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Control of nitric oxide, nitrous oxide, and ammonia emissions using microwave plasmas

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Abstract

The subject of this paper is mitigation of the undesirable side-effects of selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR): ammonia slip, residual NO_x , and N_2O emissions. The use of microwave-plasma discharge within the flue gas was explored as a potential pollution-control method. The key issues addressed were: (1) N_2O , NH_3 , and NO removal efficiencies; and (2) sustaining a stable plasma at atmospheric, or close to atmospheric, pressure. In non-oxidizing atmospheres, removal efficiencies were always close to 100% for all species. In the presence of oxygen, however, appreciable amounts of nitric oxide and ammonia were formed. Methods leading to preventing these undesirable effects were examined. In a number of runs, stable plasma operation was attained at pressures close to atmospheric. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A common way of controlling emissions of nitrogen oxides (NO_x) in coal combustion is ammonia, urea, or cyanuric-acid injection. (Urea and cyanuric acid act as convenient ammonia precursors.) The above method is known as selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR), depending on whether or not a solid catalyst is used [1,2]. Although the underlying chemistry is somewhat different for

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SNCR and SCR, both techniques have the same net result: the reaction of NO_x and NH_3 to form molecular nitrogen and water. Both techniques also have a common shortcoming known as ammonia slip, which is simply the release of unreacted ammonia into the stack. The effectiveness of SNCR and SCR critically depends on good process control as poorly chosen NH_3/NO_x ratio, temperature, or location of ammonia injection may lead to an increase in NO_x emissions. In addition, SNCR has been reported to give rise to incomplete NO_x reduction and the formation of nitrous oxide (N_2O) [2], a gas implicated in the greenhouse effect and the destruction of Earth's protective ozone layer.

The above shortcomings can be partly alleviated by improved process control, but even a perfect process-control system will not reduce N_2O levels in fluidized-bed combustion, where the source of N_2O is unrelated to SNCR. A strong need thus exists for a simple and cost-effective "polishing step" in which excess ammonia, N_2O , and residual NO_x would be removed from the combustion flue gas. The preferred location for such a gas-cleanup unit would be downstream of the air pre-heater to facilitate retrofitting. The objective of this work was to evaluate the usefulness of employing a microwave-plasma unit to decompose the three pollutants. If successful, this approach could easily be extended to applications other than SNCR and SCR.

2. Experimental methods

The experimental set-up used in this work is shown in Fig. 1. The apparatus consisted of a plasma reactor, a microwave power system, a gas flow system, and a Fourier-Transform Infrared (FT-IR) multigas analyzer. The plasma was generated in a 19-mm o.d. (~ 17 mm i.d.) vycor tube that passed axially through a microwave applicator. The height of the plasma zone in the reactor was approximately 2.5–4.0 cm, depending on process conditions.

The microwave energy system consisted of a terminated waveguide applicator [3], microwave generator, magnetic circulator, directional coupler, impedance matching device, and various waveguide sections. Microwave energy was supplied by a Cober S6F industrial microwave generator. The generator power output was adjustable from 0 to 6000 W at a fixed frequency of 2.45 GHz. The generator was connected via a magnetic circulator and a Microwave Techniques twin stub tuner to the terminated waveguide applicator. The applicator was constructed by boring a 22-mm hole through the center of the broad faces of a standard WR 284 waveguide termination. The distance from the center of the hole to the shorted end of the termination was equal to one half the width of the broad face. Hewlett Packard 432 power meters were used in conjunction with a 60-dB directional coupler to measure incident and reflected power.

