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13. ABSTRACT *(Maximum 200 Words)*

The purpose of SERDP project CP-1038 is to evaluate and develop non-thermal plasma (NTP) reactor technology for DoD air emissions control applications. The primary focus is on oxides of nitrogen (NOx) and a secondary focus on hazardous air pollutants (HAPs), especially volatile organic compounds (VOCs).

Because pollutan-containing air-emission streams within the DoD frequently span a broad range of pollutant concentrations, flow rates, and gas conditions (e.g., temperature, humidity) a single type of NTP reactor is not expected to fit all types of emissions streams. Additionally, stand alone NTP reactors may provide neither an adequate means of pollutant removal nor an acceptable economic solution. Therefore, hybrid systems (combinations of different NTP reactor types or architectures), which employ adsorbents and/or catalytic media are being examined by researchers in this field.

This report is intended to provide a preliminary summary analysis of a few representative hybrid systems as a means of introducing the hybrid or staged-system concept. For the purposes of this report, we will present qualitative, rather than quantitative, analyses of hybrid reactors. That is, primary discussing of relative advantages and/or disadvantages or example systems. Additional project work in FY98 will be required to present more quantitative data for hybrids.

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Feasibility Analysis Report for Hybrid Non-Thermal Plasma Reactors

Prepared under Strategic Environmental Research & Development Program (SERDP)
Compliance Project CP-1038: Development of Non-Thermal Plasma Reactor Technology
for Control of Atmospheric Emissions

Louis A. Rosocha
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Los Alamos National Laboratory

January 15, 1998

Introduction

The purpose of SERDP project CP-1038 is to evaluate and develop non-thermal plasma (NTP) reactor technology for Department of Defense (DoD) air emissions control applications. The primary focus is on oxides of nitrogen (NO_x) and a secondary focus on hazardous air pollutants (HAPs), especially volatile organic compounds (VOCs). Example NO_x sources are jet engine test cells (JETCs) and diesel-engine powered electrical generators. Example VOCs are organic solvents used in painting, paint-stripping, and parts cleaning.

Because pollutant-containing air-emission streams within the Department of Defense (DoD) frequently span a broad range of pollutant concentrations, flow rates, and gas conditions (e.g., temperature, humidity), a single type of NTP reactor is not expected to fit all types of emissions streams. Additionally, stand-alone NTP reactors may provide neither an adequate means of pollutant removal nor an acceptable economic solution. Therefore, hybrid systems (combinations of different NTP reactor types or architectures), which employ adsorbents and/or catalytic media are being examined by researchers in this field.

This report is intended to provide a preliminary summary analysis of a few representative hybrid systems as a means of introducing the hybrid or staged-system concept. For the purposes of this report, we will present qualitative, rather than quantitative, analyses of hybrid reactors. That is, primarily discussing relative advantages and/or disadvantages of example systems. Additional project work in FY98 will be required to present more quantitative data for hybrids.

We will discuss three representative hybrid systems: a serial-mode NTP-absorber architecture, a regenerative-mode (or 'trap and treat') architecture, and a dual-NTP-mode reactor system (namely, the use of an auxiliary reactor to inject active species into a main NTP reactor). Two companion reports discuss basic NTP reactor scaling concepts [1] and a test case hybrid system [2].

Baseline Emissions Control Technology

A common means of dealing with air emissions is to pass an exhaust stream through an adsorber system, thus capturing the entrained pollutants. Granular activated carbon (GAC) is the most commonly-employed adsorber medium for many air pollutants because it has a relatively low capital cost, has a very high surface area to volume ratio, and can adsorb a wide variety of compounds [3]. However, when the GAC loses its ability to easily adsorb pollutants, it must be regenerated, reactivated, or disposed of as waste. In the processes of regeneration or reactivation, heated gases and/or steam are usually employed to desorb or strip the pollutants from the granules. These processes usually do not restore all of the adsorption capacity and the GAC must eventually be replaced, typically within five to ten cycles. If hazardous chemical pollutants are involved, handling, transportation, and permitting issues come into play - which can significantly increase costs. In summary [3], GAC has the following properties:

- Simple and inexpensive at low exhaust-gas flow rates and low pollutants concentrations
- Desorbed compounds require ultimate disposal or further treatment
- GAC must be periodically regenerated; at moderate to high flow rates and pollutant concentrations, the costs of off-site regeneration tend to outweigh the advantages of simplicity of use
- The cost of treatment largely depends on the pollutant concentration
- GAC is best suited for short-term, low mass-flow applications
- Over a 10-year life cycle, about 90% of the cost of a GAC system is associated with operating expenses.

