in Free Convection Boundary Layer," *J. Fluid Mech.*, **30**, 225-239 (1967).

Somers, E. V., "Theoretical Considerations of Combined Thermal and Mass Transfer from a Vertical Flat Plate," *J. Appl. Mech.*, **23**, 295-301 (1956).

Szewczyk, A. A., "Stability and Transition of the Free Convection Layer Along a Vertical Flat Plate," *Intern. J. Heat Mass Transfer*, **5**, 903-914 (1962).

Wilcox, W. R., "Simultaneous Heat and Mass Transfer in Free Convection," *Chem. Eng. Sci.*, **13**, 113-119 (1961).

APPENDIX

TABLE 1. BASE FLOW QUANTITIES

Sc	N	$f''(0)$	$-T'(0)$	$-C'(0)$	f_∞	L	η_{edge}	$\Delta\eta$
0.94	0.5	0.9067	0.5455	0.6312	0.6486	0.3000	10	0.02
—	0.2	0.7727	0.5194	0.6006	0.6241	0.2619	10	0.02
—	0.0	0.6789	0.4995		0.6059	0.2353	10	0.02
—	−0.2	0.5805	0.4768	0.5506	0.5857	0.2076	10	0.02
—	−0.5	0.4211	0.4348	0.5010	0.5501	0.1634	10	0.02
—	−0.8	0.2371	0.3735	0.4283	0.5047	0.1141	12	0.02
2.0	0.5	0.8736	0.5308	0.8675	0.6238	0.2697	12	0.01
—	−0.5	0.4624	0.4590	0.7332	0.5850	0.1982	12	0.01
0.2	0.2	0.8035	0.5427	0.2728	0.8210	0.3422	20	0.05

For a plane plume flow and for a flow adjacent to an isoproperties surface, Gebhart and Pera (1971) tabulated the integral quantities

$$I_t = \int_{-\infty}^{+\infty} f'T d\eta \qquad I_c = \int_{-\infty}^{+\infty} f'C d\eta$$

However, it is more interesting to note that for the surface flow

$$\int_0^\infty T'' d\eta + 3Pr \int_0^\infty fT'' d\eta = 0$$

from which

$$[T']_0^\infty - 3Pr \int_0^\infty f'T d\eta = 0$$

$$- T'(0) - 3Pr \frac{I_t}{2} = 0$$

or

$$I_t = -\frac{2}{3} \frac{T'(0)}{Pr}$$

Similarly, one finds

$$I_c = -\frac{2}{3} \frac{C'(0)}{Sc}$$

We need not include I_t and I_c in a data tabulation which includes $T'(0)$ and $C'(0)$. Also, integrating (1), the momentum equation for the unperturbed flow, one finds

$$f''(0) + \frac{5}{2} L = \int_0^\infty (T + NC) d\eta$$

where

$$L = \int_{-\infty}^{+\infty} f'^2 d\eta$$

Table 1 lists L and $f''(0)$, so that we know the integral of the buoyancy term.

Manuscript received July 14, 1975; revision received October 1, and accepted October 2, 1975.

On the Fate of Fuel Nitrogen During Coal Char Combustion

The physical and chemical characteristics that influence the conversion of fuel nitrogen to nitrogen oxides during coal char combustion were theoretically examined by using a simplified model in which nitric oxide is an intermediate product between fuel nitrogen and N_2.

It was found that diffusion-reaction interactions were important in determining the selectivity of the char particle toward nitric oxide production. At low temperature fluidized bed combustion conditions, pore size is important, and low conversion of fuel nitrogen to nitric oxide is favored by long narrow pores. Under high temperature, pulverized coal combustion conditions, the model provided insight into mechanisms of nitric oxide formation and predicted the observed weak temperature dependence of fuel nitrogen conversion, as well as a significant effect of particle size.

J. O. L. WENDT

and

O. E. SCHULZE

Department of Chemical Engineering
University of Arizona
Tucson, Arizona 85721

Correspondence concerning this paper should be addressed to J. O. L. Wendt. O. E. Schulze is with Dow Chemical Company, Freeport, Texas.

SCOPE

Of increasing concern to researchers in the field of combustion generated air pollution is the fate of chemically bound nitrogen during the combustion process. It is known that this fuel nitrogen is partially converted to NO_x, and that the fraction so converted is a strong function of combustion conditions. The purpose of combustion modeling is to gain insight into the parameters that control this phenomenon in the hope of being able to design meaningful experiments, to interpret the data that is currently available, and to suggest practical abatement methods. Only rarely does combustion modeling result in definitive answers; rather it serves to pose specific questions which can be resolved through unambiguous experiments. Indeed, as far as coal combustion is concerned, some theoretical insight is essential in order to isolate the salient features of a very complicated process in which the phenomena of mass transfer, heat transfer, kinetics, and fluid mechanics are all combined.

When a coal particle is injected into a hot furnace environment, some of the fuel nitrogen is volatilized and some remains in the char. The fate of the volatile nitrogenous species is presently the subject of much research (Sarofim et al., 1975; DeSoete, 1975; Flagan et al., 1974), while that of the fuel nitrogen remaining in the char has generally been neglected. It is known, for example, that particle heating rates will affect the distribution of fuel nitrogen between volatiles and residue; yet it is not known which split is desirable from a pollution point of view. This work, therefore, focuses on NO_x formation during the char burnout regime of coal combustion and has, as its central theme, an elucidation of the role of diffusion-reaction interactions on fuel nitrogen conversion during coal char combustion.

In constructing a model of pollutant formation in gas solid combustion processes, it is possible to draw heavily on theories of intraparticle and external diffusion, developed primarily for gas solid catalytic processes (Peterson, 1965). Concepts of selectivity of the particle towards nitric oxide formation find ready application, especially when nitric oxide is viewed as an intermediate product between fuel nitrogen and N_2, just as carbon monoxide is an intermediate between carbon and carbon dioxide. This hypothesis can be justified on physical grounds and leads directly to the expectation that particle characteristics such as particle size, pore size, and pore length can have a significant effect on the selectivity of the char particle towards nitric oxide.

CONCLUSIONS AND SIGNIFICANCE

The project was divided into two phases. Phase 1 dealt exclusively with diffusion and reaction (heterogeneous as well as homogeneous) within the particle pores. The objectives were to determine the effect of pore diameter, pore length, temperature, and pore exit conditions on the overall conversion of fuel nitrogen to nitric oxide. Our model consisted of that of a single pore, with heterogeneous reaction of carbon to carbon monoxide and fuel nitrogen to nitric oxide at the surface and diffusion and homogeneous reactions forming carbon dioxide and N_2 inside the pore volume. Our results show that for larger particles at low temperatures, such as are applicable to fluid bed combustion, pore size is important, and that low nitric oxide emissions are favored by long narrow pores. At higher temperatures, pore size is not a major factor because then everything of interest occurs at the pore mouth, and diffusion within the pore is not a factor. At lower temperatures, however, both diffusion as well as homogeneous and surface reaction are important, leading to Thiele moduli of order unity.

