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**Author post-print (accepted) deposited in CURVE March 2014**

**Original citation & hyperlink:**

Benjamin, S.F. , Gall, M. and Roberts, C.A. (2014) Conversion of nitric oxide in an engine exhaust by selective catalytic reduction with a urea spray under steady-state and transient engine-load conditions. Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering, volume 228 (7): 758-770.

<http://dx.doi.org/10.1177/0954407013511443>

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# Conversion of NO in an engine exhaust by Selective Catalytic Reduction with urea spray under steady state and transient engine-load conditions

Stephen F Benjamin, Mirosław Gall and Carol A Roberts

## Abstract

Experiments have been carried out in the exhaust of an engine on a test bed with a selective catalytic reduction catalyst. The reductant could be introduced either as 5% ammonia in nitrogen gas or as a spray of aqueous urea droplets. Conversion of NO<sub>x</sub> was investigated at temperatures near 488 K (215 °C) and 533 K (260 °C), which are typical of a Diesel passenger car exhaust system. The experiments with urea spray were carried out for two reductant levels that were deficient and for one that was approximately stoichiometric. The experiments were run to steady state conditions. The spray was introduced into the system in two different ways, either into a mixing can and nozzle arrangement or sprayed into the system via an oblique pipe; in the latter case the spray impinged on an angled plate mixer. A transient case was also investigated where the engine load was ramped up from 6 to 10 bar bmep over 20 s and after reaching steady state was ramped back down to 6 bar bmep over 20 s and allowed to reach steady state. The NO<sub>x</sub> supplied was 100% NO in all these experiments. This was achieved by using a Pd Diesel oxidation catalyst to remove hydrocarbons and CO from the exhaust stream but without oxidising the NO. Measurements were made with a Fourier Transform Infrared gas analyser. The steady state results showed that the % NO conversion observed using urea spray had a value that was about 10% below the % conversion observed with ammonia gas when using either spray configuration. There was evidence that urea droplets were being transported unconverted through the SCR catalyst in both the steady state and transient engine load tests. The ammonia deficit was 20% or more of the potential amount of ammonia injected by the aqueous urea spray.

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## Keywords

Selective catalytic reduction (SCR), NO<sub>x</sub> reduction, urea spray, urea droplets

## Introduction

Fuel-efficient lean-burn Diesel engines are now used in passenger cars. Although overall CO<sub>2</sub> emissions are decreased as a result of this, the NO<sub>x</sub> and particulate emissions are high enough to require efficient exhaust after-treatment systems. Particulates are readily removed by filters but NO<sub>x</sub> is removed by chemical means, most commonly selective catalytic reduction (SCR). This utilises a reductant, ammonia, to react with the NO<sub>x</sub> in the exhaust and to reduce it chemically to nitrogen. The possible SCR reactions and sub-reactions that can occur are numerous but in the simplest schemes they are generally stated to comprise the following four main reactions:

Standard SCR:



Fast SCR:



Slow SCR:



N<sub>2</sub>O formation:



In heavy duty and light duty vehicles the ammonia can be supplied as a spray of aqueous urea droplets. The droplets must evaporate, leaving a particle of urea that can decompose [1] at a sufficiently high temperature, greater than 137 °C. The initial decomposition of urea forms both ammonia gas and isocyanic acid as in (5).



The isocyanic acid, HCNO, is hydrolysed by water to provide one further molecule of ammonia gas.



There is a very large volume of work in the literature that is relevant to SCR in exhaust systems. Some papers are concerned with droplet modelling and attempt to understand the mechanism of droplet evaporation, [1, 2]. Most papers, however, focus on attempts to model the NO<sub>x</sub> conversion and to describe experimental observations by developing models based on a chemical scheme and reaction rate expressions. Those rates are tuned by changing kinetic rate constants, activation energies and other parameters. Although there are similarities between the kinetic schemes developed by the different authors, the details of each scheme depend upon the nature of the catalyst. Vanadium was used [3] but now the catalyst is often a zeolite of either iron or copper [4, 5, 6]. Most studies of this type obtain their data under laboratory conditions from reactor rigs rather than from engine test studies. An exception is the work reported by Watling et al. [6] which does compare predictions from a model with engine test data. However, although that paper outlines the kinetic model that was used, it does not give model details such as the rate constants. Full details of the rate constants are given in some early papers, for example [7], but numerical values are often omitted in more recent papers. Although the modelling methodology in the published papers may be suitable for general application, rate constants specific to the catalyst are always required before the model can be applied. Therefore the models can be difficult to assess and impossible to apply to different catalysts without specific tuning of the rate constants for the catalyst under consideration. Also, although urea spray is generally used to introduce ammonia into the system, many published papers that are dedicated to modelling do not explore the fate of the urea droplets that enter the catalyst. Watling et al. [6] do not even include urea hydrolysis in their model and assume that the formation of ammonia from urea is fast. Other authors, however, do start to consider the fate of the droplets. In a paper focused on development of a model that includes ammonia storage [3] the assumption is made that the adsorbate in contact with the solid catalyst is in liquid form. In some engine test bed

studies, however, ammonia slip is investigated [8] but not specifically the fate of the urea droplets in the SCR catalyst or the possible slip of droplets.

A typical urea spray unit provides droplets of aqueous urea in the range from sub-micron diameters up to several hundred microns in diameter. The peak of the volume distribution of the droplets is, however, generally centred on a diameter below 200 microns, but is dependent upon the design of the spray unit. It would be advantageous for all the droplets to be as small as possible but commercial spray units that are able to supply sufficient flow rate do not provide mono-disperse droplets and generate a wide range of droplet sizes. Droplets from several different spray units have been measured in the laboratory, but using water in place of urea. This has given estimates for the droplet sizes being injected into the exhaust in the experiments reported in this paper.

This paper is novel because it uses an engine fitted with an exhaust designed as a one-dimensional reactor. This facilitates analysis of the composition of the reductant at the front of the SCR and an examination of the possibility that injected droplets can pass right through to the rear of the SCR monolith. The NO<sub>x</sub> supplied to the SCR in the experiments was in the form of NO. This was achieved by using a Pd Diesel oxidation catalyst (DOC) that removed the CO and hydrocarbons (HC) from the exhaust [9] but did not oxidise the NO coming from the engine to form NO<sub>2</sub>. In consequence, fewer SCR reactions were occurring and reactions between ammonia and NH<sub>3</sub> that could have produced N<sub>2</sub>O in large quantity on the copper zeolite catalyst being used [10] were avoided. Measuring NO<sub>2</sub> and NH<sub>3</sub> reliably when both are present can be difficult, even with an FTIR analyser as used in this research.

Four experiments were run to steady state using urea spray. One experiment was run as a transient case, also using urea spray, where the engine load was ramped up from 6 to 10 bar bmep over 20 s and held

