

LOAN DOCUMENT

PHOTOGRAPH THIS SHEET

DTIC ACCESSION NUMBER

LEVEL

0

INVENTORY

REFL-ML-TY-TP-2000-4560

DOCUMENT IDENTIFICATION

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

DISTRIBUTION STATEMENT

ACCESSION FOR	
NTIS	GRAM
DTIC	TRAC
UNANNOUNCED	
JUSTIFICATION	
BY	
DISTRIBUTION/	
AVAILABILITY CODES	
DISTRIBUTION	AVAILABILITY AND/OR SPECIAL
A-1	

DISTRIBUTION STAMP

DATE ACCESSIONED

DATE RETURNED

20001107 035

DATE RECEIVED IN DTIC

REGISTERED OR CERTIFIED NUMBER

PHOTOGRAPH THIS SHEET AND RETURN TO DTIC-FDAC

H
A
N
D
L
E

W
I
T
H

C
A
R
E

AFRL-ML-TY-TP-2000-4560



Microwave Process for NO_x Abatement

**Cha, C.Y. Carlisle, C.T.
and Wander, J.D.**

**CHA Corporation
372 West Lyon
Laramie, WY 82072**

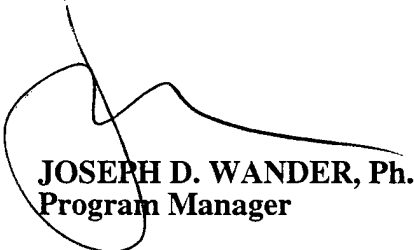
Approved for Public Release; Distribution Unlimited

**AIR FORCE RESEARCH LABORATORY
MATERIALS & MANUFACTURING DIRECTORATE
AIR EXPEDITIONARY FORCES TECHNOLOGIES DIVISION
139 BARNES DRIVE, STE 2
TYNDALL AFB FL 32403-5323**

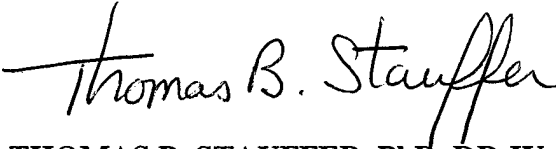
NOTICES

USING GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATA INCLUDED IN THIS DOCUMENT FOR ANY PURPOSE OTHER THAN GOVERNMENT PROCUREMENT DOES NOT IN ANY WAY OBLIGATE THE US GOVERNMENT. THE FACT THAT THE GOVERNMENT FORMULATED OR SUPPLIED THE DRAWINGS, SPECIFICATIONS, OR OTHER DATA DOES NOT LICENSE THE HOLDER OR ANY OTHER PERSON OR CORPORATION; OR CONVEY ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL ANY PATENTED INVENTION THAT MAY RELATE TO THEM.

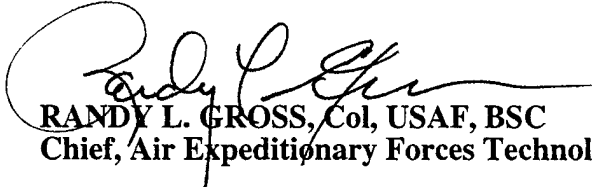
THIS TECHNICAL PAPER HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION. ORIGINALLY PRESENTED TO THE 93rd ANNUAL CONFERENCE, AIR & WASTE MANAGEMENT ASSOCIATION, SALT LAKE CITY, UTAH, 21 JUNE 2000. *PROCEEDINGS OF A&WMA'S 93rd ANNUAL CONFERENCE & EXHIBITION* IS AVAILABLE AS A CD-ROM FROM WWW.AWMA.ORG



JOSEPH D. WANDER, Ph.D
Program Manager



THOMAS B. STAUFFER, PhD, DR-IV, DAF
Chief, Weapons Systems Logistics Branch



RANDY L. GROSS, Col, USAF, BSC
Chief, Air Expeditionary Forces Technologies Division

This report is published in the interest of scientific and technical information exchange and does not constitute approval or disapproval of its ideas or findings.

Do not return copies of this report unless contractual obligations or notice on a specific document requires its return.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 22 June 2000	3. REPORT TYPE AND DATES COVERED Meeting abstract / 970301-991221
----------------------------------	--------------------------------	--

4. TITLE AND SUBTITLE Microwave Process for NOx Abatement	5. FUNDING NUMBERS Contract No : F41624-97-C-0004 JON: 3005ES6D PE: 65505F
--	---

6. AUTHORS Cha, C.Y., Carlisle, C.T., and Wander, J.D.	
---	--

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CHA Corporation 372 West Lyon Laramie, WY 82072	8. PERFORMING ORGANIZATION REPORT NUMBER
---	--

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFRL/MLQL 139 Barnes Drive, Suite 2 Tyndall AFB, FL 32403-5323	10. SPONSORING/MONITORING AGENCY REPORT NUMBER AFRL-ML-TY-TP-2000-4560
---	---

11. SUPPLEMENTARY NOTES
Technical monitor: Dr Joe Wander, AFRL/MLQL, 850-283-6240 [DSN 523-6240]
Abstract #244, *Proceedings 93rd Annual Conference Air & Waste Mangement Association, Salt Lake City, Utah*

12a. DISTRIBUTION/AVAILABILITY STATEMENT Distribution unlimited.	12b. DISTRIBUTION CODE A
---	-----------------------------

13. ABSTRACT (Maximum 200 words)
The CHA Corporation has completed an U.S. Air Force Phase II Small Business Innovation Research program to investigate the feasibility of using a novel microwave-based filter device to remove and destroy unwanted by-products of combustion in exhaust gases. A Corning ceramic monolith soot filter that has about 90% soot removal efficiency was placed in a housing that allowed for microwave regeneration. Two filters were installed in parallel into the exhaust piping of a diesel engine. After 4-hour periods of operation, the filters were successfully regenerated with microwave energy for over 50 cycles. A prototype device for the destruction of NOx in exhaust gas generated by a 58-hp diesel engine was constructed and tested. The NOx control device comprised two separate fixed-bed reactors filled with catalyst beads. In the first, a Pt/Pd catalyst was used to convert NO into NO₂ in the diesel exhaust. A reducing agent (JP-8) and microwaves were supplied to the second reactor, containing alumina-SiC pellets coated with a Pt/Rh/Pd catalyst, to destroy NO₂. Because NO oxidation efficiency (45-55%) is suppressed by the high concentration of water in diesel engine exhaust, NOx destruction efficiencies were 35-40%, 10-20% lower than the NOx destruction obtained from smaller reactors. Test results obtained for this prototype microwave device clearly identified technical and economic advantages as well as technical difficulties of applying microwave-based filter devices to control pollutants in diesel exhaust. Preliminary experimental data indicate that the microwave reactor system developed for NOx destruction can be used to destroy waste rocket fuels including hydrazine and unsymmetric dimethylhydrazine in nitrogen or air streams. Laboratory and prototype test results will be presented.

14. SUBJECT TERMS microwave, ceramic, VOC, combustion, solvent, painting, catalytic	15. NUMBER OF PAGES 22
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL
---	--	---	----------------------------------



Microwave Process for NO_x Abatement

Chang Yul Cha
University of Wyoming
Laramie, WY 82071

Charlie T. Carlisle
CHA Corporation
Laramie, WY 82072

Joseph D. Wander
AFRL/MLQE
Tyndall Air Force Base, FL 32403

ABSTRACT

The CHA Corporation has completed an U.S. Air Force Phase II Small Business Innovation Research program to investigate the feasibility of using a novel microwave-based filter device to remove and destroy unwanted by-products of combustion in exhaust gases. A Corning ceramic monolith soot filter that has about 90% soot removal efficiency was placed in a housing that allowed for microwave regeneration. Two filters were installed in parallel into the exhaust piping of a diesel engine. After 4-hour periods of operation, the filters were successfully regenerated with microwave energy for over 50 cycles. A prototype device for the destruction of NO_x in exhaust gas generated by a 58-hp diesel engine was also constructed and tested. The NO_x control device comprised two separate fixed-bed reactors filled with catalyst beads. In the first reactor, a Pt/Pd catalyst was used to convert NO into NO₂ in the diesel exhaust. A reducing agent (JP-8) and microwaves were supplied to the second reactor, containing alumina-SiC pellets coated with a Pt/Rh/Pd catalyst, to achieve NO₂ destruction. Because of lower NO oxidation efficiency (45–55%) caused by the high concentration of water in diesel engine exhaust, NO_x destruction efficiencies were 35–40%, 10–20% lower than the NO_x destruction obtained from smaller reactors. Test results obtained for this prototype microwave device clearly identified technical and economic advantages as well as technical difficulties of applying microwave-based filter devices to control pollutants in diesel exhaust. Furthermore, preliminary experimental data indicate that microwave reactor system developed for NO_x destruction can be used to destroy waste rocket fuels including hydrazine and unsymmetric demethyl hydrazine in the nitrogen or air streams. Laboratory and prototype test results will be presented.

INTRODUCTION

The CHA Corporation has completed U.S. Air Force Phase II Small Business Innovation Research project to investigate the feasibility of using a novel filter device, in which microwave energy is applied to destroy pollutants in a catalyst bed, to control unwanted combustion by-products in diesel engine exhaust gases. The microwave-based cleanup process for diesel engine exhaust gases has the potential to significantly reduce the cost of removing airborne pollutants from the exhaust of

combustion processes. The pollutants comprise nitrogen oxides (NO_x), carbon monoxide (CO), particulate matter less than 10 microns (PM₁₀), products of incomplete combustion (PICs), volatile organic compounds (VOCs), and other hazardous air pollutants (HAPs)¹. The reduction of these pollutants, as set forth by the Federal Clean Air Act, from all stationary sources is a prime goal of the U.S. Air Force, Environmental Protection Agency (EPA), and state and local air quality regulatory agencies.