In phase 2 of this project we examined the role of diffusion and reaction in a stagnant film surrounding the char particle. Here it was assumed that all diffusion and reaction occurred within this film, the thickness of which was determined by the point at which 95% of carbon monoxide produced at the surface had been converted to carbon dioxide. The work served to uncover some key critical questions which appear to control the conversion of fuel nitrogen during the char burnout regime. Most important of these is to determine what the environment surrounding a char particle is during the particle's burnout. For example, it was shown that the carbon monoxide concentration in the free stream was a more important variable than the O_2 concentration in determining the overall effect of excess air. If the effect of decreasing excess air is considered to be that of increasing carbon monoxide concentration, our model predicted the correct monotonic increase of NO_x emissions. If the effect of decreasing excess air is considered to be only that of decreasing O_2 in the free stream, then our model predicted a rarely observed dependence of NO_x emissions on excess air. Results from this model also underscored the need to determine experimentally the global order, rate, and temperature dependence of the homogeneous nitric oxide reduction mechanism, since these factors control the importance of the char burnout regime in nitric oxide formation from fuel nitrogen and can effect the type of combustion modifications that will be most effective for NO_x abatement. Our model did predict the observed (Pershing et al., 1975) weak temperature dependence of fuel nitrogen conversion and did show a significant effect of particle size. These results are new and cannot be predicted from previous models in which competitive diffusion and reaction are neglected. Further experimental work is required before all the important variables can be pinpointed more precisely.

One of the problems associated with coal combustion is the emission of nitrogen oxides, of which a major portion is attributable to oxidation of chemically bound nitrogen in the fuel (Lachapelle et al., 1974). Combustion modifications offer the best hope for NO_x abatement; yet the formation of pollutants during the combustion process is only imperfectly understood.

The chemical mechanisms of pollutant formation during combustion depend not only on the chemistry of combustion but also on the physical processes involved in creating the environment in which the chemistry takes place (Sternling and Wendt, 1974). Because of the low volatility of coal, char, and residual fuel oil, these fuels are not premixed with the combustion air to form a gaseous mixture, and combustion takes place in a diffusion flame environment. Droplet and particle combustion can be described (Sternling and Wendt, 1972) in terms of three regimes. The first regime occurs during rapid devolatilization and leads to a detached, essentially premixed combustible mixture through which (turbulent) flame fronts propagate. The second regime is formed during periods of slow devolatilization and leads to an attached diffusion flame around the particle or droplet. The third regime, or char burnout regime, is initiated after volatilization is completed, whereupon oxygen attacks the pyrolyzed surface directly. Insight into pollutant formation during char combustion can therefore be applicable to the problem of pollutant formation during coal combustion. At present, there is little data that show how fuel nitrogen is distributed among coal pyrolysis products, although it is known that particle heating rate is an important variable (Grigorev et al., 1972; Pereira et al., 1975). Sternling and Wendt (1972), using fragmentary data, indicated that a significant portion of the nitrogen in the coal may not be volatilized but will appear in the char. Data on char resulting from coal gasification (McCann et al., 1971) and on single coal particle pyrolysis (Axworthy and Schuman, 1973) tend to support this picture, while other researchers (Heap et al., 1973; Haynes and Kirov, 1974) attribute nitric oxide formation in some coal flames to conversion of the volatile nitrogen compounds present in coal. Since combustion modifications can affect the distribution of nitrogen between volatiles and char residue, it is useful to know what distribution is more desirable. The objective, then, is to determine under which conditions the fuel nitrogen in char is converted to NO_x rather than to N_2 and to determine through mathematical modeling which critical experiments must be performed to answer these questions.

This work focuses, therefore, on the conversion of fuel nitrogen during the char burnout regime. Previous fundamental work in this area has been oriented towards homogeneous gas phase kinetics both under premixed (Sarofim et al., 1975, DeSoete, 1975; Wendt and Sternling, 1974) and poorly mixed (Sternling and Wendt, 1974; Flagan and Appleton, 1974) environments. Although neglected somewhat by researchers in pollutant formation, the char burnout regime has received attention by others concerned solely with coal combustion characteristics. The pioneering work of Beér and Essenhigh (1960) indicated that in this regime both diffusion and reaction were important. Smith (1971) showed that, in addition, the combustion rates might be limited by the combined effects of diffusion into the pores of the particles and chemical reaction on the pore walls. It was then subsequently shown (Smith and Tyler, 1972) that Thiele moduli and effectiveness factors for a single first-order carbon oxidation reaction could be evaluated. In so doing, it was determined that only for very small particles was the system completely kinetically controlled.

According to Mulcahy and Smith (1969), carbon is oxidized at the surface by O_2 (rather than by carbon dioxide), to form carbon monoxide as the primary product (Ayling and Smith, 1973). The carbon monoxide so formed is subsequently homogeneously oxidized to form carbon dioxide somewhere in the particle's neighborhood (Field et al., 1967). It is possible to draw an analogy between carbon oxidation and fuel nitrogen oxidation. This leads to the hypothesis that nitric oxide is an intermediate species between fuel nitrogen and molecular nitrogen and allows theories of gas-solid reactions to provide useful leads in attacking this problem. Existing theories (Peterson, 1965) show that the selectivity of a catalyst towards an intermediate product depends strongly on particle characteristics. One might expect a similar situation to be applicable to the formation of nitric oxide in a char particle.

It should be noted, however, that a significant difference between a burning char particle and a catalyst is that in the former case, homogeneous reactions as well as heterogeneous reactions and diffusion are important. Thus, one would not expect all aspects of catalyst theory to be directly carried over to pollutant formation from char combustion, even though some useful concepts can be applied.

In this work, we modeled the char burnout regime in two phases. First, diffusion and reaction in a single pore is examined; then the processes occurring in the stagnant film surrounding the particle are modeled. The resulting models then serve to gain insight into the parameters controlling nitric oxide formation from fuel nitrogen in the char burnout regime.

THEORETICAL MODEL

The salient features of the theoretical model developed are that carbon and fuel nitrogen are converted to carbon monoxide and to nitric oxide, respectively, at the particle surface and that further reactions to carbon dioxide and molecular nitrogen occur homogeneously either inside the particle pore or outside the particle surface in a stagnant film surrounding the particle. This model was then used to investigate the effects of particle characteristics and to isolate which types of critical information must be obtained experimentally in order to confirm results of the basic model hypothesis.

That fuel nitrogen should be converted to nitric oxide at the particle surface is intuitively reasonable, since at the surface there is no obvious kinetic route by which the $N \equiv N$ bond can be formed directly, provided the O_2 concentration at the particle surface is higher than that of nitric oxide. Under the conditions examined in this work, this was shown to be the case. In char combustion, surface reaction of fuel nitrogen alone would lead to a net 100% conversion to nitric oxide, but this has seldom been observed (McCann et al., 1974). Therefore, it is reasonable to postulate that some of the nitric oxide formed at the surface then is subsequently reduced partially to N_2. Reduction of nitric oxide may occur through heterogeneous catalysis with carbon monoxide (Hammons and Skopp, 1971) or through homogeneous reaction in a fuel rich environment (Wendt et al., 1973). In this work we focus on the homogeneous reduction of nitric oxide because experimental data (Sarofim et al., 1975; Myerson, 1975) indicate that at high temperatures this process can occur fairly rapidly. Future work should incorporate both heterogeneous and homogeneous reduction mechanisms.