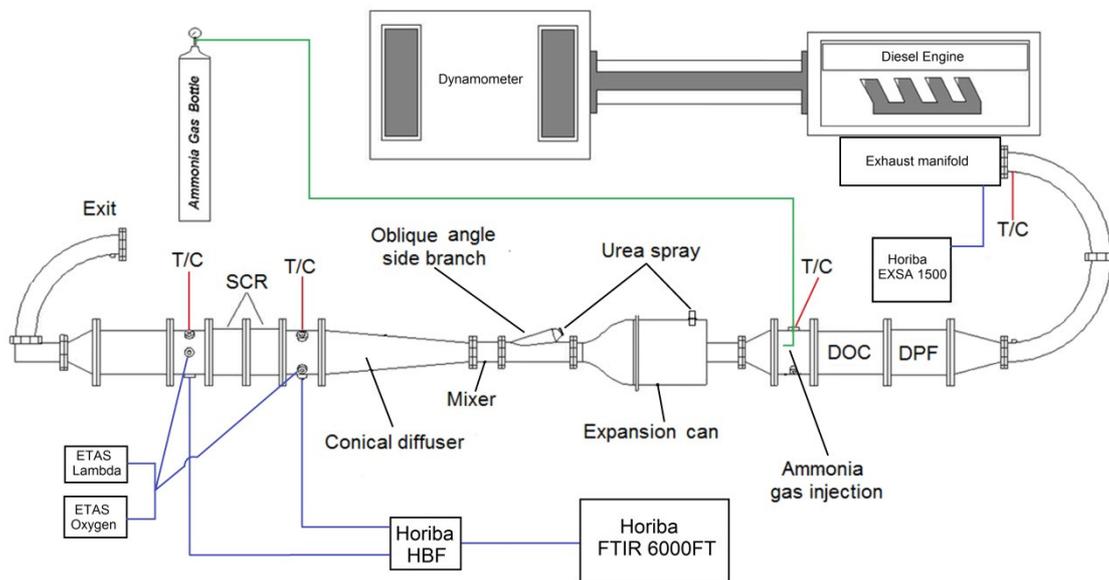
until steady state was achieved before the load was ramped down again over 20 s. As before, the experiment continued until steady state conditions were reached. These ramps are simplified versions of the accelerations and decelerations in drive cycles because the engine speed remains fixed. The results from the experiments were compared with equivalent experiments that had been carried out using 5% ammonia gas in nitrogen as the injected reductant. The aim of the experiments described in this paper was to understand the differences between supplying the ammonia in the form of droplets, rather than supplying it as ammonia gas. The difference that the method of ammonia supply makes to the conversion process that is achieved within the SCR automotive catalyst has also been investigated.

### **Description of the engine test rig**

A schematic diagram of the engine test exhaust system is shown in Figure 1. A 2.2 litre Diesel engine was run without exhaust gas recirculation (EGR) to supply significant NO<sub>x</sub> levels for experimental purposes. The exhaust passed through a Diesel particulate filter (DPF) prior to a DOC. The DPF removed the soot particulates. In these experiments the DOC catalyst was Pd and this removed HC and CO from the exhaust stream [9] without oxidising the NO to form NO<sub>2</sub>. Ammonia gas, 5% in nitrogen, was monitored with a rotameter-type flowmeter and could be introduced into the exhaust downstream of the DOC if required. Alternatively, an aqueous urea spray was used to introduce droplets in two different ways, as described later. The exhaust flow passed through a flow straightener and entered an expansion box mixing chamber. The diameter of the mixing can was 0.2 m and its length was 0.2 m. A converging nozzle downstream of the mixing chamber provided a uniform flow profile to the inlet of a long ten degree included angle diffuser. The latter expanded the duct from 0.05 m to 0.115 m diameter. This diffuser provided a uniform flow profile to the inlet of the SCR brick. Gas sampling ports upstream and downstream of the SCR brick enabled the levels of NO, NO<sub>2</sub>, NH<sub>3</sub> and N<sub>2</sub>O to be measured upstream and downstream of the SCR. Downstream of the SCR, the exhaust was vented to a stack.

The gas analysers used were an Horiba model 6000FT and an Horiba EXSA 1500. The Horiba Fourier Transform Infrared (FTIR) analyser gas sampling line temperature was 113 °C and the EXSA line temperature was 191 °C. The latter monitored the engine-out species levels to confirm consistent engine performance throughout the long duration tests that were run to steady state. The FTIR analyser measured species concentrations directly for the wet exhaust. The NO and NH<sub>3</sub> ranges were 0 – 1000 ppm (parts per million) with the noise, linearity and repeatability quoted to be better than ±1% of full scale. There was negligible drift of the readings over the period of the experiments. The oxygen levels at the monitoring points in the exhaust were measured by Etas lambda sensors with uncertainty less than 5%.

The SCR brick was 75 mm in length in the urea spray experiments described in this paper. The catalyst was a form of copper zeolite. The exhaust mass flow rate was  $0.0303 \pm 0.0002$  kg/s at 488 K (215 °C) and  $0.0326 \pm 0.0002$  kg/s at 533 K (260 °C). The engine was run at speed 1500 rpm and the load was 6 bar bmep to achieve the lower temperature and 8.5 bar bmep to achieve the higher temperature in the steady state experiments. Thermocouples monitored the exhaust gas temperature upstream of the SCR and at other locations. The rig was thoroughly lagged to avoid excessive temperature reduction between the engine and the SCR.



**Figure 1. Schematic diagram of the experimental test exhaust fitted to a 2.2 litre Diesel engine, showing the expansion can and the angled side branch pipe downstream of the converging nozzle, which were the alternative points for the introduction of urea spray.**

## **Experimental methodology for laboratory and engine tests**

### ***Droplet size measurements***

The urea spray used in the engine test studies was first characterised by some laboratory measurements made using a TSI Phase Doppler Particle Anemometry laser system. The latter provides measurements of both droplet sizes and velocities. Measurements were made of the spray in the open and also of the spray spraying into the exhaust system that is shown in Figure 1, but using an air flow rig. The laboratory measurements were made with the spray unit spraying distilled water.

The spray unit was run at a gauge pressure of 500 kPa. The droplets were injected either directly into the expansion can and nozzle arrangement or into the exhaust via an oblique-angled side branch pipe, which can be seen in Figure 1. The pipe containing the side branch was 0.215 m in length. The spray axis was inclined at  $27^\circ$  to the exhaust axis; an angled plate mixer unit was installed immediately downstream of the side branch, and immediately upstream of the entrance to the conical expansion diffuser. The mixer was located in the short pipe of length 0.12 m that can be seen in Figure 1. The design of the prototype mixer unit was confidential. The approximate location of the boss for alternatively locating the spray on the top of the expansion can for spraying downwards into the can is also seen in Figure 1. In that case, the mixer unit was replaced with an open duct of the same length. A thermocouple was soldered to the external wall of the mixer and a thermocouple was inserted through the back wall of the can into the expansion chamber about 25 mm above the bottom of the can. These thermocouples provided temperature measurements in both the laboratory studies and the engine tests.

The first spray position was on the top of the expansion can with the spray unit spraying downwards, and the droplets were measured at the can outlet in the flow rig tests in the laboratory. The droplets sizes were

measured at the outlet from the pipe downstream of the mixer when the measurements were made in the laboratory with the spray unit spraying into the angled side branch.

### ***Methodology for steady state engine experiments***

The spray unit had been calibrated with distilled water during the laboratory tests so that its discharged mass-flow rate was known. This was corrected to the rate for aqueous urea by using the known relative density of the aqueous urea. The aqueous urea used in the experiments was an Ad-blue product, which is 32.5 % urea by mass. The exhaust mass flow rate was logged during the engine experiments; hence it was possible to calculate the potential equivalent ammonia input in ppm if all the urea introduced into the exhaust by the spray was converted to ammonia gas, in accordance with equations (5) and (6). The equivalent potential ammonia level in ppm injected via the spray is defined as  $tNH_3$ , and the values applied in the experiments are shown in Table 1. Also shown are the investigated  $\alpha$  values, the ratios of  $tNH_3:NO$ , which range from deficient to stoichiometric. The alternative spray injection locations are indicated in Table 1 as either Can or Pipe, where the latter indicates injection via the oblique pipe plus mixer. Low and high T indicate the lower and higher engine load conditions.

