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# **Near-Zero NOx Control for Diesel Aftertreatment**

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Goal Line Environmental Technologies LLC

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# Near-Zero NOx Control for Diesel Aftertreatment

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## ABSTRACT

A two-chamber catalyst system for the aftertreatment of No. 2 Diesel exhaust is demonstrated. NOx conversion efficiencies greater than 95% were obtained over a broad range of operating temperatures and NOx levels. The system incorporates a NOx catalyst (SCONOx™) for the removal of CO, hydrocarbons, and NOx from the exhaust stream and a SO<sub>2</sub> catalyst (SCOSOx™) for the protection of the NOx catalyst from sulfur poisoning. Both catalysts are of sorbate or "trap" type. Hydrogen is used as the reductant and can be supplied by on-board fuel reformers. Tests of the catalysts were performed with various loads, temperatures, and NOx levels. A light-duty diesel engine with no particulate control was used for the tests. All tests were conducted using No. 2 Diesel fuel.

## INTRODUCTION

The diesel engine is fuel efficient due to its lean nature of combustion. Introduction of more lean-burn engines would reduce fossil fuel consumption and CO<sub>2</sub> emissions, which contribute to the greenhouse effect. However, control of NOx in lean exhaust is difficult, and upcoming regulations requiring more stringent NOx control present an obstacle for the introduction of lean-burn engines.

The largest reduction of NOx in lean exhaust has been obtained with sorbate, or "trap", catalysts; however, the susceptibility to sulfur poisoning of sorbate catalysts dramatically reduces catalyst lifetime.<sup>1,2</sup> Although sulfur poisoning can be reduced by moving to sulfur-free fuels, the incremental fuel cost required to remove the sulfur is high, and the additional burden on global economies would present another obstacle to lean-burn engine operation.

We present a sorbate catalyst system that dramatically reduces the effect of sulfur poisoning on a NOx sorbate catalyst. The system uses a SO<sub>2</sub> sorbate catalyst (SCOSOx™) and a NOx sorbate catalyst (SCONOx™). Sulfur poisoning is diminished by the removal of SO<sub>2</sub> with the SO<sub>2</sub> catalyst from the exhaust upstream of the NOx

sorbate catalyst. Both SCOSOx™ and SCONOx™ catalysts were originally developed for gas turbine applications where they have been declared Lowest Achievable Emission Rate and Best Available Control Technology for gas turbines in 1997 and 1998 by the U. S. EPA.<sup>3</sup>

## DIESEL AFTERTREATMENT SYSTEM DESCRIPTION

The diesel aftertreatment system is a two-chamber device. Each chamber of the device contains a SO<sub>2</sub> sorbate catalyst (SCOSOx™) upstream of a NOx sorbate catalyst (SCONOx™). Both catalysts are of sorbate type and periodically need to be regenerated. Typically, one chamber is "on-line" treating the main exhaust flow while the other chamber is regenerated "off-line". Valves control the flow of exhaust and regeneration gases. A diagram of the system is shown in Figure 1.

Aftertreatment of the exhaust begins with the SO<sub>2</sub> catalyst where SO<sub>2</sub>, SO<sub>3</sub>, and H<sub>2</sub>S are sorbed. The exhaust then flows over the NOx catalyst where NO<sub>2</sub> is sorbed; NO is converted to NO<sub>2</sub> prior to sorption. Both catalysts convert CO to CO<sub>2</sub> and destruct hydrocarbons and volatile organic compounds. At some point the catalysts sites become saturated with SO<sub>2</sub> and NOx and slippage of SO<sub>2</sub> and NOx begins. At that point the catalysts require regeneration.