Currently, no single device is available for simultaneous removal of NO_x, CO, VOCs, and PM₁₀ from oxygen-rich exhaust gases. Separate devices are required for the reduction of NO_x, oxidation of CO and VOCs, and removal of PM₁₀. Two methods for NO_x reduction currently available are selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR)^{2,3}. In both SNCR and SCR (processes originally developed for large, coal-fired power plants), a chemical reducing agent, commonly anhydrous ammonia or urea, is injected into the exhaust gas stream as it exits the combustor. In the SCR process, impregnated gases pass through a catalyst element that promotes reaction of NO_x with an injected reducing agent to form nitrogen and water. At temperatures of 900-1000 °C, NH₃ will reduce NO_x to N₂ without a catalyst. However, the SNCR process has a much lower NO_x-removal efficiency and requires higher temperatures than SCR. The SCR vendors report that 90-percent reduction in NO_x levels is achievable if the catalyst bed can be operated at temperatures between 400 and 500°C. The costs of implementing and operating the SCR process are quite high, and emissions of small amounts of unreacted ammonia are likely. Furthermore, the service conditions of non-steady-state operations that occur in much Air Force maintenance and training operations are ill suited for SNCR and SCR processes. Currently, no low-temperature (ambient to 125 °C) NO_x-removal technology is available.

CHA Corporation has developed a process employing a carbon-based adsorbent and microwave energy to treat exhaust gases. An integrated prototype system capable of treating exhaust gases for a 58-hp diesel engine was designed, fabricated, developed and demonstrated. The integrated system is a continuous adsorption/regeneration arrangement capable of 100% NO_x removals, as well as destroying the VOCs and soot present in diesel exhaust. The pollutants are first removed from the flue gases by passing the gases through a bed of relatively inexpensive carbon adsorbent. NO_x, SO_x, and VOC gases and vapors are adsorbed and stored on the carbon during this step. The pollutants are then destroyed during regeneration of the carbon by microwaves. The microwave energy decomposes NO_x to nitrogen and carbon dioxide, VOCs to carbon dioxide and water, and SO_x to elemental sulfur and carbon dioxide. A prototype unit was constructed and perfected through thorough experimentation. The unit was then transported to McClellan Air Force Base in Sacramento, California in March of 1998 for a weeklong demonstration^{4,5}. The field demonstration of the prototype was very successful. No mechanical or technical problems were encountered during frequent startup and shutdown operations. During the week of field demonstration, the outlet gas contained less than 1 ppm NO_x. In addition, this process is capable of handling frequent startup and shutdown cycles of diesel engines. However, the inlet gas needs to be cooled below 70 °C and the exhaust gas treatment system is larger in size than the diesel engine. Because of these two disadvantages, the microwave carbon adsorbent process may not be suitable for diesel engines. The process under development and reported here is intended to minimize these two weaknesses.

The emission of CO and VOCs can be lowered by a catalytic converter very similar to that found in automobiles⁶. A catalytic converter is a ceramic monolith structure that is impregnated with

oxidation catalysts, usually platinum and/or palladium. When a hot exhaust stream passes through the ceramic structure, the catalyst promotes the reaction of CO and VOCs with available oxygen. Catalytic converters are most effective when the catalyst element is above 260°C, and performance is usually best near 400°C. PM₁₀ is mainly carbonous material that is produced by engines. This PM₁₀ can be either oxidized or removed by a filter. In catalytic oxidation, the exhaust gas is sent through a catalyst element, which traps and oxidizes the soot. Removal efficiencies of up to 50 percent are achievable with this process if the average exhaust temperature can be kept near 400°C^{7,8,9}. Generally, higher removal efficiencies are not possible due to the temperature limitations of the exhaust gas stream. Very high removal efficiencies are achievable with soot filters. These paper filters for low-temperature service or ceramic-fiber filters for high-temperature service remove soot from the exhaust stream as it flows through the filter. Typical service lifetimes for these filters are short, usually less than 50 hours.

To overcome the limitations of current emission control options for stationary diesel engines, the CHA Corporation has developed a microwave-based catalytic process for the destruction of air pollutants in diesel engine exhaust gases. This filter device converts NO_x, CO, VOCs and soot into nitrogen, CO₂ and water. The device converts NO_x into nitrogen (and CO₂) through an oxidation step followed by reduction. The other pollutants are oxidized to CO₂ and water. Low-level microwave energy is used to drive each of these desired conversion reactions. The principles of operation of this device are as follows:

1. Capture the carbonaceous soot in a ceramic filter and, using microwave energy, oxidize the soot into CO₂ or CO.
2. Convert the NO into NO₂ in an oxidative-catalytic section of the device. It was learned that this reaction proceeds very quickly in the presence of a platinum catalyst, and the reduction of NO₂ by reducing agent in the presence of oxygen is more favorable than that of NO.
3. Reduce the NO₂ to nitrogen and CO₂ using a commercially available NO_x-reducing (three-way) catalyst and a reducing agent such as JP-8 jet fuel during irradiation by low-level microwave energy. This step destroys about 65 percent of the NO_x.
4. Oxidize any CO and VOC materials to CO₂ and water using an oxidizing catalyst in the presence of low-level microwave energy.

Both bench-scale and engineering prototype units have been tested for destruction of NO_x in diesel exhaust gas. A process flow diagram is shown in Figure 1.

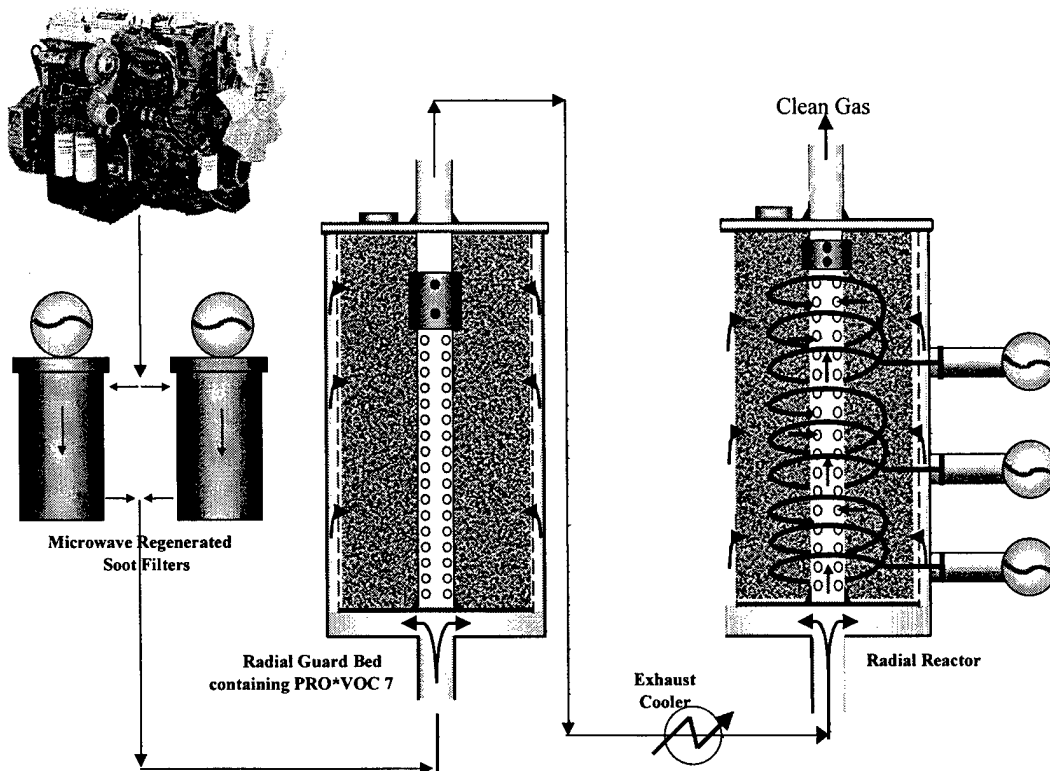


Figure 1. Microwave Catalytic Reactor System for Diesel Exhaust Treatment

LABORATORY EXPERIMENTAL RESULTS AND DISCUSSION

Removal and Destruction of Soot in Diesel Exhaust

A line of soot oxidation experiments was run using diesel exhaust gases to determine the extent of soot oxidation in a microwave field. In each experiment, 0.50 grams of devolatilized soot was placed on a SiC sponge in a 1-inch diameter quartz tube. Raw diesel exhaust was flowed through the soot sample at 6.8 standard cubic feet per hour (SCFH). Microwaves were then applied until outlet gas oxygen concentrations indicated an end to oxidation. Three samples were run for each tested power level (50, 100, and 150 W). In addition, three pulsed microwave tests were run at each condition with a 10-second-on-10-second-off pulsing cycle. Experiments to determine the optimum type of soot filter, as well as the optimum filter arrangement were also performed.

A typical microwave-induced soot oxidation reaction in the presence of raw diesel exhaust gas is presented in Figure 2. The nitric oxide in the diesel exhaust gas was initially used as the oxygen source for the soot oxidation prior to the direct use of oxygen.

Figure 3 illustrates the cumulative results of this work over all tested energy levels, both pulsed and continuous. Microwave power values for pulsed testing represent actual power applied. For example, a 10-second-on-10-second-off cycle at 150 W is reported as 75 W actual for comparison.

Oxidation rates are influenced by actual power applied, but do not differ largely between pulsed and continuous application.

