

Environmental applications of low-temperature plasmas*

B. M. Penetrante†, R. M. Brusasco, B. T. Merritt and G. E. Vogtlin

Lawrence Livermore National Laboratory, Livermore, California 94550, USA

Abstract: Treatment of NO_x in diesel engine exhaust represents a big opportunity for the environmental application of low-temperature plasmas. This paper discusses the effect of gas composition on the NO_x conversion chemistry in a plasma. It is shown that the plasma by itself cannot chemically reduce NO_x to N_2 in the highly oxidizing environment of a diesel engine exhaust. To implement the reduction of NO_x to N_2 , it is necessary to combine the plasma with a heterogeneous process that can chemically reduce NO_2 to N_2 . Data is presented that demonstrates how the selective partial oxidation of NO to NO_2 in a plasma can be utilized to enhance the selective reduction of NO_x to N_2 by a catalyst.

INTRODUCTION

Governments are becoming more conscious of the need to protect the environment and the need to conserve energy. The increasing consumption of fossil energy resources, for both stationary electrical power and transportation, has led to greater environmental pollution. The world demands better technologies that can increase the efficient use of energy but without the harmful effect of increased pollution.

In the field of catalysis, one application that has been classified as a breakthrough technology is the catalytic reduction of NO_x in oxygen-rich environments using hydrocarbons [1]. This breakthrough will require dramatic improvements in both catalyst and engine technology, but the benefits will be substantial for energy efficiency and a cleaner environment. Engine and automobile companies are placing greater emphasis on the diesel engine because of its potential for saving fuel resources and reducing CO_2 emissions. The modern direct-injection diesel engine offers demonstrated fuel economy advantages unmatched by any other commercially viable engine. The main drawback of diesel engines is exhaust emissions. A modification of existing oxidation catalyst/engine technology is being used to address the CO , hydrocarbon and particulates. However, no satisfactory solution currently exists for NO_x . Diesel engines operate under net oxidizing conditions, thus rendering conventional three-way catalytic converters ineffective for controlling the NO_x emission. NO_x reduction catalysts, using ammonia as a reductant, do exist for oxygen-rich exhausts; however, for transportation applications, the use of on-board hydrocarbon fuels is a more feasible, cost-effective, and environmentally sound approach.

Low-temperature plasmas have been shown to be effective for treating dilute concentrations of pollutants in large-volume atmospheric-pressure air streams [2]. Either electron beam or electrical discharge methods can produce low-temperature plasmas. The plasma is low-temperature in the sense that the gas remains at the ambient exhaust temperature, but the electrons have sufficient kinetic energies to produce reactive free radicals, ions and secondary electrons from electron-impact reactions. Compared to conventional catalysis, the use of a plasma has the disadvantage of requiring electrical energy. An understanding of the plasma chemistry serves as an important design tool for minimizing the electrical energy consumption of the process and identifying the process products [3].

*Lecture presented at the 14th International Symposium on Plasma Chemistry, Prague, Czech Republic, 2–6 August 1999, pp. 1809–1918.

†Corresponding author: E-mail: penetrante1@LLNL.GOV

Much work has been done on the application of plasmas to the treatment of NO_x from power plants [2]. In power plant applications, the purpose of the plasma is to oxidize NO to NO_2 , and eventually to nitric acid. The desired products, in the form of ammonium salts, are then obtained by mixing ammonia with the formed acids. Some form of scrubbing is required to collect the final products. For applications to the treatment of exhausts from cars and trucks, it is very important to make a distinction between NO removal by chemical oxidation and NO removal by chemical reduction. To avoid the need for scrubbing of plasma processing products, the desired method of NO removal is by chemical reduction, i.e. the conversion of NO to benign gaseous products like N_2 .

The objective of this paper is to examine the fate of hydrocarbons and NO_x during plasma processing of an oxygen-rich engine exhaust (often referred to as lean-burn exhaust). This study illustrates the value of understanding the plasma chemistry in order to establish the feasibility of using low-temperature plasmas for treating emissions from internal-combustion vehicles. This paper discusses the effect of gas composition on the NO_x conversion chemistry in a plasma. It is shown that the plasma by itself cannot chemically reduce NO_x to N_2 in the highly oxidizing environment of a diesel engine exhaust. To implement the reduction of NO_x to N_2 , it is necessary to combine the plasma with a heterogeneous process that can chemically reduce NO_2 to N_2 . Data is presented that demonstrates how the selective partial oxidation of NO to NO_2 in a plasma can be utilized to enhance the selective reduction of NO_x to N_2 by a catalyst.