**Table 1. Conditions upstream of the SCR brick for the steady state engine tests at low and high temperature. The quantity  $tNH_3$  is the calculated equivalent ammonia level in ppm that is injected via the spray. The ratio of  $tNH_3:NO$  is  $\alpha$ .**

	$\alpha \sim 0.5$	$\alpha \sim 0.75$	$\alpha \sim 1.0$
	$tNH_3$	$tNH_3$	$tNH_3$
	ppm	ppm	ppm
<b>Can; low T</b>	322	499	646
<b>Pipe; low T</b>	316	474	699
<b>Can; high T</b>	398	601	844
<b>Pipe; high T</b>	402	607	817

The main steady state engine tests consisted of the following procedure. The engine was warmed up at either 1500 rpm 6 bar bmep for a temperature near 488 K (215 °C) or at 1500 rpm 8.5 bar bmep for a temperature near 533 K (260 °C). The spray was turned on to the required settings and measurements were made of the amount of NH<sub>3</sub> present as gas upstream of the SCR. The spray was then turned off and the ammonia was purged from the system. The FTIR analyser was then switched to measure the levels downstream of the SCR. The experiment was run for the high spray rate setting until steady state conditions were reached, then similarly for the middle spray rate setting until steady state was reached and finally for the low spray rate setting. After steady state conditions had again been reached, the spray was turned off. The experiments took 1000 seconds or more to reach steady state at each spray rate setting. At the end of the experiment after the spray was turned off, data was logged until the NO level downstream of the SCR returned to the upstream level, indicating that ammonia had been purged from the system.

### ***Methodology for transient engine load experiment***

The transient test was carried out with the spray entering the exhaust via the oblique pipe and the droplets impinging on to the mixer. The length of the SCR brick was 75 mm, the same as in the steady state tests. The initial procedure was to warm up the engine to steady state conditions at 1500 rpm and 6 bar bmep load. Figure 2 shows the full log of the transient experiment for the period after the engine had been warmed up, so that the experimental procedure can be understood. The FTIR analyser was monitoring the levels upstream of the SCR catalyst at the start of the experiment. The spray setting was adjusted to give a tNH<sub>3</sub>:NO<sub>x</sub> ratio of 1.0 at 6 bar bmep assuming that all the potential ammonia from the spray would be released by decomposition and hydrolysis. When steady state conditions were reached, at about 5000 s in Figure 2, the engine load was ramped up to 10 bar bmep over 20 s. This had the effect of raising the NO level being supplied to the SCR, raising the exhaust temperature and the mass flow rate and lowering the

% oxygen in the exhaust stream. The temperature of the experiment varied from about 483 K (210 °C) at the 6 bar bmep load steady state condition to just over 553 K (280 °C) when steady state conditions were reached at 10 bar bmep load. At this stage the engine load was ramped down again over 20 s from 10 bar back to 6 bar, at about 7500 s in Figure 2. This lowered the NO level, the exhaust temperature and mass flow rate and raised the % oxygen in the exhaust. After steady state conditions were achieved, the FTIR analyser was moved to monitor the levels downstream of the SCR catalyst. This was at about time 10000 s in Figure 2. The experiment was repeated. The NO curve that was being logged downstream in this phase of the experiment shows a peak at about 10300 s and a dip at about 12700 s that correspond to the upward and downward engine load ramps. When the engine load was ramped upward, the NO level from the engine increased rapidly but the temperature in the SCR was slower to respond and rise, so the NO slip peaked. Conversely, when the engine load was ramped down, the NO level from the engine fell quickly, but the temperature in the SCR was slower to respond and fall, so there was a dip in the NO slip. The experiment ended at about 14900 s.

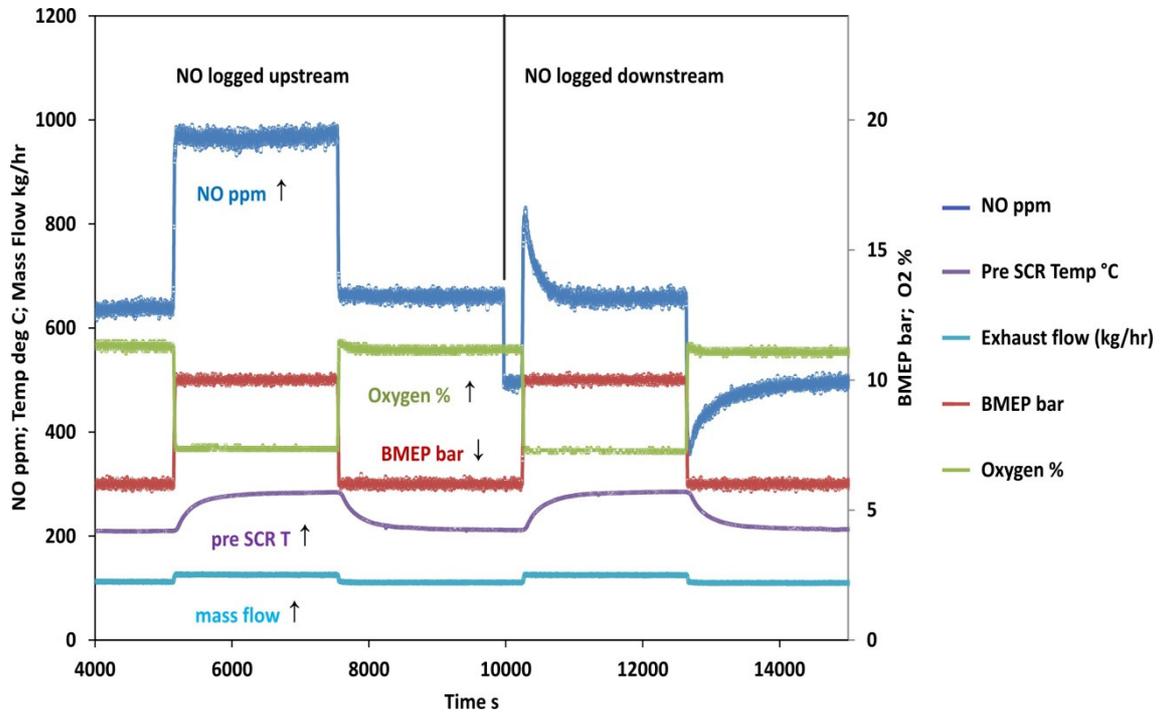


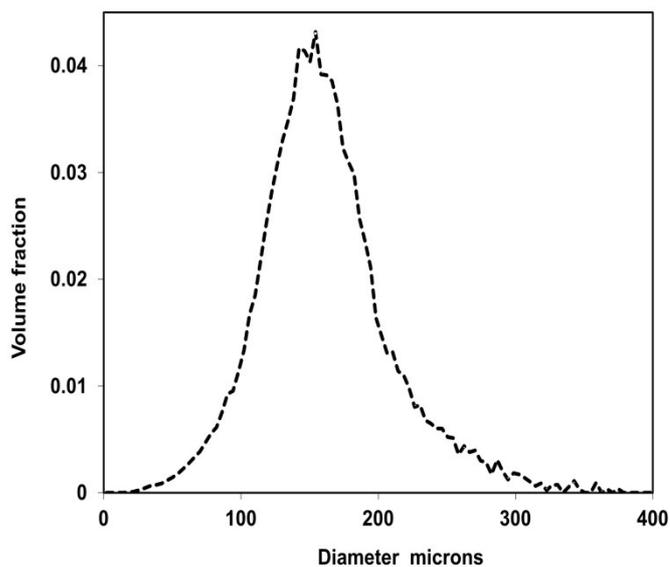
Figure 2. Log of the transient test, after initial warm up period, showing the NO level, exhaust temperature upstream of the SCR catalyst, exhaust mass flow rate, engine load and % oxygen in the exhaust.