Regeneration occurs by passing a low flow of net-reducing gas over the catalysts; typical flow rates are 1-15% of the main exhaust flow rate. During regeneration, the NOx sorbed on the NOx catalyst is reduced and released as N<sub>2</sub>, and the SO<sub>2</sub> sorbed on the SO<sub>2</sub> catalyst is released as SO<sub>2</sub>. The direction of the regeneration gas flow is reversed from the main exhaust flow so that the SO<sub>2</sub> emitted from the SO<sub>2</sub> catalyst will not come into contact with the NOx catalyst. The regeneration exhaust is bypassed around the catalyst chambers and reinserted into the exhaust line downstream. The use of an SO<sub>2</sub> sorbing cartridge in the bypass line would enable the removal of SO<sub>2</sub> from the exhaust; however, this technique has not yet been demonstrated.

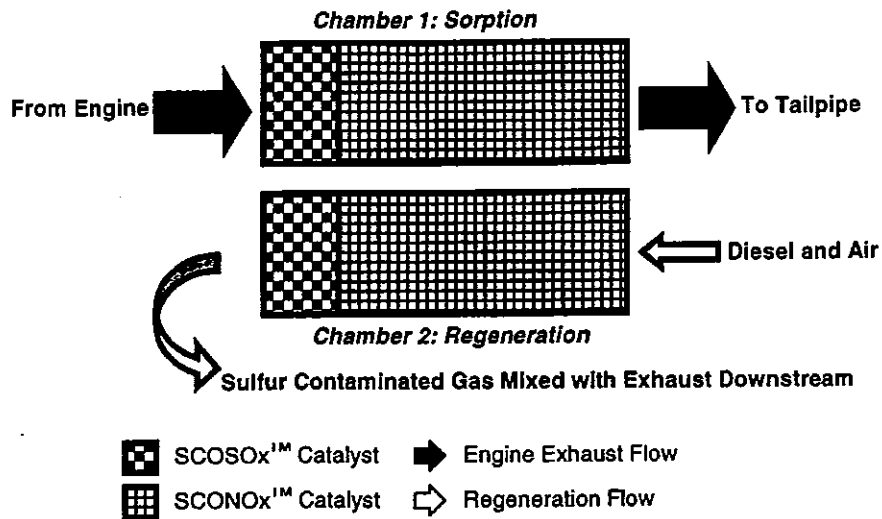


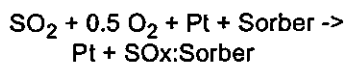
Figure 1. Diagram of the two-chamber system for diesel aftertreatment.

Hydrogen is used as the reductant which may be supplied by on-board fuel reformers. The use of on-board fuel reformers has not been demonstrated yet; however, regeneration with simulated reformer gases has been demonstrated. Diesel fuel can also be used as the reductant; bench scale studies have demonstrated regeneration with No. 2 Diesel.

### BENCH SCALE EXPERIMENTS

Development of catalyst applications begins on bench scale reactors. Catalyst chemistries and some initial results obtained from bench scale experiments will be presented here to demonstrate the catalytic effects. The bench scale results were obtained from a small (typically 15-30 cc) monolith based catalyst that is heated in a reactor with an electric furnace. Gases are passed over the catalyst and analyzed with standard analyzers.

**SULFUR SORBATE CATALYST - SCOSOx™** – The SO<sub>2</sub> catalyst is a precious metal sorbate catalyst with a proprietary sorber. The formulation of the SO<sub>2</sub> catalyst can be adjusted to release the sulfur as SO<sub>2</sub>, H<sub>2</sub>S, or a mixture of the two. The SO<sub>2</sub> releasing formulation is being used for this application. The chemistry of the sorption stage of operation is:



The chemistry of a typical regeneration reaction is:

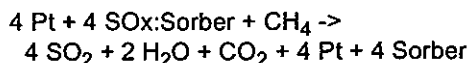


Figure 2 shows typical sorption and regeneration data obtained with the SO<sub>2</sub> catalyst on a bench scale reactor. Here the SO<sub>2</sub> catalyst has been isolated to demonstrate performance. A stream with 60 ppm SO<sub>2</sub> was passed over the catalyst; the data show the catalyst removing the SO<sub>2</sub> from the stream and then releasing the SO<sub>2</sub> during

regeneration. The conditions for the experiment were 30,000/hr space velocity and 260°C. The 60 ppm SO<sub>2</sub> inlet level was reduced to 1 ppm SO<sub>2</sub> by the catalyst; thus, 98.3% of the SO<sub>2</sub> was removed from the stream.