The Hybrid Concept

We define a hybrid NTP emissions-control system as a combination of one or more NTP reactors with an adsorber, a catalyst, or another NTP reactor. Our interest in hybrid systems arises from a major conclusion drawn from the points made in the GAC section above: if the operating lifetime and/or effectiveness of GAC can be improved, the treatment costs will decrease.

There are two simple ways to combine an NTP stage with a GAC stage: place the NTP stage in series with the GAC stage, thus lessening the load on the GAC; or place the NTP stage in parallel with the GAC stage and use it to regenerate the GAC under more favorable conditions than the heat/steam regeneration methods typically employed.

The expected advantages of such an NTP-GAC hybrid system are:

- Prolonged life of GAC filters (with an associated operating cost reduction)
- Application to a broader range of exhaust-gas flow rates and pollutant concentrations
- Potential for reducing the dependence of treatment cost on pollutant concentration
- Pollutants are destroyed by the NTP stage, rather than simply captured
- NTP system can incorporate feedback to aid in optimizing the treatment efficiency and costs.

There are several ways to combine one or more NTP reactors with other NTP stages. We will discuss one particularly promising example in this report: the corona radical shower/injector system that employs a small NTP reactor to inject beneficial active species into the main NTP reactor [4].

Example Hybrid Architectures

NTP Reactor-System Architectures

In our context, the term architecture refers to the way in which an NTP reactor system is configured to treat a gaseous-emissions stream (exhaust gas, stack/flue gas). The previously-mentioned report [1] discusses the concepts of monolithic and modular scaling architectures. In this report, we will not be concerned with the type of scale-up architecture - emphasis will be given to the method of combining a generic "black box" NTP reactor with a different stage to produce a hybrid system.

For many applications, end-of-pipe emissions treatment is the norm. However, one can also conceive of restricting the treatment closer to the point-of-use, or integrating the emissions treatment equipment directly into the process which produces the emissions. For the purposes of this report, an end-of-pipe application will sufficiently illustrate the hybrid system concept.

Serial-Mode NTP Reactor Hybrid Architecture

In a serial-mode hybrid system, an NTP reactor precedes an adsorber bank (see Figure 1). As mentioned earlier, adsorbers such as activated carbon, are commonly-employed but cost-intensive treatment methods (mainly because of regeneration, reactivation, or disposal costs). For the serial-mode hybrid, the load on the adsorber stage can be easily reduced by 50-75% by the pretreatment action of the NTP reactor. This results in a significant change in the overall treatment economics because the useful adsorber lifetime can be greatly increased, while the NTP reactor does not have to operate in an energy-demanding, high-removal regime (the energy cost per pollutant molecule destroyed is a logarithmic function of the degree of removal [1]). Additionally, one can envision tailoring the adsorber to better match the compounds which the NTP reactor produces, thereby increasing the overall process effectiveness. That is, one is not necessarily constrained to the use of GAC - superior adsorbents are most likely available (and will be sought out as part of this project).

Regenerative-Mode NTP Reactor Hybrid Architecture

In a regenerative-mode (or 'trap and treat') hybrid system, an NTP reactor is used to regenerate a pollutant-adsorber bank (see Figure 2). Here the adsorber traps the pollutants (NO_x or VOCs) while operating at a high off-gas flow rate, but is regenerated off-line at more economical conditions. Such conditions can be a lower flow rate and, hence, a lower power demand; or a lower power cost when operating at electrical utility off-peak times. This architecture is particularly attractive for episodic emissions (e.g., JETCs), where high-flow operation and regeneration can be easily divided into separate functions.

Two additional key advantages of the NTP regenerative hybrid are: the ability to incorporate electronic feedback into the process, thereby operating the system at more optimal treatment conditions and costs; and the ability to flush the adsorbent with a tailored gas mixture, thereby more effectively controlling the destruction chemistry, the formation of undesirable byproducts, and the overall effectiveness and treatment costs.

