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PLASMA AFTERTREATMENT FOR SIMULTANEOUS CONTROL OF NO_x AND PARTICULATES

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Abstract

Plasma reactors can be operated as a particulate trap or as a NO_x converter. The soluble organic fraction (SOF) of the trapped particulates can be utilized for the oxidation of NO to NO₂. The NO₂ can then be used to non-thermally oxidize the carbon fraction of the particulates. This paper examines the energy density required for oxidation of the SOF hydrocarbons and the fate of NO₂ during the oxidation of the particulate carbon. The energy density required for complete oxidation of the SOF hydrocarbons is shown to be unacceptably large. The reaction of NO₂ with carbon is shown to lead mainly to backconversion of NO₂ to NO. These results suggest that the use of a catalyst in combination with the plasma will be required to efficiently reduce the NO_x and oxidize the SOF hydrocarbons.

Introduction

Plasma reactors can be operated as a particulate trap [ref. 1-3] or as a NO_x converter [ref. 4-7].

Particulate trapping in a plasma reactor can be accomplished by electrostatic precipitation. Corona-type reactors operating as electrostatic precipitators for diesel soot are reported in refs. [1-2]. A ferroelectric pellet bed reactor, also operating as an electrostatic precipitator of diesel soot, is reported in ref. [3]. Plasma-based traps need periodic regeneration just like any other particulate trap. Regeneration by the plasma can be achieved in a thermal mode or a non-thermal mode.

The plasma reactor can be operated occasionally in the arc discharge mode to thermally oxidize the particulates. In ref. [2], this mode is referred to as the self-cleaning phase of the electrostatic muffler. Thermal oxidation of the particulates precipitated on the electrode surface is achieved in very localized regions of high temperature near the tip of the arc microdischarges.

The plasma reactor can also be operated in a non-thermal corona discharge mode to provide continuous oxidation of the particulates. The non-thermal oxidation is presumably accomplished by the O and OH radicals resulting from electron-impact dissociation of oxygen and water vapor molecules, or by negative hydronium cluster ions, [(H₂O)_nO₂⁻], resulting from electron attachment. Ref. [1] observed a self-cleaning effect in the corona mode that correlates with the production of CO and CO₂. Ref. [8] reports on the oxidation of soot in a dielectric-barrier discharge. It was conjectured that OH radicals oxidized the soot; the soot reduction did not occur in the presence of large amounts of CO, presumably because the OH radicals were consumed by CO.

Diesel particulates are composed mainly of the carbon fraction and the soluble organic fraction (SOF). The SOF could possibly be utilized for the oxidation of NO to NO₂ in a plasma. As a NO_x converter, the plasma requires hydrocarbons to achieve high oxidation efficiency with low electrical energy consumption. The NO₂ can then be used to oxidize the carbon fraction, similar to that in a Continuously Regenerated Trap (CRT) [ref. 12]. The use of NO₂ for the oxidation of trapped particulates in CRT devices is fairly well established. In CRT, a precious metal catalyst is used to oxidize NO to NO₂ upstream of a particulate filter. The CRT method requires low sulfur fuel because the catalytic oxidation of NO to NO₂ also leads to the oxidation of SO₂ to SO₃. The use of a plasma for the oxidation of NO to NO₂ can make the process more tolerant to the sulfur content of the fuel. The fate of NO₂ during the oxidation of carbon is important if one contemplates the use of plasma aftertreatment for the simultaneous removal of NO_x and particulates.

This paper examines the energy density required for oxidation of the SOF hydrocarbons and the fate of NO₂ during the oxidation of the particulate carbon.

Results

Both chemical kinetics calculations and experimental measurements are presented in this section. We used propene as the hydrocarbon surrogate in the calculations because the chemical reaction database for propene is more established and facilitates comparison of the modeling to experiments. The plasma reactor used in the experiments is a pulsed corona discharge reactor consisting of a metal wire inside a metal cylinder. The plasma chemistry is not peculiar to this type of plasma processor; all electrical discharge plasma reactors accomplish essentially the same gas-phase plasma chemistry under the same gas conditions [ref. 9-10]. The important control parameter in the plasma reactor is the electrical energy density delivered to the plasma [ref. 9-11].