Regeneration was accomplished with a 4% H<sub>2</sub> gas at a space velocity of 8,000/hr. Since the flow rate during regeneration is relatively low and reduction occurs rapidly relative to sorption, the emission of SO<sub>2</sub> occurs as a concentrated peak; however, the net SO<sub>2</sub> sorbed and released is the same. The mass balance for the data shown is 99.3%.

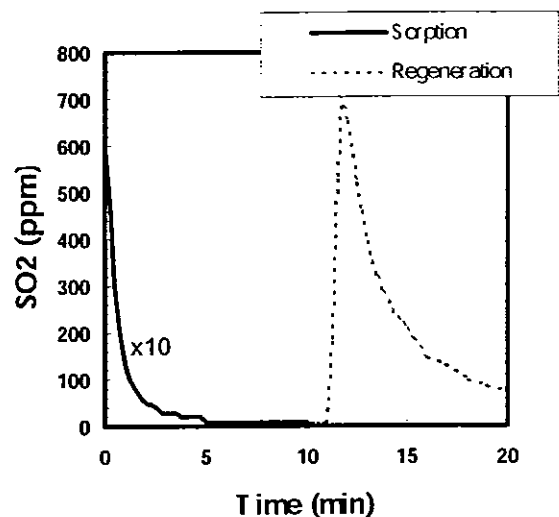
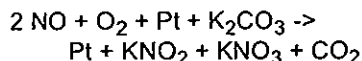


Figure 2. Bench scale data showing SO<sub>2</sub> removal and release with the SO<sub>2</sub> sorbate catalyst.

**NOx SORBATE CATALYST - SCONOx™** – The NOx sorbate catalyst is also a precious metal catalyst. The standard sorber agent is K<sub>2</sub>CO<sub>3</sub>, but many other sorber components can be used. The K<sub>2</sub>CO<sub>3</sub> forms KNO<sub>2</sub> and KNO<sub>3</sub> during sorption, and regeneration reduces the KNO<sub>2</sub> and KNO<sub>3</sub> to KOH. Sorption of CO<sub>2</sub> reverts the

potassium back to carbonate form. The chemistry of the sorption stage of operation is:



The chemistry of a typical regeneration reaction is:

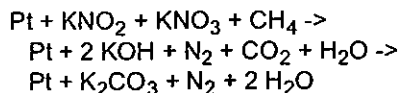


Figure 3 shows sorption data obtained with the NOx catalyst exposed to diesel exhaust on a bench scale reactor. The catalyst temperature was held constant at 315°C while diesel exhaust was passed over the catalyst. The diesel exhaust was supplied from the same engine set-up described below, but only a small portion of the exhaust was carried to the bench scale reactor via heated line. A particulate filter was used to protect the heated line. The load of the engine was varied to obtain the three different catalyst NOx inlet levels (250, 905, and 1975 ppm) shown. The space velocity was 12,300/hr for the NOx catalyst; a SO<sub>2</sub> catalyst was placed upstream of the NOx catalyst for sulfur protection (space velocity of 49,200/hr).

The NOx outlet concentration dropped dramatically for all three NOx inlet levels shown in Fig. 3; at 1 minute the NOx conversion was greater than 98% for all three NOx levels. As expected, the time that the NOx outlet level remained low was inversely proportional to the NOx inlet level; higher NOx levels cause more rapid saturation of the NOx sorbing sites. Despite the large differences between the time required for saturation, the total amount of NOx sorbed was similar (standard variance of 8.7%) for each NOx inlet level.

