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ROLE OF CHAR DURING REBURNING OF NITROGEN OXIDES

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Wei-Yin Chen¹
L.T. Fan²
Te-Chang Lu¹
Mutsuo Yashima²

1. Department of Chemical Engineering
Anderson Hall
University of Mississippi
University, MS 38677-9740

2. Department of Chemical Engineering
Durland Hall
Kansas State University
Manhattan, KS 66506-5102

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ABSTRACT

During this quarter, we have investigated the rates and product compositions of NO reduction on chars in various gaseous environments. N_2 and CO_2 internal surface areas of chars, selected from runs of various pyrolysis and reaction conditions, have been measured to assist the interpretations of experimental results. Implications of Langmuir-Hinshelwood mechanisms and mass transfer limitations have been examined in details.

Without CO_2 and O_2 , NO reduction by the bituminous coal char can be severer than that by the lignite char, particularly at high temperatures. Oxidants suppress NO reduction on the bituminous coal char more than they affect that on the lignite char. Oxygen conversion of feed NO to the gasification products, CO and CO_2 , is complete when feed gas contains only two reactive species, NO and CO_2 , indicating no carbon is gasified by CO_2 . These two observations stated above suggest that the adsorption of NO and the desorption of stable surface oxygen complexes are potentially important rate-limiting steps, and they may be catalyzed by the mineral matters during reburning with lignite char. The relative inert nature of lignite char to the presence of CO_2 may have potential value in the use of fuel system involving both solid and volatile fuels.

The lignite char produced at 950 °C and zero holding time has higher reactivity than the lignite char produced at 1100 °C and 5 min holding time. The bituminous coal chars produced at these two conditions, however, have very similar reactivity with NO. Internal surface areas of chars derived from both coals vary significantly with pyrolysis conditions and gas composition in the subsequent reaction. As an example, when oxidants are introduced in the feed, the internal surface areas of these two chars vary in opposite directions; which reflect the complexity of heterogeneous reburning and the difficulties in the interpretation of experimental data.

I. INTRODUCTION

The regulations established by the Clean Air Act Amendments of 1990 in the United States mean that a single NO_x control technology is not likely to be sufficient for boilers in the ozone non-attainment areas. Reburning is an emerging three-stage combustion technology designed for the reduction of NO by introducing a small amount of reburning fuel above the primary flame where the majority of NO is chemically reduced to nitrogen in this fuel rich environment. The concept of reburning was first introduced by Wendt *et al.* (1973). Tests on a full-scale boiler at Mitsubishi Heavy Industries (Takahashi *et al.*, 1983) resulted in over 50% NO_x reduction.

Coals, including lignites, are an economical source of carbon required for NO reduction in the fuel rich environment. Their effectiveness as a reburning fuel seem to depend on two ambivalent factors in its early stage of development. First, the conversion of the nitrogen in coal to NO in the reburning and burnout stages was not clear. Nevertheless, through an isotopical tracing technique, it has been revealed that conversion of volatile nitrogen in coal to NO during reburning is very low (Burch *et al.*, 1994). It is also known that conversion of char nitrogen to NO during combustion is less than 50% of that of volatile nitrogen (Pershing and Wendt, 1979). Second, while the homogeneous gas phase NO reduction in the fuel rich environment is relatively well understood (see, e.g., Miller and Bowman, 1989), NO reburning by chars of diverse origin and history has not been considered a viable NO reduction route until very recently.

Our initial studies of simulated reburning with reactors of two scales (Burch *et al.*, 1991a,b; 1994) have demonstrated that lignites are more effective than methane as reburning fuel. The two lignites tested were selected from Mississippi and North Dakota; both lignites have high contents of calcium. Screening with the North Dakota lignite indicated that the lignite char surface participates

in heterogeneous/catalytic NO reduction to HCN, while lignite ash enhances catalytic HCN reduction to NH₃. Both reactions are important in the overall NO reduction scheme. The effectiveness of heterogeneous reburning has recently been demonstrated in a 1.0 and a 0.1 MMBtu/hr pilot scale test facility (Payne *et al.*, 1995; Pershing, 1995).

Detailed kinetic analysis of homogeneous phase NO reduction in a fuel rich environment indicates that the majority of NO is reduced by hydrocarbon radicals C, CH and CH₂ to HCN and amine radicals (NH₂) (Miller and Bowman, 1989). The amine radicals, in turn, can be converted to N₂ or NO. The yields of these desirable hydrocarbons radicals from lignite during reburning are not known. Nevertheless, coal and lignite produce only about 50% of the volatile carbons which methane produces at the same stoichiometry, which led to the speculation that the lignite char participates in considerable heterogeneous reactions with NO.

Although NO reburning by char has not been a major area of research, investigating the interactions of NO with various carbonaceous and metallic materials has been the objective of a number of studies. An extensive review has been conducted by De Soete (1990). It has been shown that carbonaceous materials can be gasified by NO to form CO, CO₂ and N₂ (Bedjai *et al.*, 1958; Smith *et al.*, 1959; Furusawa *et al.*, 1980; Levy *et al.*, 1981; Chan *et al.*, 1983; Suuberg *et al.*, 1990; Teng *et al.*, 1992; Chu and Schmidt, 1993; Illan-Gomez *et al.*, 1993). The gasification reaction can be promoted by the addition of reducing agents, such as CO and H₂, and inhibited by O₂ when the CO₂/CO ratio is higher than one (De Soete, 1990). In addition to gasification, reaction of NO with CO on various surfaces, including char, ash and soot, can also be a major route of heterogeneous NO reduction mechanisms (De Soete, 1990). Catalytic decomposition of NO on various metallic oxides, some of which are common constituents in the lignite, has been reported by Winter (1971).

Huffman *et al.* (1990) reported that calcium is dispersed in coal macerals and is bonded to the oxygen anions. During combustion, the calcium present in lignite agglomerates, and eventually forms CaO and CaS. Recent lab-scale investigations of fluidized bed combustion (FBC) and circulating FBC (CFBC) have shown that calcium sulfide (Hansen *et al.*, 1992), CaO (Allen, 1990; Hansen *et al.*, 1992; Hansen and Dam-Johansen, 1993; Shimizu *et al.*, 1993; Lin *et al.*, 1993) and Fe₂O₃ (Allen, 1990) serve as catalysts for NO reduction in various environments. While most of these researchers claimed that these catalysts enhanced the gasification or the conversion of NO + CO to form CO₂ and N₂, Lin *et al.* indicated that CO decreases the NH₃ conversion to NO. Lin *et al.* also claimed that NO may oxidize NH₃ to form nitrogen through homogeneous and heterogeneous mechanisms in FBC or CFBC. These char gasification and mineral-catalyzed reactions in reburning environments have not been fully investigated, but can certainly be enhanced by the highly porous nature of lignite char. Various calcium-NO surface complexes have been identified by infrared studies (Low and Yang, 1974; Allen, 1990).

In the early period of this project (Chen and Ma, 1995; Chen *et al.*, 1995a, 1995b), we have been examining the reactivities of selected chars with NO. The effects of reactive gaseous species which typically exist in reburning environment, including CO₂, O₂ and CO, have been investigated sequentially. Some of the findings from this project are summarized below.

1. Heterogeneous mechanisms contribute higher NO reduction than homogeneous mechanisms over a wide range of stoichiometric ratios when the lignite is used as reburning fuel;
2. Lignite char alone can be an effective reburning fuel;
3. Surface area, estimated either by Dubinin-Radushkevich (D-R) equation with CO₂ as adsorbate or by BET with nitrogen, is not a normalization factor of char reactivity;

4. Based on limited experiments, NO reduction by bituminous coal char can be somewhat improved by impregnating the char with CaO;
5. Unlike the homogeneous phase mechanisms, oxidants, including CO₂ and O₂, inhibit the surface NO reduction over the entire range of reburning stoichiometric ratio (SR₂) studied, 0.6 to 1.1;
6. Oxidants suppress NO reduction on bituminous coal char more than they affect that on lignite char;
7. Conversion of oxygen of feed NO to the gasification products, CO and CO₂, is complete when feed gas contains only two reactive species, NO and CO₂;
8. The two observations stated above suggest desorption of stable surface oxygen complexes is a rate-limiting step, which may be catalyzed by the mineral matters during reburning with lignite char;
9. Activation energy of the NO reaction with bituminous coal char changes with temperature implying changes in mechanisms possibly through changes in pore structure;
10. Although complex, the data appear to agree qualitatively with the Langmuir-Hinshelwood kinetics.