The overall model, even in its simplest possible form, is therefore somewhat complex, involving as it does diffusion of at least three species with coupled homogeneous and heterogeneous reactions between them.

The basic four reactions can be divided into two groups:

1. Surface reactions (at pore surface or particle surface)

$$C + \tfrac{1}{2}O_2 \xrightarrow{k_1} CO \qquad \text{I}$$

$$\text{Fuel N} + \tfrac{1}{2}O_2 \xrightarrow{k_2} NO \qquad \text{II}$$

2. Homogeneous reactions (in pore volume or film volume)

$$NO + \ldots\ldots \xrightarrow{k_3} N_2 \qquad \text{III}$$

$$CO + \tfrac{1}{2}O_2 \xrightarrow{k_4} CO_2 \qquad \text{IV}$$

Diffusion of O_2 carbon monoxide, and nitric oxide occurs in the pores or in the film, where O_2 diffuses away from the free stream and nitric oxide and carbon monoxide diffuse towards it.

Parameter Evaluation

The rate coefficient k_1 for Reaction I was taken from Field et al. (1967)

$$k_1 = 59\,561.9\ T \exp(-35\,700/RT) \quad \text{cm/s} \tag{1}$$

No published data exist on the surface rate coefficient of fuel nitrogen oxidation. The rate coefficient k_2 for Reaction II was therefore estimated by assuming that fuel nitrogen is uniformly distributed throughout the char and that the ratio of k_2/k_1 was equal to the mole ratio of fuel nitrogen to carbon in the char. Thus

$$k_2 = 8.57 \times 10^{-3}\, q\, k_1(T) \quad \text{cm/s} \tag{2}$$

Little information is available on the reaction order and temperature dependence of the homogeneous nitric oxide reduction reaction (Reaction III). As a first approximation, we use a simplified constrained equilibrium kinetic model, similar to that proposed by Flagan et al. (1974). This assumes that a partial equilibrium is established between nitric oxide, NH, oxygen, and OH and that the rate controlling step forming N_2 from nitric oxide is the reverse Zeldovich reaction

$$\mathrm{NO} + \mathrm{N} \rightarrow \mathrm{N_2} + \mathrm{O} \tag{V}$$

This approach leads to an expression for the disappearance of nitric oxide

$$-R_{\mathrm{NO}} = k'\, C_{\mathrm{NO}}^2 \left(\frac{C_{\mathrm{H}}}{C_{\mathrm{OH}}}\right) \tag{3}$$

If it is further assumed that the ratio $(C_{\mathrm{H}}/C_{\mathrm{OH}})$ is a linear function of local equivalence ratio

$$-R_{\mathrm{NO}} = k_3\, C_{\mathrm{NO}}^2 (C_{\mathrm{CO}}/C_{\mathrm{O_2}}) \tag{4}$$

Equation (4) holds the key to determining the temperature dependence of the nitric oxide reburning mechanism. If it is assumed that the superequilibrium concentration of nitrogen atoms produced during reburning is roughly temperature independent, then the activation energy for k_3 is very small. If it is assumed that the ratio of hydrogen to hydroxyl concentration is roughly temperature independent, it can be calculated that the activation energy for k_3 is of the order of 48 Kcal/mole. In this work, we investigated both cases and, in addition, pegged the absolute values of k_3 to be such that fuel nitrogen conversion predictions consistent with experimental data were obtained at temperatures of 2 000° and 1 000°K. An important result from this work is the demonstration that reliable data on global reaction rates of nitric oxide reduction as a function of carbon monoxide and O_2 concentration are urgently needed. A value for k_4 (Reaction IV) was obtained by using literature values (Howard et al., 1973), and the assumption that the water vapor content was of the order of 10% vol. This gave

$$k_4 = (0.1p)^{1/2}\ 1.3 \times 10^{14} \exp(-30\,000/RT)\ \frac{\text{cm}^3}{\text{gmole s}} \tag{5}$$

In addition, it was assumed that the gaseous mixture was dilute, that the diluent was nitrogen, and that the use of constant binary diffusion coefficients was permissible.

One-Dimensional Pore Model

With the above approximations, the species balance equations for the one-dimensional pore model can be written:

For oxygen:

$$D_1 \frac{d^2C_1}{dx} - \frac{k_1}{r} C_1 - \frac{k_4}{2} C_2 C_1^{1/2} = 0 \tag{6}$$

with boundary conditions

$$\left.\frac{dC_1}{dx}\right|_{x=0} = 0; \quad C_1\big|_{x=l} = C_{1f} \tag{7}$$

For carbon monoxide:

$$D_2 \frac{d^2C_2}{dx^2} + \frac{2}{r} k_1 C_1 - k_4 C_2 C_1^{1/2} = 0 \tag{8}$$

with boundary conditions

$$\left.\frac{dC_2}{dx}\right|_{x=0} = 0; \quad C_2\big|_{x=l} = 0 \tag{9}$$

For nitric oxide:

$$D_3 \frac{d^2C_3}{dx^2} + \frac{2}{r} k_2 C_1 - k_3 C_3^2 C_2 / C_1 = 0 \tag{10}$$

with boundary conditions

$$\left.\frac{dC_3}{dx}\right|_{x=0} = 0; \quad C_3\big|_{x=l} = 0 \tag{11}$$

It should be noted that only three species were considered (O_2, carbon monoxide, and nitric oxide) and that the equation for nitric oxide was essentially decoupled from those for O_2 and carbon monoxide. This means that the concentrations of O_2 and carbon monoxide directly affected the concentration of nitric oxide but that the converse was not true.

Inspection of the boundary conditions above shows that the pore model simulates a physical situation where a stream of air with zero concentrations of carbon monoxide and nitric oxide is blowing past the pore mouth. We focus attention solely on diffusion-reaction interactions inside the pore and neglect resistance to transfer in any boundary layer surrounding the char particle. In each case examined, the quantity of interest is the percent conversion of fuel nitrogen to nitric oxide, which was calculated from the ratio of the flux of nitric oxide at the pore mouth by using an effective value for k_3 to that with k_3 set equal to zero.

Equations (6), (8), and (10) can be nondimensionalized to yield the following Thiele moduli

For oxygen $$h_{1p} = \frac{l^2 k_1}{r D_1} \tag{12}$$

For carbon monoxide $$h_{2p} = \frac{2 l^2 \alpha_1 k_1}{r D_2 \alpha_2} \tag{13}$$

For nitric oxide $$h_{3p} = \frac{2 l^2 \alpha_1 k_2}{r D_3 \alpha_3} \tag{14}$$

These expressions can be utilized to determine regimes of kinetic and diffusion control.