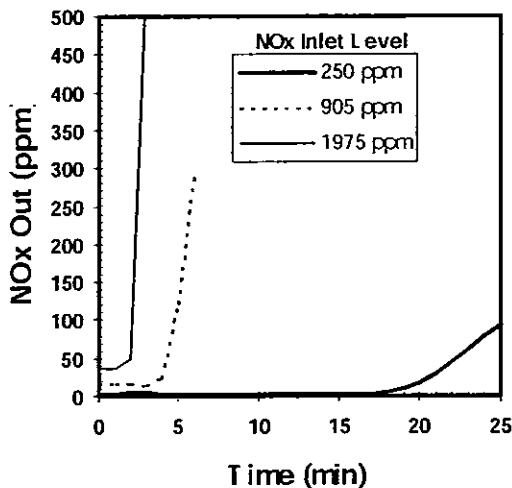


Figure 3. Bench scale data showing NOx removal from diesel exhaust with three different NOx levels.

**REGENERATION WITH DIESEL VAPOR** – Although the majority of testing to-date has been with reduction by hydrogen, diesel fuel can serve as the reductant, too. Figure 4 shows a comparison of NOx sorption performance after regeneration with hydrogen and diesel vapor

(No. 2 Diesel). The data was obtained on a bench scale reactor with a NOx inlet level of 70 ppm. The catalyst temperature was 315°C. The diesel vapor was delivered to the catalyst with a syringe pump; the carrier was N<sub>2</sub>. The performance for both reductants is comparable with hydrogen reduction being slightly better. The hydrocarbon:NOx ratio required for regeneration was 1.4.

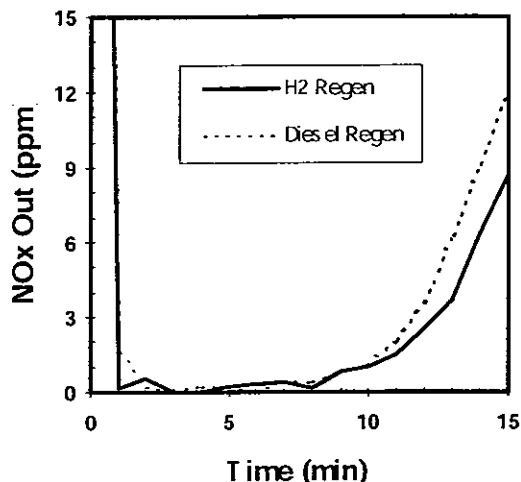


Figure 4. Bench scale data showing a comparison of NOx removal after regeneration with hydrogen and diesel vapor.

## ENGINE TEST DESIGN

The diesel aftertreatment system was tested on a light-duty platform. A 3.9 liter turbo-assisted diesel engine (Cummins 4B3.9T) produced the exhaust for testing. No particulate control or other exhaust treatment was used. The engine was attached to a generator as a gen-set, and load was applied to the engine with a resistive load bank. The engine speed was held constant. The exhaust temperature and NOx level varied with engine load.

No. 2 Diesel was used for all of the tests; thus, SO<sub>2</sub> levels in the exhaust were typically 12 to 30 ppm. Typical NOx levels ranged from 250 to 2250 ppm. CO levels were typically 100 to 700 ppm. The space velocity of the NOx catalyst was 11,800/hr, and the space velocity of the SO<sub>2</sub> catalyst was 45,700/hr.

The system was tested using a regeneration gas that simulated gases expected with on-board fuel reformers. The simulated reformer regeneration gas was 4% H<sub>2</sub> in a N<sub>2</sub> carrier; regeneration space velocities were 1,400/hr and 5,400/hr for the NOx and SO<sub>2</sub> catalysts, respectively.

