to be directly related to inaccuracies in calculating the bound water for particulate with such a high sulphate concentration. Usually a factor of 1.3 x sulphate concentration is used to calculate bound water but this factor may be inappropriate at higher sulphate concentrations.

9.1. EFFECTS OF FUEL PROPERTIES

For the evaluation of fuel effects on particulate composition the fractions of unburned fuel hydrocarbon and carbon are of interest; whereas the fraction of unburned oil hydrocarbon is considered to be only engine related and the fraction of sulphate is only affected by engine and catalyst design/technology, as discussed in **Sections 9.2** and **9.3**.

Figures 8 and **9** show the unburned fuel hydrocarbon and carbon fractions plotted versus density and cetane number respectively for each vehicle for both catalyst configurations (with and without catalyst). In general, unburned fuel hydrocarbon seems to be very similarly affected by density and cetane number as is total particulate mass reported in **Section 8.1**. However, a closer evaluation indicates that the main contributions come from fuel OC5 for any density effect and from lower cetane fuel OC1 for any cetane effect.

The highest density fuel increases unburned fuel hydrocarbon with all vehicles with the exception of vehicle V1 when the catalyst is not in place (**Figure 8**). This effect is in line with the relationship observed between fuel density and total particulate emissions. In addition the reduction of the density effect (OC5) on the unburned fuel hydrocarbon with the catalyst in place matches the observations for total particulates - see influences with vehicles V3, V5 and V6.

The lower cetane number fuel (OC1) increased unburned fuel hydrocarbon when the catalyst is <u>not</u> in operation (mainly vehicles V2, V3) (**Figure 9**). With the catalyst in place this effect is significantly reduced (V2, V3). All these observations are very similar to those found for the cetane effect on total particulates.

The above comparison confirms that, when the catalyst is <u>not</u> fitted, the effect of changing fuel properties has a direct influence on the mass of particulate through the contribution of unburned fuel.

For the carbon fraction no clear relationship with fuel properties is evident.

Figure 8 Density effect on particulates

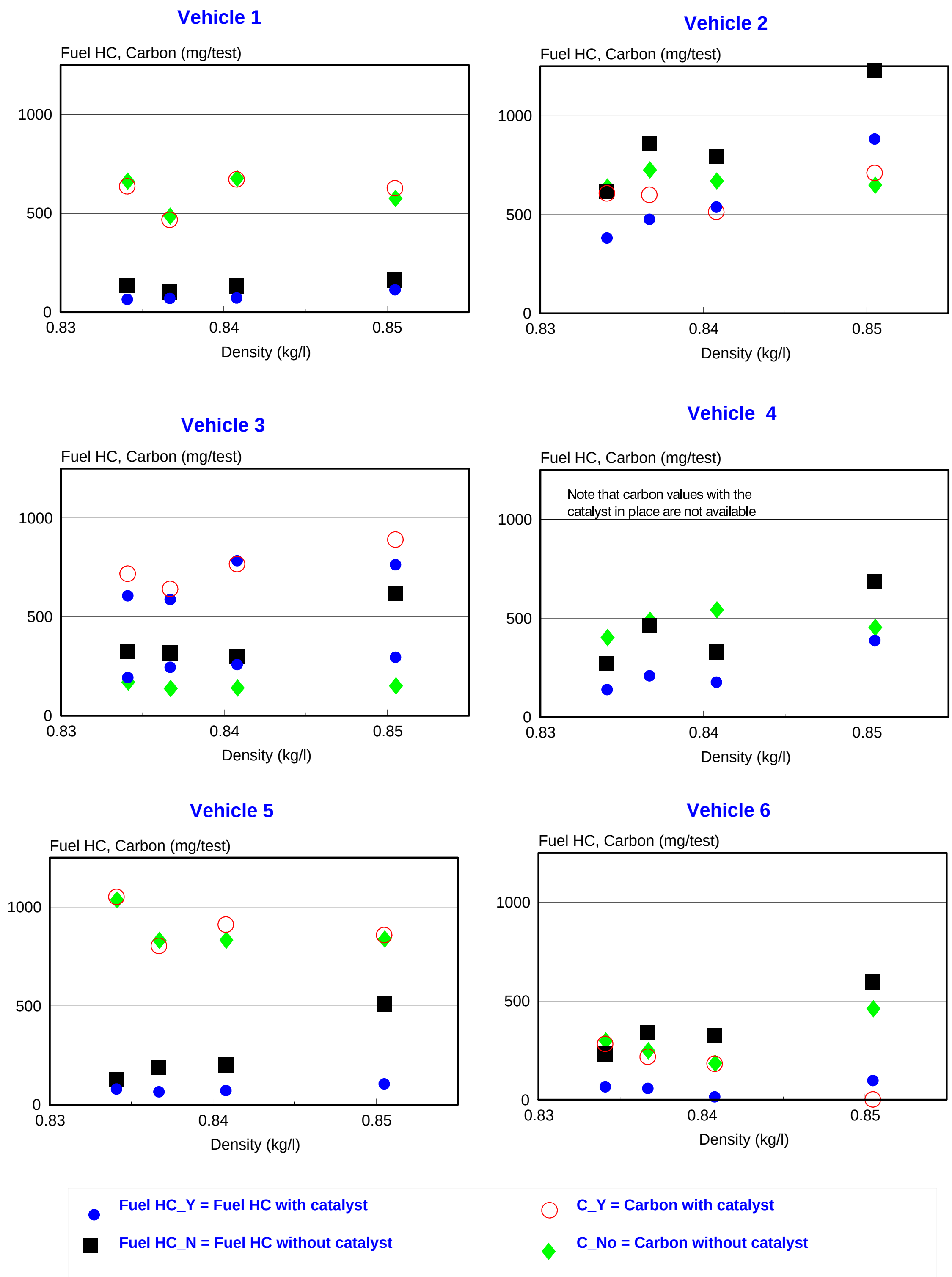
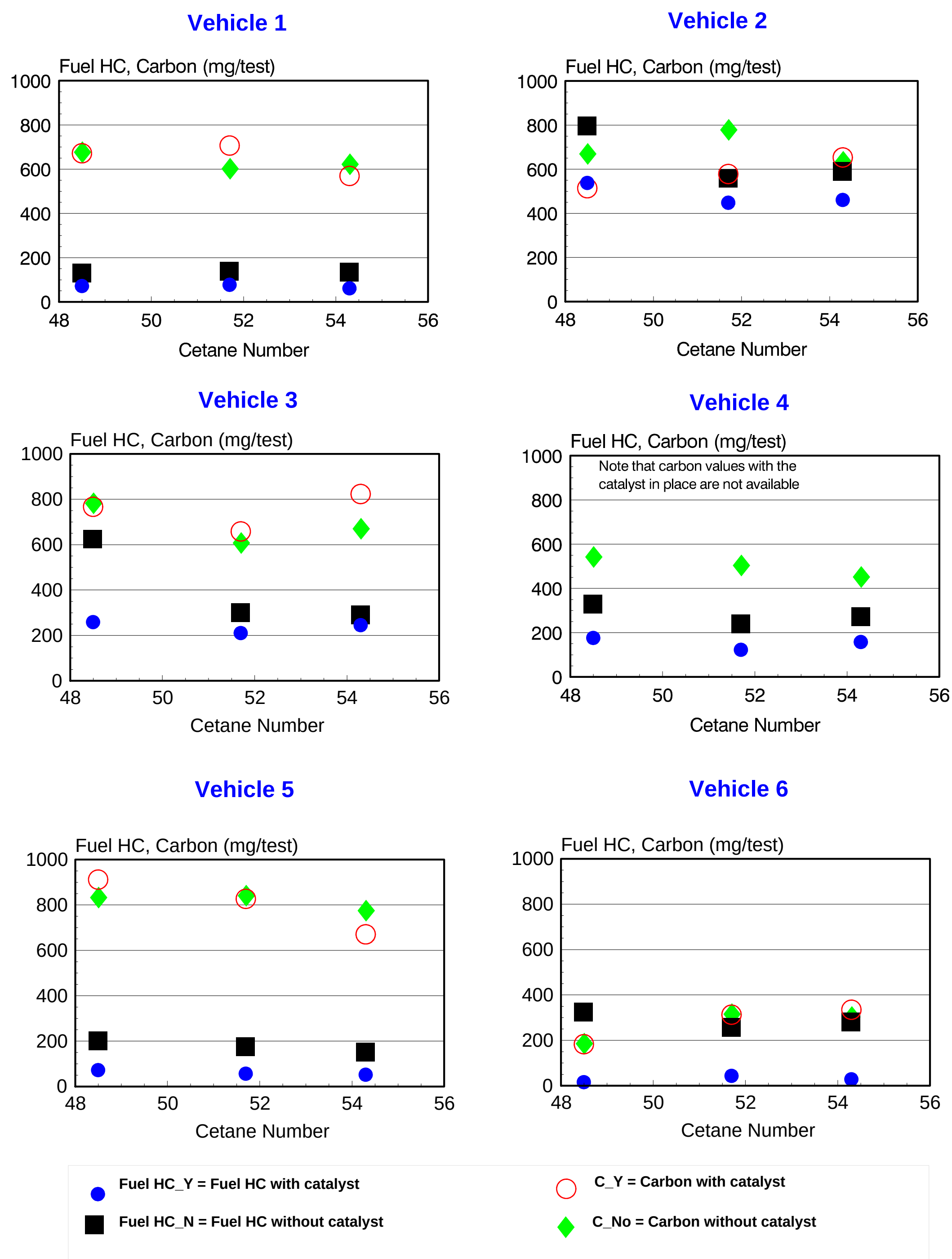