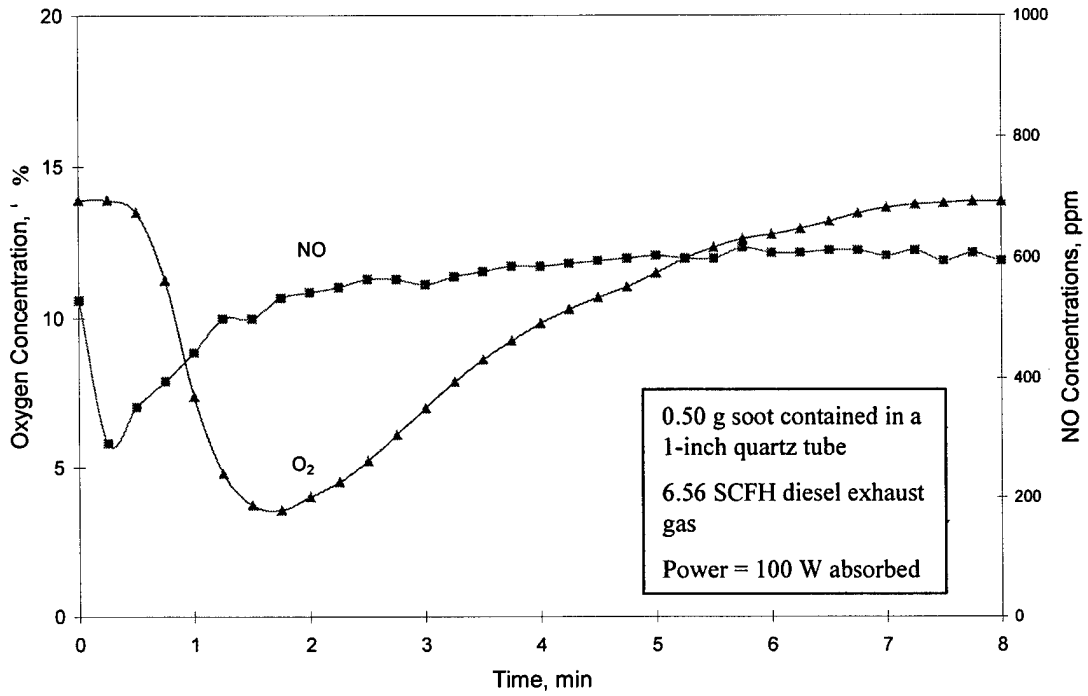


Figure 2. Typical Soot Oxidation Reaction Gas Outlet NOx and Oxygen Concentrations

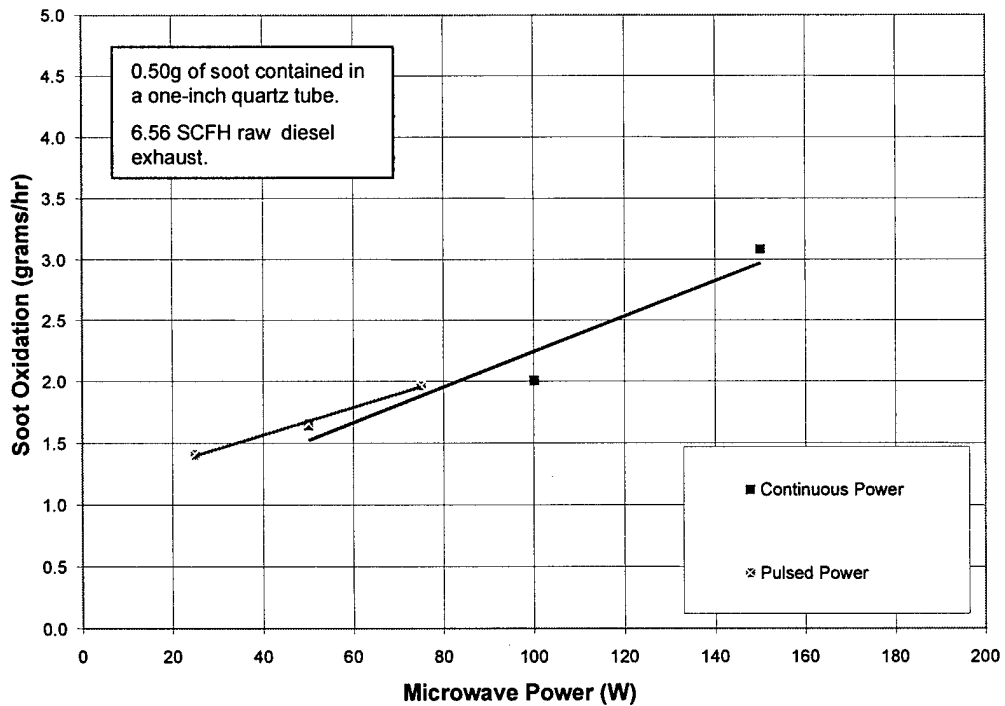


Figure 3. Soot Oxidation by Microwave Energy

Figure 4 depicts NOx destruction as a function of actual power applied for both pulsed and continuous microwave application types. For continuous microwave application, the NOx reduced per gram of soot destroyed decreases with increasing power levels. Pulsed microwave application, however, destroys more NOx per gram of soot destroyed at higher microwave levels.

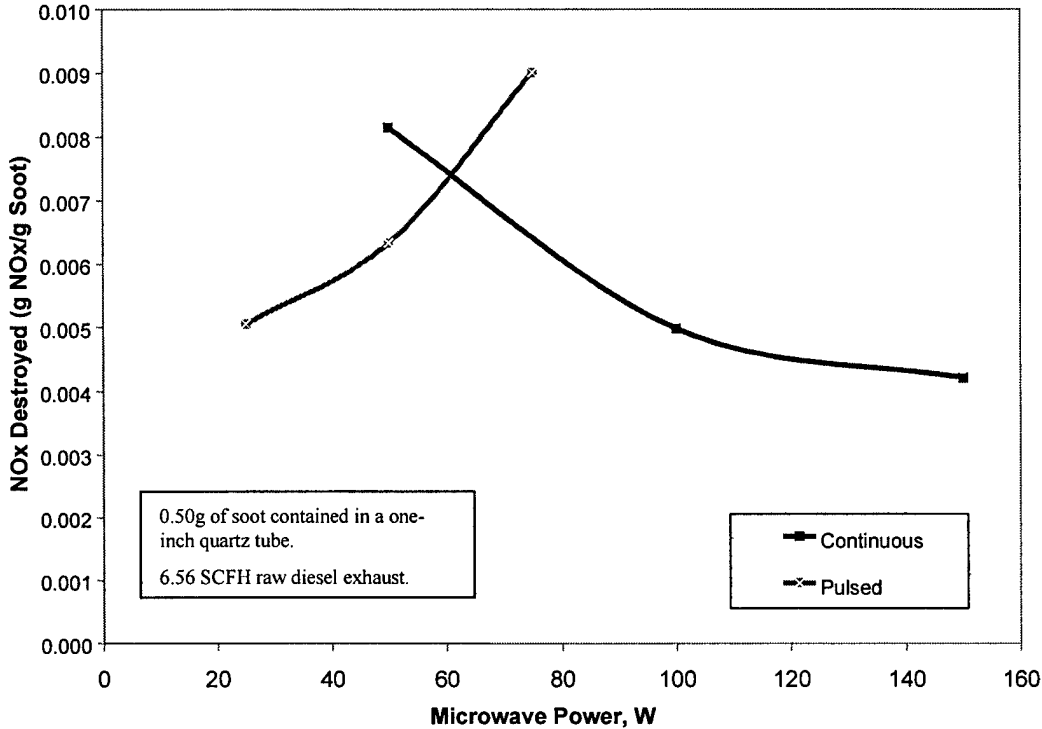


Figure 4. NOx Destruction through Microwave Induced Soot Oxidation

The Corning ceramic monolith soot filter and 3M ceramic fiber filter were tested to remove soot from the diesel exhaust gas and regenerated with microwaves. Test results show that the ceramic monolith soot filter was effectively regenerated with microwaves. This Corning ceramic monolith soot filter is commercially available and removes 87% to 92% of soot from diesel engine exhaust. This filter is made from solid ceramic material and has low thermal expansion, so it can tolerate extreme thermal cycling. Filters with and without an oxidation catalyst coating were tested to capture and destroy the soot in the diesel engine exhaust gas.

On completion of testing of the monolith filter coated with oxidation catalyst, a monolith filter without the oxidation catalyst was tested. The ability to use a filter that has not been washcoated with catalyst would significantly reduce both the costs of the filter and the initial pressure drop. Both saturation and regeneration data were gathered for the non-coated filter. The saturation testing was performed in the same way as was done for the catalyzed filter. Microwave energy was continuously applied to allow for on-line regeneration. The results for the non-catalyzed filter were better than for the filter coated in oxidation catalyst. The filter was in service for over seven hours with an acceptable manifold back-pressure. It was also apparent that on-line regeneration was taking place. The results from multiple cycles of soot loading and regeneration tests are shown in Figure 5. This data represents the pressure drop measurements recorded during the initial soot loading cycles for a dual ceramic monolith filter-arrangement installed at the 58-hp diesel engine exhaust system. The filter system has undergone more than 150 loading/regeneration cycles. Figure 5 clearly

demonstrates that soot deposits inside the filter were completely oxidized by microwave energy. Equally, the data suggest that subsequent regeneration of filter improve the single cycle duration.