The results discussed above appear to have very important values to boiler practice, and significant implications to the mechanisms of NO reduction in fuel rich environment. During this quarter, we have been continuing the investigation of products composition and rate of NO reduction on chars of two different origins by sequentially adding the three major oxidants in reburning: NO, O₂, and CO₂. N₂ and CO₂ internal surface area of chars have been determined to assist the interpretations of experimental results. These chars have been selected from runs of various pyrolysis and reaction conditions. Implications of Langmuir-Hinshelwood mechanisms and mass transfer

limitations have been examined in detailed.

II. WORK ACCOMPLISHED

The detailed flow reactor system for reburning and experimental procedure have been discussed by Burch *et al.* (1991a,b). The detailed char preparation procedure has been documented in our sixth quarterly report (Chen *et al.*, 1995a).

A. Measurements of the Surface Fractal Dimension

The BET-surface areas of samples were determined with nitrogen (N_2) as the adsorbate at a temperature of 77 K. Let P be the partial pressure of the adsorbate, and P_0 , the saturation vapor pressure of the adsorbate at the operating temperature; then, the relative pressure can be defined as P/P_0 . The measurements were carried out with the multi-point method under six different relative pressures. The values of P/P_0 ranging from 0.05 to 0.30 were within the region of the adsorption isotherm. Each P/P_0 leads to the weight of gas, W , adsorbed on the sample. The surface area of each sample has been recovered from the Brunauer-Emmett-Teller (BET) equation, the results of which are summarized in Table 1.

Additional determination of the surface areas was made with carbon dioxide (CO_2) as the adsorbate at a temperature of 273 K. The values of P/P_0 ranging from 0.001 to 0.010 were within the region of the adsorption isotherm. These values of P/P_0 are small compared to those obtained with N_2 because P_0 of CO_2 at 273 K is 2,622 mmHg and is much larger than the atmospheric pressure of 745 mmHg. The measurements were carried out under eleven different levels of P/P_0 , again with the multi-point method. The surface area of each sample has been estimated with the BET equation.

Furthermore, the micro-pore volume and surface area of each sample have been calculated with the Dubinin-Radushkevich (D-R) equation, the results of which are summarized in Table 2.

B. Effects of CO₂ and O₂ on NO Reduction with Chars of different Origins

Reburning stage contains three major oxidizing species: NO, CO₂ and O₂. The effectiveness of NO reduction by char depends on the competitive reactions of these oxidants on the char surface. In the last quarter (Chen et al., 1995b), we observed that char is gasified by these oxidants at different rates, and chars derived from a bituminous coal and a lignite follow different gasification rates. The interpretations of these reaction mechanisms are further complicated by the observations that the internal surface areas and pore volume change during gasification. The dynamical changes of these physical factors depend on its gaseous environment, and they vary significantly for chars of different origins and devolatilization history.

To initiate a systematic investigation, we designed a set of twelve experiments. Six of these runs used the chars prepared at 1100°C and with 5 min holding time, i.e., the high temperature chars; and six others used the chars prepared at 950°C and with 0 holding time, i.e., the low temperature chars. The N₂ and CO₂ surface areas of the two bituminous coal chars produced at two different temperatures (ID #3-6 and 4-1P) and the two lignite chars (ID#3-1 and 4-1L) are shown in Tables 1 and 2. The ultimate analyses of these coals and chars have been reported by the Huffman Laboratory, and are shown in Table 3. Each of the four chars are subject to three experiments: NO+char, NO+char+CO₂, and NO+char+CO₂+O₂. The reactant gas contains, if any, 1000 ppm NO, 16.8% CO₂ and 1.95% O₂, balanced with helium. Char feeding rates are 0.0640 g/min for the lignite char, and 0.0446 g/min for the bituminous coal char. These feed compositions correspond to

reburning at $SR_2 = 0.97$ and 0.90 for the high temperature chars derived from the bituminous coal and the lignite, respectively. All experiments were conducted at 1100°C , with 0.2 s residence time. The results of the six experiments with the high temperature chars are discussed in this section, and data are presented in Figures 1 through 3.

Figure 1 presents the exit NO concentrations from runs where major oxidants in reburning, CO_2 and O_2 , are sequentially added. The exit NO concentrations suggest two interesting observations. First, the reactivity of the bituminous coal char is comparable or even higher than lignite char when CO_2 and O_2 are absent. Second, CO_2 and O_2 are more detrimental to the bituminous coal char than that to the lignite char.

Figure 2 illustrates the net yields of gasification products, CO_2 and CO , from these six experiments discussed above. Addition of 16.8 volume % of CO_2 in the feed does not seem to increase the total yields of these gasification products from reburning either with the lignite char or with the bituminous coal char. But the presence of CO_2 results in notably higher NO concentration from reburning with bituminous coal char, and results in only small increase in NO from reburning with lignite char. Using the Langmuir-Hinshelwood interpretation, this observation seems to suggest that NO adsorption on lignite char is much faster than CO_2 adsorption, but CO_2 and NO are competitive for the active sites on the char derived from the bituminous coal.

The exit concentrations of NO, CO_2 , and CO from reactions of lignite char appear to be insensitive to the presence of 16.8 volume % of CO_2 . **This observation may be rather important to NO reburning with mixed fuels containing both volatiles and solid carbon.** Since the volatile fuels usually burn much faster than char, CO and CO_2 produced from burning of mixed fuels is not expected to compete with NO for the active sites on lignite char. Furthermore, we have observed

the catalytic conversion of HCN to NH₃ by lignite char or ash (Burch *et al.*, 1991b), which is a ✱
desired reaction when volatile fuel is used in reburning. Thus, with O₂ already depleted, the ✱
NO/char reaction will take place in an environment "richer" to NO than nominally observed, ✱
and the NO reduction should not be the sum of of the reduction from each fuel taken ✱
separately. ✱

When both O₂ and CO₂ are added in the feed, the yields of gasification products notably increase, and more carbon of lignite char is gasified than that of bituminous coal char. Again, using Langmuir-Hinshelwood kinetics, the observed NO concentrations imply that NO competes with O₂ for the formation of surface complexes on lignite char, but NO can not compete with O₂ on the bituminous coal char. Furthermore, due to the formation of large amount of gasification products, turnover of the oxygen surface complex on the lignite char seems to be faster than that on the bituminous coal char. The accelerated desorption is likely a result of catalysis.

Interestingly, the char gasification literature has offered some helpful support to what we have observed here, particularly through the concepts of "stable oxides," "labile oxides," and "reactive surface area" which have been well documented by Laine *et al.* (1963), Lizzio (1990) and Radovic *et al.* (1991). In the study of gasification of carbon by N₂O, Strickland-Constable (1938) distinguished two types of surface oxides: 1) stable oxides, i.e., those C-O complexes which accumulate on the surface and inhibit oxidation, and 2) labile oxides, i.e., those C(O) complexes which have a shorter lifetime and are active in the combustion mechanisms. Lizzio (1990), Lizzio *et al.* (1990), and Radovic *et al.* (1991) developed temperature-programmed desorption techniques for the quantifications of both C-O and C(O) complexes. They concluded that the surface area occupied by the labile oxides, i.e., C(O), is a better normalization parameter of char reactivity and is called

"reactive surface area (RSA)." This technique is tested in the determinations of CO_2 -gasification rates of chars derived from lignite and bituminous coal (Lizzio *et al.*, 1990).

Lizzio (1990) also theorized and verified that RSA increases with decreasing structure order during gasification. His hypothesis is consistent with our observation that lignite char, a carbonaceous material having lower structure order than the bituminous coal char, has a higher reactivity in our gasification environments involving NO.