Plasma-Catalyst Hybrids

In either the serial-mode hybrid or the regenerative-mode hybrid, the use of catalysts, rather than adsorbents, is also considered. Recently, there has been considerable interest in combining non-thermal plasmas and catalysts for de-NOx applications [5-8]. Much of this work has been focused on lean-burn diesel engines, whose oxygen-rich exhaust streams tend to enhance the oxidative conversion path NO → NO_2 when only plasma treatment is employed. With plasma-assisted catalysis, the goal is to develop a de-NO_x system that favors the reductive path NO → $N_2 + O_2$ (or other products which are not oxides of nitrogen).

In oxygen-rich environments, several types of catalytic materials can promote the selective catalytic reduction (SCR) of NO_x by hydrocarbons normally present in the exhaust stream. Combining an NTP with a catalyst has been shown to enhance the SCR process. Additionally, one can conceive of multi-stage plasma-catalytic systems, whereby either a catalytic material or an NTP is applied to enhance particular reaction steps in the SCR process. For example, the highly-efficient, yet undesirable reaction NO → NO_2 can be used to advantage if the plasma stage which produces the NO_2 is followed by an efficient catalytic stage for converting the NO_2 to a more-desirable terminal product: NO_2 + catalyst + hydrocarbon → $N_2 + CO_2 + H_2O$. Such systems are being explored by other researchers in fundamental, benchtop studies. In our future SERDP work, we intend to more fully evaluate plasma-catalytic systems for DoD applications (in particular JETCs and diesel motor-generator exhausts).

Dual-NTP Reactor Hybrid System (Corona Radical Injection/Shower)

Yet another promising configuration is the hybrid "Corona Radical Shower" (CRS) system of J.-S. Chang et al [4]. This device is described in the earlier-mentioned companion report [2]. Here, a brief summary of the system will be presented.

In the CRS system (see Figure 3), arrays of small nozzles or showers, each with a small bleed-gas flow, are introduced into a wire-plate DC corona reactor. The purpose of the nozzles is to create desirable active species and inject them into the larger main corona treatment region, which enhances the overall pollutant-removal effectiveness. The injected active species can be tailored to the particular pollutant stream being treated by selecting the shower-injector bleed-gas so that it produces active species that are particularly effective in decomposing the target pollutant.

Experiments by our collaborators at McMaster University have shown that, for NO removal, ammonia (NH_3) and a hydrocarbon like methane (CH_4) are useful injector-gas additives. It is interesting to note that McMaster has also shown that, for JETC de-NO_x, normally-present hydrocarbons in the exhaust stream can enhance the de-NO_x process. In this case, air or a slipstream of the JETC exhaust itself is effective as a shower-injector gas, without requiring additional external additives (like NH_3).

Future Work

Under this project, our future work on hybrid systems will focus on: evaluation of potential adsorbents and/or catalysts for serial-mode or regenerative-mode hybrid systems; further quantification of comparisons among different NTP reactors (e.g., including ancillary equipment costs); improving our understanding of the role entrained hydrocarbons play in plasma de-NOx; exploring methods to arrive at easily-handled final de-NO_x products (e.g., ammonium nitrate powders useful for fertilizer; scrubbable nitric acid).