NO_x CONVERSION CHEMISTRY IN THE PLASMA

Oxidation is the dominant process in the plasma for exhausts containing dilute concentrations of NO in mixtures of N_2 , O_2 and H_2O , particularly when the O_2 concentration is 5% or higher. The kinetic energy of the electrons is deposited primarily into the major gas components, N_2 and O_2 . The most useful deposition of energy is associated with the production of N and O radicals through electron-impact dissociation:



where $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$ are ground-state and metastable excited-state nitrogen atoms, respectively, and $\text{O}(^3\text{P})$ (simply referred to as O) and $\text{O}(^1\text{D})$ are ground-state and metastable excited-state oxygen atoms, respectively. The $\text{N}(^4\text{S})$ is the only plasma-produced species that could effectively lead to the chemical reduction of NO [4,5]:



In the presence of O_2 , the oxidation pathway becomes dominant for two reasons:

(a) The dissociation energy of O_2 is smaller than that of N_2 . For electrical discharge plasma reactors, the average electron kinetic energy is low, around 3–6 eV [6–8]. Under this condition the rate for electron-impact dissociation of O_2 is much higher compared to that of N_2 . The dissociation of O_2 will produce only oxidative radicals. The ground-state oxygen atom, $\text{O}(^3\text{P})$, will convert NO to NO_2 via



The metastable oxygen atom, $\text{O}(^1\text{D})$, will react with H_2O to produce OH radicals:



The OH radicals will convert NO and NO_2 to nitrous and nitric acid, respectively.

(b) High electron energies are required to optimize the production of $\text{N}(^4\text{S})$ by electron-impact dissociation of N_2 . Under conditions optimum for the dissociation of N_2 , a large number of excited nitrogen atoms, $\text{N}(^2\text{D})$, is produced [9,10]. The $\text{N}(^2\text{D})$ species can lead to undesired reactions in the presence of O_2 . Rather than reduce NO, the $\text{N}(^2\text{D})$ species would react with O_2 to produce NO:



Because of the large rate constant [11] for reaction (7) and the large concentration of O_2 relative to NO, the $N(^2D)$ species preferentially reacts with O_2 to produce NO. In an oxygen-rich exhaust, the production of NO by $N(^2D)$ will counterbalance the reduction of NO by $N(^4S)$, thus effectively leaving oxidation as the only pathway for NO conversion.

The number of NO molecules converted to NO_2 is determined by the number of O radicals produced by the plasma, not by the initial NO concentration. The number of O radicals is determined only by the energy density input to the plasma. The efficiency for oxidation of NO to NO_2 drops as the temperature is increased. At high temperatures, the NO to NO_2 oxidation reaction is counteracted by the reduction reaction:



Because of reaction (8), the oxidation of NO by the O radical is not efficient at high temperatures.

At typical engine exhaust temperatures, the efficiency for conversion of NO to NO_2 is very poor in the absence of hydrocarbons in the gas stream. Figure 1a shows a comparison of our experiment to our chemical kinetics model for the case of plasma processing of 500 p.p.m. NO in 10% O_2 , balance N_2 at 300 °C, without any hydrocarbon. Even with high electrical energy input, the maximum oxidation of NO to NO_2 in the plasma at 300 °C is only 10%. Back-conversion of NO_2 to NO by the O radical is responsible for the low oxidation efficiency.