The total amount of oxygen in the gasification products, CO and CO_2 , normalized by the amount of converted NO during reaction suggests the competition for char among the three oxidants: NO, CO_2 , and O_2 , Figure 3. When the feed contains NO and char only, the conversions of oxygen of NO indicate that CO and CO_2 are the major products of NO reduction. When CO_2 is added, the oxygen conversions are also about 100 percent, suggesting NO is a stronger oxidizing agent than CO_2 . However, since the NO reduction on the bituminous coal char is retarded when CO_2 is introduced, oxygen conversions to gasification products imply that CO_2 poisons the active sites for NO reduction probably through forming stable surface complex on the bituminous coal char. When NO, CO_2 and O_2 are all introduced in the feed, the gasification products increase sharply (the scale for these two runs is reduced by a factor 60). Although significant amounts of carbon are gasified by oxygen, NO and O_2 are competitive for lignite char; this is not what observed for the bituminous coal char.

C. Effects of Pyrolysis Severity on Char Reactivity

Similar to the experiments with the high temperature chars discussed in Section II.B, the low temperature chars were subject of six experiments: NO+char, NO+char+ CO_2 , and NO+char+ CO_2 + O_2 .

The reactant gas contains, if any, 1000 ppm NO, 16.8% CO₂, and 1.95% O₂, balanced with helium. Char feeding rates are 0.0640 g/min for the lignite char, and 0.0446 g/min for the bituminous coal char. These feed compositions correspond to reburning at SR2 = 0.93 for the bituminous coal char, and 0.88 for the lignite char. All experiments were conducted at 1100°C, with 0.2 s residence time.

The results presented in Figures 4 through 6 indicate that the low temperature bituminous coal char behaves almost identical to the high temperature bituminous coal char in various gaseous environments, when they are compared with the data presented in Figures 1 through 3. We observed shift of calibration values of the CO/CO₂ analyzer when the experiment with NO+char+CO₂+O₂, therefore, the CO₂ and O₂ yields tend to be low and will have to be confirmed in the next quarter. The low temperature lignite char demonstrates notably higher NO reduction activity, Figure 4, than the high temperature lignite char, Figure 1, regardless if the oxidants are present. The loss of reactivity of high temperature char could be caused by a number of reasons. First, it has been reported that pyrolysis of Pittsburgh #8 coal generates a small amount of H₂ (<0.4 wt % of as received coal) in the temperature range of 950 to 1100 °C (Howard, 1981), and this hydrogen yield may assist the removals of oxidants, CO₂ and O₂, and direct reduction of NO. The ultimate analyses shown in Table 3, however, demonstrate that the elemental compositions of high and low temperature bituminous coal chars are about the same; the low temperature lignite char does have slightly higher atomic H/C ratio than that of the high temperature char. Second, it has been speculated that the a hydrogen complex forms on the partially devolatilized char, which also assists the removal of oxidants and NO (De Soete, 1990). Third, high temperature causes closures of pores due to a structure ordering of carbon, or graphitization (Radovic *et al.*, 1983a,b; Sahu *et al.*, 1988; Wong *et al.*, 1995), and therefore reduces the contact area of char with NO. The low temperature lignite char (ID#3-1)

does have higher CO₂ surface area, but lower N₂ surface area, than those of the high temperature lignite char (ID#4-1L), Tables 1 and 2. Our observation is consistent with an earlier study of char reaction with air (Radovic *et al.*, 1983b), in which char's reactivity was found to decrease with increasing pyrolysis severity, including temperature, heating rate, and holding time.

D. Variations of Internal Surface Area and Char Reactivity

Char internal surface areas reflect the complexity of heterogeneous reburning. First, based on per unit CO₂ surface area, NO yields presented in Figure 1 seem to imply that bituminous coal char is more reactive than lignite char when CO₂ and O₂ are absent. For the NO reaction with the high temperature char without oxidants, CO₂ surface area of bituminous coal char reduces from 36.2 to 24.6 m²/g (ID#4-1P and 4-2P), while the surface area of lignite char reduces from 255 to 235 m²/g (ID#4-1L and 4-2L).

Second, both N₂ and CO₂ surface areas of lignite chars reduce to 20% of their original levels when oxidants, CO₂ and O₂ are introduced in the feed, see samples with ID#4-1L and 4-4L in Table 1 and 2. This is very different from what we have observed with the bituminous coal char. The low temperature bituminous coal char (ID#3-6) has much higher N₂ and CO₂ surface areas than those of the high temperature bituminous coal char (ID#4-1P), Tables 1 and 2. The surface areas of these two chars vary significantly when they react with NO, CO₂ and O₂, see samples with ID# 3-7, 4-2P, 4-3P, and 4-4P in Tables 1 and 2. These data seem to imply that higher pyrolysis temperature and reactions of bituminous coal char with NO cause closure of pores, but these pores open up to a level near the low temperature char range when the oxidants are introduced.

Since the high and low temperature bituminous coal chars have no noticeable differences in

the observed NO reduction efficiency shown in Figures 1 and 4, the observed large difference in their internal surface areas reflects the complexities of heterogeneous reburning. One possibility is that the mass transfer limitation exists, and the micropores do not contribute to NO reduction. This is part of the reason we have started estimating the mass transfer limitations this quarter based on the newly obtained nominal reaction rates and surface areas, see the next section. Nevertheless, the low temperature char used in the surface area measurement was derived from an old Pittsburgh #8 coal sample in our collection, but the chars from the new Pittsburgh #8 coal were used in the reaction study. What we have observed about the variations in surface areas will be reexamined in the next quarter.

What we have observed about the internal surface areas may be very significant to the understanding of various physical and chemical mechanisms of NO reactions on chars of different origins. If the closure of the pores of lignite char occurs in the early stage of the reaction, the exit NO concentrations presented in Figure 1 demonstrate that reduction of NO by O₂ may be due to closure of pores, or poisoning of active sites of the char by CO₂ and O₂. If the closure of the pores of lignite char occurs in the later stage of the reaction time, i.e., ~0.2 s, then the NO yields in Figure 1 reflect poisoning, and, more importantly, the lignite char activity is to diminish after 0.2 s. In the study of air staging, Mereb and Wendt (1994) observed sharp decrease in NO concentration during the first 1.5 s of burning of bituminous coal at SR = 0.83. They also observed that the variation of the concentration of total exit nitrogen species in NO / lignite reaction is lower than that of bituminous coal in the first 1.8 s, but it undergoes a sharp fall between 1.8 and 2.4 s. It would certainly be interesting to investigate if these variations in NO are related to the changes in pore structures in the future studies.

E. Rates of NO Reactions with Chars

During this quarter we continue the investigation of the effects of feed NO concentration on the rate of NO reaction with chars of two different origins. From the stand point of reburning practice, these rate data are desirable because recent successful developments in low NO_x burners have significantly lowered the NO concentration of flue gas coming into the reburning stage. From the stand point of basic research, these rate data are needed for the understanding of the heterogeneous reburning mechanisms in various periods of reburning.

Six series of experiments with feed NO at 800, 600, and 400 ppm, and two different chars have been conducted in the temperature range 800 and 1100°C. The two high temperature chars include one derived from the Pittsburgh #8 bituminous coal and the other from the Mississippi lignite. No oxidants are included in the feed. Char preparation and reaction study with a flow reactor system have been discussed in our previous publications (Chen and Ma, 1995; Chen *et al.*, 1995a; Chen *et al.*, 1995b). Figures 7 and 8 present the exit NO concentrations observed in these six series of experiments. These two figures also contain data discussed in the last quarterly report (Chen *et al.*, 1995b) and in the last section, i.e., data with feed NO at 1000 and 800 ppm, and those with feed containing oxidants.

Due to the low surface reaction rate of NO and char reported in the literature (see, e.g., De Soete, 1990), we have been assuming that mass transfer limitations are negligible and our interpretation of the reburning mechanisms has been based on Langmuir-Hinshelwood models (Chen and Ma, 1995; Chen *et al.*, 1995b). Two of our recent findings, however, have revealed the need for further examination of the significance of mass transfer limitations. First, surface areas of the high temperature bituminous coal char is much smaller than that of the low temperature char measured

previously, yet the two chars demonstrate very similar reactivity with NO. The observed low surface area of high temperature char results in higher estimated NO activity per unit char surface area, and the reaction is more likely to suffer the mass transfer limitations. Second, as discussed in the last section, the internal surface areas of lignite char vary significantly when CO₂ and O₂ are introduced, and the pore-closure process can potentially lead to mass-transfer controlled mechanisms.