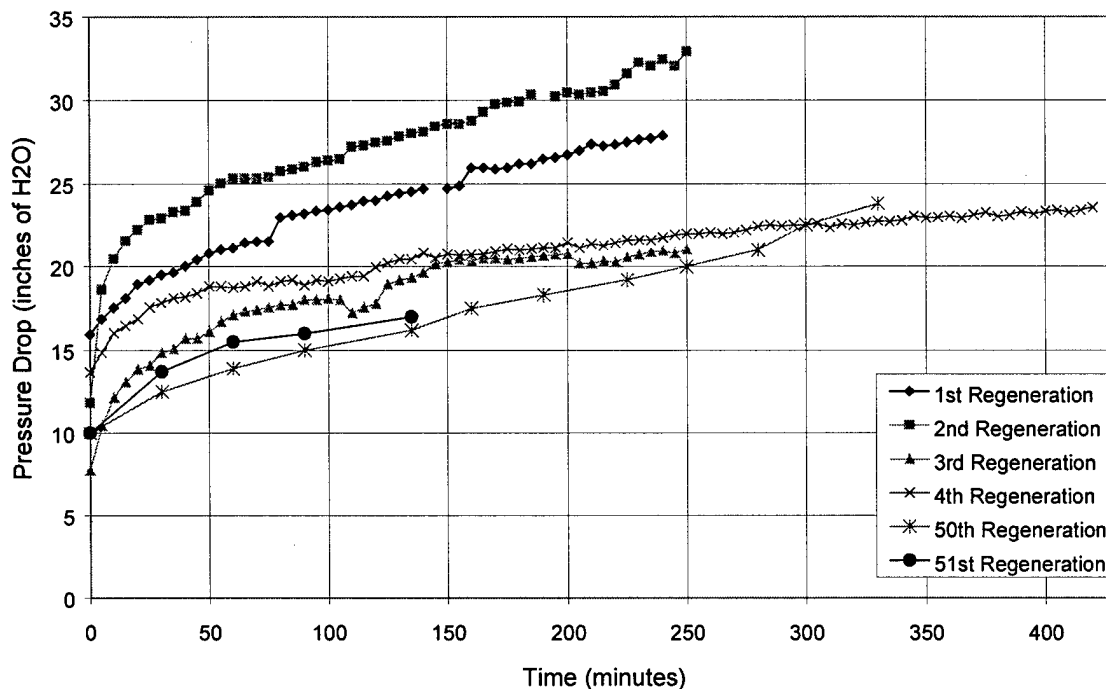


Figure 5. Pressure Drop Across Non-Catalyzed Monolith Filter During Saturation Cycles

NO_x Destruction by JP-8 over the Catalyst Bed

NO_x destruction experiments were carried out using a 1-inch inside diameter (ID) reactor containing 6 inches of Pt/Rh catalyst (PRO*VOC 7 made by Prototech Company) on SiC or 6 inches of PRO*VOC 7 on zeolite evenly mixed with SiC. A 1-inch ID guard bed was set in front of the reactor and contained 10 inches of PRO*VOC 7 on zeolite. The guard bed was heated to 520 °F. The guard bed catalyzed the reaction of NO to NO₂ consequently, allowing improved destruction efficiencies within the main reactor. A JP-8 sparger introduced reducing agent above the reactor chamber. The JP-8 temperature was maintained at 200 °F. A pre-heated nitrogen flow of 0.1 standard liters per minute (SLPM) carried the vaporized JP-8 into the reactor column. The diesel exhaust gas flow rate was held at 6.5 SCFH through the column. Diesel exhaust NO_x concentrations during testing averaged 700 ppm. NO_x destruction efficiency as a function of applied microwave power was tested over a range from 50 to 250 W in 25-W increments.

Microwave-induced catalytic reduction testing was performed on raw diesel exhaust gas to determine CO and VOC destruction efficiency as a function of microwave input power. These experiments were performed using a 60-mm-ID quartz tube reactor bed in a microwave helix reactor chamber. Input power was varied from 50 to 200 W in 25-W increments. The diesel exhaust gas flow rate was

35 SCFH. Average inlet concentrations were 412 ppm and 43 ppm for CO and VOCs, respectively. The reactor bed contained two ¾-inch Prototech PRO*VOC 7 / zeolite / SiC catalyst sponges. A soot pre-filter made of Nextel 312 AF-62 fabric was also used to prevent possible catalyst contamination by soot.

Guard bed testing was performed to determine optimum temperature ranges for efficient conversion of NO into NO₂. The guard bed uses PRO*VOC 7 coated on zeolite to catalyze oxidation of NO to NO₂. Diesel exhaust contains primarily NO, whereas only NO₂ is reduced in the presence of oxygen. Testing was performed using 125 grams of zeolite in a 1-inch-ID chamber, which provided a bed height of 10 inches. The bed was then saturated with NOx prior to temperature dependence experimentation. Raw diesel exhaust was passed through the guard bed at a flow rate of 5 SCFH. Diesel exhaust NO concentrations averaged 690 ppm. Inlet and outlet NO and NOx concentrations were recorded using a NO/NOx analyzer attached to our Camile data acquisition system. Bed temperature was varied between 150 and 600 °F.

Figure 6 depicts the microwave-induced NOx destruction efficiencies for raw diesel exhaust and simulated gases using JP-8 as the reducing agent. Synthesized exhaust gas data is presented in this figure for comparison. Both exhaust types exhibit similar NOx destruction efficiency trends. Raw diesel exhaust NOx destruction outperformed test data for simulated gas at microwave power levels above 100 W. The raw diesel exhaust gas testing results are broken down between the PRO*VOC 7 coated on SiC and the PRO*VOC 7 on zeolite mixed with SiC. Catalyst efficiencies were similar for catalysts on these two substrates. This similarity of efficiencies verifies the feasibility of using catalyst-coated SiC for NOx reduction.

Figure 7 indicates catalyst destruction performance as a function of microwave power for CO and VOCs. VOC destruction occurred at low microwave energy levels, but showed a pronounced increase after 125 W. Carbon monoxide was unaffected at energy levels below 100 W, but was completely oxidized at power levels above 150 W. These data indicate that power densities corresponding to 150 W at test conditions are sufficient to remove CO and VOCs from raw diesel exhaust with the PRO*VOC 7 catalyst.

The NO/NOx conversion efficiency as a function of guard bed temperature-using PRO*VOC 7 on zeolite is illustrated in Figure 8. Beneficial conversion rates were achieved above 500 °F. Placing the treatment device near the exhaust manifold can easily attain this temperature. As a result of this favorable temperature range, no cooling or heating of the exhaust gas is required to obtain maximum guard bed and reactor conversions.

