0273-2289/01/91–93/0205/$11.75

Effect of Temperature on Biofiltration of Nitric Oxide

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Index Entries: Nitric oxide; *Paracoccus denitrificans*; denitrification; trickle-bed biofilter; mass transfer.

Introduction

In 1997, a record level of 3.13 trillion kilowatt-hours (kWh) of electricity was generated in the United States. Coal-fired power generation accounted for 57% of this production, generating an estimated 7.2 million t of nitrogen oxide (NO_X) compounds. Generally, >95% of the NO_X compounds in combustion gas streams will be in the form of NO. Titles I and IV of the 1990 Clean Air Act Amendments list an overall goal of reducing total NO_X emissions to 697–775 kg/million kWh *(1)*.

The NO_X compounds consist of nitric oxide (NO) and nitrogen dioxide (NO_2). NO and NO_2 contribute to photochemical smog, acid rain, visibility degradation, and fine particulates in the atmosphere *(1)*. NO_X compounds tend to be local and regional concerns, because of their relatively short lifetime in the atmosphere. The other NO_X, nitrous oxide (N_2O), has a long life span in the atmosphere and is a strong absorber of infrared radiation in the troposphere. It is claimed that it is a major component of global warming and depletion of ozone *(1)*. Because N_2O is stable in the troposphere, it is transported to the stratosphere, where it is the largest source of stratospheric NO. By being the major natural chemical sink, N_2O helps establish the stratospheric ozone concentration.

Recent scientific articles report daily increases in particle air pollution. These are associated with daily increases in harmful human health effects,

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primarily among the elderly and children with increased hospitalizations for respiratory diseases *(2)*. NO is considered a signaling molecule that acts primarily in the nervous and cardiovascular systems, and it diffuses freely across cell boundaries to activate nearby "target" cells *(3)*. Moreover, NO has cytotoxic properties and is implicated as the causative factor for neuron degeneration associated with Parkinson disease, autoimmune deficiency syndrome, dementia, and stroke. NO is produced by a variety of cell types, including neurons in the central and peripheral nervous systems, endothelial cells, platelets, and certain activated cells of the immune system *(3)*.

One possible alternative for NO_X treatment is microbial denitrification. Denitrification is the process in which nitrate is reduced to nitrogen through nitrite, NO, and N_2O intermediates via the following reaction *(4)*:

$$NO^{3-} \Rightarrow NO^{2-} \Rightarrow NO \Rightarrow N_2O \Rightarrow N_2 \quad (1)$$

The goal of the present study was to examine the effect on operating temperature in a trickle-bed biofilter when using the bacterium *Paracoccus denitrificans* (renamed from *Thiosphaera pantotropha*) to carry out the last two steps in the aforementioned denitrification process with a simulated combustion gas containing NO.

Materials and Methods

The bacterium *P. denitrificans* (ATCC 35512) was obtained from the American Type Culture Collection (Manassas, VA) and was maintained on a *Thiosphaera* mineral medium consisting of 3.0 g of KNO_3, 2.7 g of $CH_3COONa{\cdot}3H_2O$, 0.8 g of K_2HPO_4, 0.3 g of KH_2PO_4, 0.4 g of NH_4Cl, 0.4 g of $MgSO_4{\cdot}7H_2O$, and 2 mL of trace metal solution *(5)* per liter of medium. The pH of the medium was adjusted to 8.0 with NaOH before autoclaving at 121°C for 30 min. The cells were aerobically grown in the medium for 2 d at 30°C before they were placed in a refrigerator (4°C) for later use in the reactor. To inoculate the trickle-bed reactor, 90 mL of refrigerated culture was added to the liquid recycle loop, and the system was used in full recycle with an air purge for 2 d, after which the continuous feed medium was started at a flow rate of 0.2 mL/min. After 7 d the medium was replaced with a medium with sodium acetate and KNO_3 concentrations of 8.25 and 1.5 g/L, respectively. After an additional 13 d, the medium was replaced with a medium without nitrate and a sodium acetate concentration of 8.25 g/L. The gas feed was also changed to a mixture of ~500 ppmv of NO and 15.5% CO_2 in N_2. Finally, after 10 d the medium was again changed to the *Thiosphaera* medium, less the KNO_3. By changing the medium in this manner, we were able to establish rapid cell growth on the packing under aerobic conditions and slowly transition the system to a nitrate-free medium under anaerobic conditions. The total start-up period was 30 d, and the data presented were collected over a 72-d period.