One-Dimensional Film Model

In a pulverized coal furnace, the smallest scale of turbulence is usually much greater than typical particle diameters (Field et al., 1967). This rationalizes the physical picture of a particle surrounded by an infinite stagnant film, in which diffusion and reaction processes occur. Assuming spherical particles, and employing approximations analogous to those in the pore model, we can write the equations for the stagnant film model:

For oxygen

$$D_1 \frac{d^2C_1}{dr^2} + \frac{2}{r} D_1 \frac{dC_1}{dr} - \frac{k_4}{2} C_2 C_1^{1/2} = 0 \tag{15}$$

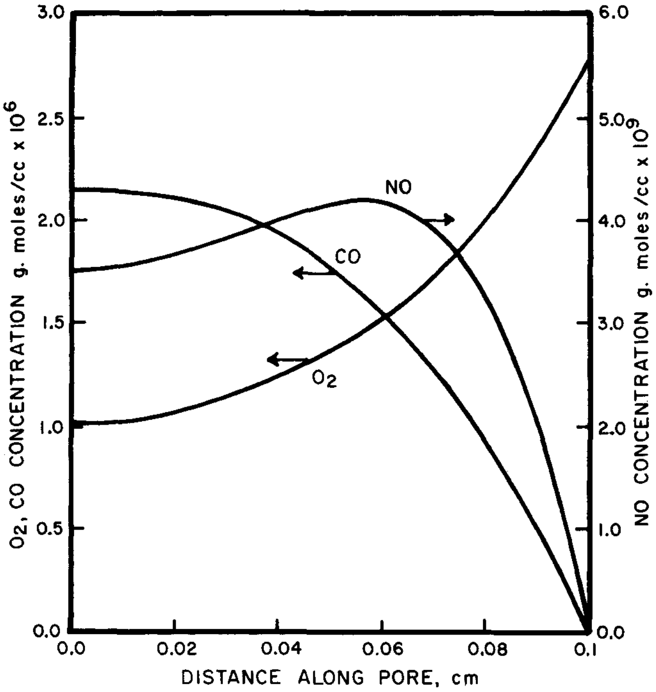

Fig. 1. Pore model: typical concentration profiles (T = 1000°K, $k_3 = 2.0 \times 10^{11}$ cc/mole sec, l = 0.1 cm, r = 0.01 cm).

with boundary conditions

$$\left.\frac{dC_1}{dr}\right|_{r=r_i} = \left.\frac{k_1C_1}{2D_1}\right|_{r=r_i} \; ; \quad C_1|_{r=r_i+\delta} = C_{1f} \quad (16)$$

For carbon monoxide

$$D_2 \frac{d^2C_2}{dr^2} + \frac{2}{r} \frac{dC_2}{dr} - k_4C_2C_1^{1/2} = 0 \qquad (17)$$

with boundary conditions

$$\left.\frac{dC_2}{dr}\right|_{r=r_i} = -\left.\frac{k_1C_1}{D_2}\right|_{r=r_i} \qquad C_2|_{r=r_i+\delta} = 0 \quad (18)$$

For nitric oxide

$$D_3 \frac{d^2C_3}{dr^2} + \frac{2}{r} D_3 \frac{dC_3}{dr} - k_3C_3{}^2C_2/C_1 = 0 \qquad (19)$$

$$\left.\frac{dC_3}{dr}\right|_{r=r_i} = -\left.\frac{k_2C_1}{D_3}\right|_{r=r_i} \qquad C_3|_{r=r_i+\delta} = 0 \quad (20)$$

An important difference between the pore model and the film model is that in the former case the surface reactions enter into the equations, while in the latter case the surface reactions enter through the boundary conditions.

The quantity of interest is, again, the net percent conversion of fuel nitrogen to nitric oxide. An important parameter in the film model is the thickness δ of the stagnant film surrounding the char particle. Field et al. (1967) indicated that at least 95% of the carbon monoxide is oxidized to carbon dioxide in the neighborhood of the particle. As a first approximation, we therefore chose as our film thickness that thickness that would allow 95% of the carbon monoxide produced at the particle surface to be converted to carbon dioxide. Film thickness then becomes a dependent parameter and changes with temperature, particle diameter, etc. The salient feature of the film model is, therefore, a quantitative description of the competition between the nitric oxide reburning reaction (Reaction III) and the carbon monoxide oxidation reaction (Reaction IV). This competition may be the key to the partial oxidation of fuel nitrogen to nitric oxide.

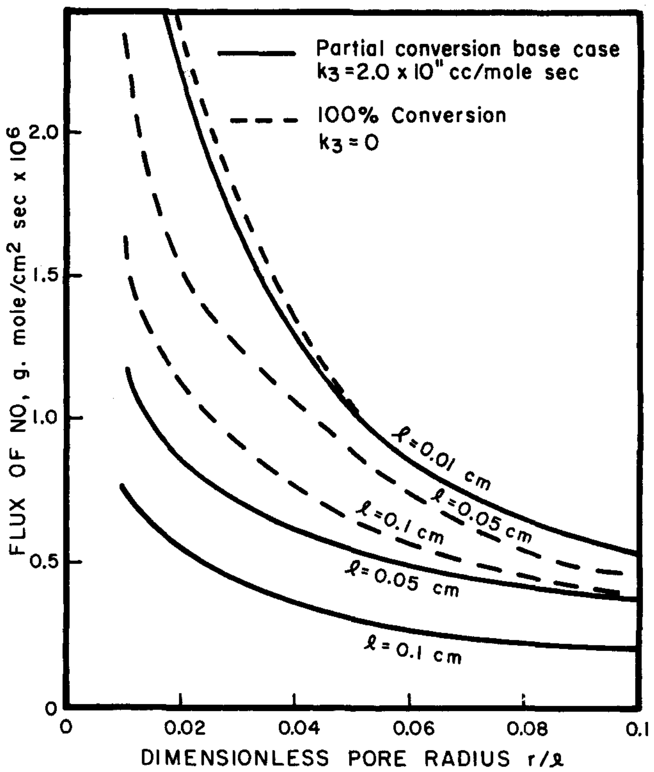

Fig. 2. Pore model: effect of pore characteristics on NO flux.

To solve the above boundary value problems, a numerical integration method utilizing both a fourth-order Runge Kutta Gill and a multivariable optimization algorithm was utilized. Details of the computer codes developed are described by Schulze (1974).

RESULTS

Pore Model

Typical concentration profiles are shown in Figure 1 for a temperature of 1 000°K. The concentration profiles of O_2, carbon monoxide, and nitric oxide vary smoothly along the pore, indicating that pore diffusion and reaction are important under these conditions. At temperatures much above 1 000°K, essentially all the oxygen is consumed at the pore mouth at the particle surface, and pore diffusion is not important. The low temperature case corresponds to combustion in a fluidized bed, which is of practical interest. It should be noted from Figure 1 that the nitric oxide concentration is significantly lower than the O_2 concentration everywhere in the pore, and this supports our hypothesis that the most likely surface reaction of fuel nitrogen is with O_2 to form nitric oxide. Results were computed for two values of k_3, the homogeneous nitric oxide reduction reaction rate coefficient. The high value ($k_3 = 2.0 \times 10^{13}$ cm^3/mole s) is in line with high temperature data of Sarofim et al. (1975). The low value ($k_3 = 2.0 \times 10^{11}$ cm^3/mole s) is that which gave reasonable conversions of fuel nitrogen to nitric oxide at 1 000°K and was used as the base value for this study at 1 000°K. A zero value for k_3 simulates the case where complete conversion of fuel nitrogen to nitric oxide is obtained. Clearly, further experimental data on k_3 would be desirable.