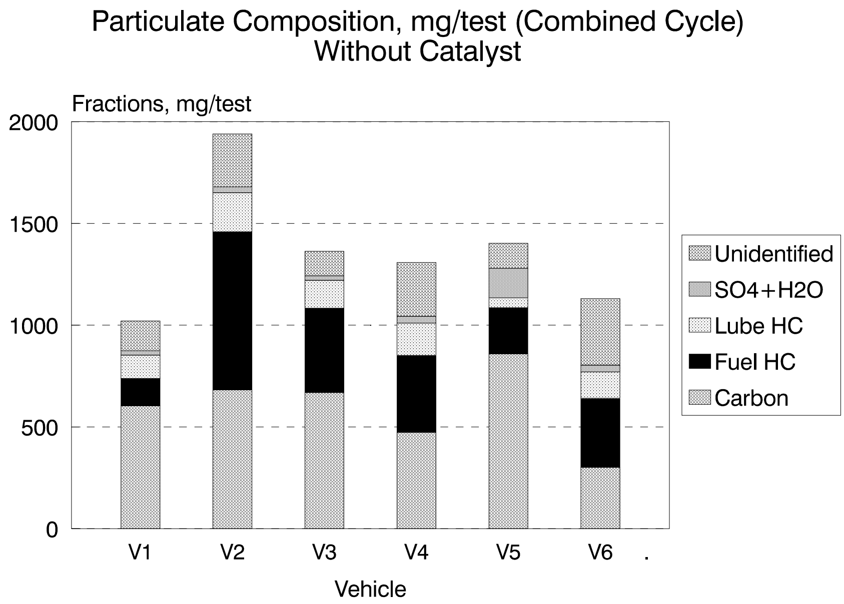
Figure 9 Cetane effect on particulate fractions



9.2. EFFECTS OF VEHICLE TECHNOLOGY

The impact of vehicle technology both in terms of total particulate mass and particulate composition (**Tables 9 to 13**) is shown in **Figure 10**. This shows engine out particulate composition for all vehicles. Compositions are averaged across the low sulphur fuels to provide overall effects for the individual vehicles. Detailed information is given in **Figures 16 to 21**, which additionally show individual fuel effects.