The trickle-bed biofilter consisted of a jacketed glass column (51 mm id, 600 mm high), packed with porous foam material (Fluval Foam; Rolf C.

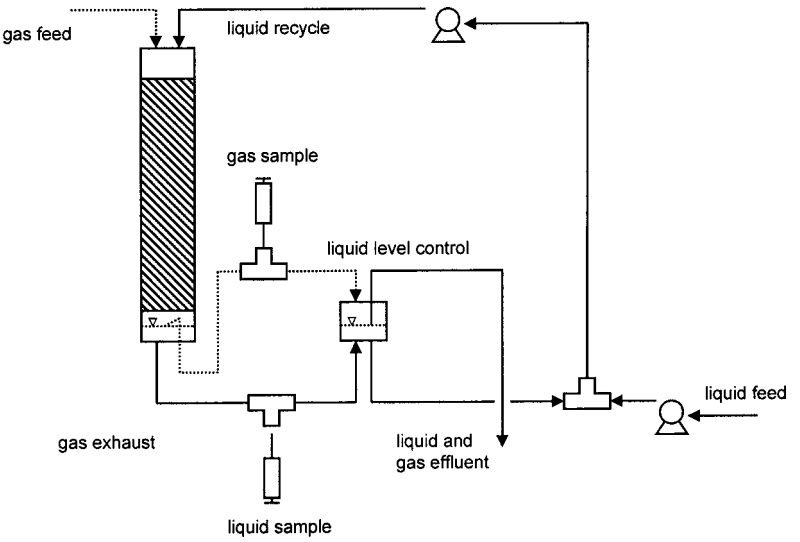

Fig. 1. Schematic of trickle-bed bioreactor. Fresh gas feed entered the top of the reactor and passed over plastic foam packing acting as a solid support for the biofilm. NO is removed by the microbial consortium as it is transferred into the liquid phase. Trickling mineral medium containing acetate as the carbon and energy source is recirculated through the reactor.

Hagen, Montreal, P.Q., Canada) to a height of 525 mm. Both the gas and the liquid recycle streams entered from the top and were separated below the packing. Figure 1 presents a schematic of the system.

The liquid recycle was kept at 200 mL/min and the fresh medium feed rate was 0.2 mL/min. The temperature of the reactor was maintained by circulating heated water through the jacket surrounding the column. The gas flow rate was varied with a calibrated rotameter control valve.

The gas analysis ($NO/O_2/CO_2$) was performed by collecting approx 2 L of gas in a Tedlar PVF gas sample bag and immediately analyzing the content of the bag using a Micro Emissions Analyzer (Model Enerac 400 EMS; Energy Efficiency Systems, Westbury, NY). Because of the already high concentration of N_2 in the inlet gas (80–85%), N_2 produced by the conversion of NO could not be measured.

Results and Discussion

Figure 2 depicts conversion of gaseous NO within the trickle bed during the course of the work. As noted, the removal of NO was 100% at gas flow rates corresponding to an empty bed residence time of approx 2 min in the packed section of the bed. Interestingly, there was no apparent temperature effect over the interval studied. A few of the data points collected at 42°C were below expected removal efficiency (Fig. 2); however, these points were collected immediately after a few days of interrupted gas supply (thus, the electron acceptor, NO, was not present). Also note that the