## Discussion of Results

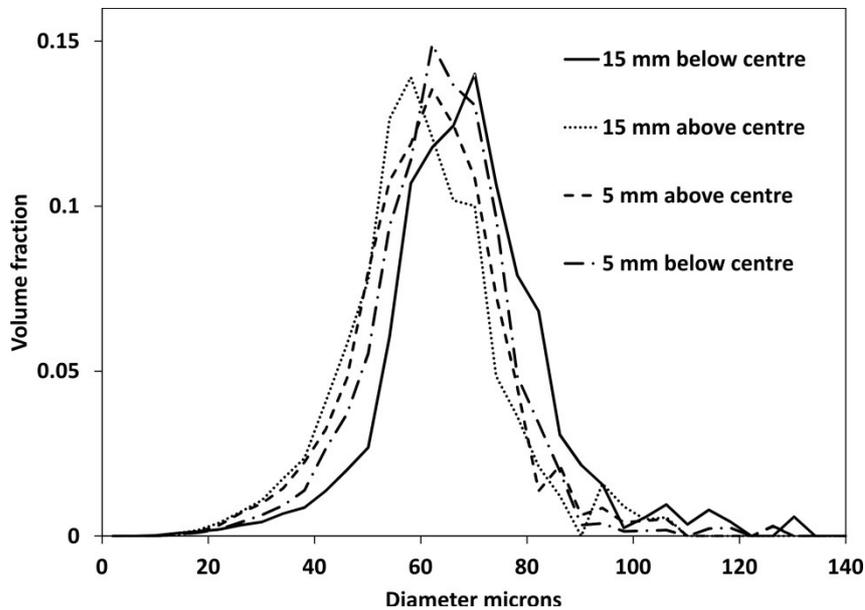
### *Effect of urea spray position on droplet sizes*

Figure 3 shows a typical measurement of the droplet sizes from the spray when spraying cold distilled water into open air in the laboratory. It is seen that the measured volume distribution shows a droplet size at the peak of the distribution that is less than 200 microns, being close to 150 microns. This is still larger than the ideal value for use in SCR exhaust systems but is typical of sprays in current use in the automotive sector. All the droplets are subject to evaporation and to break up mechanisms as they pass through the exhaust system so the size distribution will change. The first spray position was on the top of the expansion can and spraying downwards. This should have allowed the injected droplets to mix with

the 180 °C air stream. As the measured droplet injection velocity was in the region of 22 to 26 m/s, however, and the flow velocity in the large diameter expansion can was relatively low, many droplets would have been able to impinge on the base of the can. This impact could have resulted in either a droplet bounce or a splash that broke up the droplet, or possibly the droplet could have stuck to the can inner surface and evaporated from that surface. A droplet that bounced from the surface may have had a long path length as a result of further bounces within the can. The droplets emerging from the nozzle downstream of the can were measured in the air flow in the laboratory and were found to have the distribution shown in Figure 4. The peak of the volume distribution is seen to be at a diameter near 65 microns so that those measured droplets that had emerged from the can in the air stream from the nozzle were much smaller than those injected by the spray.

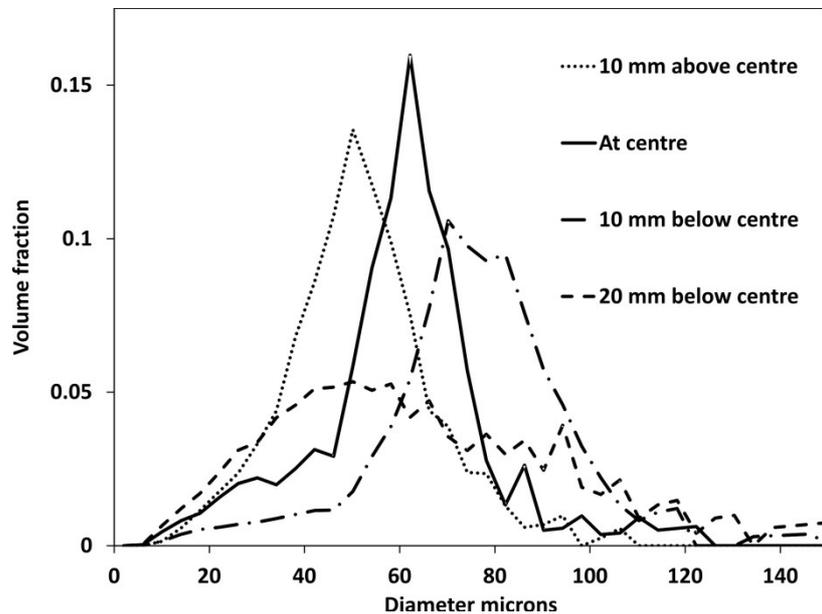


**Figure 3. Distribution of droplet size measurements for peak of spray pattern when spraying cold water droplets into open air.**



**Figure 4. Examples of droplet size distribution measurements at the converging nozzle exit when the spray was sprayed into the top of the expansion can with 180 °C air flow temperature. The legend indicates the position of the measurement point relative to the converging nozzle axis.**

When the droplet sizes downstream of the mixer were measured in the laboratory they were more variable as can be seen in Figure 5. The droplets were nevertheless significantly smaller than those seen in Figure 3. The mixer design would have allowed some droplets to pass through it without any impingement whereas others would have impacted the mixer plates and either been broken up or evaporated on the plate surfaces. Both methods for the introduction of the droplets into the exhaust significantly decreased the size of the droplets injected by the spray unit.



**Figure 5.** Examples of droplet size measurements made downstream of the angled plate mixer when the spray was sprayed into the duct through the oblique angled side branch with 180 °C air flow temperature. The legend indicates the position of the measurement point relative to the duct axis.

### *Measured ammonia levels upstream of SCR in steady state engine tests*

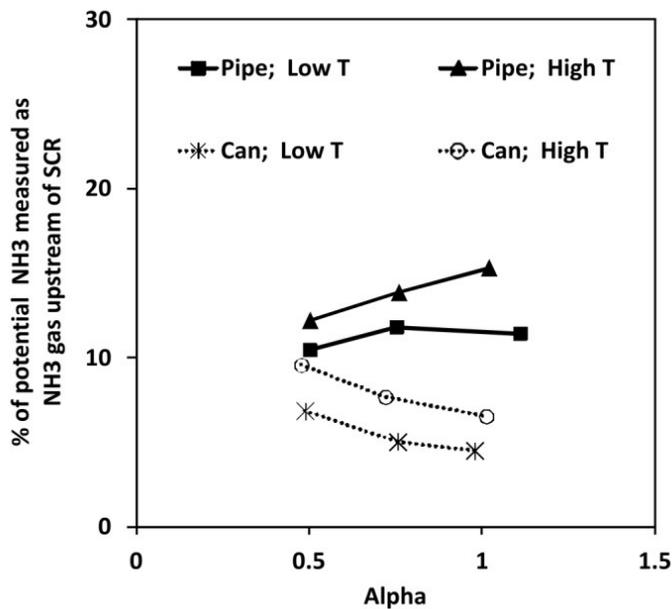
Table 2 shows the experimental measurements of ammonia and NO upstream of the SCR in the engine tests that were run to steady state. The tests were run at three different  $\alpha$  values near 0.5, 0.75 and 1.0, based on the potential ammonia supplied by the spray unit.

Some of the potential ammonia available in the spray was converted to ammonia gas upstream of the SCR. Hence this was measurable with the FTIR analyser when measuring upstream of the SCR. The % of ammonia released upstream is slightly higher with the spray spraying into the oblique pipe than into the can. This is illustrated in Figure 6, which shows some of the information from Table 2 in graphical form. It can be seen that very little of the potential ammonia is released upstream of the SCR, although more is

released when the temperature is higher. It is clear from Figure 6 that more ammonia is released with the pipe and mixer arrangement of the spray than with the spray spraying directly into the expansion can.