## ENGINE TEST RESULTS

Figure 5 shows NOx and SO<sub>2</sub> catalyst performance data on the diesel engine system. For the data shown the gas sample was collected on the downstream side of one of the system chambers during the sorption cycle for that

chamber. Thus, the sorption performance of the catalysts was isolated. The engine load was 25 kW. The exhaust temperature was 222°C, and the inlet NO<sub>x</sub>, CO, and SO<sub>2</sub> levels were 890 ppm, 148 ppm, and 15 ppm, respectively. The catalyst outlet CO and SO<sub>2</sub> levels are near zero and near the detection limits of the analyzers throughout the 15 minute sorption period. The NO<sub>x</sub> level is dramatically reduced from the 890 ppm inlet level. The NO<sub>x</sub> level does rise with time due to the start of catalyst site saturation.

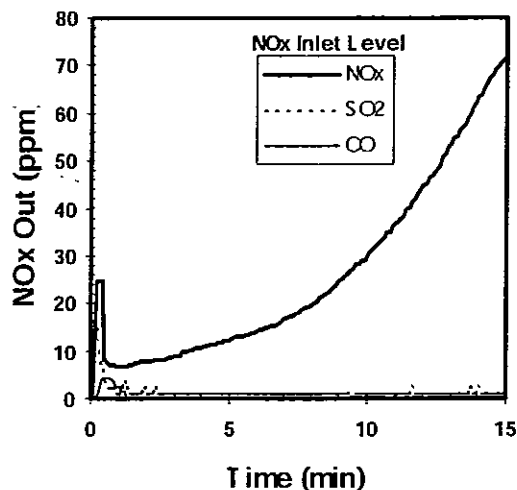


Figure 5. Exhaust gas downstream of one chamber of the system collected during the sorption cycle. The exhaust temperature was 222°C; the engine load was 25 kW. The NO<sub>x</sub>, SO<sub>2</sub>, and CO inlet levels were 890, 15, and 148 ppm, respectively. SO<sub>2</sub> and CO are removed to near zero levels;

Figure 6 shows the regeneration period immediately after the sorption period shown in Fig. 5. The regeneration gas sample was obtained from the system by-pass line that allows the regeneration exhaust to be mixed with the main exhaust downstream of the catalysts. Thus, the high concentrations shown in Fig. 6 are a direct result of the low flow of gas used in regeneration. Recall that the flow of regeneration gas is in a reversed direction from the main exhaust flow. The regeneration exhaust shows some NO<sub>x</sub> emitted during regeneration of the NO<sub>x</sub> catalyst. After the NO<sub>x</sub> catalyst regeneration is complete (just before 5 minutes), regeneration of the SO<sub>2</sub> catalyst begins. The level of CO in the regeneration exhaust is zero with the exception of a small CO peak at the beginning of the regeneration period due to the untreated CO in the volume of gas trapped between the catalyst and main valve when regeneration begins. A similar peak occurs for NO<sub>x</sub>.

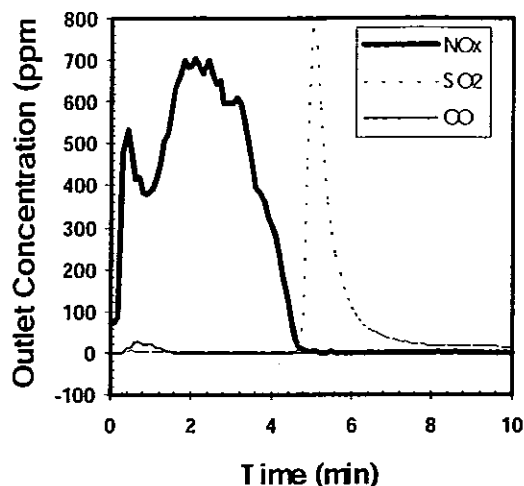


Figure 6. Regeneration exhaust sample taken from the by-pass line. Note that the low flow of gas used for regeneration results in high NO<sub>x</sub> concentrations, but the NO<sub>x</sub> mass contribution to total emissions from regeneration is small. The presence of sharp SO<sub>2</sub> peaks indicates that SO<sub>2</sub> is being released from the SO<sub>2</sub> catalyst during regeneration. Test conditions were the same as for Fig. 5 data.