Figure 2 shows the effect of pore length and pore radius on the flux of nitric oxide leaving the pore. Clearly, smaller particles with narrow pores burn out more rapidly and give a higher nitric oxide flux than those with long wide pores. For short pores ($l = 0.01$, $r = 0.001$), the Thiele modulus evaluated for oxygen has a value $h_{1_p} = 0.11$ which indicates that under these conditions the system is reaction controlled.

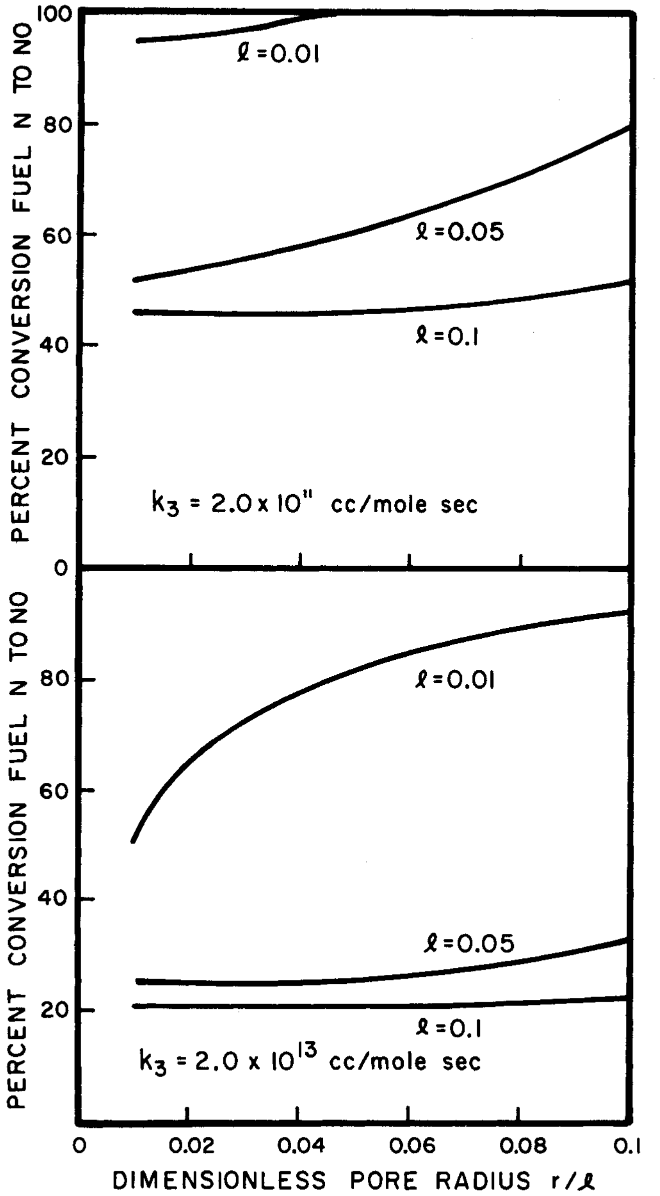

Fig. 3. Pore model: effect of pore characteristics on fuel nitrogen conversion.

As pointed out by Fine et al. (1971) and substantiated by this work, reaction controlled conditions tend to maximize fuel nitrogen conversion to nitric oxide. However, as the pore length is increased, the Thiele modulus h_{1_p} increases and has a value close to unity for $l = 0.1$, $r = 0.01$. Figure 3 indicates that under these conditions, which might be representative of fluid bed combustion, both diffusion and reaction are important, and then fuel nitrogen is only partially converted to nitric oxide. This agrees with experimental findings of Jonke et al. (1969) and Pereira et al. (1975), although our results are applicable strictly only to coal char rather than to coal. Figure 3 shows the effect of pore radius and pore length on the percent conversion of fuel nitrogen to nitric oxide for both high and low values of k_3. It is apparent that the selectivity of the particle towards low yields of nitric oxide are favored by long, narrow pores, that is, at large values of Thiele moduli. This result is consistent with conventional gas solid reaction theory (Peterson, 1965).

Film Model

The important results obtained from the film model are the effects of temperature, fuel nitrogen content, particle diameter, and free stream O_2 and carbon monoxide concentrations on fuel nitrogen conversion.

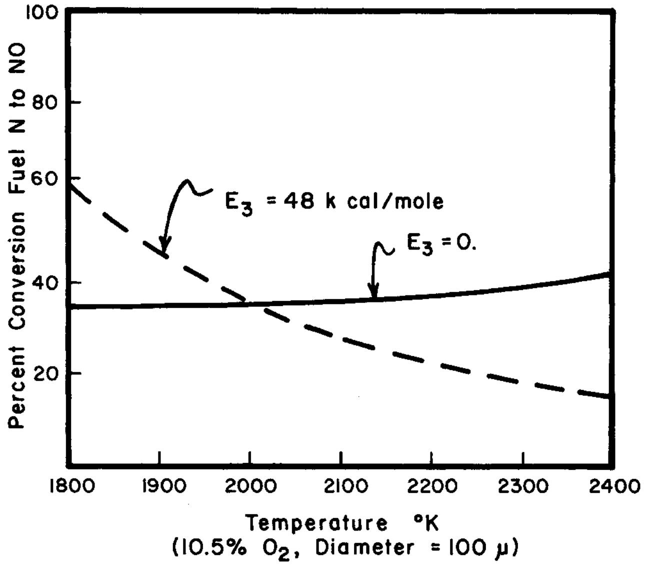

Fig. 4. Film model: effect of temperature on fuel nitrogen conversion.

As in the pore model, results showed that the concentration of oxygen at the surface is over an order of magnitude greater than that of nitric oxide and that the overall conversion of fuel nitrogen was sensitive to the value of k_3, the rate coefficient of the homogeneous reburning reaction. For the results subsequently reported here, we settled on a value of k_3 to give 36% conversion of fuel nitrogen to nitric oxide at 2 000°K, at 10.5% O_2 in the free stream, and a particle diameter of 100μ. This value is identical to the high value in the pore model and is consistent with high temperature data of Sarofim et al. (1975).