Figure 10



Vehicle V1 produces predominantly a very dry particulate hence fuel effects are small. Consequently the lubricant contribution is approximately equal to that of the fuel.

Vehicle V2 produces particulate of which approximately 50% is VOF. There is a significant contribution of lubricant. As a consequence of the wetter particulate, fuel effects will be more pronounced.

Vehicle V3 particulate is predominantly dry but shows a significant fuel influence on the VOF. Lubricant contribution corresponds to approximately a third of the total hydrocarbons.

The particulate of vehicle V4 is, like vehicle V2, about 50% VOF with a significant lubricant contribution. Again the hydrocarbons show a strong sensitivity to changes in fuel characteristics.

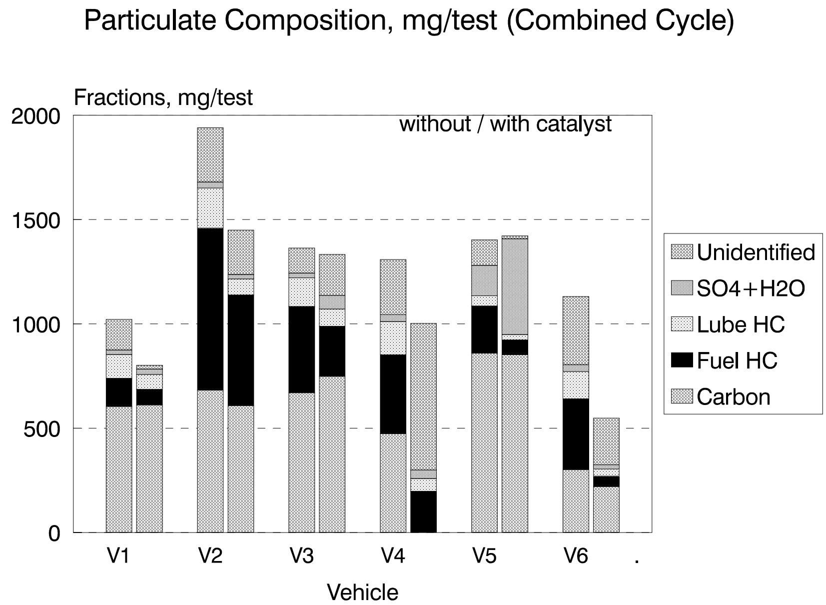
Vehicle V5 produces very dry particulate for all fuels except OC5. The lubricant contribution is the least of all vehicles tested.

Vehicle V6 produces particulate with 30-50% VOF of which approximately 30% is lubricant. Again, the only fuel to show a significant effect on the particulate is OC5.

9.3. EFFECT OF CATALYST TECHNOLOGY

The same **Figures** (**16 to 21**) comparing particulate composition with and without catalyst give valuable information about the operation of the catalyst and show clearly how the composition varies from vehicle to vehicle. An overview with averaged compositions across all low sulphur fuels is provided in **Figure 11** for each individual vehicle.

Figure 11



Vehicles V1, V2 and V4 all show similar catalyst efficiencies although the composition of the particulate is very different. The catalyst on vehicle V1 appears to be fairly active as the particulate is very dry and there is a limited amount of VOF for the catalyst to oxidize. However, the catalyst is not so active that sulphate production is a problem. Despite the slight reduction of efficiency with OC7 the catalyst is still effective.

Vehicle V2 produces a very wet particulate and there is plenty of scope for oxidation which is not fully utilized. Despite the reduction achieved it would appear that the catalyst employed with this vehicle is not very active, although there is a small increase in the sulphate contribution when the catalyst is employed with the higher sulphur fuel.

The catalyst on vehicle V4 appears to be similar to that on vehicle V2 in terms of activity. There is a large amount of VOF to oxidize and interestingly the lubricant hydrocarbon appears to be reduced to a greater extent than that of the unburned fuel. Despite the mediocre activity with respect to hydrocarbon oxidation this catalyst promotes sulphate formation with the higher sulphur fuel whilst still effecting a particulate reduction.

Vehicles V3 and V5 have a very different catalyst activity. Both show a great sensitivity to fuel sulphur (even at 0.05%) which obviates the effectiveness of the catalyst. This is especially noticeable for vehicle V5. The particulate is extremely dry and it appears that very active catalyst technology has been used to oxidize the small amount of hydrocarbon present. However, the activity is so high that sulphate formation is promoted to such an extent as to make the use of the catalyst counter productive.

Although Vehicle V3 has a catalyst activity which is deleterious with respect to sulphate formation the particulate is wetter. As a consequence, the extent of hydrocarbon oxidation is marginally greater than sulphate formation where there is an increase in hydrocarbons due to a fuel effect. In these instances the net effect from the use of the catalyst is a small reduction in particulate but over all fuels the use of the catalyst is not beneficial.

Vehicle V6 is fitted with a very efficient catalyst which shows excellent hydrocarbon oxidation with only a slight tendency to promote sulphate formation.

Figure 12

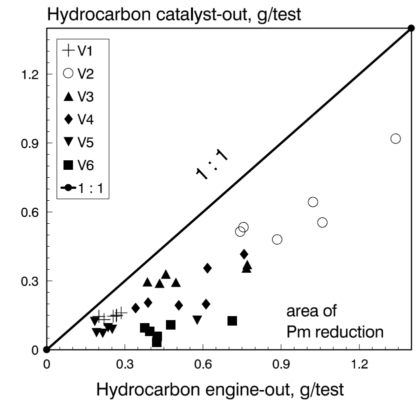
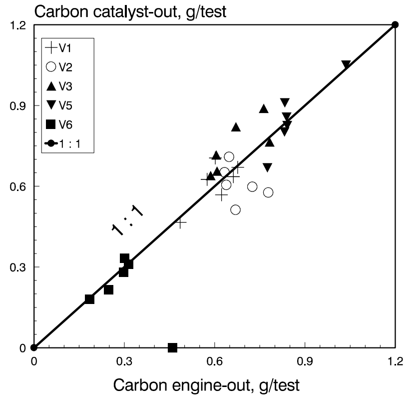


Figure 13



Catalysts reduce particulates through the selective removal of unburned hydrocarbons associated with the particulate matter (**Figure 12** above) while the carbon fraction remains unaffected (**Figure 13** above). This selective hydrocarbon removal explains the lower sensitivity to fuel quality of vehicles fitted with oxidation catalysts.