During the last two quarters (Chen *et al.*, 1995a; Chen *et al.*, 1995b), we have derived the following expression which relates the reaction rate with the reaction conditions inside a tubular flow reactor containing three temperature zones in the axial direction: constant heating-rate period, isothermal zone, and constant cooling-rate period.

$$\ln(1 - X) = \int 0.765 W_1 A k_0 \frac{1}{T} e^{-\frac{E_a}{RT}} dT - t_h W_1 A k_0 e^{-\frac{E_a}{RT}} - \int (-0.765) W_1 A k_0 \frac{1}{T} e^{-\frac{E_a}{RT}} dT \quad (1)$$

where X is the NO conversion,

W₁ is the char feeding rate, in g s⁻¹,

A is the specific, internal surface area of char, in m² g⁻¹,

k₀ is the frequency factor of the surface reaction, in mole s⁻¹ m⁻² atm⁻¹,

E_a is the activation energy of the surface reaction, in kcal mole⁻¹,

T is temperature, in °C, and,

t_h is gas residence time in the isothermal temperature region, in s.

For a system involving internal mass transfer limitation, the observed Arrhenius rate in the above expression can be considered the product of the true surface reaction rate the effectiveness factor,

η, i.e.,

$$\ln(1 - X) = \int 0.765 W_1 A \eta k_0 \frac{1}{T} e^{-\frac{E_a}{RT}} dT - t_h W_1 A \eta k_0 e^{-\frac{E_a}{RT}} - \int (-0.765) W_1 A \eta k_0 \frac{1}{T} e^{-\frac{E_a}{RT}} dT \quad (2)$$

The effectiveness factor has been theoretically shown a function of the Thiele modulus, ϕ (see, e.g., Satterfield, 1970)

$$\eta = \frac{3}{\phi} \left[\frac{1}{\tanh \phi} - \frac{1}{\phi} \right] \quad (3)$$

where the Thiele modulus is defined as

$$\phi = R \left[\frac{2ka}{D_{eff}r} \right]^{0.5} \quad (4)$$

where R is the radius of particles, in cm,
 k is the rate constant, in mole sec⁻¹ m² atm⁻¹,
 a is the ideal gas conversion constant, 2.445×10^4 atm cm³ mole⁻¹,
 D_{eff} is effective diffusion coefficient, in cm² sec⁻¹, and,
 r is the pore radius, in cm.

The mass transfer resistance in terms of the effective diffusivity can be considered the linear combination of the resistances contributed by the Knudsen and the bulk diffusivity (Satterfield, 1970; Chan, 1980),

$$\frac{1}{D_{eff}} = \frac{1}{D_{k,eff}} + \frac{1}{D_{12,eff}} \quad (5)$$

$$D_{k,eff} = 19400 \left[\frac{\theta^2}{T_m A \rho_p} \right] \left[\frac{T}{M} \right]^{0.5} \quad (6)$$

$$D_{12, \text{eff}} = \frac{0.001858 T^{1.5} \left[\frac{M_1 \cdot M_2}{M_1 + M_2} \right]^{0.5}}{P \sigma_{12}^2 \Omega_D} \quad (7)$$

where $D_{k, \text{eff}}$ is the Knudsen diffusion coefficient for a porous solid, in $\text{cm}^2 \text{s}^{-1}$,
 $D_{12, \text{eff}}$ is the bulk diffusion coefficient, in $\text{cm}^2 \text{s}^{-1}$,
 θ is the particle void fraction,
 τ_m is the tortuosity factor based on the mean pore radius, assumed 2,
 ρ_p is the particle density, $0.4 \text{ cm}^3 \text{g}^{-1}$,
 M, M_1 are the molecular weights of diffusing molecules, $M_{\text{NO}} = 30$, $M_{\text{HE}} = 4$,
 M_2 is the molecular weight of the gas medium,
 P is pressure, 1 atm,
 Ω_D is the "collision integral", a function of $K_B * T / \epsilon_{12}$, dimensionless,
 ϵ, σ are the force constant of the Lenard-Jones potential function, ϵ in $\text{g cm}^2 \text{s}^{-2}$, σ in \AA , and,
 k_B is the Boltzmann constant, $1.38 \times 10^{-16} \text{ g cm}^2 \text{s}^{-2} \text{K}^{-1}$.

The subscript 12 in the Eqs. 5 and 7 means that species 1 is diffusing in species 2. Equations 5 through 7 allow the calculation of the effectiveness diffusivity for the NO + char reaction at 1100°C . For instance, we have examined the pore volumes presented in Tables 1 and 2, and obtained the average pore volumes for the MS lignite char and the Pitt#8 coal char, $0.1 \text{ cm}^3/\text{g}$ and $0.01 \text{ cm}^3/\text{g}$, respectively. We can further assumed that the bulk density of both chars is 2.07 g/cm^3 . Based on these values, we obtain

$$\begin{aligned} \theta &= \text{pore volume} \times \text{density} \\ &= 0.2 \text{ for the MS lignite char and } 0.02 \text{ for the Pitt\#8 char.} \end{aligned}$$

From Bird *et al.*, (1960):

$$\begin{aligned} \epsilon_{\text{He}}/k_B &= 10.2^\circ \text{K}, \quad \sigma_{\text{He}} = 2.576 \text{ \AA}, \\ \epsilon_{\text{NO}}/k_B &= 119^\circ \text{K}, \quad \sigma_{\text{NO}} = 3.47 \text{ \AA}, \\ \sigma_{\text{He-NO}} &= 1/2 * (\sigma_{\text{He}} + \sigma_{\text{NO}}) = 3.023 \text{ \AA}, \\ \epsilon_{\text{He-NO}} &= (\epsilon_{\text{He}} \epsilon_{\text{NO}})^{0.5} = 34.84 k_B \text{ g-cm}^2/\text{sec}^2, \\ k_B T / \epsilon_{\text{He-NO}} &= 23.83, \quad \Omega_D \approx 0.6776. \end{aligned}$$

Substituting the above constants into Eqs. 5 through 7, we obtain

$$\begin{aligned}D_{k, \text{eff}} &= 3.98 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ for lignite char at } 1100 \text{ }^\circ\text{C}, \\D_{12, \text{eff}} &= 8.127 \text{ cm}^2/\text{sec}, \\D_{\text{eff}} &= 3.98 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ for lignite char at } 1100 \text{ }^\circ\text{C}.\end{aligned}$$

This results show that Knudsen diffusion controls the overall diffusion rate.

The significance of what has been discussed is that Eqs. 2 through 4 can be solved simultaneously by MathCad for η , ϕ and k . Since the micropore volume reported in Tables 1 and 2 is for the pores in the range 0 to 20 Å only, more accurate determination of pore volume is currently under way by BET N₂. It is expected that, by the end of next quarter, we will be able to know more about the extent of the mass transfer limitation and provide more accurate rate constant.

Figure 9 illustrates the current knowledge about the nominal NO reduction rates based on Eq. 1 and the CO₂ surface areas reported in Tables 1 and 2. Due to the temporal variations of char internal surface areas, average CO₂ surface areas have been used in the estimations of the reaction rate. For example, for the NO reactions with the high temperature chars, specific surface areas of lignite char bituminous coal chars have been assumed to be 255 m²/g, and 31.9 m²/g, respectively.

IV. WORK FORECAST

In the succeeding quarter, we will continue the measurements of the rates of NO/char reactions with feed NO concentration at 200 ppm. Experiments will be conducted with sequential addition of CO₂ and oxygen. Better measurement of pore fraction and pore size distribution will be obtained by BET N₂. This information will be used in the estimation of the Thiele modulus, effectiveness factor, and surface reaction rate; therefore provide accurate information about the mass transfer limitations. After the rates are corrected by the effects of mass transfer limitations, we will establish a Langmuir adsorption/desorption/surface reaction model.

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Table 1a. Specific surface areas measured with nitrogen as the adsorbate at a temperature of 77K.
 (Data from two repeated experiments are shown in the table.)