Based on a typical gas flow of 100 ml/min (STP) and a system pressure of 15 mm Hg, estimated residence times were 0.02–0.03 s, assuming a mean gas temperature in the plasma zone of ~ 1300 K. The inlet gas flow was controlled using mass-flow controllers, and the outlet gas composition was measured using an FT-IR analyzer. The outlet gas was diluted with nitrogen to increase the flow rate through the analyzer gas cell (reduced purge time and better response to changes in gas composition). In experiments in which the effect of moisture was studied, one of the inlet gas streams

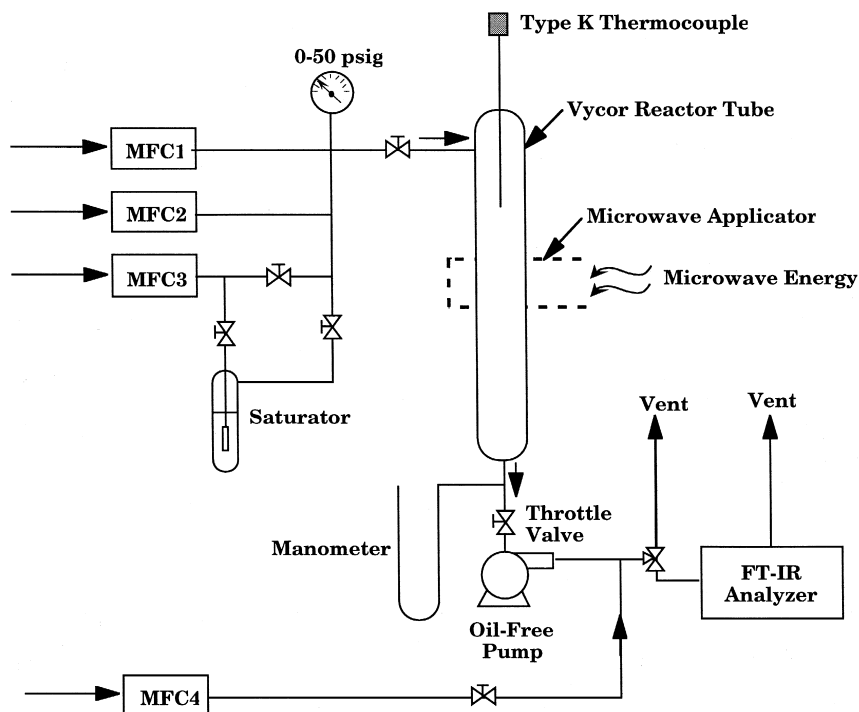


Fig. 1. Schematic representation of the experimental set-up used in this study. MFC1, MFC2, MFC3, and MFC4 are mass-flow controllers.

was saturated with water vapor using a standard laboratory bubbler equipped with a fritted-plate gas distributor. Water content varied between 0.5% and 1.1%, and was limited by the dew point at the conditions prevailing in the vacuum pump. Condensation of water downstream of the reactor had to be avoided to prevent difficulties with the ammonia measurement (absorption of ammonia by condensed water). A mercury manometer was used to measure the system pressure.

3. Results and discussion

The following issues were addressed in this project: (1) N_2O removal efficiency using an $\text{N}_2\text{O}/\text{N}_2$ gas mixture; (2) NO removal efficiency using an NO/N_2 gas mixture; (3) NH_3 removal efficiency using an NH_3/N_2 gas mixture; (4) the maximum pressure at which a microwave plasma can be sustained; (5) the effect of microwave power input; (6) the behavior of multicomponent gas mixtures (the effect of water, oxygen, and carbon dioxide).

A number of runs were carried out using several N_2O input concentrations, reactor pressures, and microwave power inputs. The data related to the $\text{N}_2\text{O}/\text{N}_2$, NO/N_2 , and NH_3/N_2 experiments are summarized in Tables 1–3, respectively.

Table 1

Summary of microwave-plasma runs involving a mixture of nitrous oxide and nitrogen (C_i is inlet concentration of species i ; X_i is percent conversion of species i in the reactor; P is reactor pressure (mm Hg); and MP is microwave power input)

Run #	P (mm Hg)	MP (W)	C_{N_2O} (ppm)	X_{N_2O} (%)
1	11–349	50–300	313	96
2	5	50	778	99
3	15	100	313	99
4	15	100	401	100

A general observation was made that nearly complete N_2O decomposition took place in the plasma reactor as long as a stable plasma was maintained. In the case of plasma extinction, e.g., during a sudden surge in pressure, the N_2O conversion dropped to zero. Thus, the only critical parameter for N_2O removal seems to be the existence vs. non-existence of the plasma. Excellent N_2O decomposition efficiency was observed in the entire range of N_2O inlet concentrations.