The effect of temperature on fuel nitrogen conversion is shown in Figure 4. If an activation energy of $E_3 = 48$ kcal/mole for the nitric oxide reburning mechanism is assumed, then fuel nitrogen conversion decreases with increasing temperature. This is unexpected, and it is more usual to postulate that temperature dependence of fuel nitrogen conversion is slight (Pershing et al., 1975). Therefore, it appears more reasonable to set $E_3 = 0$, implying that the concentration of superequilibrium N atoms is roughly independent of temperature. Then, Fig-

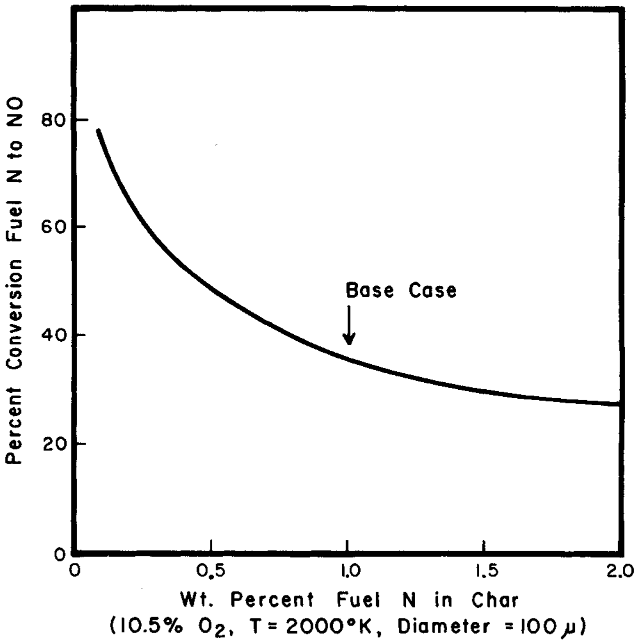

Fig. 5. Film model: effect of char fuel nitrogen content on fuel nitrogen conversion.

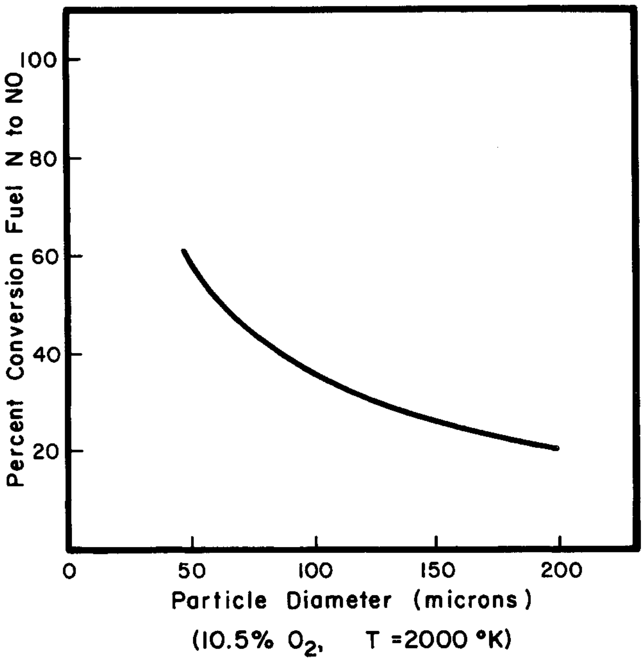

Fig. 6. Film model: effect of particle diameter on fuel nitrogen conversion.

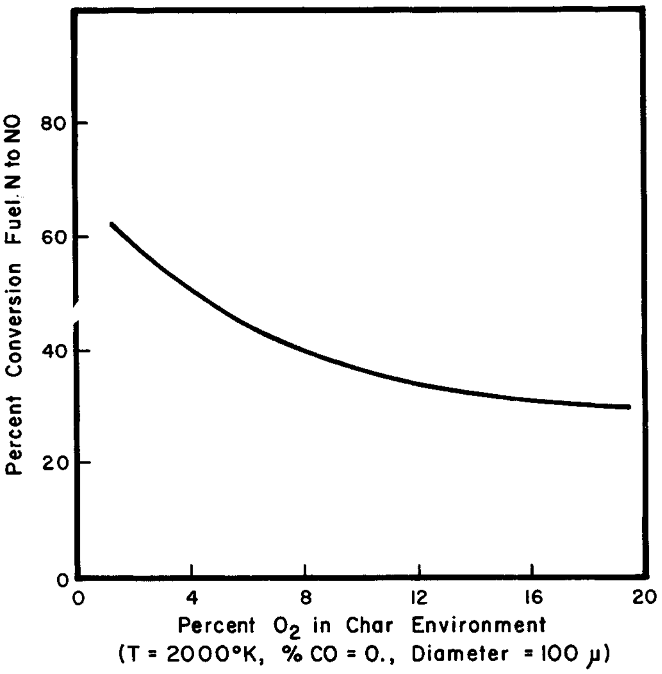

Fig. 7. Film model: effect of free stream O_2 concentration on fuel nitrogen conversion.

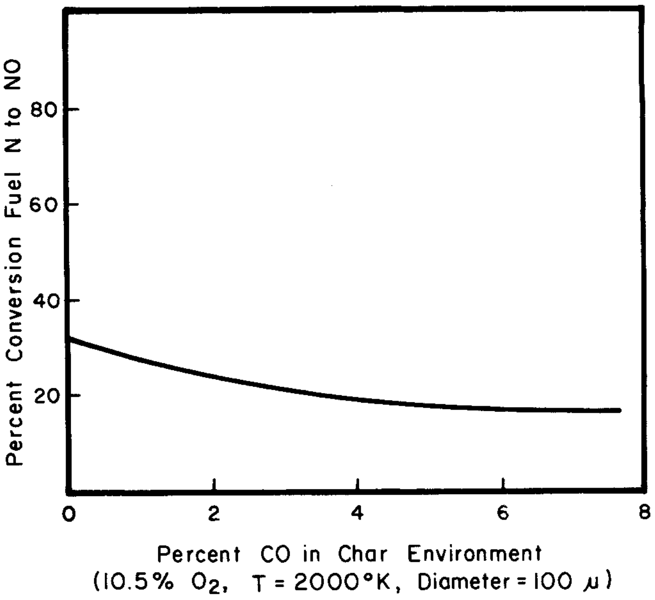

Fig. 8. Film model: effect of free stream carbon monoxide concentration on fuel nitrogen conversion.

ure 4 shows that, indeed, the dependence of fuel nitrogen on temperature is very slight, even though the surface reaction forming nitric oxide has an activation energy of 35.7 kcal/mole. This is because diffusion of O_2, carbon monoxide, and nitric oxide and homogeneous reaction are very important in controlling the resulting fuel nitrogen conversion. The results on Figure 4 are thus consistent with the data of Armento (1975) and Pershing et al. (1975), which indicated that flue gas recirculation was not effective in lowering fuel nitrogen conversion to nitric oxide. However, this comparison with experimental data on coal presupposes that the char burnout regime is important as far as NO_x formation is concerned.

The effect of char fuel nitrogen content on fuel nitrogen conversion is shown on Figure 5. Increasing fuel nitrogen content decreases conversion to nitric oxide. This is because the nitric oxide reduction mechanism is second order with respect to nitric oxide, while the surface reaction forming nitric oxide goes linearly with fuel nitrogen content. Our results are consistent with those obtained on fuel nitrogen conversion from doped fuel oils (Martin and Berkau, 1972). Char particle diameter has a significant effect on fuel nitrogen conversion, as shown on Figure 6. This effect is related to changes in the ratio of surface area forming nitric oxide to film volume destroying nitric oxide.

Figures 7 and 8 show the effect of changing the free stream concentrations of O_2 and carbon monoxide in the char environment. It is to be expected that decreasing overall excess air should lead to decreasing O_2 and increasing carbon monoxide in the free stream. Although our results relate directly only to the char burnout regime of coal combustion, some comparison with coal fuel nitrogen experimental data is useful.