Catalyst efficiency in reducing *overall* particulate emissions is, however, dependent on three main factors:

1. Engine-out particulate composition

These emissions were dominantly influenced by engine design; fuel quality showed some smaller effect (**Section 9.1**). Two vehicles in particular (V1 and V5) produced very dry particulates thus providing little hydrocarbon for the catalyst to oxidize.

2. Sulphate forming activity

Sulphate formation can partly counterbalance the reduction of the hydrocarbon fraction and hence reduce the catalyst efficiency in reducing overall particulate emissions. This can be seen in **Figure 14** where two vehicles (V3 and V5) showed a propensity for sulphate formation even with low sulphur fuels (0.05%). This can be related to the vehicle design/optimization which, in these particular cases, led to high exhaust gas temperatures in the catalyst (see CONCAWE Report No. 94/55, Table in Section 8.1) and hence promotion of sulphate formation. [3, 9]

3. Catalyst oxidation efficiency and technology

All catalysts in this study were effective in oxidizing hydrocarbons with vehicles V5 and V6 showing the highest conversion efficiency (**Figure 14**). Though no detailed knowledge of the individual catalysts is available it can be expected that the individual design/technology of the catalyst will influence the catalyst performance as well.

The overall poor performance of V5 can thus be explained by a combination of dry engine-out particulate and high exhaust gas temperatures leading to sulphate formation. The catalyst can of course play an additional role, see CONCAWE report No. 94/55. On the other hand, the excellent performance of vehicle V6 can be related to its wet engine-out particulate and lower exhaust gas temperature. This clearly shows that it is possible to decouple sulphate formation from hydrocarbon conversion by appropriate vehicle and catalyst design to maintain the catalyst below the temperature at which sulphate formation occurs (**Figure 15**).

Figure 14

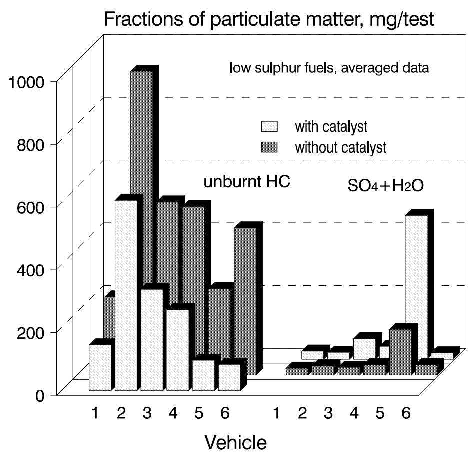
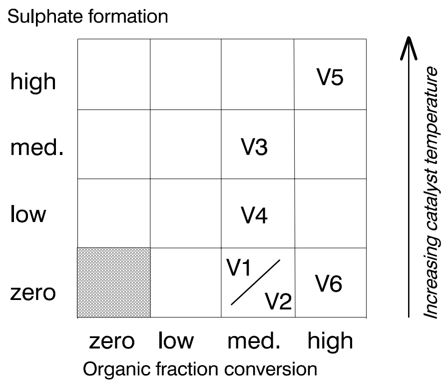


Figure 15



10. CONCLUSIONS

A series of emissions tests have been conducted on diesel passenger vehicles fitted with oxidation catalysts, and also with the catalyst substituted by an ordinary exhaust pipe system. Tests were carried out over European ECE15+EUDC cycle procedures.

It was found that,

- Oxidation catalysts are effective in decreasing HC, CO and particulate emissions by oxidizing unburned hydrocarbons. The carbon fraction of the particulate matter remains unaffected.

- Catalysts markedly decrease the influence of fuel characteristics on exhaust emissions performance.

- Oxidation catalysts are generally tolerant to fuel sulphur, but in two vehicles high catalyst temperatures (as identified in this study) promoted sulphate formation. This was counterproductive to particulate reduction.

- Optimization of vehicle system design can achieve efficient hydrocarbon conversion without excessive sulphate formation by ensuring that the catalyst operates in an optimum temperature range.

Individual fuel properties showed the following effects, which are greatly reduced with the catalyst fitted:

- **Particulates**: density was the dominating fuel property influencing particulate emissions with an increase in density leading to increased particulates. A similar relationship could be identified in this fuel set with T95, but this was because the two properties were intercorrelated. Regression analysis showed a better fit for density. This finding is supported by studies in which the inter-correlation between these parameters has been successfully broken. Cetane number affected particulates when the catalyst was not in place showing decreasing particulate emissions with increasing cetane number. With the catalyst in place this effect was negligible. Total aromatics showed no effect on particulates.

- **Hydrocarbons, carbon monoxide** : cetane number was the main influential fuel property. An increase in cetane number led to a reduction in hydrocarbon and carbon monoxide emissions. Increasing density increased both hydrocarbon and carbon monoxide emissions. Effects on hydrocarbons were larger than on carbon monoxide.

- **Nitrogen oxides** : no fuel effects on NOx emissions were detected.

The range of modern, catalyst equipped diesel passenger cars used in this study indicates the major impact vehicle/engine technology development continues to have on emissions in contrast with the limited effects of fuel characteristics.