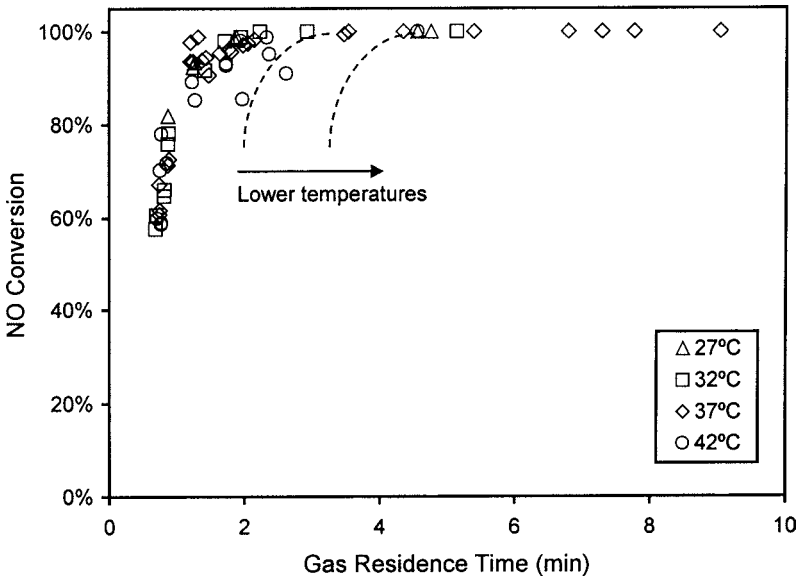

Fig. 2. Typical NO removal efficiency profiles as function of gas residence time and temperature.

temperature was changed in the order of 37° → 32° → 27° → 42°, and that gas flow rates were altered between high and low values in a random pattern. Each flow rate was allowed to stabilize for at least 30 gas residence times.

Production of the intermediate N_2O was not measured in the experiment. However, in batch serum bottle experiments with a gas phase of He and NO, complete conversion of NO to N_2 was noted without accumulation of any intermediates (data not shown). If the system were operating in a kinetic limited region, it would be expected to perform worse at lower temperatures, because the culture becomes less active. Dashed lines in Fig. 2 have been constructed to illustrate this point. Because the system was unaffected by temperature, we may assume that the conversion of NO was mass transfer limited. We have discussed in detail the use of temperature control to investigate kinetic and mass transfer operational limits in previous articles *(6,7)*. (Note that in ref. *7* K_La and K_La_{eff} incorporate ε_L.)

To estimate the mass transfer coefficient, we followed the approach taken by Cowger et al. *(8)* and Barton et al. *(9)* by focusing on the data collected at <100% NO conversion (Fig. 3). (Note that Eq. 3 in ref. *9* is incorrect; the left-hand side should be $\ln([y_i]_{outlet}/[y_i]_{inlet})$.) The slope of the line in Fig. 3 is proportional to the mass transfer coefficient. Using a value of Henry's law constant of 455 atm·L/mol for NO (in water at 34.5°C) *(10)*, we can calculate a value of approx 2100 h^{-1} for the mass transfer coefficient ($K_La\varepsilon_L$) in the experiments. This value is six times higher than those given by Bredwell et al. *(11)*, who list mass transfer coefficients of 36–360 h^{-1} for trickle-bed reactors with conventional packing materials. (Note that in ref. *11* the K_La values listed in Table 1 incorporate ε_L.)

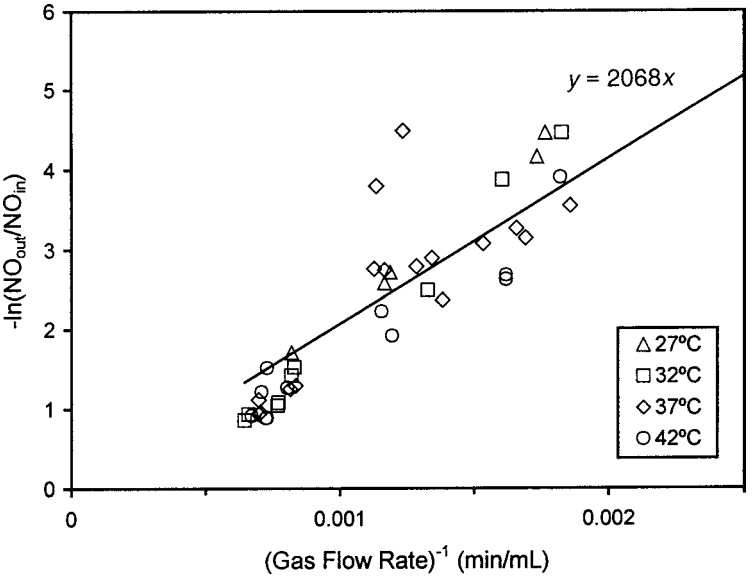

Fig. 3. Determination of mass transfer in a trickle-bed system *(8,9)*.