ID	Sample Description	Nitrogen
No. 1	low temp. MS lignite char, first trial	15.09 17.52
No. 2	low temp. MS lignite char after rxn., first trial	40.79 41.56
No. 3-1	low temp. MS lignite char	67.52 63.42
No. 3-2	low temp. MS lignite char after reburning @ SR=0.70 1100°C	35.19 37.65
No. 3-3	low temp. MS lignite char after reburning @ SR=0.94 1100°C	51.86 51.04
No. 3-4	low temp. ND lignite char	33.26 35.23
No. 3-5	low temp. ND lignite char after reburning at 1100°C	43.12 44.68
No. 3-6	low temp. Pitt. #8 bituminous coal char	18.53 18.49
No. 3-7	low temp. Pitt. #8 bituminous coal char after reburning	10.66 11.62
No. 4-1 P	high temp. Pitt.#8 coal char pyr. = 1100°C	.872 .865
No. 4-2 P	high temp. Pitt. #8 coal char after (NO + char) rxn pyr.= 1100°C, rxn.= 1100°C	.218 .210
No. 4-3 P	high temp. Pitt. #8 coal char after (NO + Char) rxn pyr.= 1100°C, rxn.= 800°C	.318 .317

Table 1b. Specific surface areas measured with nitrogen as the adsorbate at a temperature of 77K.
 (Data from two repeated experiments are shown in the table.)

ID	Sample Description	Nitrogen
No. 4-4 P	high temp. Pitt. #8 coal char afetr (NO+O ₂ +CO ₂ +char) rxn pyr.= 1100°C, rxn.= 1100°C	67.3 68.8
No. 4-1 L	high temp. MS lignite char pyr.= 1100°C	116 114
No. 4-2 L	high temp. MS lignite char after (NO + char) rxn pyr.= 1100°C, rxn.= 1100°C	13.7 13.7
No. 4-3 L	high temp. MS lignite char after (NO + char) rxn pyr.= 1100°C, rxn.= 800°C	10.8 8.67
No. 4-4 L	high temp. MS lignite char after (NO +O ₂ +CO ₂ + char) rxn pyr.= 1100°C, rxn.= 1100°C	18.1 17.8
No. 4-5-L	high temp. MS lignite char after (NO +CO ₂ + char) rxn pyr.= 1100°C rxn.= 800-1000°C all samples	42.3 42.8
No. 5-1	high temp. Pitt. coal char in 1.5M calcium acetate solution for 32 h	.478 .501
No. 5-2	high temp. Pitt. coal char in 1.0M calcium acetate solution for 5 h	.516 .450
No. 5-3	undoped char	.302 .293

Table 2a. Specific surface areas evaluated with the BET equation and the micro pore volumes and micro pore surface areas evaluated with the D-R equation: adsorbate CO₂, operating temperature 273 K. (Data from two repeated experiments are shown in the table.)

ID	Sample Description	Surface area [m ² /g]	Micro pore volume [cc/g]	Micro pore surface area [m ² /g]
No. 1	low temp. MS lignite char, first trial	124 118	.076 .085	209 235
No. 2	low temp. MS lignite char after rxn., first trial	38 29	.024 .019	66 53
No. 3-1	low temp. MS lignite char	172 168	.108 .109	299 300
No. 3-2	low temp. MS lignite char after reburning @ SR=0.70 1100°C	114 117	.075 .070	206 193
No. 3-3	low temp. MS lignite char after reburning @ SR=0.94 1100°C	121 124	.083 .082	228 227
No. 3-4	low temp. ND lignite char	200 210	.147 .152	406 420
No. 3-5	low temp. ND lignite char after reburning at 1100°C	192 186	.134 .132	371 365
No. 3-6	low temp. Pitt. #8 bituminous coal char	158 146	.115 .108	317 298
No. 3-7	low temp. Pitt. #8 bituminous coal char after reburning	128 115	.080 .085	222 235
No. 4-1 P	high temp. Pitt.#8 coal char pyr. = 1100°C	32.4 29.9	.013 .013	36.8 35.6
No. 4-2 P	high temp. Pitt. #8 coal char after (NO + char) rxn pyr.= 1100°C, rxn.= 1100°C	N/A	.009 .009	23.5 25.7

Table 2b. Specific surface areas evaluated with the BET equation and the micro pore volumes and micro pore surface areas evaluated with the D-R equation: adsorbate CO₂, operating temperature 273 K. (Data from two repeated experiments are shown in the table.)

ID	Sample Description	Surface area [m ² /g]	Micro pore volume [cc/g]	Micro pore surface area [m ² /g]
No. 4-3 P	high temp. Pitt. #8 coal char after (NO + Char) rxn pyr.= 1100°C, rxn.= 800°C	24.2 24.1	.007 .009	20.5 23.6
No. 4-4 P	high temp. Pitt. #8 coal char afetr (NO+O ₂ +CO ₂ +char) rxn pyr.= 1100°C, rxn.= 1100°C	141 140	.100 .100	276 276
No. 4-1 L	high temp. MS lignite char pyr.= 1100°C	142 130	.096 .089	265 245
No. 4-2 L	high temp. MS lignite char after (NO + char) rxn pyr.= 1100°C, rxn.= 1100°C	134 116	.088 .083	241 229
No. 4-3 L	high temp. MS lignite char after (NO + char) rxn pyr.= 1100°C, rxn.= 800°C	129 120	.092 .086	255 236
No. 4-4 L	high temp. MS lignite char after (NO +O ₂ +CO ₂ + char) rxn pyr.= 1100°C, rxn.= 1100°C	26.0 26.0	.017 .018	52.6 50.0
No. 4-5 L	high temp. MS lignite char after (NO +CO ₂ + char) rxn pyr.= 1100°C rxn.= 800-1000°C all samples	113 122	.081 .087	225 239

Table 2-c. Specific surface areas evaluated with the BET equation and the micro pore volumes and micro pore surface areas evaluated with the D-R equation: adsorbate CO₂, operating temperature 273 K. (Data from two repeated experiments are shown in the table.)

ID	Sample Description	Surface area [m ² /g]	Micro pore volume [cc/g]	Micro pore surface area [m ² /g]
No. 5-1	high temp. Pitt. coal char in 1.5M calcium acetate solution for 32 h	N/A	.056 .065	154 179
No. 5-2	high temp. Pitt. coal char in 1.0M calcium acetate solution for 5 h	N/A	.064 .063	177 172
No. 5-3	undoped char	N/A	.047 .048	130 132

Table 3. Ultimate Analysis of Coals and Chars

Contents, %	MS lignite	Pitt #8 bituminous coal	MS lignite char (Low temperature 950 °C)	Pitt #8 coal char (Low temperature 950 °C)	MS lignite char (High temperature 1100 °C)	Pitt #8 coal char (High temperature 1100 °C)
Moisture	0.29	1.75	0.55	0.304	0.11	0.7
Carbon	53.07	77.23	56.54	90.63	51.55	88.28
Hydrogen	5.34	5.34	0.77	0.53	0.67	0.61
Oxygen	0*	8.75	0*	0*	1.38	0.43
Nitrogen	0.58	1.55	0.41	1.05	0.31	1.31
Sulfur	0.94	0.71	1.33	2.38	1.79	1.14
Ash	23.75	6.42	45.2	8.93	53.01	9.99

* by difference.

Moisture was determined by loss on drying in air at 105 °C for one hour. Char results are reported on a dried sample basis.

Table 4. Summary of Arrhenius' constants obtained under various feed concentrations and from two different chars

	k_0 , mole/(s*m ² *atm)	Ea, Kcal/mole
MS lignite w/o CO ₂	10.112	15.58
MS lignite w/ CO ₂	4.8313	15.01
MS lignite w/o CO ₂ , 800 ppm	5.43×10 ²	26.54
MS lignite w/o CO ₂ , 600 ppm	2.089×10 ³	30.20
MS lignite w/o CO ₂ , 400 ppm	2.641×10 ⁵	36.60
Pitt #8, low temp. char, w/o CO ₂	0.05229	8.024
	2.38 x 10 ⁵	38.95
	2.73 x 10 ⁹	62.56
Pitt #8, high temp. char, w/o CO ₂	0.09596	11.90
	4.521 x 10 ¹⁵	103.40
	1.719 x 10 ⁸	34.12
Pitt #8, high temp. char, w/ CO ₂	0.0458	10.21
	6.467 x 10 ¹¹	83.87
	1.615 x 10 ⁶	49.92
Pitt #8, high temp. char, w/o CO ₂ , 800 ppm	4.00 x 10 ³	27.68
	8.47 x 10 ⁶	45.86
	3.11 x 10 ⁸	54.93
Pitt #8, high temp. char, w/o CO ₂ , 600 ppm	1.997 x 10 ⁵	37.52
	1.229 x 10 ⁶	41.90
	1.368 x 10 ¹⁰	71.22
Pitt #8, high temp. char, w/o CO ₂ , 400 ppm	1.75 x 10 ⁶	41.18

* The feeding rate of Mississippi lignite char w/ CO₂ at [NO]_m = 1000 ppm is 0.064 g/min.