The following reaction, known to occur in non-plasma systems [1], is believed to be responsible for N_2O destruction:



where M denotes a gas molecule.

If traces of water are present, which is often difficult to avoid, the following two reactions may also play a role:



and:



In the case of NO/N_2 gas mixtures, it was again observed that a nearly complete NO decomposition occurred as long as a stable plasma was maintained (see Table 2). High

Table 2

Summary of microwave-plasma runs involving a mixture of nitric oxide and nitrogen (C_i is inlet concentration of species i ; X_i is percent conversion of species i in the reactor; P is reactor pressure (mm Hg); and MP is microwave power input)

Run #	P (mm Hg)	MP (W)	C_{NO} (ppm)	X_{NO} (%)
6	25	100	1463	100
7	11	50	600	100
8	31	50	600	89
9	28	100	600	94
10	28–68	200	600	90–100
12	126–156	200	600	100
13	236	300	600	100
14	6	50	600	100
118	11	50	6000	100
119	10–234	250	6000	98

Table 3

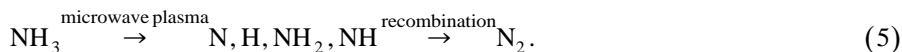
Summary of microwave-plasma runs involving a mixture of ammonia and nitrogen (C_i is inlet concentration of species i ; X_i is percent conversion of species i in the reactor; P is reactor pressure (mm Hg); and MP is microwave power input)

Run #	P (mm Hg)	MP (W)	C_{NH_3} (ppm)	X_{NH_3} (%)
22	12	300	205	100
23	512	300	205	100
25	11	50	205	91
27	609	300	205	100
28	10	200	366	100

decomposition efficiencies were obtained in a wide range of NO concentrations. The following reaction may be responsible for NO destruction:



Ammonia-destruction data are shown in Table 3. It is quite clear that, within experimental error, virtually all ammonia is destroyed by the reactive species present in the microwave plasma. The mechanism of ammonia decomposition may be schematically represented as follows:



Microwave plasmas are usually employed in vacuum applications, and one of the critical issues addressed in this project was the viability of microwave-plasma operation at pressures close to atmospheric. Due to budget and time constraints, only preliminary exploration of the problem was possible in this study. In a number of runs, system pressure was gradually raised to the point of plasma extinction. It was found that the system was sensitive to the rate of pressure increase, and to some extent also to gas composition (e.g. traces of ammonia seemed to help sustain plasma at higher pressures, but the underlying chemistry of this effect is unclear). In many cases, stable plasma operation was attained at pressures only slightly below or equal to atmospheric, and in several runs, favorable conditions for plasma existence were accomplished at a pressure 20 mm Hg *above* atmospheric. Reactor operation was stable over a long period of time, and this result was fully reproducible in independent replicate experiments.

Several runs were carried out in which the $\text{N}_2\text{O}/\text{N}_2$ gas stream was introduced about 1 cm downstream of the plasma zone. A flow of nitrogen was maintained through the reactor for nitrogen-plasma generation, and both gas streams were combined below the bottom part of the plasma zone. Under these conditions, N_2O conversions were below 100%, and the effect of microwave-power input could be assessed. The results are presented in Fig. 2, and they show that as microwave power increases from 50 to 250 W, the efficiency of N_2O decomposition increases from 55% to 82%. It is interesting to note that high N_2O removal efficiencies were observed although N_2O never passed through the plasma reactor. This provides a proof of concept for the idea of generating a nitrogen plasma *ex situ*, and then injecting the reactive plasma species into the flue gas.