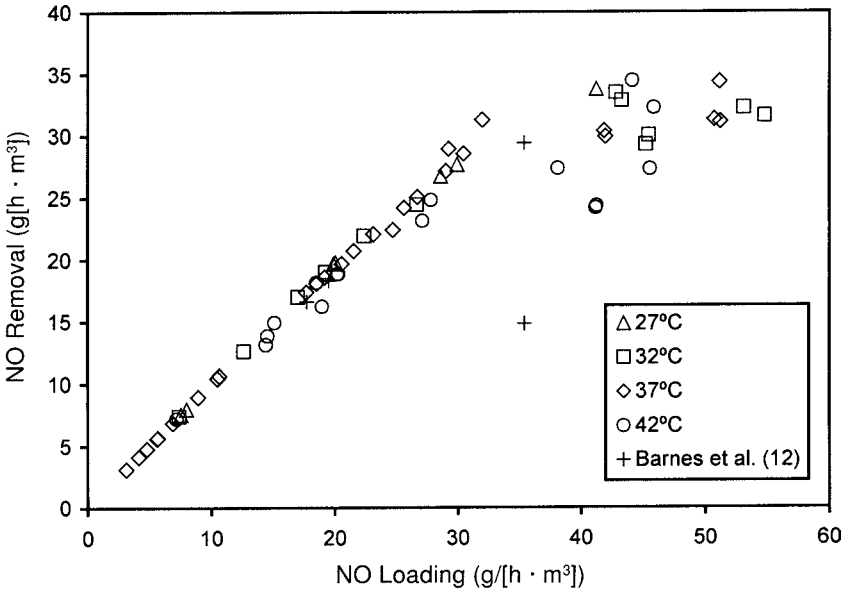

Fig. 4. Volumetric removal rate as a function of loading rate.

The reactor removal rate is displayed in Fig. 4, where it has been plotted as a function of the loading based on empty packed-bed volume. The obtained removal rate in our current studies compares well with the maximum rates obtained by Barnes et al. *(12)* in an anaerobic compost biofilter augmented with dextrose or lactate. These results have been incorporated

into Fig. 4 for comparison. The maximum NO removal at loading rates above 35 g/(h·m^3) was approx 32 g/(h·m^3). This indicates that the system capacity is reached, corresponding to mass transfer limiting condition in our case.

The normally anaerobic trickle bed was also operated under aerobic conditions by mixing air with the gas stream before entering the reactor. The aerobic studies were conducted at 27°C and with a gas residence time of approx 7.5 min. The oxygen concentration was varied between 0.5 and 4.5% with the system responding with a near linear decrease in NO conversion from 75 to 45%. This corresponds to a decrease in reactor removal rate of 3.2–1.4 g/(h·m^3) for a loading of 4.2–3.1 g/(h·m^3). Under anaerobic conditions, NO conversion would be 100% at 7.5-min residence time (*see* Fig. 2); less was achieved because of the presence of O_2. The removal rate compared favorably to results presented by du Plessis et al. *(13)*, who found the NO removal rate to be 0.53–0.73 for a loading of 0.75 g/(h·m^3) in an aerobic biofilter. Nagase et al. *(14)* reported an NO removal rate of 0.82 for a loading of 1.4 g/(h·m^3) in an aerobic bubble column inoculated with *Dunaliella tertiolecta*. In an aerobic soil biofilter, Okuno et al. *(15)* observed a removal rate of 0.018 at a loading rate of 0.12 g/(h·m^3). NO can arguably be converted to NO_2 in the presence of oxygen; however, this is a slow reaction at low NO concentrations *(14)*. Because this reaction rate is proportional to the oxygen concentration, the abiotic conversion of NO should increase with increasing oxygen levels. This was not observed in our biotic studies with oxygen in which the NO conversion decreased as the oxygen concentration increased. This indicates, indirectly, that the abiotic conversion was small in our aerobic studies.

The formation of N_2 from the conversion of NO (*see* Eq. 1) could not be confirmed in the trickle bed because of the low concentration of NO in the system. However, in separate batch experiments (not shown), conducted with elevated concentrations of NO in a helium atmosphere, accumulation of N_2 was noted to increase with time. Also, at the end of experimentation, the temperature of the reactor was increased to 50°C, which inactivated the culture. The abiotic reactor stopped converting NO at that point, and the effluent gas composition was the same as the inlet gas composition, within experimental error (10–15% for a single measurement).

Acknowledgment

This work was supported by the U.S. Department of Energy's Office of Fossil Energy Advanced Research and Technology Program. Oak Ridge National Laboratory is operated by UT-Battelle, LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

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