The feeding rate of Mississippi lignite char w/o CO₂ at [NO]_m = 1000 ppm is 0.0325 g/min.

† The feeding rate of Pitt #8 bituminous coal char at [NO]_m = 1000 ppm is 0.0446 g/min.

*

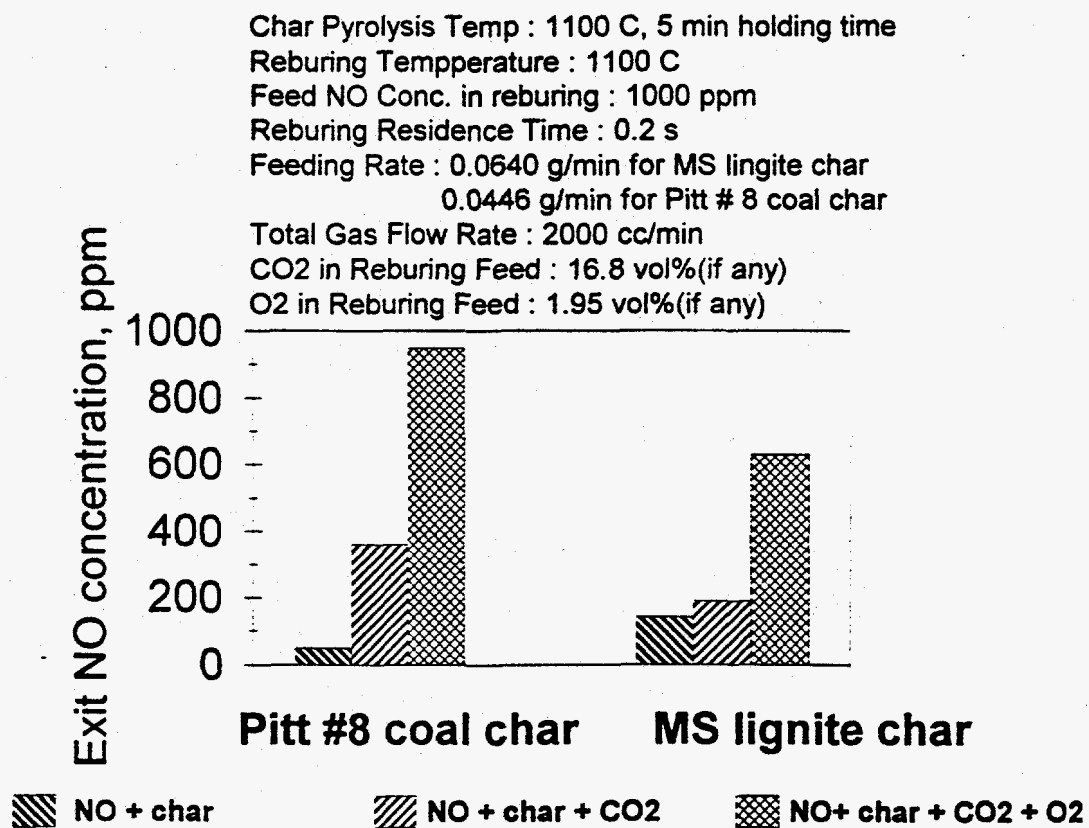


Figure 1. Effects of oxidants and char origins on exit NO concentrations. The chars were prepared at 1100 °C. The NO to char ratios correspond to that used in reburing at SR = 0.97 and 0.90 for the lignite char and bituminous coal char, respectively.

*

Char Pyrolysis Temp : 1100 C, 5 mins holding time
Reburing Temperature : 1100 C
Feed NO Conc. in reburing : 1000 ppm
Reburing Residence Time : 0.2 s
Feeding Rate : 0.0640 g/min for MS lignite char
0.0446 g/min for Pitt # 8 coal char
Total Gas Flow Rate : 2000 cc/min
CO₂ in Reburing Feed : 16.8 vol%(if any)
O₂ in Reburing Feed : 1.95 vol%(if any)

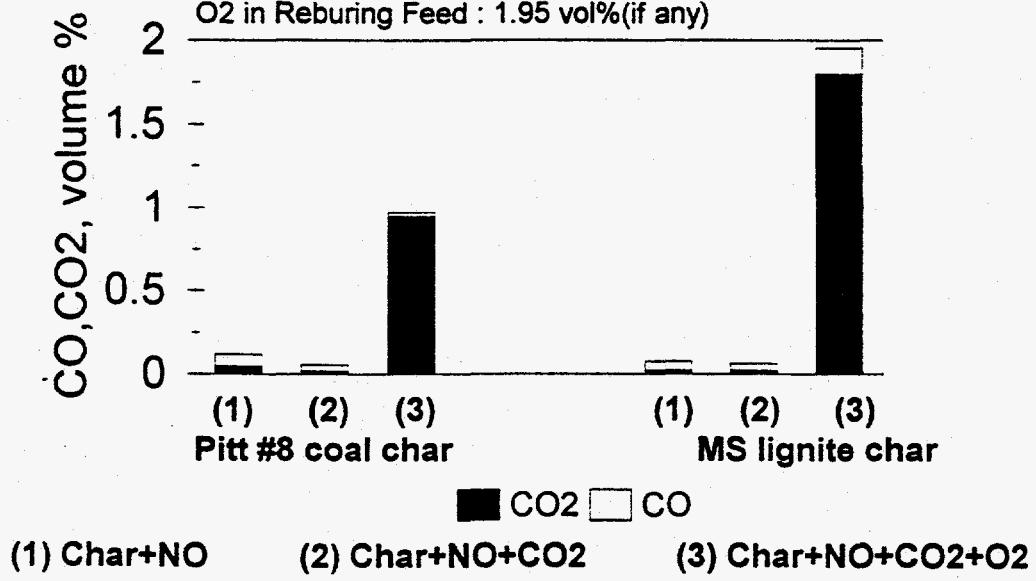


Figure 2. Yields of carbon oxides (in volume percentage) from the reactions of NO with the chars prepared at 1100 °C.

*

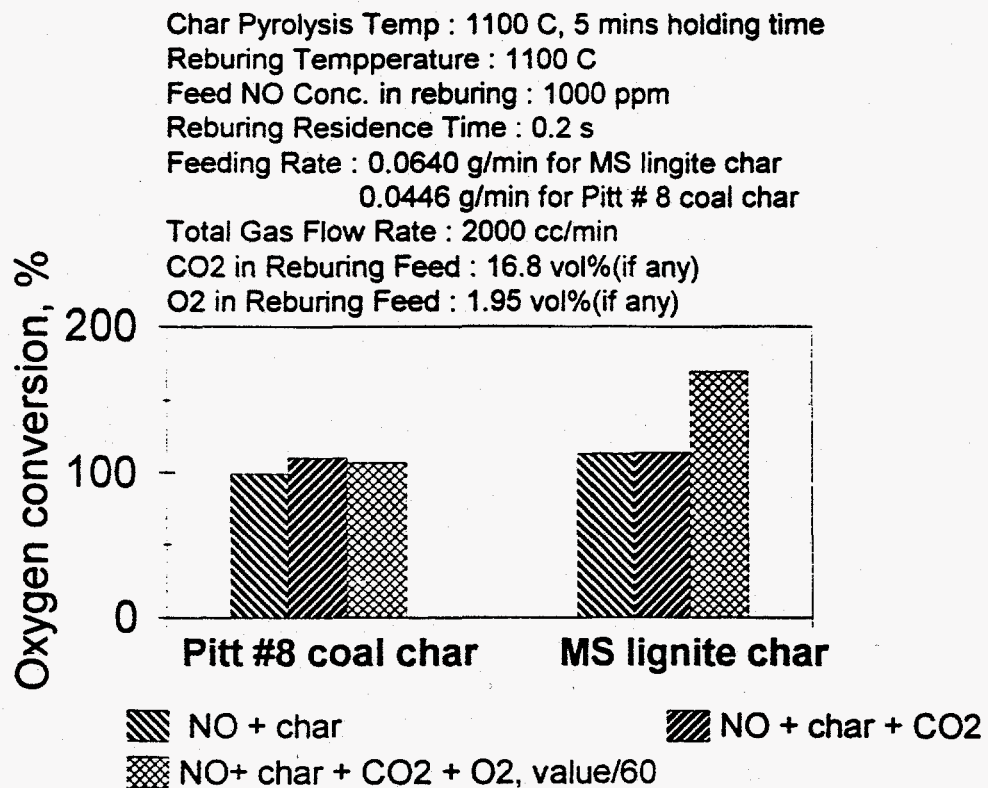


Figure 3. Percentage conversion of oxygen in feed NO to the gasification products, CO and CO₂. Note that the scales for the (NO+char+CO₂+O₂) reactions are reduced by a factor 60. Chars were prepared at 1100 °C.