**Table 2. Conditions upstream of the SCR brick for the steady state tests at low and high temperature. The quantity  $tNH_3$  is the calculated equivalent ammonia level in ppm that is injected via the spray. The ratio of  $tNH_3:NO$  is  $\alpha$ .**

	Upstream Measured NO ppm	$\alpha \sim 0.5$ Measured $NH_3$ ppm & %	$\alpha \sim 0.75$ Measured $NH_3$ ppm & %	$\alpha \sim 1.0$ Measured $NH_3$ ppm & %	$\alpha \sim 0.5$ $tNH_3$ ppm	$\alpha \sim 0.75$ $tNH_3$ ppm	$\alpha \sim 1.0$ $tNH_3$ ppm
Can; low T	660	22 (6.8%)	25 (5.0%)	29 (4.5%)	322	499	646
Pipe; low T	630	33 (10.4%)	56 (11.8%)	80 (11.4%)	316	474	699
Can; high T	834	38 (9.5%)	46 (7.7%)	55 (6.5%)	398	601	844
Pipe; high T	801	49 (12.2%)	84 (13.8%)	125 (15.3%)	402	607	817



**Figure 6. The % of the potentially available ammonia,  $tNH_3$ , detected as ammonia gas upstream of the SCR catalyst in the engine tests.**

### ***Results of engine tests run to steady state***

Figure 7 shows temperatures measured during the steady state tests. The temperatures shown in Figure 7 are from the thermocouple soldered to the external wall of the mixer and the thermocouple inserted through the back wall of the expansion can, and also the thermocouple recording the gas temperature upstream of the SCR. Low temperature experiments were carried out at gas temperatures of about 488K (215°C) upstream of the SCR and high temperature experiments corresponded to 533 K (260 °C). The measurements recorded cooler temperatures from the mixer thermocouple than from the thermocouple inserted into the can. It can be seen in Figure 7 that the temperature at these locations varied as the spray rate was changed during the experiment. In the experiment, after the spray was turned on, its rate was stepped down from high to low; this is the explanation for the cooler temperatures observed during the experiment in Figure 7 when the spray was turned on at about 200 s. It also explains the temperature rise in these locations when the spray rate was adjusted and eventually turned off at the end of the experiment. Although both locations were cooled by the spray, the temperatures observed were high enough to boil off the water from impinging droplets and to dissociate the urea. Figure 7 shows that the temperatures measured pre the SCR changed much less during the experiments than the measurements at the bottom of the can or on the mixer, and were effectively constant throughout each experiment.

Figure 8 shows the NO and NH<sub>3</sub> levels logged downstream of the SCR during the steady state experiments. The slip of ammonia measured in the gaseous state was observed to be greater when the spray was injected via the side branch pipe than when it was injected into the top of the expansion can. The logged traces in Figure 8 show a period of 200 s prior to the commencement of the experiment, following which the NO level falls and the ammonia slip rises as the spray is injected, at first at a level that is approximately stoichiometric in quantity. The observed NO level rises slightly, i.e. conversion is

less, when the spray is set to the increasingly deficient settings but finally returns to its initial value after the spray is turned off.

Figure 9 shows conversion from these experiments compared with some equivalent experiments at similar temperatures where the ammonia was supplied as 5% ammonia gas in nitrogen. Clearly there is higher conversion of NO with the ammonia supplied as a gas. There is negligible difference between the can experiment and the pipe experiment at low temperature but there are small differences at high temperature. Spraying into the can gives better conversion than spraying into the pipe when the potential ammonia in the spray is deficient, but the difference is small. Because the measured level of ammonia gas, ppm, supplied to the SCR brick is less than the amount of NO converted, ppm, see Table 3, this implies that the HCNO is hydrolysed within the SCR brick. It also suggests that some droplets are converted within the SCR brick itself, rather than upstream, to provide the ammonia necessary to convert the NO. The amount of NO converted is relatively large so that it must have demanded conversion of droplets within the brick, not just hydrolysis of the HCNO assumed to be entering the brick. The latter should be the same in quantity as  $m\text{NH}_3$  in Table 3, which is the ammonia gas measured upstream of the SCR brick. It is assumed that the conversion occurs via the standard SCR reaction (1) with the stoichiometry of one ammonia molecule converting one NO molecule. The temperatures are too low to convert NO to  $\text{NO}_2$  in significant quantity on the SCR catalyst so that it is assumed that the other SCR reactions involving  $\text{NO}_2$  do not contribute to the net conversion under these conditions.

**Table 3. Measured NH<sub>3</sub> gas upstream and converted NO at low and high temperature at steady state. Measured NH<sub>3</sub> is indicated by mNH<sub>3</sub> and total (potential) ammonia supplied by the spray is indicated by tNH<sub>3</sub>.**

	Upstream tNH <sub>3</sub> :NO	Upstream mNH <sub>3</sub> ppm	Converted NO ppm
Pipe; low T	0.50	33	124
Pipe; low T	0.75	56	136
Pipe; low T	1.11	80	148
Pipe; high T	0.50	49	222
Pipe; high T	0.76	84	272
Pipe; high T	1.02	125	300
Can; low T	0.49	22	132
Can; low T	0.76	25	149
Can; low T	0.98	29	155
Can; high T	0.48	38	258
Can; high T	0.72	46	290
Can; high T	1.01	55	312

The ammonia slip levels downstream were examined. The amount of potential ammonia supplied to the SCR by the spray is a known quantity, tNH<sub>3</sub>. The amount measured to have converted to gas upstream of the SCR is also known, shown as mNH<sub>3</sub> in Table 3. It is assumed that the amount of ammonia that is required to convert the NO is one mol per one mol. It is known how much ammonia slips from the SCR in the form of NH<sub>3</sub> gas, as illustrated in Figure 8. There is, however, a net deficit observed in measurable ammonia. This missing ammonia could have been adsorbed in the SCR brick itself or elsewhere in the test rig so that it is consequently unavailable to be measured by the FTIR gas analyser. A possible form for such storage would be as a nitrate but this is unlikely at the temperature [4, 11] of these experiments and in the absence of NO<sub>2</sub>. The difference in NO conversion efficiency at the low and high temperatures in Figure 9 is partly explained because the net ammonia stored is different in the two cases. Because the tests are run to steady state, the level of ammonia storage will adjust during the early part of each experiment but will remain constant in the steady state part. The ammonia deficit, however, cannot be fully explained at steady state by the level of storage. It is inferred that the apparently missing ammonia

exits from the SCR brick in the form of non-hydrolysed HCNO or it could be still in the form of urea droplets. This is possible because some of the droplets are large and they could therefore survive the heating [1] caused by their passage through the catalyst. The level of the ammonia deficit is shown in Figure 10. The deficit is dependent upon  $\alpha$ , particularly for the configuration where the spray was sprayed into the expansion can. Thus the deficit is larger with higher spray rate. The deficit is also larger for both configurations at the lower temperature.