11. ACKNOWLEDGEMENTS

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Esso Research Centre, Abingdon

Euron, Milan

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12. REFERENCES

1. Montagne, X., Phillipet, A. (1993) Oxidation exhaust catalyst of diesel engines and diesel fuel sulphur content. Symposium on fuels for automotive and industrial diesel engines. London: Institution of Mechanical Engineers

2. Ketcher, D.A., Horrocks, R.W. (1990) The effect of fuel sulphur on diesel particulate emissions when using oxidation catalyst. London: Institution of Mechanical Engineers

3. Zelenka, P., Ostgate, K., Lox, E. (1990) Reduction of diesel exhaust emissions by using oxidation catalysts. SAE Paper 902111. Warrendale, Pa: Society of Automotive Engineers

4. Betts, W.E., Floysand, S.A, Kvinge, F., (1992) The influence of diesel fuel properties on particulate emissions in European cars. SAE Paper 922190. Warrendale, Pa: Society of Automotive Engineers

5. Floysand, S.A., Kvinge,F., Betts, W.E. (1993) The influence of diesel fuel properties on particulate emissions in a catalyst equipped European car. SAE Paper 932683. Warrendale, Pa: Society of Automotive Engineers

6. Lange, W.W et al (1993) The influence of fuel properties on exhaust emissions from advanced Mercedes Benz diesel engines. SAE Paper 932684. Warrendale, Pa: Society of Automotive Engineers

7. Lange, W.W. (1991) The effect of fuel properties on particulate emissions in heavy-duty truck engines under transient operating conditions. SAE Paper 912425. Warrendale, Pa: Society of Automotive Engineers

8. Cowley, L.T., Stradling, R.J., Doyon, J. (1993) The influence of composition and properties of diesel fuel on particulate emissions from heavy-duty engines, SAE Paper 932732. Warrendale, Pa: Society of Automotive Engineers

9. Bürgler, L., Herzog, P.L., Zelenka, P. (1991) Strategies to meet 1994/95 diesel engine federal emission legislation for HSDI-diesel engine powered vehicles. London: Institution of Mechanical Engineers

13. TABLES

Table 1 Analytical data on test fuels used in the programme (mean values)

Fuel No		OC1, OC2*, OC3*	OC4	OC5	OC6	OC7
Property	Unit					
Sulphur content	%m	0.052	0.053	0.046	0.048	0.199
Density @ 15°C	kg/l	0.8408	0.8341	0.8505	0.8367	0.8427
KV @ 20°C	cSt	3.98	3.47	4.91	5.02	4.02
KV @ 40°C (3)	cSt	2.62	2.34	3.18	3.11	2.75
Flash point	ºC	69	67	67	72	69
Cloud point	ºC	-1	-10	+6	+2	-2
CFPP	ºC	-20	-24	-5	-7	-18
Water content	ppm	64	50	68	63	70
Copper corrosion		1a	1a	1a	1a	1a
Carbon residue	%m	0.05	0.03	0.02	0.02	0.03
AROMATICS AND IGNITION QUALITY						
FIA (4)	%v	30.0	28.6	29.8	23.2	31.7
HPLC (2)	%m	27.1	26.0	26.7	17.0	27.3
HPLC:						
mono aromatics (3)	%v	19.7	22.0	16.5	11.6	20.0
di aromatics (3)	%v	4.0	3.3	5.1	3.5	4.1
tri aromatics (3)	%v	0.5	0.4	0.6	0.5	1.1
total aromatics (3)	%v	24.2	25.7	22.2	15.6	25.2
HPLC:						
mono aromatics (2)	%m	20.9	22.5	18.1	13.4	19.7
di aromatics (2)	%m	5.3	4.2	6.6	4.4	4.8
tri aromatics (2)	%m	0.8	0.7	0.6	0.7	1.4
total aromatics (2)	%m	27.0	27.4	25.3	18.5	25.9
Cetane number		48.5, 51.7, 54.3	49.5	48.3	52.8	48.2
Calculated Cetane Index		49.0	49.7	47.6	54.1	48.4
DISTILLATION DATA						
IBP	ºC	176	175	175	180	176
10%	ºC	207	201	215	223	207
20%	ºC	220	213	231	239	220
30%	ºC	234	226	245	251	235
40%	ºC	248	240	258	263	249
50%	ºC	262	255	270	274	263
60%	ºC	276	269	283	285	276
70%	ºC	290	283	299	300	290
80%	ºC	307	299	318	318	307
90%	ºC	332	319	346	341	330
95%	ºC	354	337	367	358	351
FBP	ºC	369	356	387	372	368
Recovery (5)		98.4	98.6	98.5	98.3	98.4
Loss (5)		0.2	0.1	0.2	0.2	0.2
Residue (5)		1.4	1.3	1.3	1.5	1.4

(All values are the mean of six analyses, except where indicated)

* Contain ignition improver additive

Table 2 Intercorrelation of fuel properties

Sample Correlation of all six fuels

	Cetane number	Density	95%-Point	Total aromatics
Cetane number	1.00 (6) 0.00	-0.3451 (6) 0.5029	-0.20 (6) 0.970	-0.3054 (6) 0.5561
Density	-0.3451 (6) 0.5029	1.00 (6) 0.00	0.8234 (6) 0.0440	0.0407 (6) 0.9389
95%-Point	-0.0200 (6) 0.9700	0.8234 (6) 0.0440	1.00 (6) 0.00	-0.4842 (6) 0.3305
Total aromatics	-0.3054 (6) 0.5561	0.0407 (6) 0.9389	-0.4842 (6) 0.3305	1.00 (6) 0.00

Legend: Coefficient
(Sample size)
Significance level

Table 3 Inspection data on the unused oil

Reference L92/10091
Grade SAE 15W/40, API SF, DB 227.1

Pour point	°C	-33
Sulphur content	% mass	0.475
KV 40°C	mm^2/sec	112.3
KV 100°C	mm^2/sec	14.6
Viscosity Index		133
Volatility (DIN 51581)	% mass	11.1
1 hour, 250°C		
Phosphorus	% mass	0.11
Calcium	% mass	0.21
Magnesium	% mass	0.11
Zinc	% mass	0.12
<u>Hydrocarbon Distribution</u>		
IBP	°C	133
FBP	°C	534