References

1. L.A. Rosocha and R.A. Korzekwa, “First Report on Non-Thermal Plasma Reactor Scaling Criteria and Optimization Models, ” *Los Alamos National Laboratory Unpublished Report*, LA-UR-98-125 (January 1998).
2. M. Matsuoka, S.J. Kim, P.C. Looy, and J.S. Chang, “Development of Scaling and Economic-Evaluation Algorithms for Non-Thermal Plasma Reactors for Control of NO_x Emissions,”, McMaster University (October 27, 1997).
3. M. Cummings and S.R. Booth, “An Evaluation of the Cost Effectiveness of Innovative Off-Gas Treatment Technologies,” *Los Alamos National Laboratory Unpublished Report*, LA-UR-96-1253 (1996).
4. J.-S. Chang, P.C. Looy, J. Pevler, K. Nagai, and T. Yoshioka, “Reduction of NO_x from a Combustion Flue Gas by a Corona Radical Injection Method, ” *Conference Record of 1993 IEEE IAS Meeting*, pp. 1969-1975 (1993); and T. Ohkubo, S. Kanazawa, Y. Nomoto, and J.-S. Chang, “NO_x Removal by a Pipe with Nozzle-Plate Electrode Corona Discharge System,” IEEE Trans. Industry Applications, 30, pp. 856-861 (1994).
5. B.M. Penetrante, M.C. Hsiao, B.T. Merritt, and G.E. Vogtlin, “Enhanced Selective Catalytic Reduction of NO_x from Lean-Burn Engine Exhausts,” *Abstracts of 1997 Diesel Engine Emissions Reduction Workshop,* San Diego, CA (July 27-31, 1997).
6. M.C. Hsiao, B.M. Penetrante, B.T. Merritt, and G.E. Vogtlin, “Plasma-Assisted Heterogeneous Catalysis for NO_x Reduction in Lean-Burn Engine Exhausts,” *Abstracts of 1997 Diesel Engine Emissions Reduction Workshop,* San Diego, CA (July 27-31, 1997).
7. R.G. Tonkyn, M.L. Balmer, S.E. Barlow, D. Goulette, J. Hoard, and T.M. Orlando, “Vehicle Exhaust Treatment Using Electrical Discharge and Materials Chemistry,” *Abstracts of 1997 Diesel Engine Emissions Reduction Workshop,* San Diego, CA (July 27-31, 1997).
8. V. Palekar, V. Puchkarev, M. Ramavajjala, and R. Stone, “Plasma Assisted Catalyst Technology for NO_x and Particulate Removal from Heavy Duty Vehicles,” *Abstracts of 1997 Diesel Engine Emissions Reduction Workshop,* San Diego, CA (July 27-31, 1997).

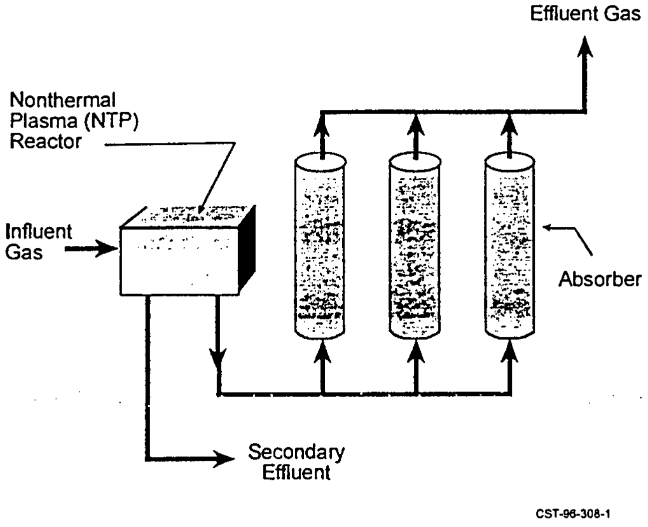

Figure 1: Serial-mode NTP-absorber architecture. Disposal and/or regeneration economic advantage comes from reducing the load on the absorber. Treatment effectiveness can also be increased if the NTP reactor converts the initial pollutant into more easily-absorbed compounds.