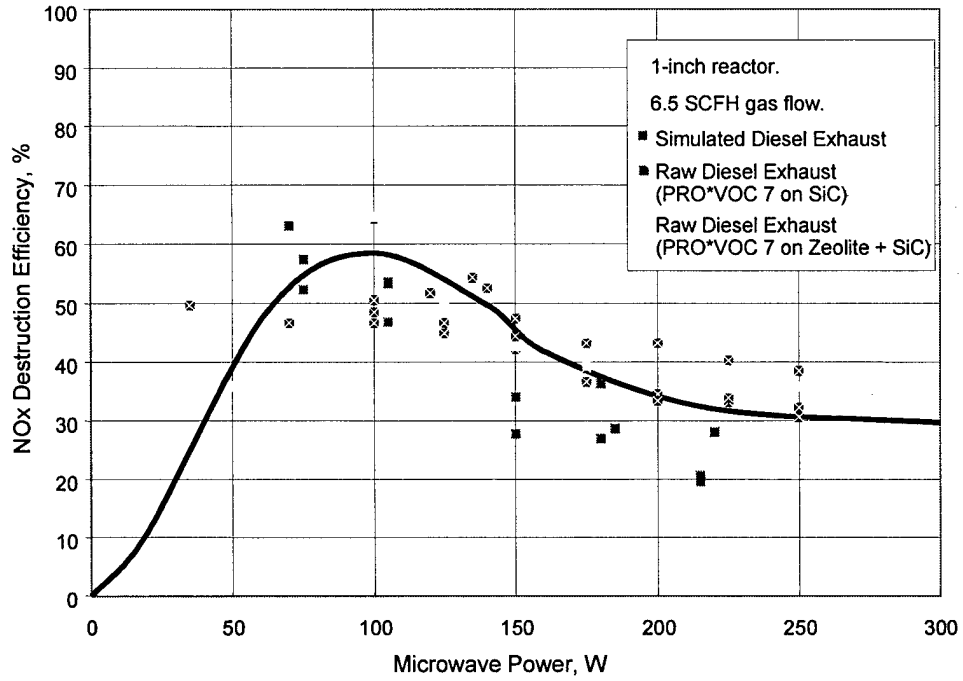


Figure 6. NOx Destruction Efficiency with Microwave Power Variance

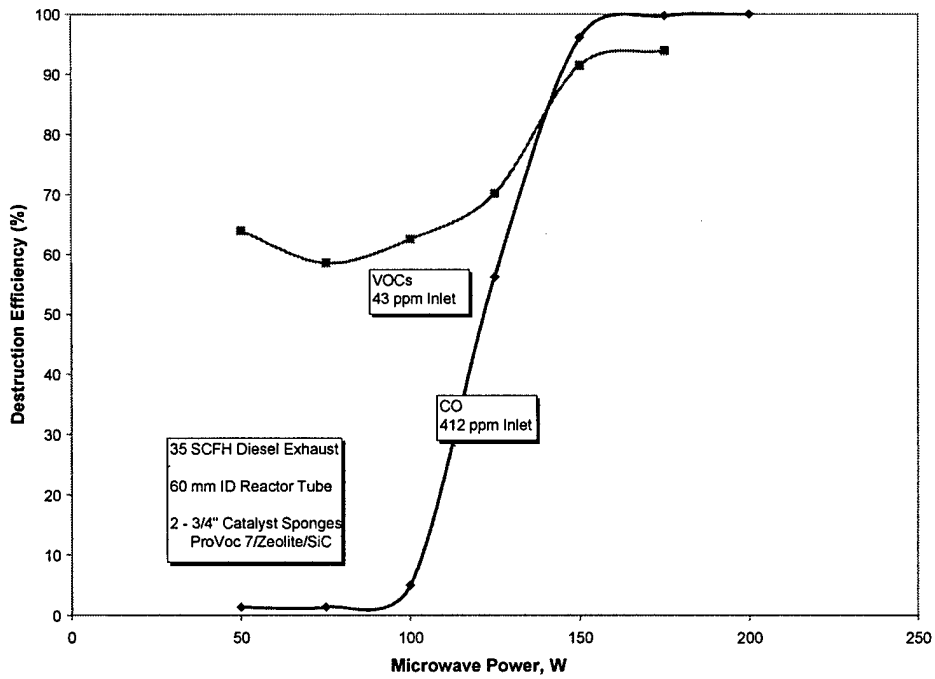


Figure 7. Catalytic Oxidation of CO and VOCs

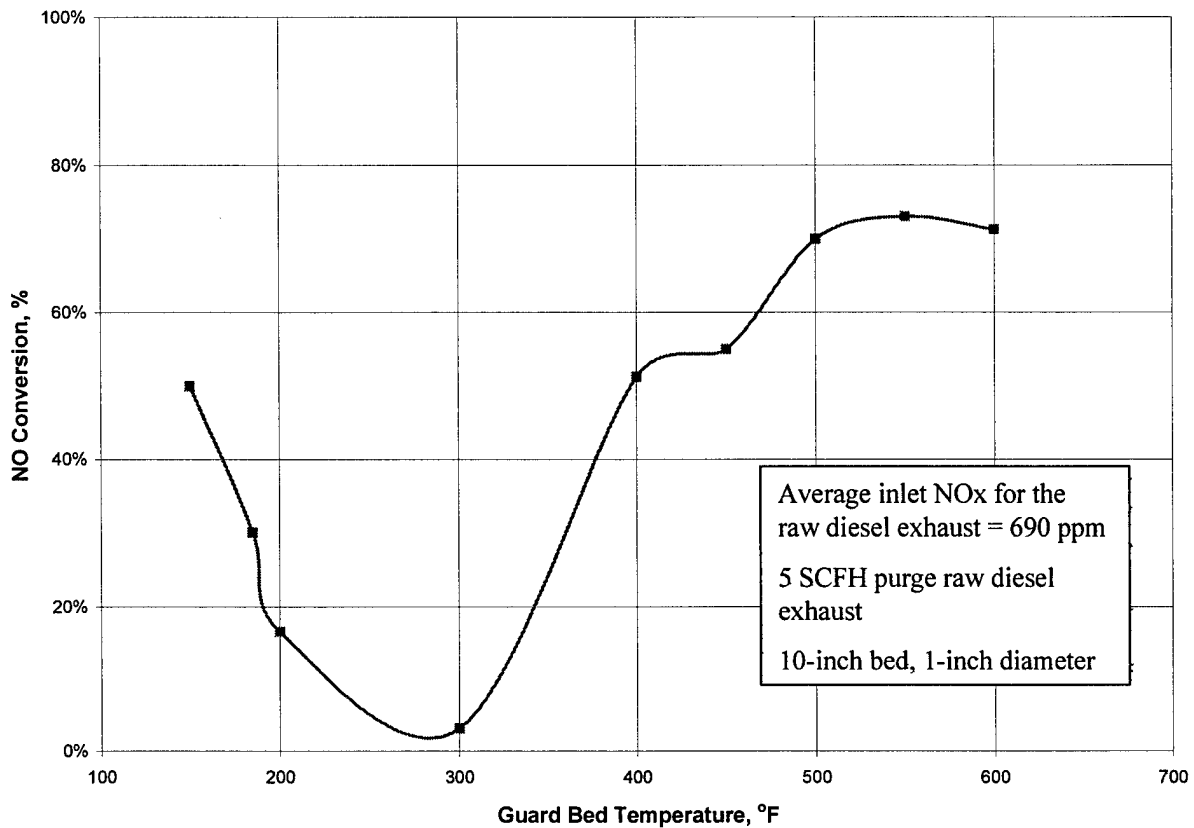


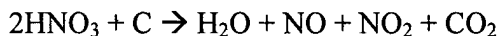
Figure 8. NO/NOx Conversion Efficiency as a Function of Temperature

Conversion of NO₂ to HNO₃ in Guard-Bed

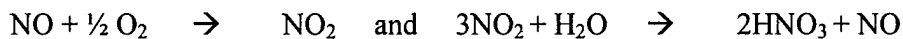
In the presence of moisture NO₂ interacts with alumina in the following reaction¹⁰:



If both moisture and oxygen are in presence, NO is converted into NO₂ and HNO₃ on the carbon surfaces, which are then adsorbed onto the carbon¹¹. From mass balance it was estimated that 89% of NO₂ was converted into HNO₃. Nearly 90% of the HNO₃ and NO₂ adsorbed on the FMC char was reduced into N₂ and carbon oxides during microwave regeneration¹¹. The capacity for NO adsorption and the catalytic activity for NO oxidation of activated carbon were also investigated by Jontgen et al¹². From thermal desorption spectrometry, they proposed the following reaction for the decomposition of HNO₃ adsorbed on the activated carbon:



After comparing guard bed data obtained using dry gas with diesel exhaust guard-bed data, we speculated that the following reactions are likely occurring in the guard bed:



Assuming NO_2 reacts with water vapor to produce HNO_3 and NO , and using NO and NO_2 concentration data, the conversions of NO into NO_2 and NO_2 into HNO_3 were calculated by material balances and are presented in Table 1. The conversion of NO into HNO_3 is approximately the same as the NO -to- NO_2 conversion. Since NO needs to be converted to NO_2 in the guard bed to be destroyed in the microwave reactor, the maximum destruction efficiency of NO is limited to 67%. Furthermore, HNO_3 has to be destroyed in the microwave reactor by reacting with JP-8. The maximum destruction efficiency of NO_x obtained from a single microwave reactor was 65% using a 1-inch reactor and 55% using an 8-inch reactor. To increase the destruction efficiency, it is necessary to convert NO into NO_2 after HNO_3 is destroyed. This indicates the need of a second guard bed after the microwave reactor. Use of the second guard bed is not practical because of difficulties involved in heating.

Table 1. NO and NO_2 Concentrations in Guard Bed.

Guard Bed	Inlet Gas		Outlet Gas		NO to NO_2	NO_2 to HNO_3
Temp, °F	NO , ppm	NO_2 , ppm	NO , ppm	NO_2 , ppm	Conversion	Conversion
535	690	78	312	139	77.8%	77.3%
540	642	70	286	148	77.1%	73.8%
542	620	100	295	178	72.3%	67.6%

A small stream of the diesel exhaust gas (2 SCFH) flowing out from the guard bed was taken and introduced into one liter of water to determine the concentration of HNO_3 in the guard bed outlet gas. After 2 hours, the concentration of HNO_3 in water measured by the colorimetric method was 5 ppm. With this value the concentrations of HNO_3 and NO_2 in the guard bed outlet gas are estimated to be 16 ppm. NO_x concentrations of inlet and outlet gas were 798 and 525 ppm, respectively. The difference in the inlet and outlet NO_x concentration is 273 ppm, that should be the concentration of HNO_3 in the guard bed outlet gas if NO_2 reacts with water vapor to produce HNO_3 and NO . Furthermore, the concentration of NO_2 in the guard bed outlet gas was 239 ppm. If NO_2 and HNO_3 in the guard bed outlet gas are dissolved in one-liter water for 2 hours, the NO_3^- concentration should be 68 ppm. To check the solubility of NO_2 in water, nitrogen gas containing one percent NO_2 was introduced at one SCFH into one liter of water for two minutes. The concentration of HNO_3 in water was measured to be 8 ppm. The HNO_3 concentration should be 14 ppm if 100% NO_2 in nitrogen was dissolved in water. As expected, this confirms that NO_2 is not easily absorbed in water. Furthermore, some gaseous component in the diesel exhaust might hinder the absorption rate of NO_2 and HNO_3 in water. This clearly indicates that the colorimetric method followed by saturation of guard bed outlet gas in water is not adequate to determine the concentration of HNO_3 in the guard bed outlet gas.

PROTOTYPE DEVICE FOR DESTRUCTION OF NO_x IN 58-HP DIESEL ENGINE EXHAUST GAS

Design and Construction of Microwave Reactor and Radial Guard-Bed

Based on experimental data obtained from the 2.31-inch-diameter reactor and 8-inch x 8-inch reactors, a radial guard bed and microwave reactor were designed for treating exhaust gas generated by 58-hp diesel engine and are presented in Figures 9 and 10, respectively.

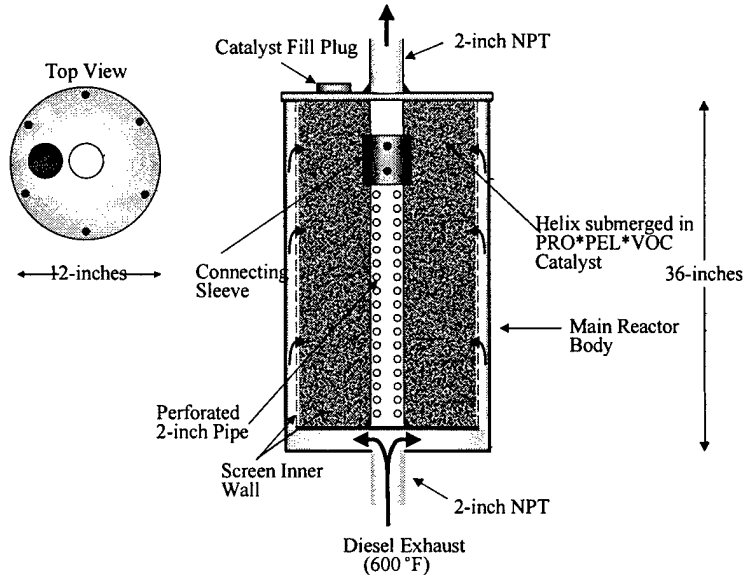


Figure 9. Radial Guard Bed for 58-hp Diesel Engine Exhaust

Two separate units were constructed for the full-scale prototype system. First, the three-foot radial guard bed was completed. The guard bed holds a total catalyst volume of 1.83 ft³ and the exhaust gas flow navigates from outside to inside through the bed. These conditions were obtained by scaling up the most-efficient unit that had been tested. The second unit that we built was the microwave reactor. Figure 11 is a picture of the finished reactor. The reactor was filled with 1.83 ft³ of catalyst, and irradiated with a 2.7 kW of microwave energy during operation. Gas flows through the reactor from bottom to top and from outside to inside of catalyst bed.