Table 4 Mean particulate data (g/km) combined ECE 15 + EUDC cycle (Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	0.100	0.173	0.146	0.110	0.125	0.114
	2	0.092	0.158	0.103	0.111	0.120	0.094
	3	0.088	0.154	0.107	0.098	0.121	0.090
	4	0.099	0.154	0.117	0.118	0.131	0.088
	5	0.099	0.228	0.146	0.154	0.149	0.142
	6	0.086	0.175	0.107	0.118	0.114	0.092
	7	0.092	0.175	0.129	0.141	0.126	0.098
After catalyst	1	0.075	0.125	0.120	0.082	0.127	0.046
	2	0.078	0.119	0.109	0.081	0.134	0.048
	3	0.070	0.127	0.115	0.079	0.120	0.046
	4	0.076	0.107	0.113	0.092	0.129	0.047
	5	0.073	0.159	0.134	0.111	0.130	0.060
	6	0.073	0.129	0.110	0.104	0.121	0.047
	7	0.074	0.125	0.146	0.106	0.200	0.059

Table 5 Mean carbon monoxide data (g/km) combined ECE 15 + EUDC cycle (Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	0.483	1.522	0.584	0.689	0.624	0.851
	2	0.478	1.240	0.475	0.605	0.579	0.764
	3	0.461	1.137	0.478	0.591	0.582	0.665
	4	0.480	1.422	0.550	0.657	0.603	0.743
	5	0.530	1.675	0.620	0.811	0.671	0.898
	6	0.461	1.237	0.496	0.665	0.598	0.678
	7	0.511	1.453	0.546	0.713	0.602	0.784
After catalyst	1	0.352	1.393	0.378	0.510	0.194	0.658
	2	0.351	1.205	0.338	0.454	0.172	0.626
	3	0.304	1.180	0.351	0.406	0.157	0.568
	4	0.328	1.272	0.378	0.499	0.166	0.668
	5	0.386	1.425	0.424	0.668	0.221	0.779
	6	0.306	1.120	0.386	0.495	0.177	0.589
	7	0.377	1.356	0.412	0.664	0.201	0.750

Table 6 Mean hydrocarbon data (g/km) combined ECE 15 + EUDC cycle (Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	0.103	0.313	0.109	0.191	0.118	0.238
	2	0.100	0.243	0.063	0.135	0.099	0.198
	3	0.095	0.231	0.064	0.146	0.108	0.156
	4	0.107	0.289	0.094	0.177	0.118	0.183
	5	0.107	0.353	0.092	0.256	0.149	0.250
	6	0.087	0.247	0.085	0.188	0.100	0.167
	7	0.099	0.420	0.108	0.240	0.107	0.194
After catalyst	1	0.063	0.330	0.083	0.143	0.054	0.141
	2	0.065	0.283	0.072	0.115	0.050	0.131
	3	0.051	0.277	0.081	0.110	0.055	0.117
	4	0.059	0.309	0.081	0.128	0.055	0.140
	5	0.079	0.326	0.084	0.229	0.067	0.172
	6	0.069	0.231	0.081	0.156	0.050	0.116
	7	0.074	0.315	0.082	0.207	0.056	0.174

Table 7 Mean nitrogen oxides data (g/km) combined ECE 15 + EUDC cycle (Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	0.684	0.655	0.604	0.620	0.597	0.573
	2	0.675	0.653	0.613	0.592	0.686	0.576
	3	0.685	0.643	0.623	0.598	0.702	0.593
	4	0.689	0.647	0.616	0.603	0.627	0.572
	5	0.679	0.613	0.615	0.591	0.595	0.582
	6	0.659	0.613	0.593	0.582	0.653	0.590
	7	0.643	0.644	0.610	0.621	0.613	0.595
After catalyst	1	0.682	0.641	0.614	0.651	0.617	0.661
	2	0.711	0.646	0.606	0.648	0.659	0.666
	3	0.709	0.658	0.609	0.655	0.648	0.665
	4	0.682	0.650	0.609	0.636	0.604	0.649
	5	0.713	0.616	0.598	0.615	0.630	0.687
	6	0.681	0.609	0.609	0.625	0.598	0.640
	7	0.665	0.648	0.608	0.632	0.624	0.674

Table 8 Particulate mass (g/test) of analysed filters (combined ECE 15 + EUDC cycle)
(Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	1.139	1.962	1.692	1.18	1.335	1.271
	2	0.996	1.758	1.130	1.26	1.339	0.964
	3	0.943	1.692	1.135	1.12	1.321	0.979
	4	1.064	1.746	1.313	1.31	1.400	0.993
	5	1.091	2.545	1.670	1.65	1.741	1.535
	6	0.894	1.937	1.239	1.33	1.280	1.045
	7	1.027	1.982	1.440	1.63	1.391	1.090
After catalyst	1	0.834	1.420	1.372	0.91	1.446	0.518
	2	0.870	1.363	1.182	0.82	1.445	0.520
	3	0.785	1.403	1.351	0.89	1.330	0.536
	4	0.811	1.221	1.309	1.04	1.505	0.501
	5	0.847	1.849	1.580	1.18	1.447	0.669
	6	0.663	1.438	1.202	1.17	1.357	0.544
	7	0.822	1.381	1.709	1.13	2.034	0.647

Table 9 Particulate VOF content (mg/test) of analysed filters (combined ECE 15 + EUDC cycle)
(Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	255	1023	766	611	235	423
	2	268	756	433	341	215	396
	3	200	744	386	502	191	425
	4	266	885	495	388	184	377
	5	285	1340	770	757	577	713
	6	220	1059	457	617	251	478
	7	198	1001	508	717	236	441
After catalyst	1	145	642	356	199	95	33
	2	150	533	290	182	71	80
	3	144	514	296	194	74	58
	4	146	479	294	205	123	96
	5	160	919	371	416	128	126
	6	130	553	330	355	88	109
	7	166	488	393	167	76	139

Table 10 Particulate fuel hydrocarbon content (mg/test) of analysed filters (combined ECE 15 + EUDC cycle), (Engine out and after catalyst data)