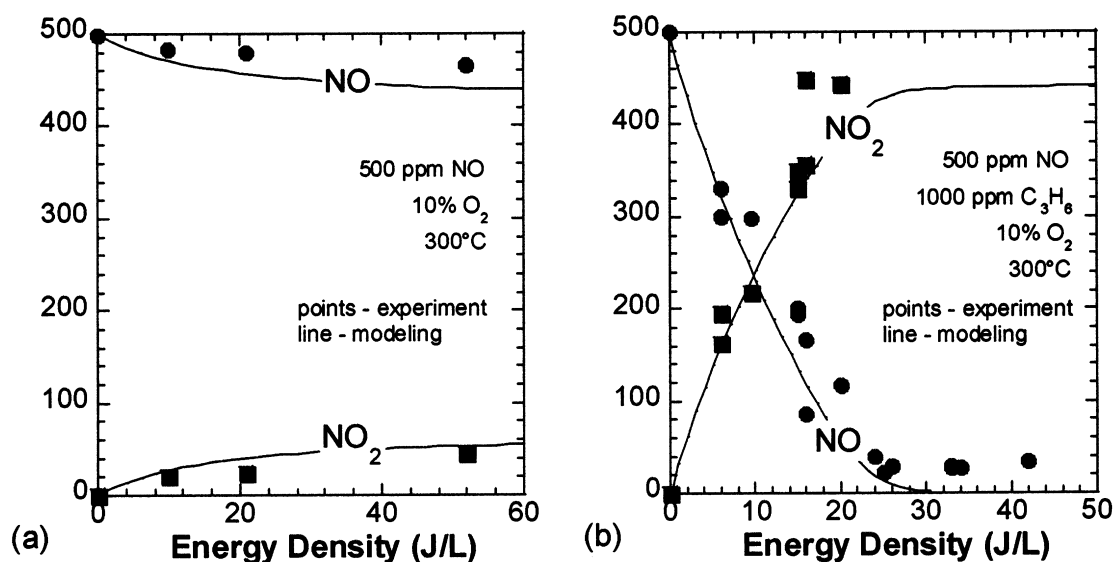


Fig. 1 Plasma processing of: (a) 500 p.p.m. NO in 10% O_2 , balance N_2 at 300 °C, and (b) 500 p.p.m. NO, 1000 p.p.m. C_3H_6 in 10% O_2 , balance N_2 at 300 °C.

The effect of hydrocarbons on the oxidation of NO is the key to making the plasma process electrically efficient. Figure 1b shows a comparison of our experiment to our chemical kinetics model for the case of plasma processing of 500 p.p.m. NO in 10% O_2 , balance N_2 at 300 °C, with 1000 p.p.m. C_3H_6 . Note the dramatic increase in NO oxidation efficiency. The O radicals that normally would react with NO or NO_2 are now consumed in reactions with C_3H_6 .

Consider, for example, the following $O + C_3H_6$ reaction:



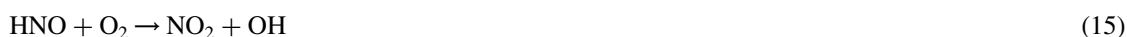
The H would quickly be converted to the strong oxidizing radical HO_2 upon reaction with O_2 :



and then oxidize NO:



Similarly, the CH₃ will react with O₂, followed by a series of reactions that effectively oxidize NO to NO₂:



The OH radical would in turn break up more C₃H₆ molecules and lead to additional hydrocarbon radicals that could oxidize more NO to NO₂. Thus, in the presence of hydrocarbons, one O radical could initiate the oxidation of many NO molecules. Furthermore, the O radical will be prevented from back-converting NO₂ to NO. Nearly all the O atoms for conversion are supplied by electron impact, which has an associated cost in electrical energy. The hydrocarbon lowers the energy requirement by production of HO₂ radicals that then become the main radical for conversion of NO to NO₂.

PLASMA-ASSISTED CATALYTIC REDUCTION OF NO_x

Selective catalytic reduction (SCR) by hydrocarbons [12] is one of the leading catalytic after-treatment technologies for the reduction of NO_x in lean-burn engine exhaust (often referred to as ‘lean-NO_x’). The objective is to chemically reduce the pollutant molecules of NO_x to N₂. After-treatment schemes have focused a great deal on the reduction of NO because the NO_x in engine exhaust is composed primarily of NO. However, catalyst studies have shown that the oxidation of NO to NO₂ serves an important role in enhancing the efficiency for reduction of NO_x to N₂ [13–21]. It has become apparent that preconverting NO to NO₂ could improve both the efficiency and durability of lean-NO_x catalysts. As we have shown in the previous section, a low-temperature plasma can be an efficient means for selective partial oxidation of NO to NO₂. The use of a low-temperature plasma in combination with a lean-NO_x catalyst opens the opportunity for catalysts that are more efficient and more durable compared to conventional catalysts [22].