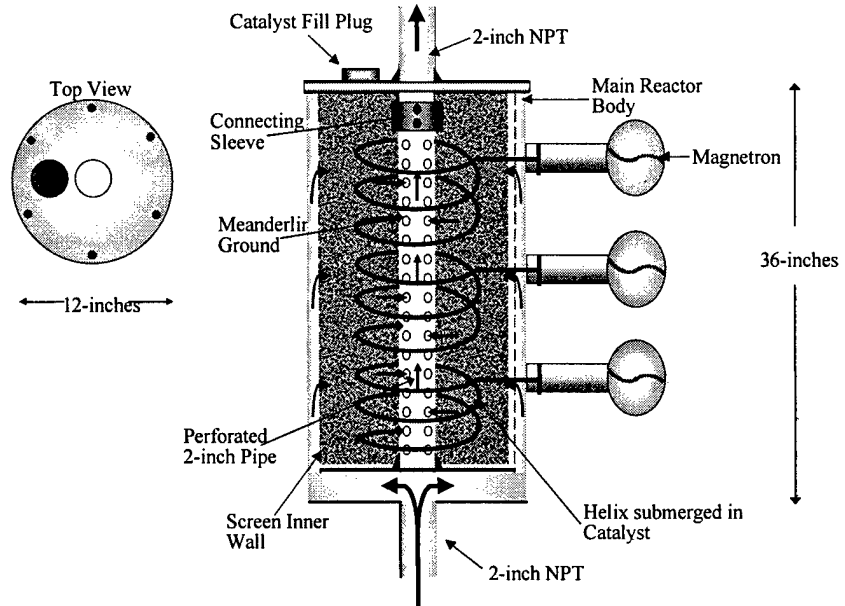


Figure 10 Radial Microwave Reactor for 58-hp Diesel Engine Exhaust.

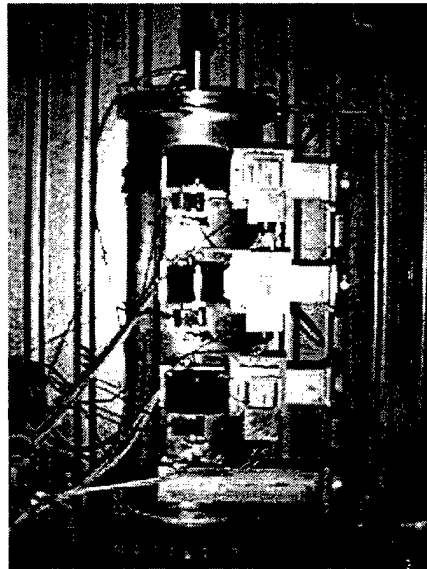


Figure 11. Microwave Radial Reactor for NOx Abatement

The final installed full-scale treatment system for 58-hp diesel engine is shown in Figure 12.

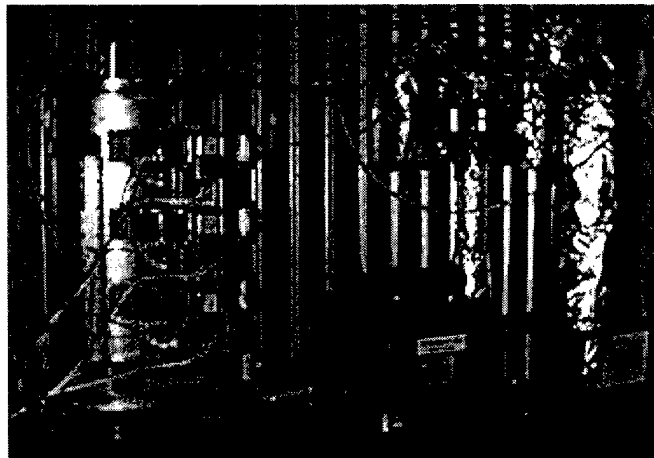


Figure 12. Prototype NO_x Treatment System for 58-hp Diesel Exhaust

Test Operation of Prototype NO_x Abatement System

The initial stage in test operation of the full-scale treatment system was to perform shake down tests to determine the effects of several variables on the system. The effect of reducing agent injection rate, microwave power, inlet NO_x concentration, and inlet gas temperature were investigated.

The pressure drop across the guard bed was 6 inches of water at the exhaust gas flow rate of 120 CFM. The NO conversion efficiency of the full-scale guard bed ranged from 45 to 55%. JP-8 was used as the reducing agent for NO_x destruction testing. Figure 13 presents NO_x destruction efficiency as a function of JP-8 injection rate. As shown in this figure, adding JP-8 had minimal effect on the NO_x destruction efficiency. From these results it was decided to run further tests with a JP-8 injection rate of 11 mL/min. Once the reducing agent injection rate had been established the effects of varying microwave power were tested. To perform these tests the three microwave magnetrons on the reactor were pulsed. This pulsing of the microwaves varied the average applied power to the system. For example, when the microwaves are operated at 80% on and 20% off, the equivalent average input power was 2,160 W compared to the 2,700 W applied when all three magnetrons were operated continuously. Four separate pulse settings were tested to determine the most efficient power level for microwave application. The results are shown in Figure 14, which indicates that input power levels of 2,160 and 2,700 W provided the highest NO_x destruction efficiency. Through further testing it was decided that the best operating power for the system was 2,700 W.

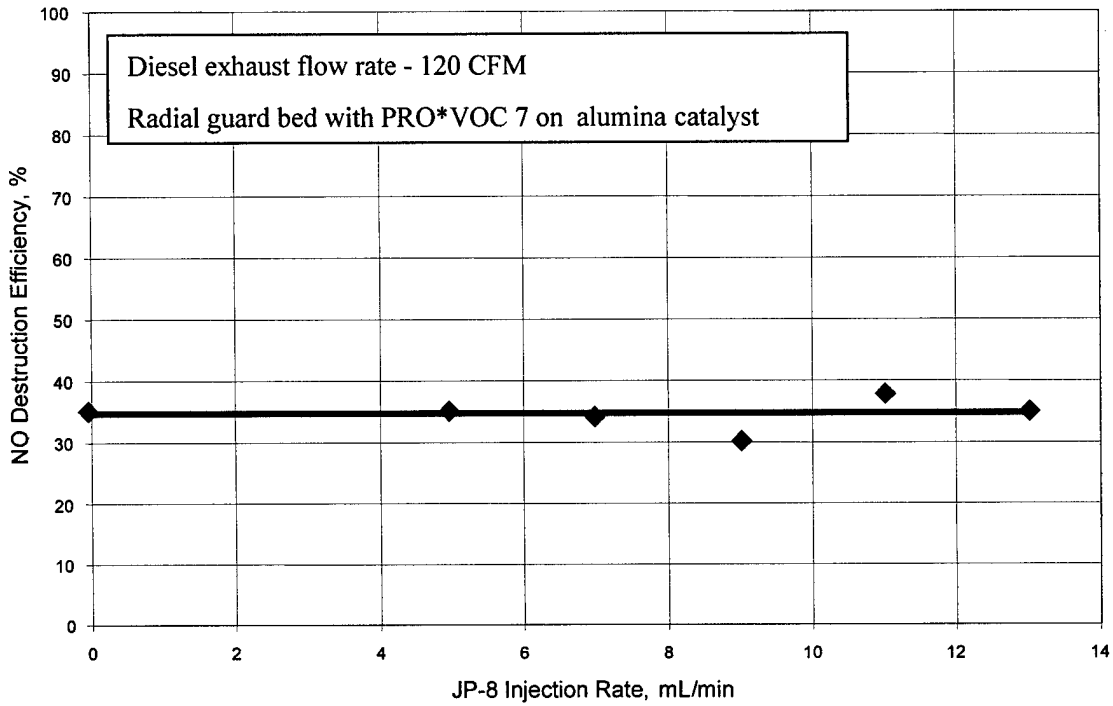


Figure 13. NOx Destruction Efficiency in Radial Microwave Reactor as a Function of JP-8 Injection Rate

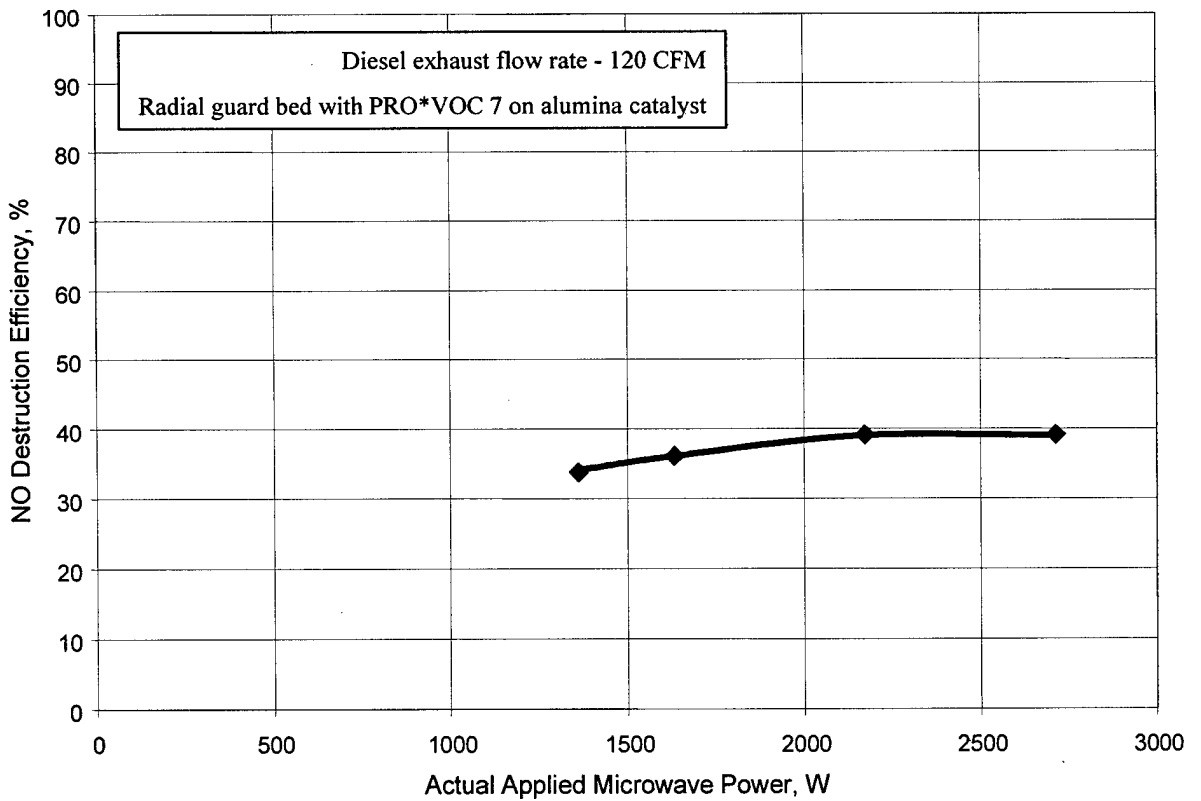


Figure 14. NO Destruction Efficiency as a Function of Applied Microwave Power

The third test series performed was to determine the effect of inlet NOx concentration on both guard bed conversion and total NO destruction. Four different NOx concentrations (600, 800, 1,000, and 1,200 ppm) were tested. The total microwave power applied to the system was held at a constant level of 2,700 W. JP-8 was injected at a rate of 11 mL/min. For all of the tests the inlet gas temperature to the microwave reactor was held at 120 °F. Figure 15 illustrates the results of this testing.