Figure 1 shows the calculated concentration of aldehydes formed during plasma processing of 100 ppm NO in a simulated diesel exhaust at 200°C with a C₁/NO_x of 6. Formaldehyde is the major product of the partial oxidation of propene in the plasma. Note that the electrical energy density required to convert NO to NO₂ is much less than that required to fully oxidize the aldehydes. Whereas it is possible to convert 100 ppm of NO to NO₂ with less than 10 J/L, conversion of the resulting 50 ppm of formaldehyde to H₂O and CO_x requires more than 150 J/L. This result shows that the electrical power required by the plasma to completely oxidize the hydrocarbons is unacceptably large.

Some of the minor products shown in Figure 1 include CH₃CHCO and C₂H₃CHO. Species CH₃CHCO is methyl ketene and species C₂H₃CHO is acrolien. Acrolien is experimentally observed as an intermediate product in the low temperature oxidation of propene [ref. 13]. The addition of O atom to propene to form a biradical and its decomposition forms methyl ketene. The rate of this process is based on the current understanding of the O + propene reaction as reviewed in Ref. [14]. Reactions to consume acrolien and methyl ketene by radical attack are included in the detailed chemical kinetic mechanism.

Figure 2 shows the calculated concentration of other species formed during plasma processing of 100 ppm NO in a simulated diesel exhaust at 200°C with a C₁/NO_x of 6. Large amounts of CO are formed during the plasma oxidation of hydrocarbons.

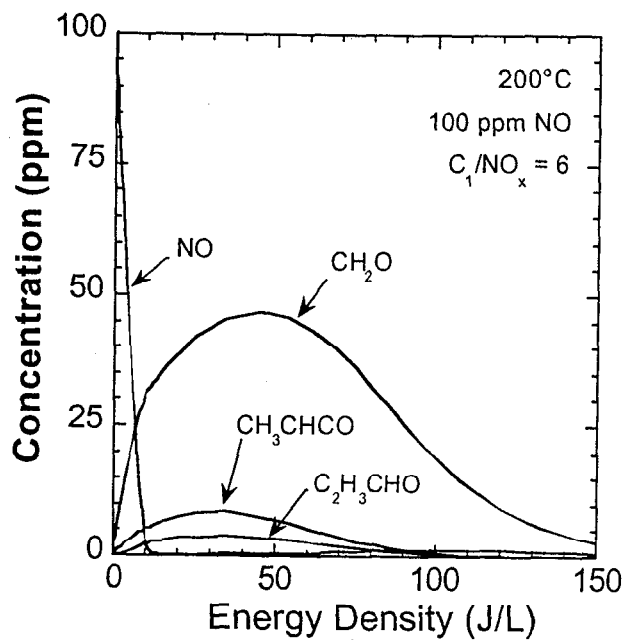


Figure 1. Chemical kinetics calculation of the concentration of aldehydes formed during plasma processing of 100 ppm NO in a simulated diesel exhaust with 10% O₂, 10% CO₂, 5% H₂O, balance N₂. Propene additive, $C_1/NO_x = 6$. Gas temperature = 200°C.

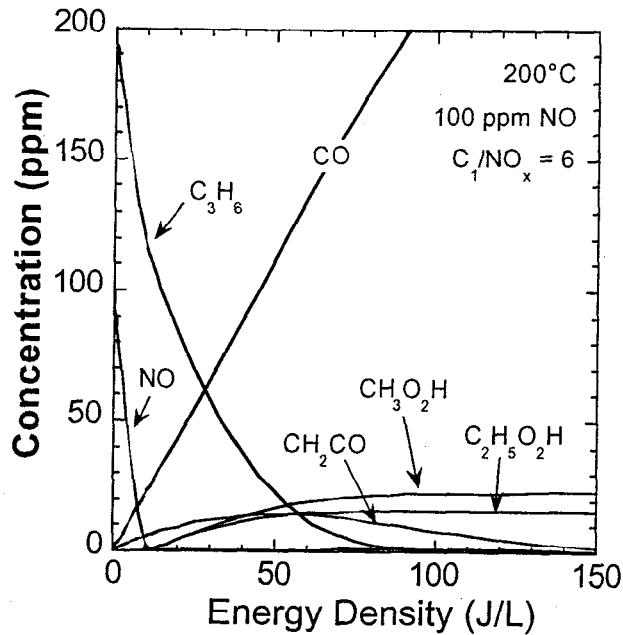


Figure 2. Chemical kinetics calculation of the concentration of various species during plasma processing of 100 ppm NO in a simulated diesel exhaust with 10% O₂, 10% CO₂, 5% H₂O, balance N₂. Propene additive, $C_1/NO_x = 6$. Gas temperature = 200°C.