The plasma-assisted catalytic reduction of NO_x is accomplished in essentially two steps. First, the plasma oxidizes NO to NO₂ in the presence of a hydrocarbon:



where HC refers to a hydrocarbon and HC-products refers to partially oxidized hydrocarbons. Second, the catalyst reduces NO₂ to N₂ by selective reduction using the hydrocarbons:



Figure 2 is a schematic of a plasma-assisted catalyst processor. There are many ways of producing a low-temperature plasma. The schematic shown in Fig. 2 shows a pulsed corona plasma produced by short pulses of high voltage on a metal wire inside a metallic cylinder. Although we have used a pulsed corona reactor, this type of reactor is not necessarily the only type that produces the same effect. It can be used with any type of plasma reactor and does not require a specific type of high-voltage power supply. All electrical discharge plasma reactors accomplish essentially the same gas-phase plasma chemistry for the same gas mixture [6–8,23]. In Fig. 2 the plasma reactor is located upstream of the catalyst reactor. The same result is achieved if the catalyst is placed inside the plasma reactor.

Figure 3 shows Fourier transform infrared (FTIR) spectra illustrating the effect of catalyst, plasma and plasma-plus-catalyst combination on the NO_x and hydrocarbons. In this example, propene is used as the hydrocarbon reductant. When the electrical power to the plasma reactor is turned off and the gas mixture is passed through the catalyst, the efficiencies for both the NO_x reduction and the hydrocarbon oxidation are very low, as shown in the second box (‘catalyst only’). When the electrical power to the plasma reactor is turned on, the NO is oxidized to NO₂ and the propene is partially oxidized to formaldehyde, as shown in the third box (‘plasma only’). When the NO₂-containing gas stream from the plasma is then passed through the same catalyst, both the NO_x and the hydrocarbons are eliminated, as shown in the bottom box (‘plasma + catalyst’). The plasma-plus-catalyst combination efficiently removes NO_x and hydrocarbons under conditions in which the plasma or the catalyst alone is ineffective.

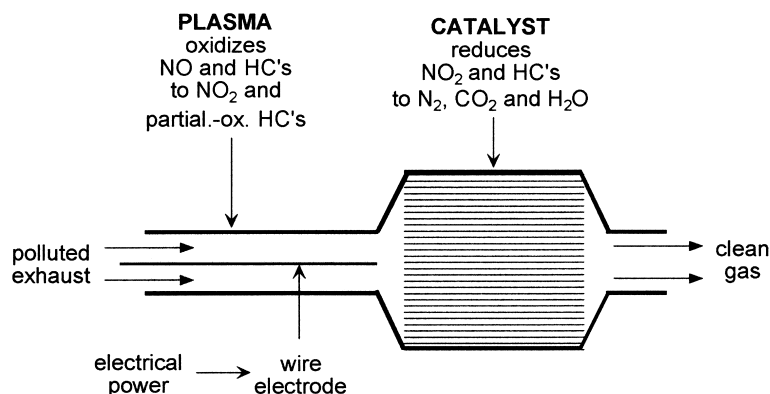


Fig. 2 The plasma-assisted catalytic reduction process. US patents: no. 5711 147, no. 5891 409 and no. 5893 267.