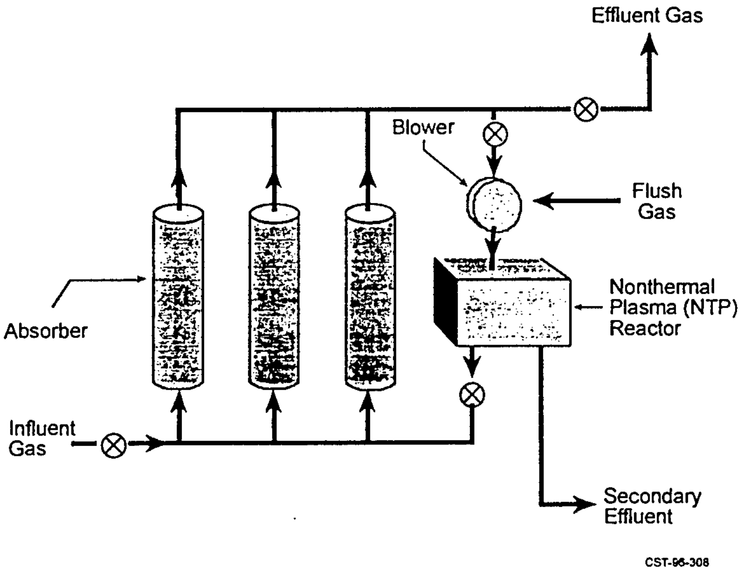

Figure 2: Regeneration-mode NTP-absorber architecture. Economic and performance advantages may be gained by regenerating the absorbers off-line from pollutant capture, but employing on-site, rather than off-site handling.

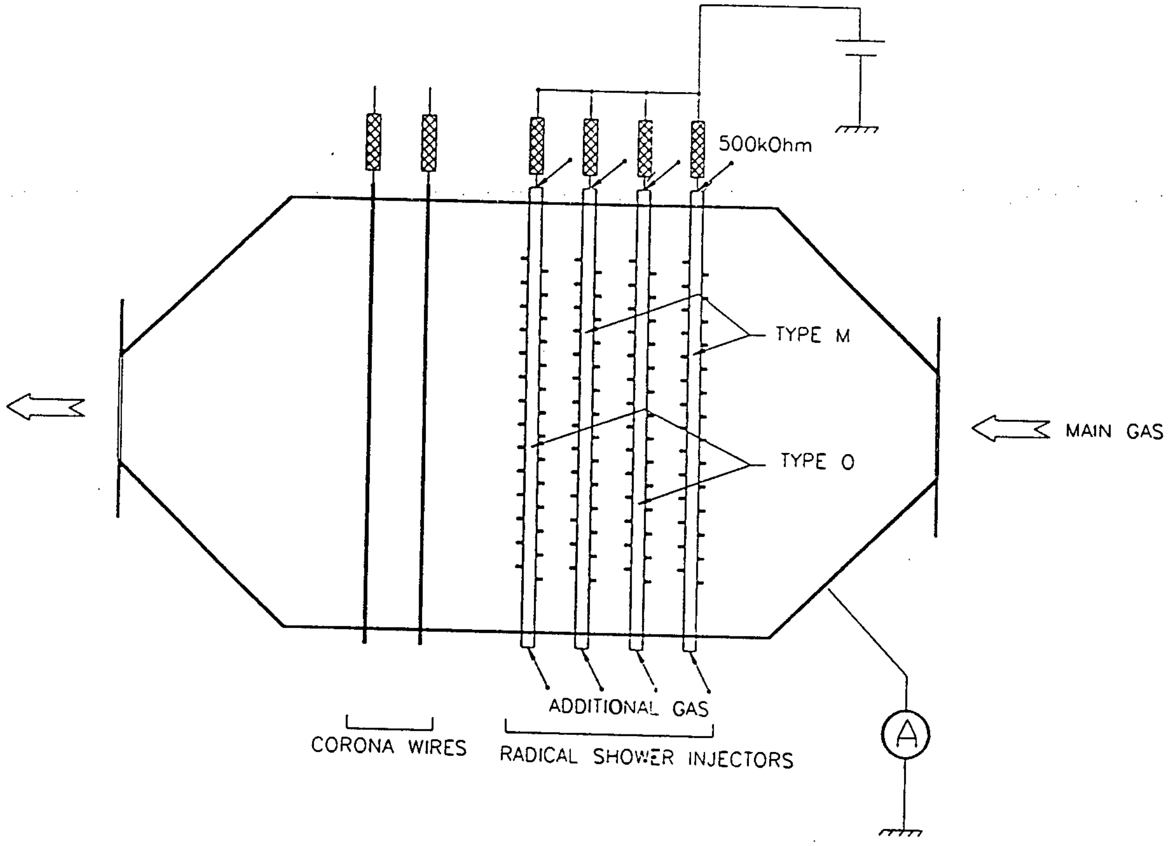

Figure 3: Cross-section view of corona radical shower reactor [2]. Active species are introduced to the main wire-plate DC corona reactor through an electrical discharge in a bleed gas fed through the small "shower" tubes.