	Fuel	Vehicle 1	2	3	4	5	6
Engine out	1	132	797	626	329	202	326
	2	140	560	302	240	175	257
	3	135	592	291	273	152	282
	4	137	617	326	271	129	234
	5	162	1231	619	687	509	596
	6	102	861	320	464	190	341
	7	127	804	352	370	150	297
After catalyst	1	70	537	257	175	71	14
	2	76	447	209	121	55	42
	3	60	459	244	156	50	27
	4	63	380	192	138	78	65
	5	112	882	294	386	105	97
	6	68	475	244	208	64	57
	7	116	413	249	161	57	88

Table 11 Particulate lubricant hydrocarbon content (mg/test) of analysed filters (combined ECE 15 + EUDC cycle), (Engine out and after catalyst data)

	Fuel	Vehicle 1	2	3	4	5	6
Engine out	1	122	226	140	282	33	98
	2	128	197	131	100	40	139
	3	65	152	95	233	39	144
	4	130	269	170	117	55	143
	5	124	109	151	71	68	117
	6	118	198	137	153	61	137
	7	72	188	155	347	86	143
After catalyst	1	75	105	99	23	25	18
	2	74	86	81	61	16	38
	3	84	54	52	37	24	31
	4	83	99	102	67	44	31
	5	48	37	77	30	24	29
	6	62	78	86	148	24	53
	7	50	75	144	6	19	50

Table 12 Particulate sulphate content (mg/test) of analysed filters (combined ECE 15 + EUDC cycle), (Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	9	10	9	13	125	22
	2	12	11	8	22	45	18
	3	10	6	13	12	72	9
	4	12	10	3	13	68	10
	5	6	14	10	14	35	16
	6	7	25	16	13	35	10
	7	16	25	23	39	50	19
After catalyst	1	10	10	33	14	236	10
	2	10	8	27	12	214	9
	3	12	6	27	20	201	9
	4	15	11	29	10	148	7
	5	10	11	25	25	181	9
	6	10	8	29	26	217	9
	7	15	34	121	65	343	17

Table 13 Particulate carbon content (mg/test) of analysed filters (combined ECE 15 + EUDC cycle), (Engine out and after catalyst data)

	Fuel	Vehicle					
		1	2	3	4	5	6
Engine out	1	677	670	783	542	833	185
	2	602	779	607	504	841	315
	3	623	633	670	452	775	302
	4	662	639	605	402	1036	298
	5	575	649	763	453	839	461
	6	485	726	586	489	832	248
	7	555	633	770	622	995	361
After catalyst	1	670	512	765	nd	910	181
	2	705	576	656	nd	825	310
	3	568	651	821	nd	668	332
	4	635	605	717	nd	1050	281
	5	625	709	889	nd	857	nd
	6	465	598	640	nd	802	216
	7	541	578	837	389	766	265

(nd - not determined)

14. FIGURES

Figure 16

Vehicle 1 - Particulate Composition, (Combined Cycle)

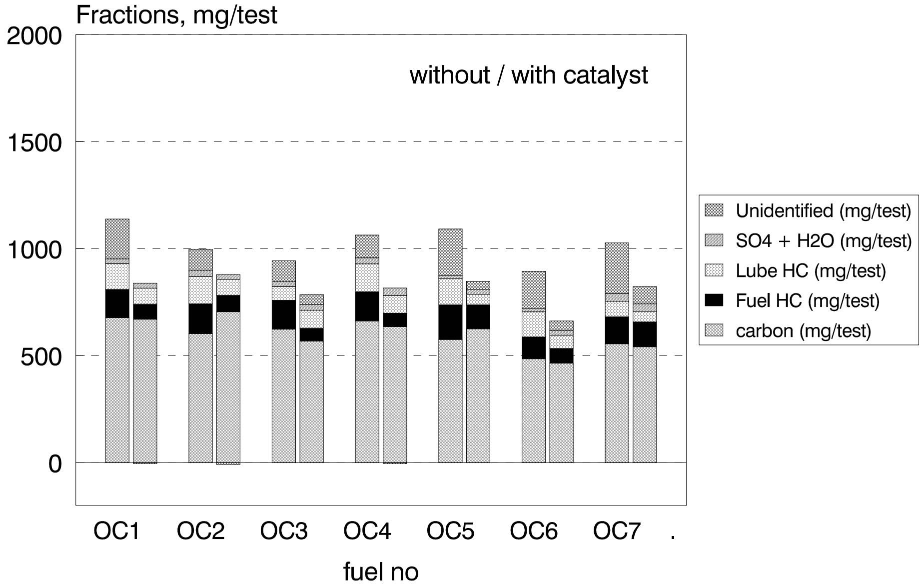

Figure 17

Vehicle 2 - Particulate Composition, (Combined Cycle)

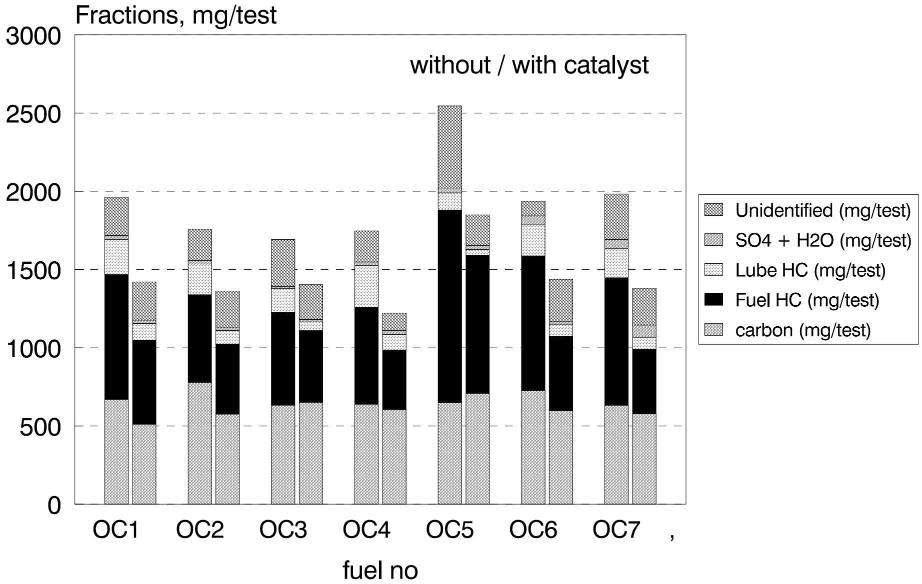

Figure 18

Vehicle 3 - Particulate Composition, (Combined Cycle)