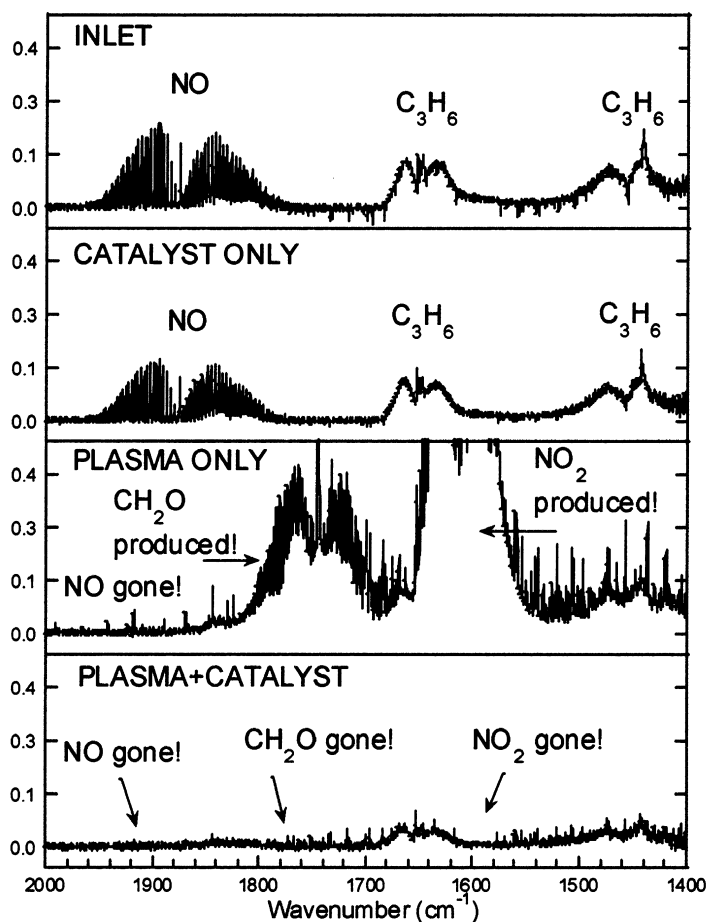


Fig. 3 Fourier Transform Infrared (FTIR) spectroscopy data showing the effect of catalyst, plasma and plasma-plus-catalyst combination on the NO_x and hydrocarbons.

There is a heated debate between engine and oil companies over the need to reduce sulfur in the fuel so that catalyst technologies can efficiently reduce tailpipe emissions of NO_x . State-of-the-art lean- NO_x catalysts require precious metals (e.g. platinum) to convert NO_x to N_2 with high efficiency, particularly at the relatively low temperatures (300°C and below) of diesel engine exhaust. In addition to oxidizing NO to NO_2 , the precious metal is very effective in oxidizing SO_2 to SO_3 . The SO_3 forms sulfate on the catalyst sites, leading to degradation of the NO_x reduction. The SO_3 also leads to the production of sulfuric acid,

which adds to particulate emission. Furthermore, the precious metal is also very active in the oxidation of the hydrocarbons; this results in a decrease in the availability of the hydrocarbon as a reductant for NO_x .

Plasma-assisted catalysis can efficiently reduce NO_x without requiring precious metals or low-sulfur fuel. The plasma oxidizes NO to NO_2 , but does not oxidize SO_2 to SO_3 . This makes the plasma-assisted process more tolerant to the sulfur content of fuel compared to conventional lean- NO_x technologies [24]. Furthermore, in a plasma, the hydrocarbons are converted to partially oxygenated hydrocarbons, but not completely oxidized to CO_x and H_2O . For some catalysts, the partially oxygenated hydrocarbons could be more effective compared to the original hydrocarbons in reducing NO_x to N_2 . The plasma can efficiently oxidize NO to NO_2 over a wide range of temperature without depleting the amount of hydrocarbon available for reduction of NO_x to N_2 .

CONCLUSIONS

The diesel engine is the most commercially viable technology for reducing fuel consumption in the transportation industry. Treatment of NO_x in diesel engine exhaust represents a big opportunity for the environmental application of low-temperature plasmas. A low-temperature plasma by itself cannot chemically reduce NO_x to N_2 in the highly oxidizing environment of a diesel engine exhaust. To implement the reduction of NO_x to N_2 , it is necessary to combine the plasma with a heterogeneous process that can chemically reduce NO_2 to N_2 . The selective partial oxidation of NO to NO_2 in a plasma can be utilized to enhance the reduction of NO_x to N_2 by a catalyst. One of the approaches currently offering the greatest hope of reducing NO_x in diesel exhaust is a catalyst working in conjunction with a low-temperature plasma.

ACKNOWLEDGEMENTS

This work was performed at Lawrence Livermore National Laboratory under the auspices of the US Department of Energy under Contract Number W-7405-ENG-48, with support from the Chemical Sciences Division of the DOE Office of Basic Energy Sciences, the DOE Office of Fossil Energy, the DOE Office of Transportation Technologies, the Strategic Environmental Research and Development Program, and a Cooperative Research and Development Agreement with Cummins Engine Company.