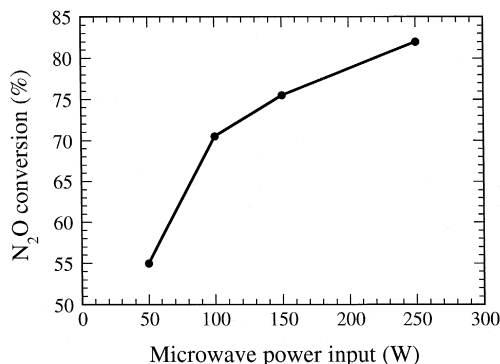


Fig. 2. N₂O conversion in a microwave reactor at 12 mm Hg pressure. A mixture of 300 ppm N₂O in nitrogen was introduced into the reactor approximately 1 cm below the plasma zone, while a small flow of nitrogen was introduced at the top of the reactor for nitrogen-plasma generation.

The effect of water was studied within the limitations of the existing system, i.e., at concentrations up to 1.1%. In actual flue gas, water levels are much higher, and it is expected that the overall behavior of the plasma system would be different from what is observed at low water-vapor concentrations. Nevertheless, some insights into the chemistry of microwave-plasma reactions can be gained from the experiments carried out in this work.

A series of runs involving 300 ppm N₂O/N₂ mixtures in the presence of water were carried out, and nearly 100% N₂O destruction efficiencies were observed. This is not surprising as water vapor provides H and OH radicals known to be instrumental in gas-phase N₂O decomposition according to reactions (2) and (3).

The negative effect of the presence of water was the generation of 77–808 ppm NO, and up to 315 ppm of NH₃. Although a great number of radical and other reactions are involved in the overall plasma chemistry, it seems likely that NO formation observed in these experiments is caused by reactions that are part of the thermal NO_x formation mechanism:



and:



Thus, the formation of nitric oxide in the presence of water may be attributed to the atomic oxygen generated from water at elevated temperatures. If the above conjecture is correct, it should be possible to detect nitric oxide in the products of reactions occurring in the plasma formed from O₂–N₂ mixtures. Such tests were carried out, with and without water addition, and the relevant results are shown in Fig. 3. The following three observations can be made: (1) an oxygen–nitrogen plasma does give rise to nitric oxide formation; (2) small amounts of water enhance NO formation; and (3) the amount of nitric oxide formed increases as system pressure increases.

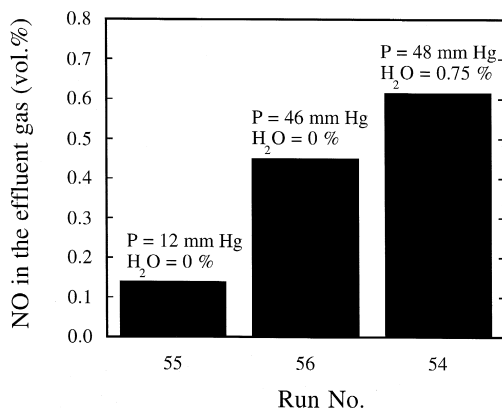


Fig. 3. Nitric oxide formation in an oxygen–nitrogen plasma (3.3% O₂, 96.7% N₂; microwave power input: 250 W).

The formation mechanism of NH₃ in an N₂O/N₂/H₂O system is less clear. NH₃ formation has been reported as a result of reactions involving N and H atoms when nitrogen and hydrogen mixtures were passed through a discharge [4]. The highest yields of ammonia were obtained at low temperatures because, at such temperatures, high NH₃ concentrations are thermodynamically favored. In one study, a pressure of 100 mm Hg was reported as optimum for high NH₃ formation, and a nitrogen-to-hydrogen ratio of 5 was unexpectedly found to result in the highest yields of NH₃ [5,6]. With electrode discharges, NH₃ yields were also found to depend on current strength, pressure, and also the shape of the reaction tube. It is fair to say that there remains a lot to be learned about ammonia chemistry in plasma systems, and a more systematic investigation of reaction fundamentals is warranted.

The effect of CO₂ on NO and NH₃ conversion was also studied, and nitric oxide formation was found to occur, although in smaller amounts than in the case of oxygen. It is interesting to note that CO₂ itself underwent appreciable decomposition, similar to that experienced by N₂O, NO and NH₃ in non-oxidizing atmospheres, with carbon monoxide as the main product.