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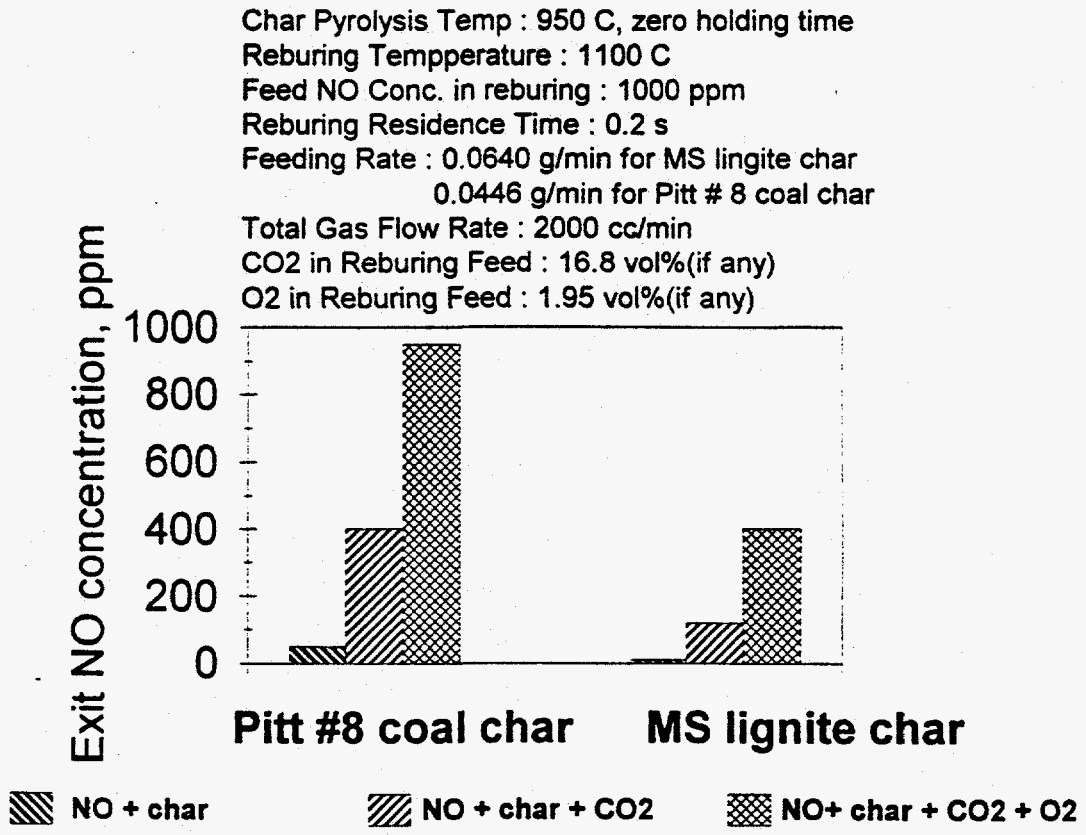


Figure 4. Effects of oxidants and char origins on exit NO concentrations. The chars were prepared at 950 °C. The NO to char ratios correspond to that used in reburing at SR = 0.93 and 0.88 for the lignite char and bituminous coal char, respectively.

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Char Pyrolysis Temp : 950 C, zero holding time
Reburing Temperature : 1100 C
Feed NO Conc. in reburing : 1000 ppm
Reburing Residence Time : 0.2 s
Feeding Rate : 0.0640 g/min for MS lingite char
 0.0446 g/min for Pitt # 8 coal char
Total Gas Flow Rate : 2000 cc/min
CO₂ in Reburing Feed : 16.8 vol%(if any)
O₂ in Reburing Feed : 1.95 vol%(if any)

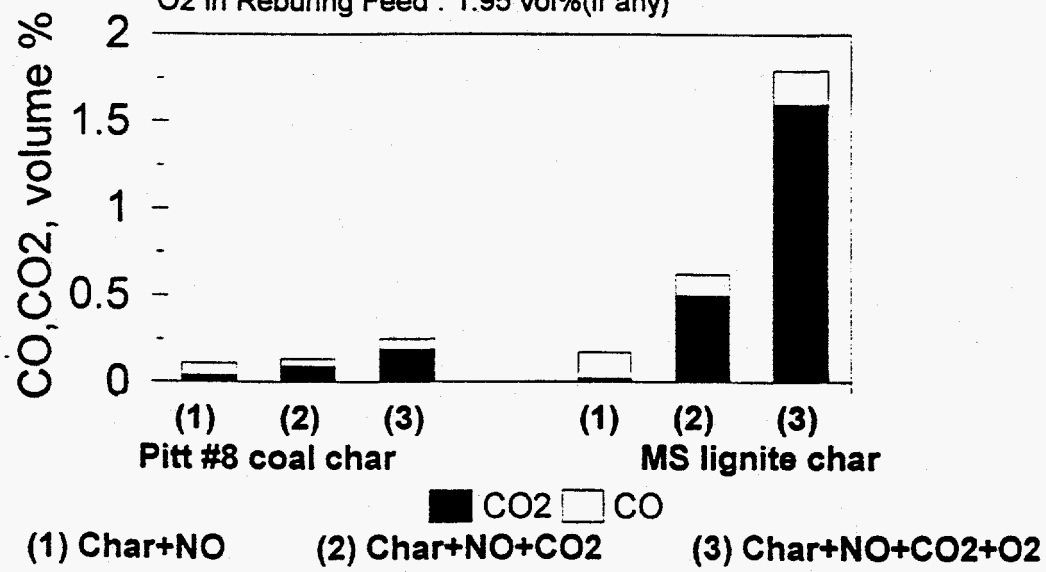


Figure 5. Yields of carbon oxides (in volume percentage) from the reactions of NO with the chars prepared at 950 °C.

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Char Pyrolysis Temp : 950 C, zero holding time
 Reburing Temperature : 1100 C
 Feed NO Conc. in reburing : 1000 ppm
 Reburing Residence Time : 0.2 s
 Feeding Rate : 0.0640 g/min for MS lignite char
 0.0446 g/min for Pitt # 8 coal char
 Total Gas Flow Rate : 2000 cc/min
 CO₂ in Reburing Feed : 16.8 vol%(if any)
 O₂ in Reburing Feed : 1.95 vol%(if any)

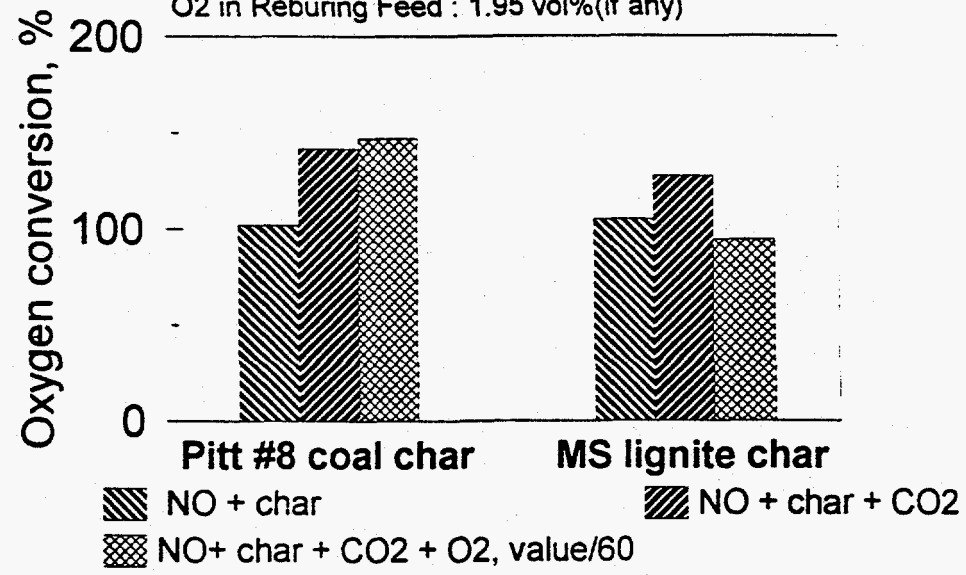


Figure 6. Percentage conversion of oxygen in feed NO to the gasification products, CO and CO₂. Note that the scales for the (NO+char+CO₂+O₂) reactions are reduced by a factor 60. Chars were prepared at 950 °C.