It is known that decreasing excess air decreases fuel nitrogen conversion (Armento, 1975; Pershing et al., 1975). However, Figure 7 shows an apparent anomalous effect, that decreasing free stream O_2 concentration increases the percent conversion. This is because as the free stream O_2 is decreased, the concentration of O_2 carbon monoxide, and nitric oxide at the surface fall proportionately. Since the nitric oxide reduction reaction is overall second order while the nitric oxide formation reaction is overall first order, the net result is to decrease nitric oxide reduction relative to nitric oxide formation. This increases the overall fuel nitrogen conversion to nitric oxide at low free stream O_2 concentrations, even though the flux of nitric oxide (and particle burnout rate) has decreased. We believe that the observed effect of excess air on fuel nitrogen can be explained by the effect changes in excess air have on the free stream concentration of carbon monoxide during char burnout. Increasing free stream carbon monoxide concentration leads to decreasing fuel nitrogen conversion (Figure 8), which is consistent with the observed dependence on excess air. In Figure 8, the film thickness was fixed at the base case value of 0.0529 cm because 95% conversion of carbon monoxide within the film does not have physical significance when there is carbon monoxide outside the film which is not reacting.

CONCLUSIONS

The char combustion models developed have led to new insight into how and why fuel nitrogen is converted to nitrogen oxides. A simple one-dimensional model of diffusion and reaction within a single particle pore showed that the selectivity of the char particle towards nitric oxide formation was likely to be affected by pore radius and pore length, provided the temperature was below 1 000°K. This is especially applicable to fluidized bed combustion, and our results indicate that the method by which char is formed will affect the resultant conversion of fuel nitrogen to nitric oxide.

It was shown that under fluidized bed combustion conditions, both diffusion and reaction were important in determining the resulting nitric oxide flux. The Thiele modulus was a useful parameter to quantify the relative effects of surface reaction and diffusion, and low values of the Thiele modulus for O_2 led to high conversions of fuel nitrogen to nitric oxide. Our results were based on the use of Field's (1967) recommended value for the carbon oxidation rate coefficient. Should the lower value of Smith and Tyler (1972) be used, reevaluation of Thiele moduli then indicates that our conclusions are still valid, but for smaller particles and at higher temperatures. The concentration of oxygen at the particle surface was always greater than that of nitric oxide, and this would support the contention that all the fuel nitrogen is converted to nitric oxide at the particle surface.

When attention is focused on the particle surface and on the surrounding film rather than on internal burning, a film model can be used to pinpoint some key areas requiring further investigation. One of the most important is an accurate experimental determination of the magnitude, order, and temperature dependence of the homogeneous nitric oxide reduction reaction. The importance of the char burnout regime with respect to nitric oxide formation hinges on how rapidly nitric oxide can be reburned back to N_2.

The work served to uncover some key critical questions which appear to control the conversion of fuel nitrogen during the char burnout regime. Most important of these is to determine what the environment surrounding a char particle is during the particle's burnout, and, specifically, how this environment is affected by overall excess air. This work indicated that the carbon monoxide concentration in the free stream was a more important variable than the O_2 concentration in determining the overall effect of excess air. It was assumed, arbitrarily, that the film thickness was determined by the conversion of carbon monoxide to carbon dioxide so that, at the outer edge, 95% of carbon monoxide had been converted. The problem of nitric oxide conversion in this film is thus one of competition with carbon monoxide conversion and is quite complex. What is needed are data to show how much carbon monoxide is converted to carbon dioxide in the neighborhood of the particle, how much escapes to the free stream, and how this depends on the environment around the particle. Our model did predict the observed weak temperature dependence of fuel nitrogen conversion and did show a significant effect of particle size.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation through Grant GK-37459.

NOTATION

C_1, C_2, C_3 = concentration of O_2, carbon monoxide, and nitric oxide, respectively, g mole/cm^3
C_{1f}, C_{2f}, C_{3f} = final concentration of O_2, carbon monoxide, and nitric oxide, respectively, g mole/cm^3
D_i = diffusivity of species i in N_2, cm^2/s
E_3 = activation energy Reaction III, cal/g mole
h_{ip} = Thiele parameter for pore, evaluated for species i, dimensionless
k_0 = preexponential factor
k_1 = kinetic rate coefficient, Reaction I, cm/s
k_2 = kinetic rate coefficient, Reaction II, cm/s
k_3 = kinetic rate coefficient, Reaction III, cm^3/g mole s
k_4 = kinetic rate coefficient, Reaction IV, adjusted, cc$^{1.5}$/g mole$^{1.5}$ s
l = pore length, cm
q = weight percent fuel nitrogen in char
r = radius of pore, cm
R = universal gas constant, cal/g mole °K
R_i = rate of formation of component i, g mole/s
r_i = particle radius, cm
T = temperature, °K
x = distance inside the pore, cm
α_i = characteristic concentration differences for species i, g mole/cal
δ = thickness of stagnant film surrounding particle, cm
ρ = molar density, g mole/cm^3

LITERATURE CITED

Armento, W. J., "Effects of Design and Operation Variables on NO_x Formation in Coal Fired Furnaces," Babcock and Wilcox Company, Alliance, Ohio. Environmental Protection Technology Series Report EPA-650/2-74-002b (1975).

Axworthy, A. E., and M. Schuman, "Investigation of the Mechanisms and Chemistry of Fuel Nitrogen Conversion to Nitrogen Oxides in Combustion," Proceedings EPA Coal Combustion Seminar, p. 9, Environmental Protection Technology Series Report EPA-650/2-73/021 (1973).

Ayling, A. G., and I. W. Smith, "Measured Temperatures of Burning Pulverized Fuel Particles and the Nature of the Primary Reaction Product," *Comb. Flame*, **18**, 173 (1973).

Beér, J. M., and R. H. Essenhigh, "Control of Reaction Rate in Dust Flames," *Nature*, **187**, 1106 (1960).

DeSoete, G. G., "Overall Reaction Rates of NO and N_2 Formation from Fuel Nitrogen," *Fifteenth Symposium (International) on Combustion*, p. 1093, The Combustion Institute, Pittsburgh, Pa. (1975).

Field, M. A., D. W. Gill, B. B. Morgan, and P. G. W. Hawksley, *Combustion of Pulverized Coal*, BCURA Leatherhead, Cherey and Sons, Ltd., Banbury, England (1967).

Fine, D. W., S. M. Slater, A. R. Sarofim, and G. C. Williams, "The Importance of Nitrogen in Coal as a Source of Nitrogen Oxide Emissions from Furnaces," paper presented at 64th Annual AIChE Meeting, San Francisco, Calif. (1971).

Flagan, R. C., S. Galant, and J. P. Appleton, "Rate Constrained Partial Equilibrium Models for the Formation of Nitric Oxide for Organic Fuel Nitrogen," *Comb. Flame*, **22**, 299 (1974).

Flagan, R. C., and J. P. Appleton, "A Stochastic Model of Turbulent Mixing with Chemical Reaction: Nitric Oxide Formation in a Plug Flow Burner," *ibid.*, **23**, 249 (1974).