REFERENCES

- 1 R. M. Heck, R. J. Farrauto. Breakthrough catalytic technologies: the future. In *Catalytic Air Pollution Control: Commercial Technology*, Chap. 12. Van Nostrand Reinhold, New York (1995).
- 2 B. M. Penetrante, S. E. Schultheis, eds. Non-thermal plasma techniques for pollution control, Part, A. Overview. Fundamentals and supporting technologies, Part B. In *Electron Beam and Electrical Discharge Processing*. Springer-Verlag, Berlin/Heidelberg (1993).
- 3 B. M. Penetrante, M. C. Hsiao, J. N. Bardsley, B. T. Merritt, G. E. Vogtlin, A. Kuthi, C. P. Burkhart, J. R. Bayless. *Plasma Sources Sci. Technol.* **6**, 251 (1997).
- 4 B. M. Penetrante, J. N. Bardsley, M. C. Hsiao. *Jap. J. Appl. Phys.* **36**, 5007 (1997).
- 5 B. M. Penetrante, M. C. Hsiao, B. T. Merritt, G. E. Vogtlin. *Fundamental limits on NO_x reduction by plasma*. SAE Paper 971715 (1997).
- 6 B. M. Penetrante, M. C. Hsiao, B. T. Merritt, G. E. Vogtlin, P. H. Wallman, M. Neiger, O. Wolf, T. Hammer, S. Broer. *Appl. Phys. Lett.* **68**, 3719 (1996).
- 7 B. M. Penetrante, M. C. Hsiao, B. T. Merritt, G. E. Vogtlin, P. H. Wallman, A. Kuthi, C. P. Burkhart, J. R. Bayless. *Appl. Phys. Lett.* **67**, 3096 (1995).
- 8 B. M. Penetrante, M. C. Hsiao, B. T. Merritt, G. E. Vogtlin, P. H. Wallman. *IEEE Trans. Plasma Sci.* **23**, 679 (1995).
- 9 E. C. Zipf, P. J. Espy, C. F. Boyle. *J. Geophys. Res.* **85**, 687 (1980).
- 10 P. C. Cosby. *J. Chem. Phys.* **98**, 9544 (1993).
- 11 K. Schofield. *J. Phys. Chem. Ref. Data* **8**, 723 (1979).
- 12 M. Shelef. *Chem. Rev.* **95**, 209 (1995).
- 13 H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito, M. Tabata. *Appl. Catal.* **70**, L15 (1991).

- 14 J. O. Petunchi, W. K. Hall. *Appl. Catal. B. Environ.* **2**, L17 (1993).
- 15 M. Shelef, C. N. Montreuil, H. W. Jen. *Catal. Lett.* **26**, 277 (1994).
- 16 C. Yokoyama, M. Misono. *J. Catal.* **150**, 9 (1994).
- 17 M. Shimokawabe, A. Ohi, N. Takezawa. *React. Kinet. Catal. Lett.* **52**, 393 (1994).
- 18 Z. Chajar, M. Primet, H. Praliaud, M. Chevrier, C. Gauthier, F. Mathis. *Catal. Lett.* **28**, 33 (1994).
- 19 K. A. Bethke, C. Li, M. C. Kung, B. Yang, *et al.* *Catal. Lett.* **31**, 287 (1995).
- 20 G. R. Bamwenda, A. Ogata, A. Obuchi, H. Takahashi, K. Mizuno. *React. Kinet. Catal. Lett.* **56**, 311 (1995).
- 21 M. Iwamoto, T. Zengyo. *Chem. Lett.* 1283 (1997).
- 22 B. M. Penetrante, R. M. Brusasco, B. T. Merritt, W. J. Pitz, G. E. Vogtlin, M. C. Kung, H. H. Kung, C. Z. Wan, K. E. Voss. Plasma-assisted catalytic reduction of NO_x. SAE paper number 982508. In *Plasma Exhaust Aftertreatment* (J. Hoard, H. Servati, eds). SAE/SP-98/1395, pp. 57–66. Society of Automotive Engineers, Warrendale, PA (1998).
- 23 C. R. McLarnon, B. M. Penetrante. Effect of reactor design on the plasma treatment of NO_x. SAE paper number 982434. In *Plasma Exhaust Aftertreatment* (J. Hoard, H. Servati, eds), SAE/SP-98/1395, pp. 49–55. Society of Automotive Engineers, Warrendale, PA (1998).
- 24 B. M. Penetrante, R. M. Brusasco, B. T. Merritt, G. E. Vogtlin. Sulfur tolerance of selective partial oxidation of NO to NO₂ in a plasma. SAE paper number 1999-01-3687. Society of Automotive Engineers, Warrendale, PA (1999).