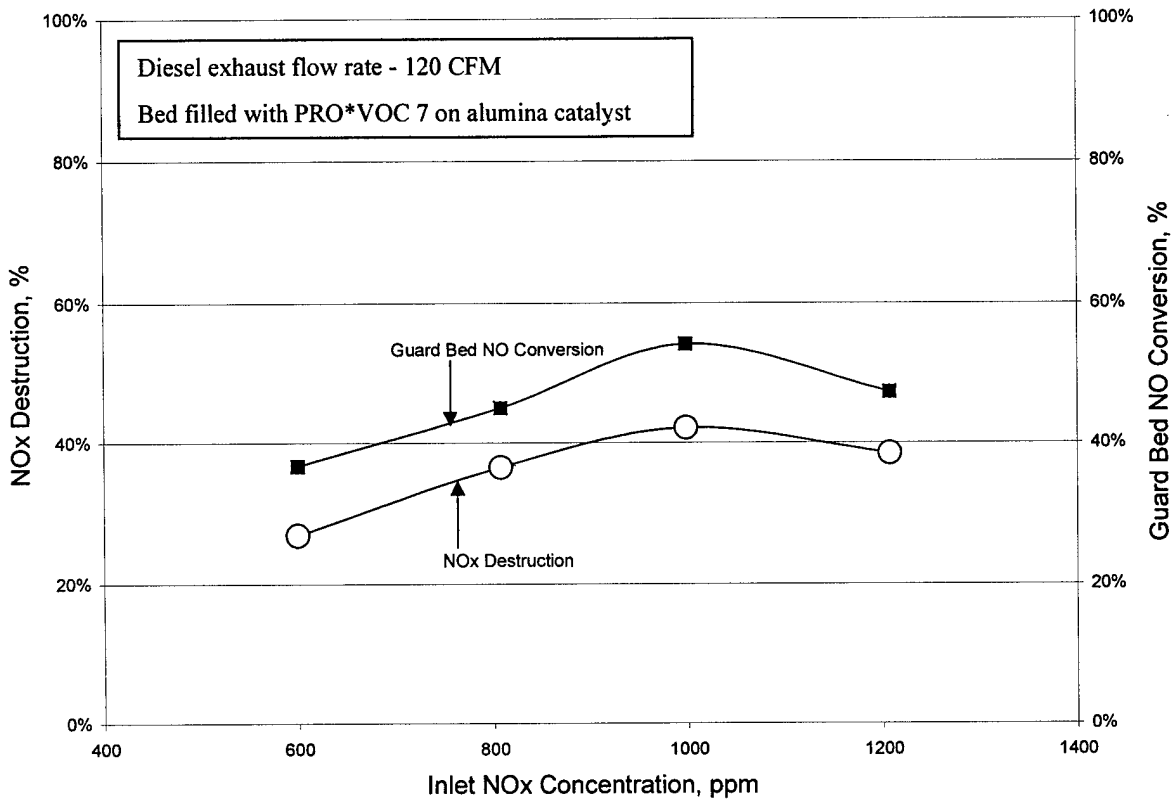


Figure 15. NOx Destruction Efficiency as a Function of Inlet NOx Concentration

The final shakedown tests performed were those examining the effect of inlet gas temperature on NOx destruction, and bed temperature on NO → NO₂ conversion in the guard bed. Increases in bed temperature up to 600 °F resulted in higher conversion efficiencies in the guard bed, but any temperature increase beyond 600 °F caused the conversion efficiency to decrease. This trend is illustrated in Figure 16.

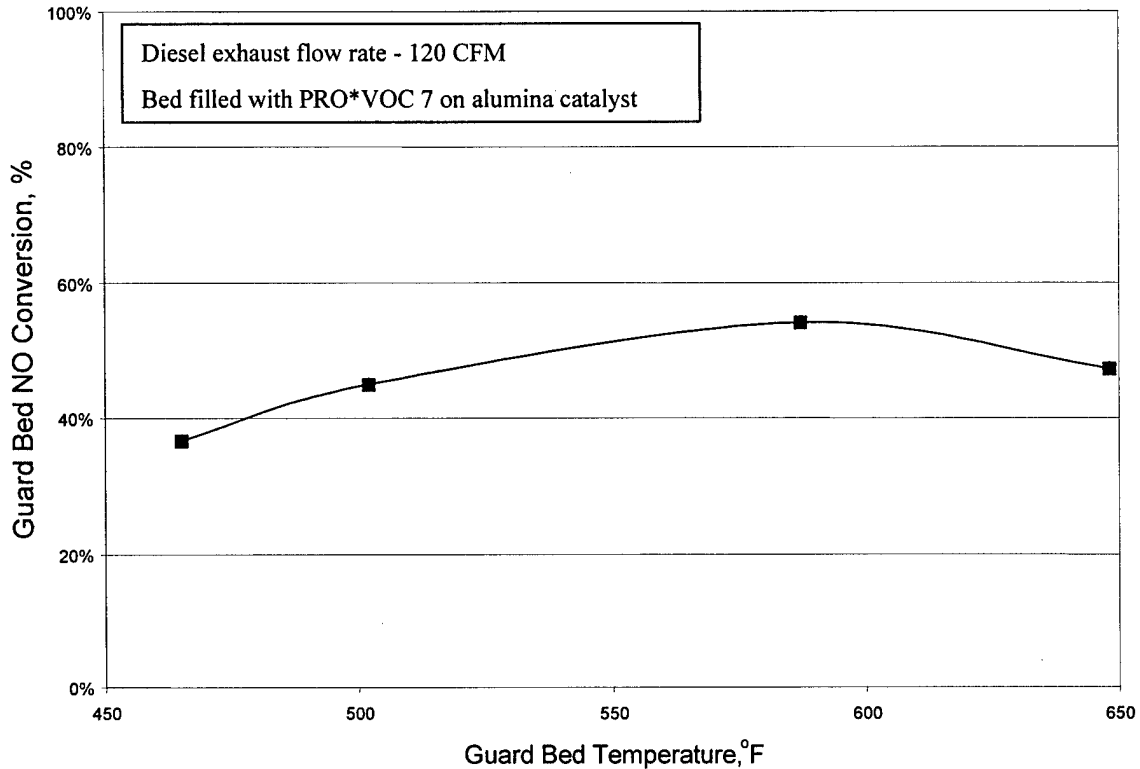


Figure 16. NO Conversion in Full-Scale Guard Bed as a Function of Temperature

When the inlet reaction temperature was varied, it was found that lower and higher temperatures were not beneficial for NOx conversion. The convenient way to vary the reactor inlet temperature is to increase and decrease the load on the engine, which also increases and decreases the exhaust gas and guard bed temperature. Since this is the case, it is necessary to maximize guard bed conversion by operating at 600 °F, so the reactor inlet temperature remained constant at 140 °F. Changing the insulation of exhaust pipe can also vary the temperature of inlet gas to the guard bed.

Upon completion of the shakedown tests, the reactor was run at the determined optimum conditions for several other sets of experiments. During the first experimental run, gas flow through the reactor was varied. Flow rates of 60, 80, 100, and 115 CFM were flowed through the radial reactor. Each test was run for three hours to be sure that the system reached at the steady state operating conditions.

The NOx destruction efficiency from these experiments is shown in Figure 17 as a function of exhaust gas flow rate. Duplicate experiments were performed at each gas flow rate.

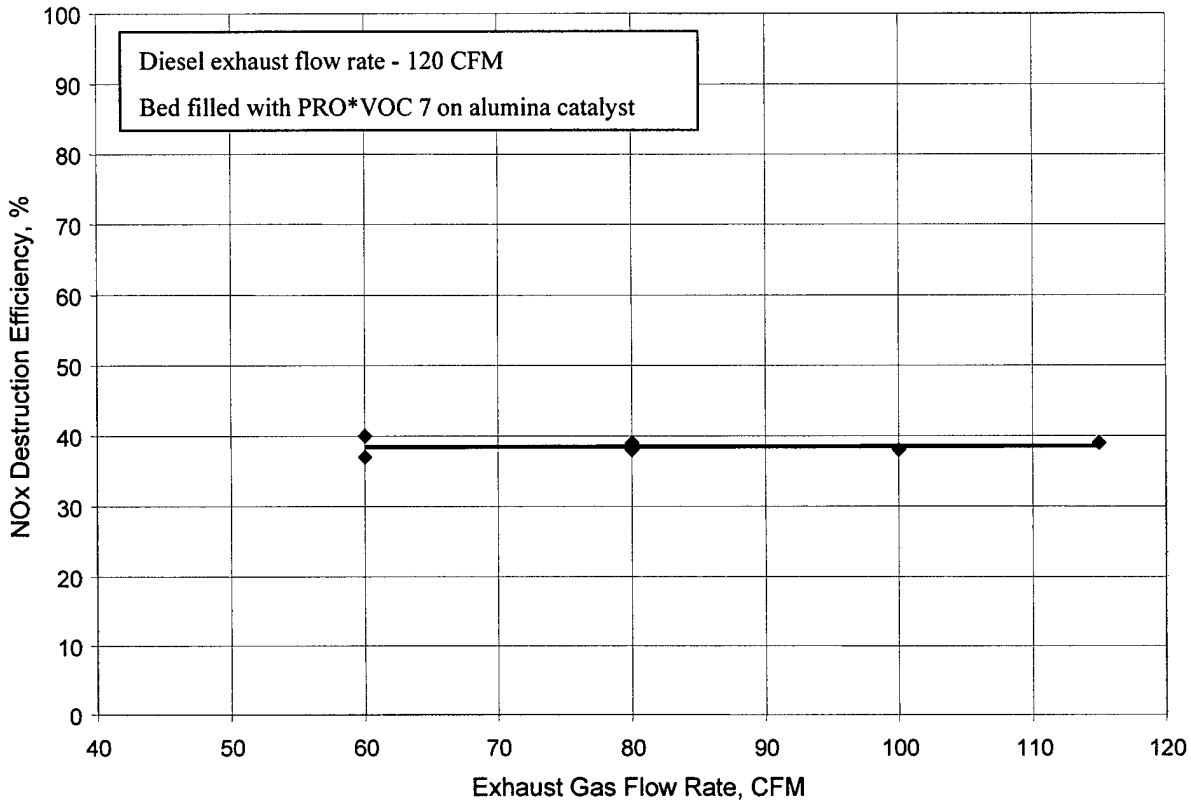


Figure 17. NOx Destruction in Radial Reactor as a Function of Exhaust Gas Flow Rate