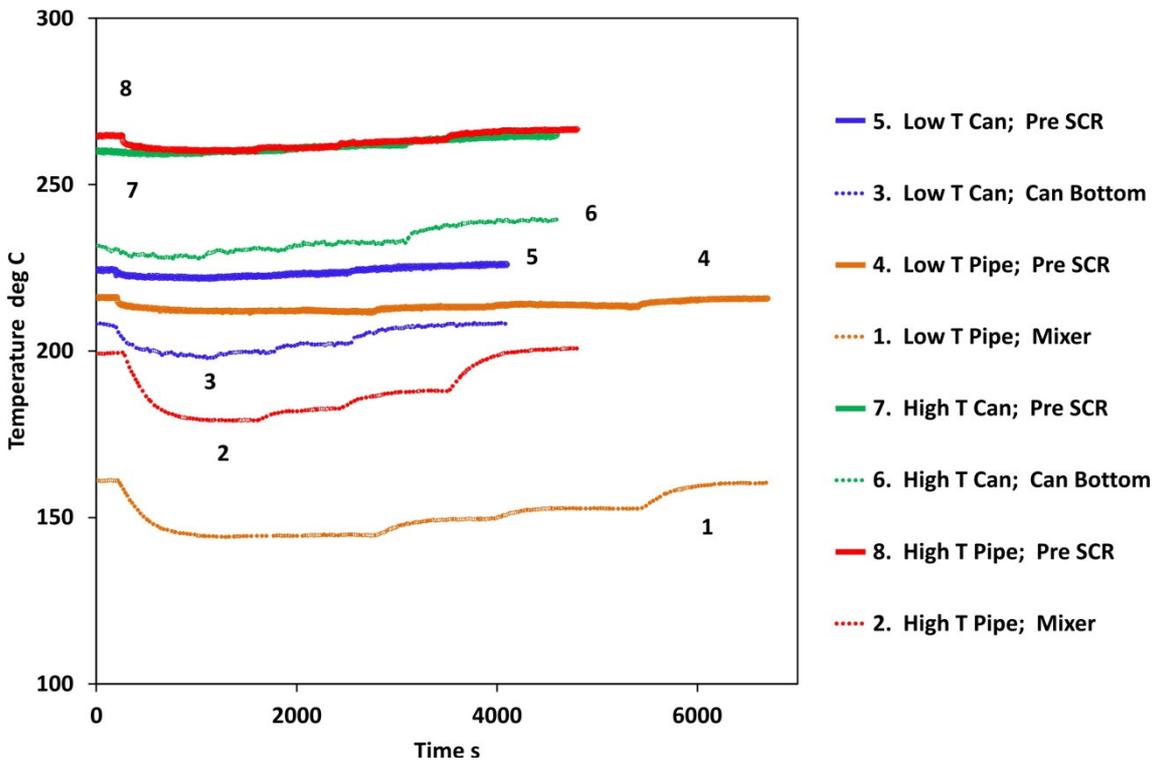


Figure 7. Temperature measurements made during the steady-state spray experiments. Note that the time scale in this figure is the same as in Figure 8.

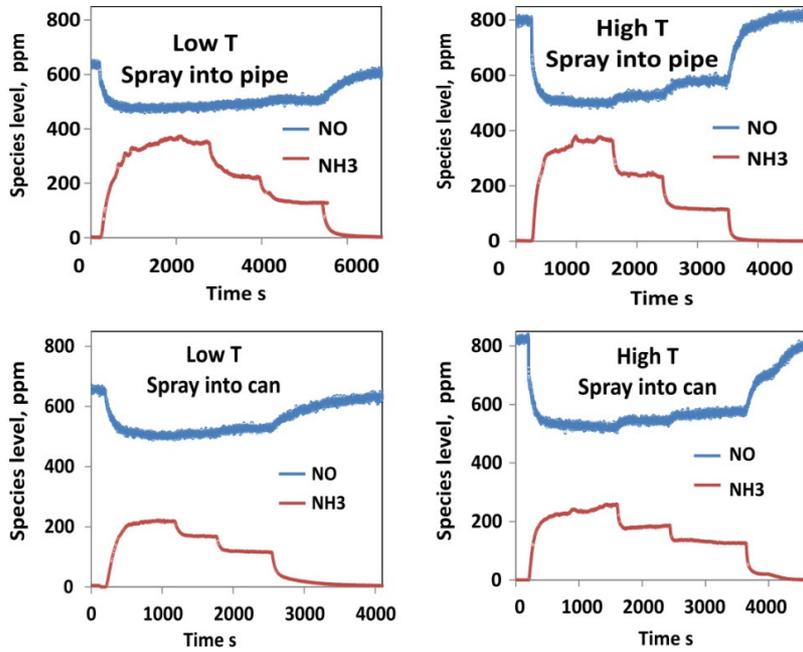


Figure 8. Logged data, NO and NH<sub>3</sub> levels measured downstream of the SCR catalyst, during the urea spray experiments.

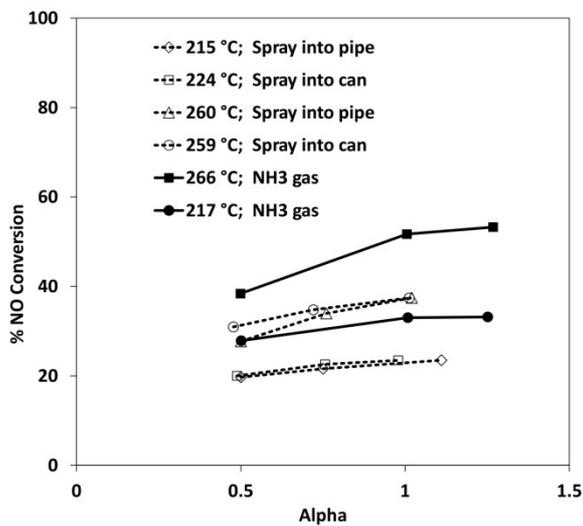
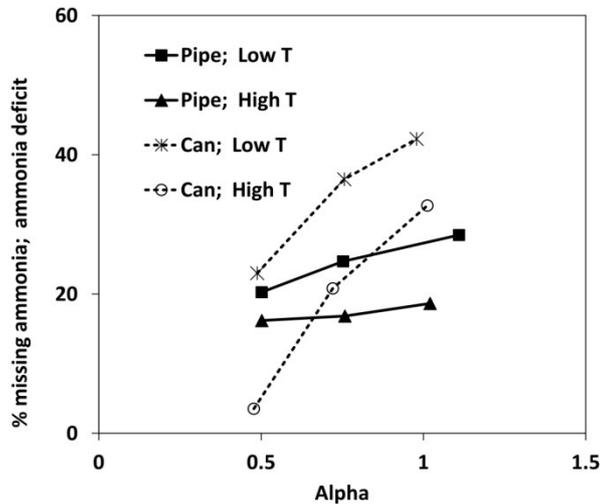


Figure 9. Conversion of NO at steady state conditions achieved by 75 mm length SCR catalyst in urea spray experiments at low and high temperatures.



**Figure 10.** Apparent ammonia deficit, i.e. ammonia unaccounted for at steady state. The ammonia has passed through the SCR in a form not detectable by the gas analyser, either as HCNO or urea droplets.

### *Results of tests with transient engine load*

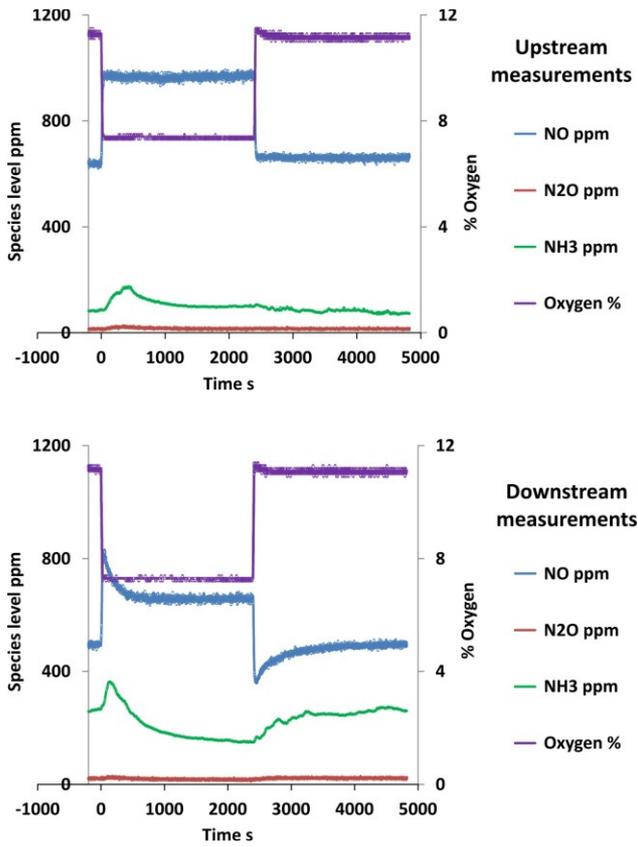
Figure 11 shows the log of the transient test. The two parts of the experiment that were illustrated in Figure 2 are now each plotted separately so that time zero in Figure 11 corresponds to the start of each part of the experiment. The upstream measurements show that the NO level is about 660 ppm when the load is 6 bar bmep and is just under 1000 ppm when the load is 10 bar bmep. A relatively small amount of ammonia in gaseous form is detected upstream. Ad-blue was sprayed at a rate of 65.5 mg/s into the rig throughout the experiment, which was equivalent to  $\alpha \sim 1$  at engine load 6 bar bmep, so that  $t\text{NH}_3$  was about 660 ppm at the lower engine load. The exhaust mass flow rate changes with engine load so that the potential amount of ammonia available is effectively at a lower ppm level when the engine load and mass flow rate are high. There is negligible  $\text{N}_2\text{O}$  measured upstream of the SCR but a small amount is detected downstream, which is normally unexpected in the absence of  $\text{NO}_2$ , but is possible for a copper zeolite catalyst [10]. The gaseous ammonia slip measured downstream is larger than the amount of ammonia

entering the SCR catalyst in gaseous form. Figure 12 shows an analysis of the implications of this, which are similar to the steady state tests discussed above. The time scale in Figure 12 corresponds with Figure 11.