In a limited number of experiments, the effect of reactor size (surface-to-volume ratio) was studied. A strong indication was found that the NO formation chemistry was dominated by heterogeneous reactions occurring on the walls of the reactor (a factor of two increase in the surface-to-volume ratio brought about a factor of two increase in NO levels). This finding may have practical implications for the process, as discussed below.

It is likely that the NO formation mechanisms that compete with the microwave-assisted NO decomposition were strongly enhanced in the experiments reported in this study. This could have happened due to the following factors: (1) the low pressures used in most runs; (2) the small size of the plasma reactor (high surface-to-volume ratio); and (3) the high quench rates (see the discussion below).

It is well known that under vacuum conditions heterogeneous reactions play a more important role than the same reactions occurring at atmospheric pressure. It can then be

expected that the undesirable NO formation would be less severe in atmospheric-pressure operations in large-scale reactors. Evidence for the wall-induced nitric oxide generation was reported by Timmins and Ammann [7]. According to them, the following reaction is responsible for NO formation on reactor walls:



Another way of explaining the results obtained in a small reactor is in terms of the effect rapid quenching has on nitric oxide concentration in the flue gas. It is well known that high-temperature conditions favor the formation of nitric oxide, with low temperatures promoting NO decomposition in favor of molecular nitrogen. High transient temperatures, which may be encountered within the plasma region, are detrimental to the gas-cleanup process (thermal NO_x), but what is even worse is the dramatic temperature drop to room temperature. Under such conditions, which prevailed in most of our experiments, the high levels of NO were “frozen” without giving the gas a chance to reach equilibrium concentrations. Although at low temperatures chemical equilibrium favors nitric oxide decomposition, the slow kinetics make this process take too much time to be of practical importance. A gradual decrease of temperature, instead of rapid quenching, would presumably allow nitric oxide to reach lower concentrations in the transition zones of the reactor.

A detailed analytical study by Ammann and Timmins [8] has shown that nitric oxide concentrations are extremely sensitive to the time–temperature history of the gas. If the quench rate is maintained above 10^{10} K/s, the surface reactions can dominate the recombination kinetics. This problem is particularly severe when quenching occurs at low pressures, and this phenomenon has been reported to affect even gas-sample collection into evacuated containers [7]. Several investigators have obtained up to 10–12% NO from dissociated air at very low pressures [9]. In another study, LaRoche [10] used high-frequency discharges and found that rapid quench rates produced twice the levels of NO than were formed in low quench rate experiments.

In view of the fact that considerable technical challenges still need to be addressed, an economic assessment of the plasma-induced cleanup technology seems premature. At this time, a reference can be made to a preliminary study of the cost of a plasma process in a 200-MW utility boiler carried out by Burns and Roe [11]. The study concluded that the costs of SCR and the plasma injection were similar, and that further improvements in plasma energy efficiency and radical production could increase the process viability. The main difference between the two technologies is the fact that the capital costs for SCR are higher than for the plasma process, whereas the opposite is true about the operating costs.

4. Conclusions

The use of microwave-plasma discharge within the flue gas was explored as a potential pollution-control method. The key issues addressed were: (1) N_2O , NH_3 , and NO removal efficiencies; and (2) sustaining a stable plasma at atmospheric, or close to

atmospheric, pressure. In non-oxidizing atmospheres, removal efficiencies were always close to 100% for all species. In the presence of oxygen, however, appreciable amounts of nitric oxide and ammonia were formed. In a number of runs, stable plasma operation was attained at pressures close to atmospheric.

Clearly, future research should focus on preventing the undesirable NO and NH₃ formation in the plasma zone, e.g., through the use of a pulsed plasma source. This technique has been successfully used in an E-beam process, but pulsed microwave-plasma applications are not unusual. Pulsed corona discharge has also been reported to improve NO_x-emission control [12].

Another method may involve the generation of reactive plasma species *ex situ* in a small stream of nitrogen that would be added to the flue gas. In this way, the harmful oxidizing environment would be eliminated from the plasma zone. The concern here is whether sufficient amounts of long-lived species would be created for this method to be effective. A similar approach has been applied to NO_x-emission control using an argon plasma [13].

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