Figure 17 indicates that microwaves were not uniformly distributed in this radial reactor. NOx destruction was lower and not dependent on gas flow rate. If microwaves were uniformly distributed in the catalyst bed, NOx destruction efficiency should decrease with increasing the gas flow rate. Therefore, it was decided that different reactor designs should be tested to find the optimum reactor design for NOx removal from diesel exhaust gases. These tests could not be completed because of time constraints in the experimental phase of this project.

CAPITAL AND OPERATING COST ESTIMATE

Diesel engine capacities of 35, 100, and 250 kW used for electric power generation were chosen for the economic evaluation of a NOx-treatment device. The purchased equipment cost for three different-sized NOx treatment systems were estimated from the known cost of our previously constructed system, and through the use of scale-up factors¹³. The raw exhaust gas flow rates produced from diesel engines are 115 SCFM from 35 kW, 400 SCFM from 100 kW and 1,000 SCFM from 250 kW of generator output, respectively. By assuming 5% freight and 65% installation cost factors, the total installed equipment cost for each system was calculated. For the 115-CFM treatment system the total installed equipment cost is \$18,054, for the 400-CFM treatment system the cost is \$30,430, and for the 1,000-CFM treatment system the cost is \$51,340. The total cost of the catalyst for each system was then determined from supplier purchase price and a 5% freight charge. The catalyst for the 115-CFM system will cost \$2,305, for the 400-CFM system the catalyst cost will be \$9,225, and for the 1,000-CFM system the catalyst cost will be \$23,060. The total capital investment for each system is calculated by adding the total installed equipment cost and the total

cost of the catalyst. The total capital investments for the three systems are \$20,360 (\$582/kW), \$39,655 (\$397/kW), and \$74,400 (\$298/kW) for 35 kW, 100 kW, and 250 kW, respectively.

The operating cost was estimated only for a 250 kW diesel engine power generator. The plant is assumed to operate at the treatment rate of 1,000 SCFM of diesel exhaust gas containing NO_x, CO, VOCs, hydrocarbons, and dry particulate matter (DPM) for 365 days per year. It is also assumed that the plant is operated automatically and controlled by a computer. Hence, no personnel attendance will be required. Assuming that the labor equivalent of 1/4 person will be required to operate the plant, the loaded direct labor cost is \$18,000 per year. Supplies and material costs, including the price of replacement microwaves and catalyst are estimated at \$18,900/year. The maintenance cost is assumed to be 3% of the capital investment, or \$2,230/year. The annual cost for taxes and insurance are taken as 3% of the capital investment, or \$2,230/year. The annual plant power demand is estimated at 96,360 kW-hr and the cost of power is estimated to be \$0.075 per kW-hr resulting in an annual cost of \$7,227. The total annual operating cost is \$48,590. However, the majority of diesel engines are used only approximately 175 to 2,080 hours per year. Therefore, the annual operating cost will be between \$970 and \$11,540 per year.

CONCLUSIONS AND RECOMMENDATIONS

The CHA Corporation has completed an investigation of the feasibility of using a novel, microwave-based filter device to remove and destroy unwanted by-products of combustion in exhaust gases. The prototype device for the destruction of NO_x in exhaust gas generated by a 58-hp diesel engine has clearly identified technical and economic advantages and technical difficulties of applying microwave-based filter device for control of diesel exhaust. The following summarizes our conclusions and recommendations.

- Corning ceramic monolith filter captures more than 85% of soot in diesel exhaust gas. The oxidation of soot captured on the filter can be easily accomplished by microwave energy but requires a minimum accumulation of soot to sufficiently absorb microwaves. Because of high-pressure drop caused by the accumulated soot, an off-line microwave regeneration of the soot filter is a more practical means of soot oxidation.
- In the absence of oxygen, NO can be easily destroyed in a Pt/Rh catalyst bed using a reducing agent and microwaves. When the oxygen concentration exceeds 6%, microwave-induced destruction of NO by a reducing agent is less than 10%. To achieve any significant catalytic destruction of NO in diesel exhaust by microwaves, the oxidation of NO to NO₂ is necessary. The maximum conversion of NO to NO₂ in the oxidation catalyst bed tested was achieved at temperatures of 550-600 °F that can be easily obtained by insulating the exhaust pipe. Because of high moisture content in diesel exhaust gas, NO₂ further reacts with H₂O to produce HNO₃ and NO in the guard-bed. This reaction limits NO conversion in the guard-bed and NO₂ destruction in the microwave reactor to 45 to 60%. The maximum NO_x destruction efficiencies were 65% for the 1-inch reactor, 50% for the 8-inch reactor and 40% for the full-scale prototype reactor for a 58-hp diesel engine. Lower NO_x destruction of the full-scale microwave reactor is due to both poor distributions of microwaves in the reactor and low conversion of NO to NO₂ in the guard-bed. Using better oxidizing catalysts that improve the oxidation of NO and improving the design of microwave reactor can increase NO_x destruction efficiency.

- A single housing accommodating a guard-bed and catalytic microwave reactor may be better for NO_x destruction. A helix coupling device distributes microwave energy uniformly in a small reactor but may not be suitable for larger reactors. A cavity reactor is more suitable to large-scale reactors if 915-MHz microwave power is utilized. Catalyst impregnated with silicon carbide (25% by weight) absorbs microwaves and can be used in other microwave applications. A helix-coupling device placed inside this catalyst transmits microwave energy to the catalyst bed and can effectively be used in a fluidized-bed.
- Estimated capital cost (\$300/kW) of the microwave-catalyst device for removal and destruction of NO_x in diesel exhaust is much lower than that of microwave-activated carbon process (\$490/kW). Because of low capital cost and smaller size, we recommend that the microwave-catalyst device for NO_x removal be further developed. NO_x destruction efficiency can be increased above the 40% barrier by using a better oxidizing catalyst and improving microwave reactor design.

ACKNOWLEDGMENTS

We wish to express our appreciation to the U.S. Air Force for providing financial support to this project.

REFERENCES

1. Alternative Control Techniques Document—NO_x Emissions from Stationary Reciprocating Internal Combustion Engines, EPA Report # EPA-453/R-93-032, July 1993.
2. Johnson, R., NALCO Fuel-Tech, Private Communications.
3. Cooper, C.D. and F.C. Alley, "Air Pollution Control, 2nd Edition," Waveland Press, 1994, Chapters 15 and 16.
4. Cha, C.Y. and C. Carlisle, "Indirect Microwave Treatment of Diesel Exhaust Gas for NO_x Control". Proceedings of the 1997 Diesel Engine Emissions Reduction Workshop", University of California-San Diego, La Jolla, CA, July 28-31, 1997, p. 319-322.
5. Rennie, D.C., P.H. Mook and C.Y. Cha, "Prototype Demonstration of CHA NO_x Removal System for Treatment of Stationary Diesel Exhaust", Presented at the 1999 AIChE Spring National Meeting, Houston, Texas, March 15-18, 1999.
6. CanTech International, "Catalyst Slays Volatile Organic Compounds," CanTech International, Feb./Mar. 1995, p.30-33.
7. Watts, W., "Health Risks Associated with the Use of Diesel Equipment Underground," In Proceedings; Diesels in Underground Mines: Measurement and Control of Particulate Emissions, Bureau of Mines Information and Technology Transfer Seminar, Sept. 1992, p. 24-29.

8. Bickel, K. L., Thomson, P., Hillman, T. L., "In-service Performance of Catalyzed Ceramic Wall-Flow Diesel Particulate Filters," In Proceedings; Diesels in Underground Mines: Measurement and Control of Particulate Emissions, Bureau of Mines Information and Technology Transfer Seminar, Sept. 1992, p. 74-81.
9. Taubert, T. R., Cordova, C. G., "Application of Urban Bus Diesel Particulate Control Systems to Mining Vehicles," Proceedings; Diesels in Underground Mines: Measurement and Control of Particulate Emissions, Bureau of Mines Information and Technology Transfer Seminar, Sept. 1992, p. 83-90.
10. Lee, M.R.; Allen, E.R.; Wolan, J.T.; Hoflund, G.B. "NO₂ and NO Adsorption Properties of KOH-Treated γ -Alumina." *Ind. Eng. Chem. Res.* 1998, 37, 3375.
11. Cha, C., Yougen, K., "NO_x Abatement with Carbon Adsorbents and Microwave Energy." *Energy & Fuels*, Volume 9, No. 6, 1995.
12. Jontgen, H., Kleinschmidt, R., Knoblauch, K., Pilarczyk, E., Richter, E., "Thermal Desorption of Nitrogen Oxides from Activated Carbon." *Thermochimica Acta*, 1985, p. 311-314.
13. Baasel, William D., "Preliminary Chemical Engineering Plant Design, 2nd Edition," Van Nostrand Reinhold Publishing, New York, 1990, 271.