Figure 7 shows data obtained downstream of the system. Here the sorption and regeneration exhaust gases from both chambers are combined to produce the system exhaust. Only NO<sub>x</sub> and SO<sub>2</sub> are shown since CO levels were near zero, and the NO<sub>x</sub> data is offset by 40 ppm to show the SO<sub>2</sub> data more clearly. The conditions for the experiment are the same used for Figs. 5 and 6; however, 5-minute sorption and regeneration cycles were used. A combination of the effects from Figs. 5 and 6 is shown in the Fig. 7 data. The NO<sub>x</sub> and SO<sub>2</sub> peaks occur from the NO<sub>x</sub> and SO<sub>2</sub> emitted in regeneration. The size of the SO<sub>2</sub> peak increases with size due to an increase in catalyst temperature during the run. The NO<sub>x</sub> and CO conversions obtained in the data were 97.5% and 98.1%, respectively.

NO<sub>x</sub> conversion as a function of temperature is shown in Figure 8. The data was obtained by varying engine load; engine out NO<sub>x</sub> level (listed on the plot) and exhaust temperature increased with increasing load. The data was obtained with 5-minute sorption and regeneration cycles; the total NO<sub>x</sub> conversions given were obtained over a 20-minute interval. The peak NO<sub>x</sub> conversions represent the minimum catalyst out NO<sub>x</sub> level occurring in the 5-minute cycle. The decrease in NO<sub>x</sub> conversion at the higher temperatures (>250°C) occurred due to catalyst saturation from the higher NO<sub>x</sub> levels. The peak NO<sub>x</sub> conversion represents the potential NO<sub>x</sub> conversions that could be obtained by using shorter sorption and regeneration cycles.

CO conversion as a function of temperature is shown in Figure 9. The CO conversion is excellent over the entire temperature range. The engine out CO levels are listed; 5-minute sorption and regeneration cycles were used.

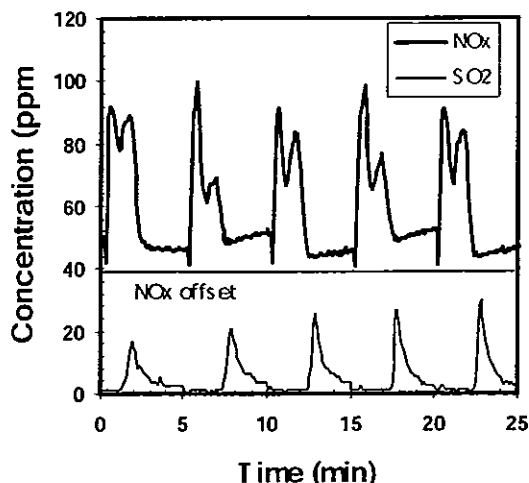


Figure 7. Typical emission profile obtained downstream of the catalyst system. Test conditions were the same as for Fig. 5 data. The outlet CO level was near zero and not shown.

### CONCLUSION

The use of a SO<sub>2</sub> sorbate catalyst to protect a NO<sub>x</sub> sorbate catalyst from sulfur poisoning has been demonstrated on a diesel engine system running on No. 2 Diesel. The catalyst system utilizes a two-chamber design to efficiently reduce the catalysts. By taking the

catalysts off-line during regeneration, the complications of reduction in the oxygen-rich diesel exhaust have been avoided. Excellent NO<sub>x</sub> and CO conversions have been obtained over a wide temperature range. Although hydrogen was used as the reductant for the engine tests, regeneration of the catalysts with diesel vapor has been demonstrated on a bench scale reactor.

### ACKNOWLEDGMENTS

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3. US Patents 5451558, 5599758, 5607650, 5650127, 5665321, and 5762885.