Figure 3 shows the comparison between the model predictions and experimental measurements of the concentration of formaldehyde and CO formed during plasma processing of 500 ppm NO in a gas mixture with 10% O₂, balance N₂, at 100°C with a C₁/NO_x of 6. This level of NO is typical of that in heavy-duty diesel engine exhaust. There is fairly good agreement between the modeling and the experiment. With a C₁/NO_x of 6, about 25 J/L is required to get maximum oxidation of NO to NO₂. At this energy density, about 150 ppm of formaldehyde has already been formed. The amount of aldehydes increases further as the energy density is increased. Oxidation of these aldehydes will require very large electrical energy density input to the plasma.

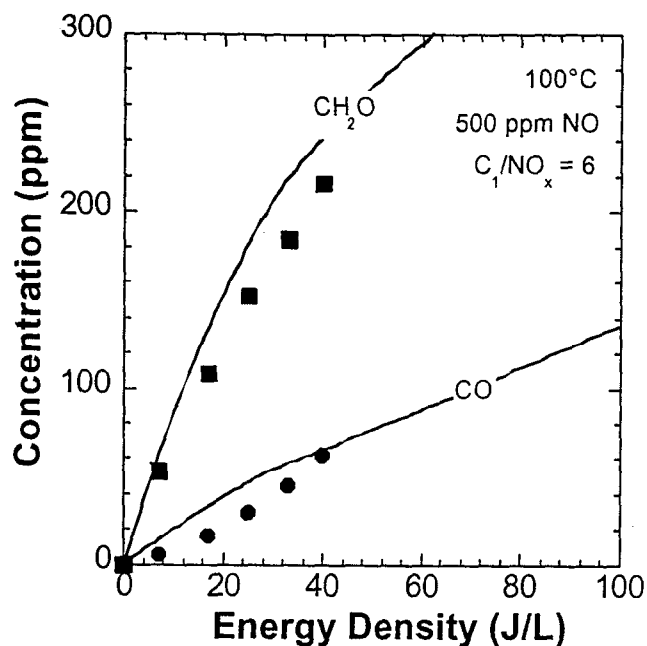


Figure 3. Experimental measurements (points) and modeling predictions (lines) of the concentration of formaldehyde and CO formed during plasma processing of 500 ppm NO in a gas mixture with 10% O₂, balance N₂. Propene additive, C₁/NO_x = 6. Gas temperature = 100°C.

The oxidation of the carbon by NO₂ can lead to reduction of NO_x or backconversion of NO₂ to NO. The following experiments measure the NO_x reduction efficiency and the amount of backconversion of NO₂ to NO.

Figure 4 shows the fate of NO₂ during its reaction with carbon pellets at 250°C in a gas stream containing only N₂. There is about 20% NO_x reduction. The NO_x remaining after the reaction is composed mostly of NO.

Figure 5 shows the same type of experiment conducted in a gas stream containing 10% O₂, balance N₂. The oxygen seems to have promoted the NO_x reduction efficiency to about 30%. Again the NO_x remaining after the reaction is composed mostly of NO.

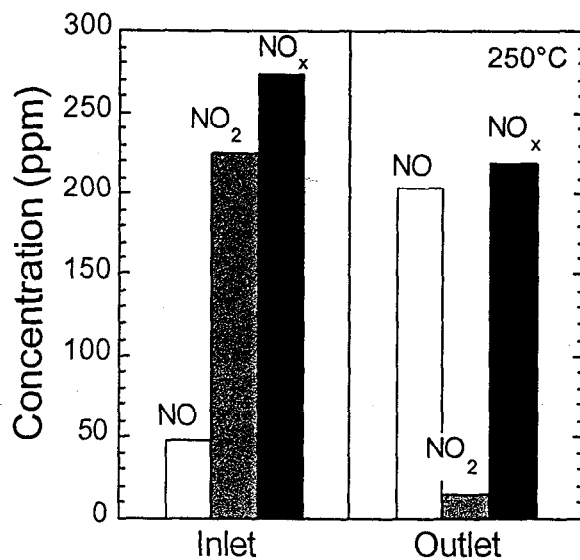


Figure 4. Oxidation of carbon by NO₂ in N₂. Gas temperature = 250°C.