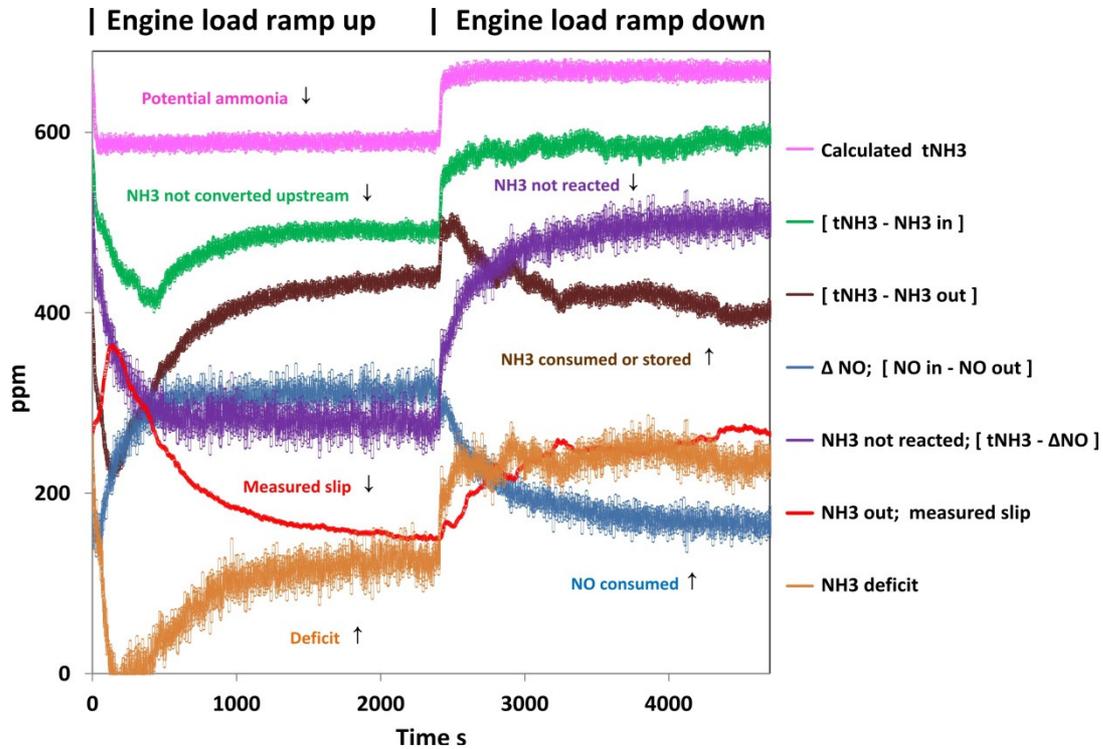
The calculated equivalent level of ammonia injected via the spray,  $t\text{NH}_3$ , is shown in Figure 12. This drops rapidly at the start of the upward engine load ramp, after time 0 s, but then stays constant until it rises rapidly at the start of the downward ramp, about 2500 s. As stated above, this is a consequence of the changes in mass flow rate during the experiment. The difference between  $t\text{NH}_3$  and the ammonia gas level measured upstream of the SCR is shown in Figure 12. Figure 11 showed that the ammonia gas level upstream was approximately constant throughout, apart from a peak after the upward engine load ramp. The difference between  $t\text{NH}_3$  and the ammonia gas measured upstream is relatively large, as shown by the green line in Figure 12, because most of the potential ammonia is not released as ammonia gas upstream of the SCR. There is a dip after the upward engine load ramp at about 500 s, consistent with more ammonia gas being temporarily available upstream; this is stored ammonia released from surfaces in the exhaust system as the temperature rises in response to the engine load upward ramp. The measured gaseous ammonia slip downstream of the SCR is shown in red in Figure 12, and is also shown in Figure 11; this peaks after the upward engine load ramp because there is breakthrough in response to the higher space velocity until the temperature rises sufficiently to increase the reaction rate. After the downward engine load ramp, at about 2400 s, the slip returns to its initial level, corresponding to the low temperature, 6 bar bmep engine load condition. The difference between  $t\text{NH}_3$  and the measured gaseous ammonia slip is shown by the brown line in Figure 12; this is the net amount of ammonia apparently consumed or stored. This quantity falls to a minimum after the upward engine load ramp, because the measured gaseous ammonia slip rises at this point. After the downward engine load ramp this difference peaks but then falls. Immediately following the engine load transients there may be changes in the amount

of ammonia stored by the SCR but at steady state the brown line represents the amount of ammonia apparently consumed by reactions. This is notably different from the amount of NO consumed in the SCR, which is shown by the blue line in Figure 12. Just before the start of the upward engine load ramp the amount of NO consumed is 150 ppm, which is the low value that corresponds to the 6 bar bmep steady state engine condition for the 75 mm brick. The NO consumed rises to a steady state value near 300 ppm for the 10 bar bmep engine load condition. After the downward engine load ramp, the amount of NO consumed decays back to the value for 6 bar bmep load. At steady state the amount of NO consumed by the SCR would be expected to be exactly equal to the amount of ammonia consumed. So the difference between  $t\text{NH}_3$  and the amount of NO consumed is shown by the purple line in Figure 12; this is the amount of potential ammonia supplied to the SCR but not reacted. This is larger than the measured gaseous ammonia slip throughout, except near 100 s where changes in ammonia storage will be contributing to the balance of gaseous ammonia. The difference between the non-reacted ammonia (purple line) and the gaseous ammonia slip (red line), and the difference between  $[t\text{NH}_3 - \text{NH}_3 \text{ out}]$  (brown line) and NO reacted (blue line), both represent a discrepancy that must be explained. This discrepancy is ammonia that is unaccounted for and the deficit is shown by the orange line in Figure 12. This can be accounted for if some of the ammonia is not present to be detected as gaseous slip but is either stored or slips in a form undetectable by the FTIR gas analyser, i.e. as HCNO or as droplets. Just after the engine load upward or downward ramps, changes in net ammonia storage will be a factor, but at steady state the net storage rate of ammonia is zero and thus only undetected slippage can be the explanation under those conditions. The most likely reason is that possibly HCNO, or more likely urea droplets, have survived to pass through the SCR. The amount of potential ammonia that can be inferred to be slipping in this form is a significant percentage of the total, as can be seen from the  $\text{NH}_3$  deficit line in Figure 12. This deficit has value near zero just after the upward engine load ramp when slightly more ammonia was apparently present in gaseous form upstream of the SCR; but after this the deficit rises to

about 100 ppm, rising further to above 200 ppm after the downward engine load ramp. The latter is approaching 30% of the potentially available injected ammonia.