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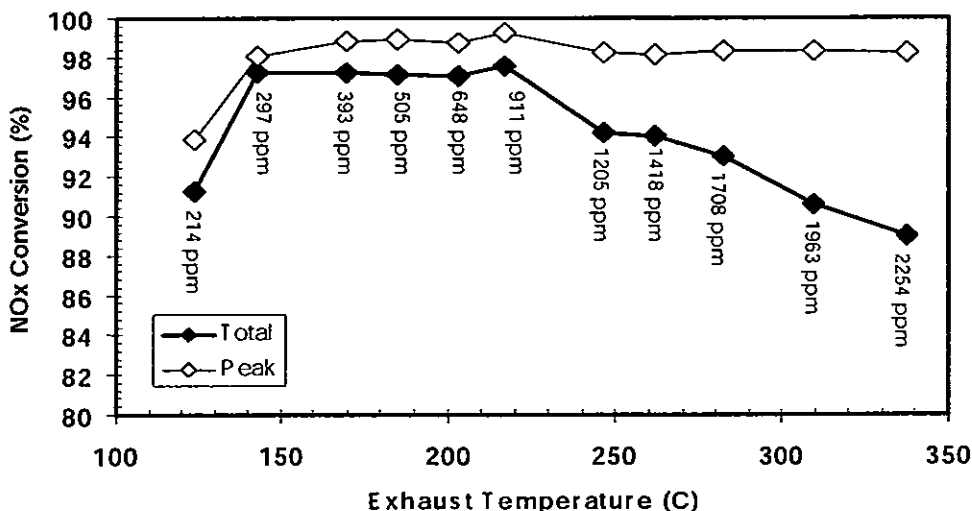


Figure 8. NO<sub>x</sub> conversion as a function of temperature. The NO<sub>x</sub> inlet levels for each data point are listed. Total conversions represent the average conversion over a 20-minute steady-state test; 5-minute cycles were used. Peak conversions represent the minimum catalyst out NO<sub>x</sub> level obtained during the 5-minute cycle.

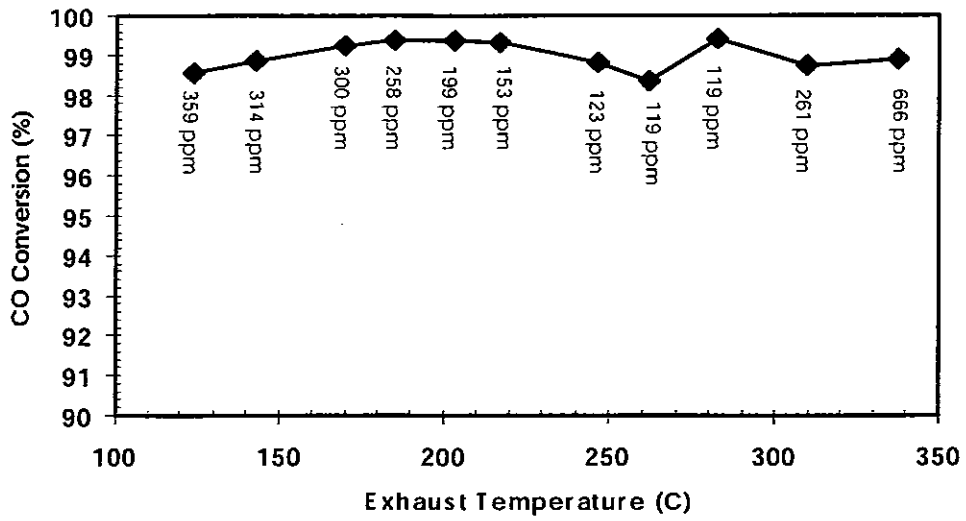


Figure 9. CO conversion as a function of temperature. The temperature was varied by varying engine load. The CO inlet level varied with load and temperature and is shown for each data point.