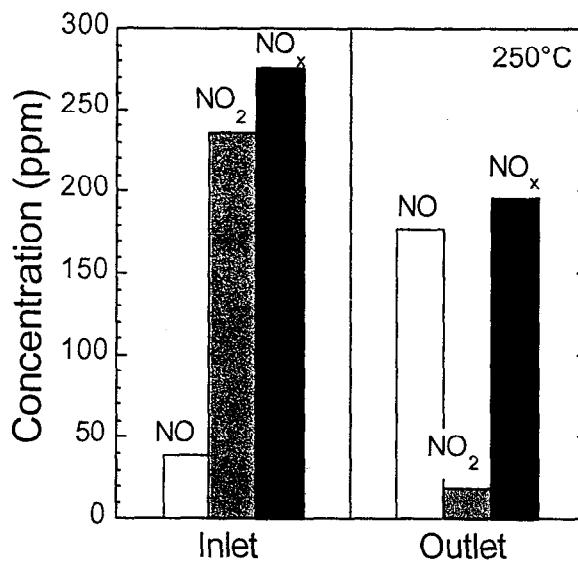


Figure 5. Oxidation of carbon by NO₂ in 10% O₂, balance N₂. Gas temperature = 250°C.

Figure 6 shows the result of another experiment to simulate the effect of the volatile organic fraction of particulates on the NO₂ reduction. The gas stream in this experiment contains 10% O₂ and 1500 ppm C₁ kerosene. The NO_x reduction efficiency is about 35%, with the remaining NO_x being composed mostly of NO.

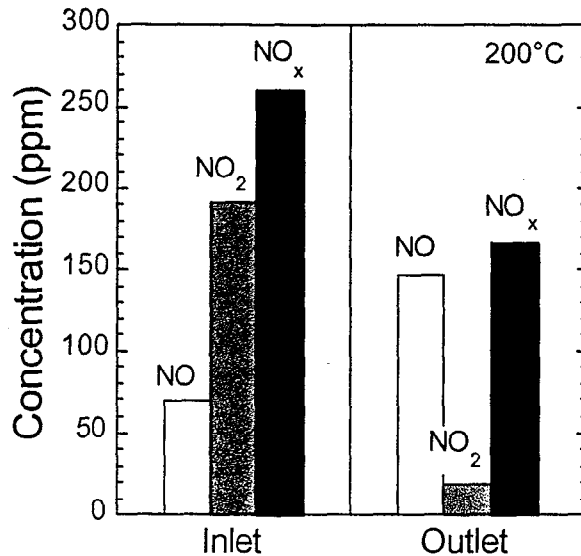


Figure 6. Oxidation of carbon by NO₂ in 10% O₂ + 1500 ppm C₁ kerosene. Gas temperature = 200°C.

The results in Figures 4-6 show that even though the NO₂ could be utilized for the oxidation of the carbon fraction of the particulates, the reaction with the carbon fraction cannot provide a high level of NO_x reduction. Another means will have to be provided to achieve a high NO_x reduction efficiency. If one is going to use plasma-assisted SCR for the NO_x reduction, the regeneration of the particulate trap will have to be done without the NO₂. A way to do this would be to operate the plasma reactor occasionally in the arc mode to thermally oxidize the carbon fraction of the particulates. Ref. [2] describes an example of the effectiveness of this technique and how it can be implemented.

Conclusions

The electrical energy density required for complete oxidation of hydrocarbons in a plasma is much greater than that required to achieve maximum NO_x conversion. Aldehydes and CO will be formed. The energy density required to oxidize the aldehydes will be unacceptably large even for light-duty applications. A catalyst in combination with the plasma will be required to take care of the aldehydes and CO.

The NO₂ from the plasma can be used to non-thermally oxidize the carbon fraction of trapped particulates. However, the reaction of NO₂ with carbon cannot provide a high level of NO_x reduction and leads mostly to the backconversion of NO₂ to NO. If one is going to use plasma-assisted SCR for the NO_x reduction, the regeneration of the particulate trap will have to be done without the NO₂. A way to do this would be to operate the plasma reactor occasionally in the arc mode to thermally oxidize the carbon fraction of the particulates.

Acknowledgments

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