Grigorev, N. P., I. S. Titova, A. P. Bronshtein, and G. N. Makarox, "Formation of Nitrogen Compounds During Coal Carbonization," *Coke and Chemistry (USSR)*, **9**, 10 (1972).

Hammons, G. A., and A. Skopp, "NO_x Formation in Fluidized Bed Coal Combustion Processes," ASME Paper No. 71-WA/APC-3 (1971).

Haynes, B. S., and N. Y. Kirov, "Nitric Oxide During the Combustion of Coal," *Comb. Flame*, **23**, 277 (1974).

Heap, M. P., T. M. Lowes, R. Walmsley, and H. Bartelds, "Burner Design Principles for Minimum NO_x Emissions," *Proceedings, EPA Coal Combustion Seminar*, p. 141, Environmental Protection Technology Series Report EPA-650/2-73-021 (1973).

Howard, J. B., G. C. Williams, and D. H. Fine, "Kinetics of Carbon Monoxide Oxidation in Post Flame Gases," *Fourteenth Symposium (International) on Combustion*, p. 975, The Combustion Institute, Pittsburgh, Pa. (1973).

Jonke, A. A., E. L. Carls, R. L. Jarry, M. Haas, W. A. Murphy, and C. B. Schoffstoll, "Reduction of Atmospheric Pollution by the Application of Fluidized Bed Combustion," Argonne

National Laboratory, Report ANL/ES-CEN-1001 (1969).

Lachapelle, D. G., J. S. Bowen, and R. D. Stern, "Overview of Environmental Protection Agency's NO_x Control Technology for Stationary Combustion Sources," paper presented at 67th Annual Meeting, AIChE, Washington, D.C. (Dec., 1974).

Martin, G. B., and E. E. Berkau, "Evaluation of Various Combustion Modifications Techniques for Control of Thermal and Fuel Related Nitrogen Oxides Emissions," paper presented at 14th Symposium (International) on Combustion, University Park, Pa. (1972).

————, "An Investigation of the Formation of Various Fuel Compounds to Nitrogen Oxides in Oil Combustion," *AIChE Symposium Ser. No. 68*, 45-54 (1972).

McCann, C. R., J. M. Henry, J. J. Demeter, and D. Bienstock, "Control of NO_x Emissions in Pulverized Coal Combustion," U.S. Bureau of Mines, Pittsburgh Energy Center, Pa. U.S. Bureau of Mines Report of Investigations (1974).

McCann, C. R., J. J. Demeter, A. A. Orning, and D. Bienstock, "Combustion of Pulverized Char," paper presented at Am. Chem. Soc. Meeting, Washington, D.C. (1971).

Mulcahy, M. F. R., and I. W. Smith, "Kinetics of Combustion of Pulverized Fuel: A Review of Theory and Experiment," *Rev. Pure Appl. Chem.*, **19**, 81 (1969).

Myerson, A. L., "The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixtures," *Fifteenth Symposium (International) on Combustion*, p. 1085, The Combustion Institute, Pittsburgh, Pa. (1975).

Pereira, F. J., J. M. Beér, B. Gibbs, and A. B. Hedley, "NO_x Emissions from Fluidized Bed Coal Combustors," *Fifteenth (International) Symposium on Combustion*, p. 1149, The Combustion Institute, Pittsburgh, Pa. (1975).

Pershing, D. W., G. B. Martin, and E. E. Berkau, "Influence of Design Variables on the Production of Thermal and Fuel NO from Residual Oil and Coal Combustion," AIChE Symposium Series No. 148, **71**, 19 (1975).

Petersen, E. E., *Chemical Reaction Analysis*, Prentice Hall, Englewood Cliffs, N. J. (1965).

Sarofim, A. G., G. C. Williams, M. Modell, and S. M. Slater, "Conversion of Fuel Nitrogen to Nitric Oxide in Premixed and Diffusion Flames," AIChE Symposium Series No. 148, **71**, 51 (1975).

Schulze, O. E., "Formation of Pollutants During Char Combustion," M.S. thesis, Univ. Ariz., Tucson (Aug., 1974).

Smith, I. W., "The Kinetics of Combustion of Pulverized Semi-Anthracite in the Temperature Range 1400-2200°K," *Comb. Flame*, **17**, 421 (1971).

———, and R. J. Tyler, "Internal Burning of Pulverized Semi-Anthracite: The Relation Between Particle Structure and Reactivity," *Fuel*, **51**, 312 (1972).

Sternling, C. V., and J. O. L. Wendt, "Kinetic Mechanisms Governing the Fate of Chemically Bound Sulfur and Nitrogen in Combustion," NTIS Report No. PB-230895, U.S. Department of Commerce, Springfield, Va. (1972).

————, "On the Oxidation of Fuel Nitrogen in a Diffusion Flame," *AIChE J.*, **20**, 81 (1974).

Wendt, J. O. L., and C. V. Sternling, "Effect of Ammonia in Gaseous Fuels on NO_x Emissions," *J. Air Poll. Control Assoc.*, **24**, 1055 (1974).

————, and M. A. Matovich, "Reduction of Sulfur Trioxide and Nitrogen Oxides by Secondary Fuel Injection," *Fourteenth Symposium (International) on Combustion*, p. 897, The Combustion Institute, Pittsburgh, Pa. (1973).

Manuscript received February 25, 1975; revision received October 15, and accepted October 17, 1975.

Secondary Nucleation of Two Fast Growth Systems in a Mixed Suspension Crystallizer: Magnesium Sulfate and Citric Acid Water Systems

Secondary nucleation of magnesium sulfate and citric acid was studied in a seeded back mixed crystallizer. The MSMPR type of exponential population density distribution was obtained above 8 μm size in quasi steady state operation. Growth rates were satisfactorily correlated with supersaturation. Nucleation rates correlated with supersaturation and slurry properties. Agitation level (RPM) did not have any significant effect on the nucleation rates, presumably implying surface regeneration limited nucleation.

SUBHAS K. SIKDAR
and
ALAN D. RANDOLPH

Department of Chemical Engineering
University of Arizona
Tucson, Arizona 85721

SCOPE

Mixed suspension crystallizers of the kind used in this study proved to be an excellent tool for the determination of kinetics of fast growth systems such as magnesium sulfate heptahydrate and citric acid monohydrate. Continuous on-line measurement of the fines distribution created by secondary nucleation with a short average fluid retention time and with the parent seed crystals totally retained in the crystallizer is a desirable feature of this technique. In addition to measuring effective growth and nucleation kinetics, the technique furnishes insight into the fundamental mechanisms of secondary nucleation. The mini-crystallizer of this study operates as a realistic MSMPR crystallizer, yet offers distinct advantages over conventional MSMPR techniques. For example, the supersaturation and the retention time can be independently varied, while the time scale of the entire experiment is shortened considerably. The effect of the different moments of macrosized crystals can be independently measured. The kinetic correlations obtained in this study could be gainfully utilized in the design of crystallizers. Continuous fines distribution measurement was possible by the use of a multichannel Coulter Counter.

Correspondence concerning this paper should be addressed to A. D. Randolph. S. K. Sikdar is with Garrett Research and Development Company, Inc., La Verne, California 91750.