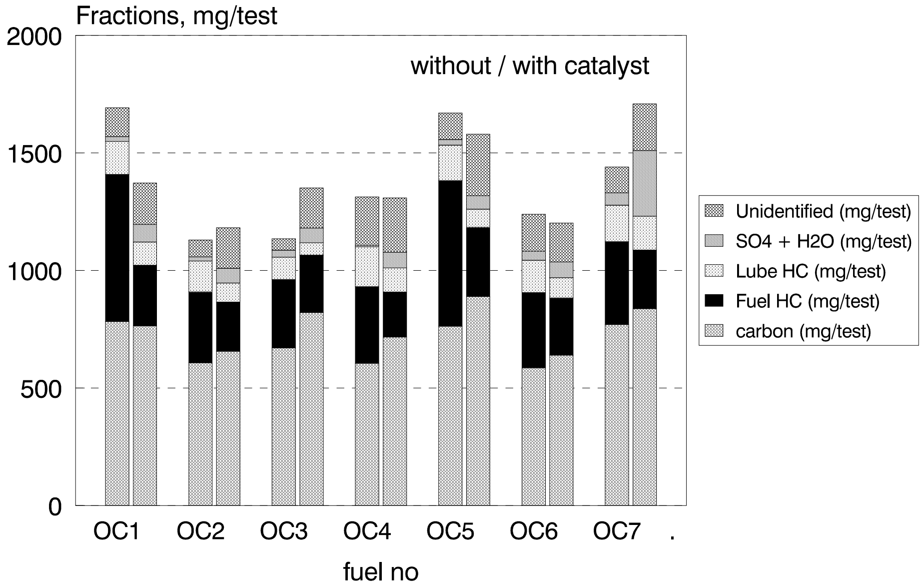

Figure 19

Vehicle 4 - Particulate Composition, (Combined Cycle)

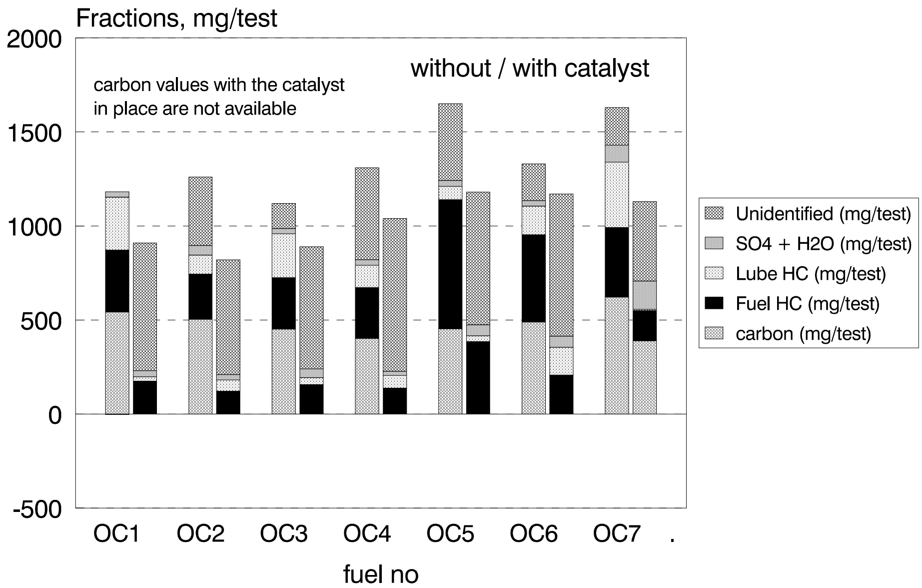

Figure 20

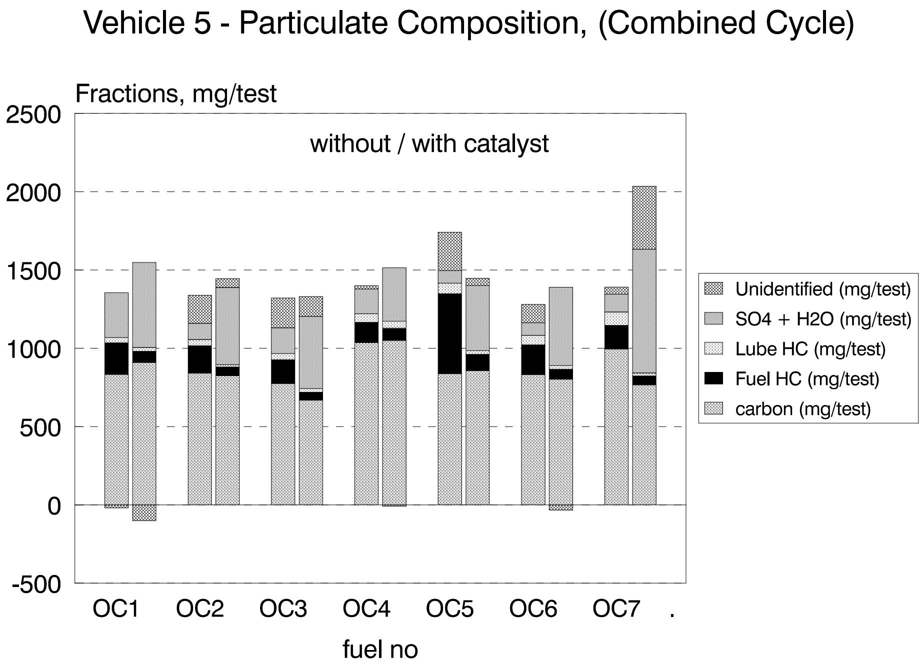

Figure 21