**Figure 11. Measured NO, ammonia and N<sub>2</sub>O levels upstream and downstream of the SCR catalyst in the transient engine load experiment. Time is shown as zero at the start of each phase of the experiment. Oxygen level is also shown for reference.**



**Figure 12. Analysis of data from the transient engine load experiment showing the missing ammonia,  $\text{NH}_3$  deficit, which it is inferred has passed through the SCR catalyst in droplet form.**

Figure 13 shows the NO conversion observed in the transient test. The NO conversion is a minimum just after the upward engine load ramp, when the NO level is high, the temperature is relatively low, and the ammonia supply is deficient. The NO conversion peaks just after the downward engine load ramp, when the NO level is low, the temperature is high and the ammonia supply is stoichiometric. The conversion levels at steady state, i.e. at about 2000 s and 4500 s in Figure 13, agree approximately with Figure 9. Figure 13 can be compared with Figure 14 where the results from a similar study are shown where the ammonia was not supplied as spray but as 5% ammonia gas in nitrogen. In that study, however, the SCR brick was shorter, just 45 mm in length; the conversion rates achieved are lower as would be expected for a shorter brick. Superficially, the logged curves from the urea spray test in Figure 13 look very similar to

the ammonia gas test in Figure 14 but it is the numerical values achieved at steady state that are important.

Table 4 shows approximate conversion efficiencies observed in a series of steady state tests using ammonia gas. In Figures 13 and 14, the first phase of the experiment ends in a steady state condition at high temperature and the second phase of the experiment ends in a steady state condition at low temperature. Figure 13, which was obtained using the urea spray, does not achieve the expected steady state conversion efficiencies from Table 4; whereas Figure 14 obtained in a transient experiment using ammonia gas does perform as expected. The high temperature achieved in the transient spray test described in this document was nearer 553 K (280 °C) than 533 K (260 °C), which should have promoted conversion, yet even this did not enable attainment of the Table 4 levels of 42 % and 34 % at steady state in Figure 13.

**Table 4. Approximate conversion (%) of NO in exhaust measurements at steady state using Pd DOC and 5% ammonia gas in nitrogen.**

<b>Temperature &amp; SCR brick length</b>	<b>NH<sub>3</sub>:NO<sub>x</sub> ratio 0.6</b>	<b>NH<sub>3</sub>:NO<sub>x</sub> ratio 1.0</b>
260 °C; 75 mm	42 %	
210 °C; 75 mm		34 %
260 °C; 45 mm	26%	
210 °C; 45 mm		18%

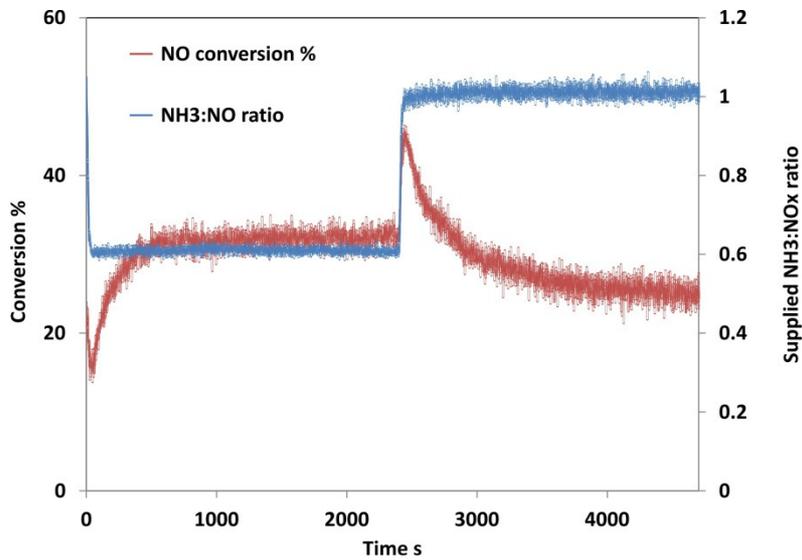


Figure 13. Supplied NH<sub>3</sub>:NO<sub>x</sub> ratio and observed % conversion of NO in the urea spray transient engine load experiment. The SCR catalyst length was 75 mm in this experiment.

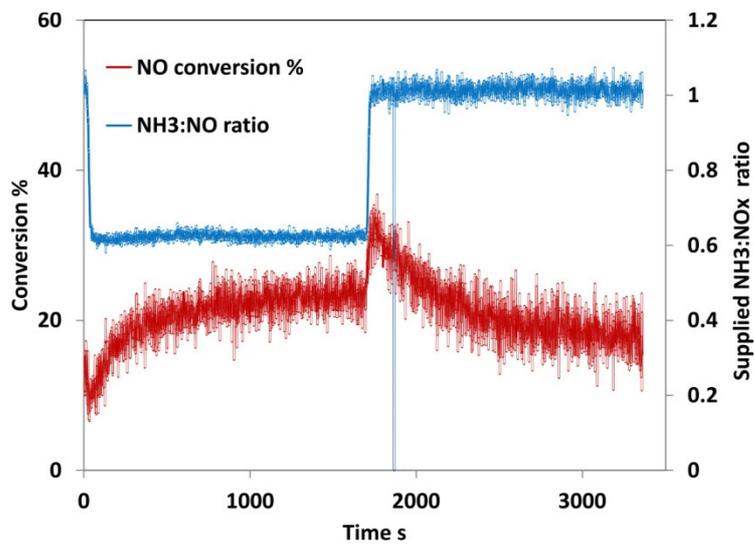


Figure 14. Supplied NH<sub>3</sub>:NO<sub>x</sub> ratio and observed % conversion of NO in ammonia gas transient engine load experiment. The SCR catalyst length was 45 mm in this experiment.

## Summary & Conclusions

An experimental study of SCR in an engine exhaust at low, 210 - 215 °C, and high, 260 - 280 °C, temperature conditions has been performed. These temperatures are typical of Diesel exhaust systems in passenger cars. NO conversion was studied in two types of tests. In the first set of tests the engine load was maintained constant but the dosing of urea was varied through the test. In the second type of test the urea dosing was maintained constant but the engine load was ramped up from 6 to 10 bar bmep bar over 20 s, and after steady state conditions were reached, the load was ramped down over 20 s and the test was continued to reach steady state. NO conversion has been shown to be relatively low in the urea dosing tests, when compared with ammonia gas tests.

In the steady state experiments, less than 15% of the ammonia injected as urea spray was detected by an FTIR gas analyser to be available as ammonia gas upstream of SCR in the experiments. This implied that the majority of the potentially available ammonia was entering the SCR brick as either urea droplets or HCNO under the experimental conditions. The % NO conversion observed in the steady state experiments with urea spray, shown in Figure 9, had a value about 10 % below the % conversion observed in equivalent experiments where the ammonia was supplied as a gas. This was observed in both low and high temperature experiments for  $\alpha$  in the range 0.5 to 1.0, i.e. between deficient ammonia and stoichiometric conditions. Observations showed that a significant amount of ammonia was unaccounted for by ammonia gas measurements made upstream and downstream of an SCR brick under steady state conditions. The deficit was near 20 % of the amount of ammonia known to be injected into the exhaust via an aqueous urea spray into an oblique pipe. An even larger amount was unaccounted for under stoichiometric conditions when the spray was injected into the experimental exhaust via an expansion can. It was inferred that the ammonia was passing through the SCR in the form of HCNO or urea

droplets. The deficit approached 30 % of the potentially available ammonia in the downward engine ramp phase of a transient engine load experiment where the spray was injected via the oblique pipe.

The main conclusion from this study is that it has been demonstrated that ammonia that is potentially available from the spray is unaccounted for in the gaseous emissions measurements in both types of test carried out in this research. These tests were steady state and transient engine load experiments with stoichiometric or deficient levels of urea spray supplied to the exhaust. It is concluded that ammonia entering the exhaust in the form of an aqueous urea spray does pass through the SCR in urea droplet form to emerge downstream in the exhaust. Careful control of the spray dosing would be required to avoid this outcome in real systems.

## **Funding**

EPSRC Grant No. EP/F036175/1 supplied funding for this project.

## **Acknowledgements**

Technical support was received from Jaguar Land Rover plc, Faurecia and Johnson Matthey plc. Robert Gartside of Coventry University provided technical assistance with the engine test measurements.

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