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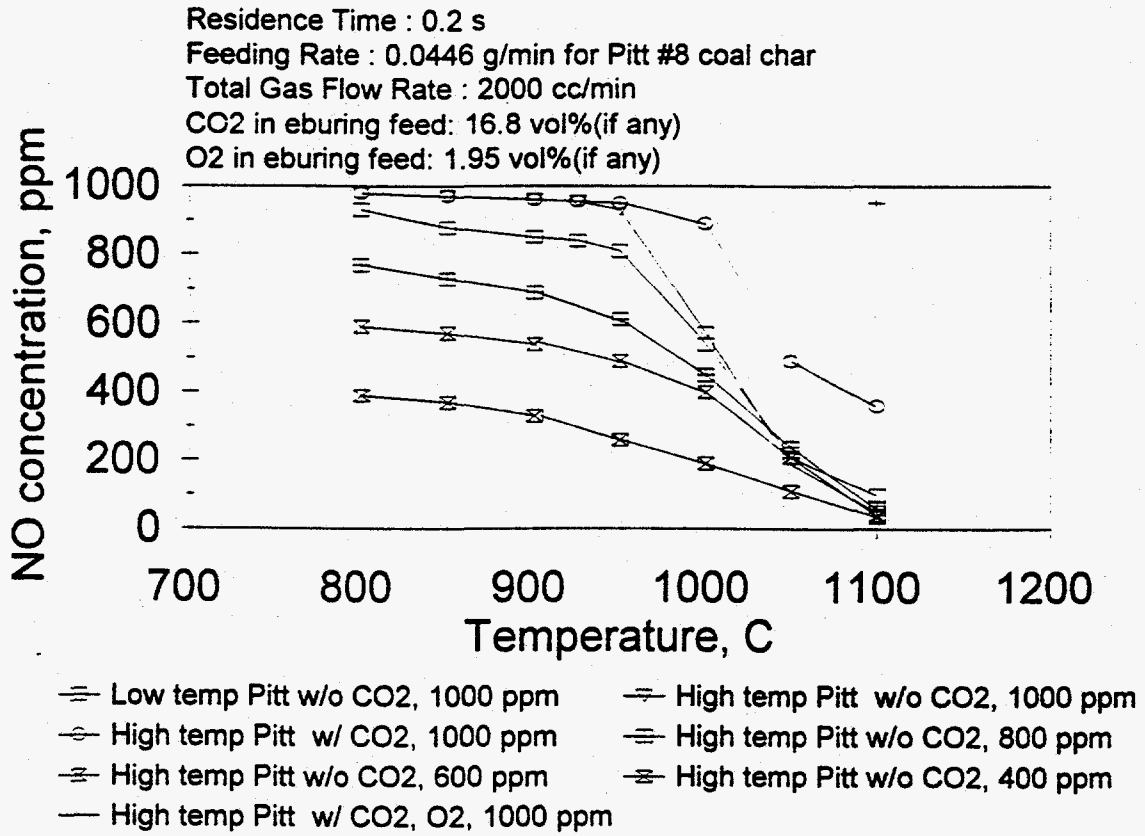


Figure 7. Exit NO concentrations from reburning with the bituminous coal chars as functions of temperature, char pyrolysis temperature, and feed compositions. The NO to char ratios correspond to those used in reburning at SR = 0.9 and 0.88 for the high and temperature chars, respectively.

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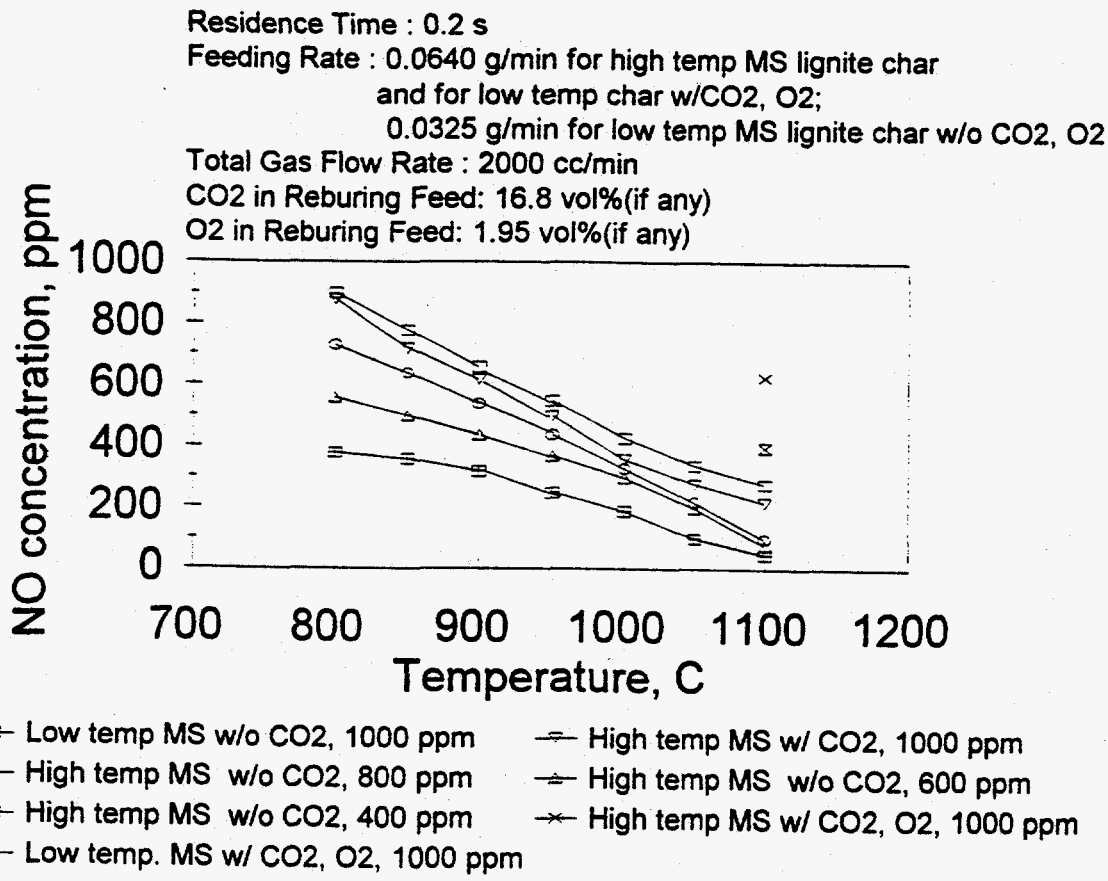


Figure 8. Exit NO concentrations from reburing with the Mississippi lignite chars as functions of temperature, char pyrolysis temperature, and feed compositions. The NO to char ratio for the runs with high char feeding rate corresponds to that used in reburing at SR = 0.97 and 0.93 for the high and low temperature chars.

Char Pyrolysis Temp : 1100 C, 5 mins holding time
 Reburing Residence Time : 0.2 s
 Feeding Rate : 0.0446 g/min for Pitt #8 coal char
 0.0640 g/min for high temp MS lingite char w/ CO2
 0.0325 g/min for low temp MS lignite char w/o CO2
 Total Gas Flow Rate : 2000 cc/min
 CO2 in Reburing Feed : 16.8 vol%(if any)
 O2 in Reburing Feed : 1.95 vol%(if any)

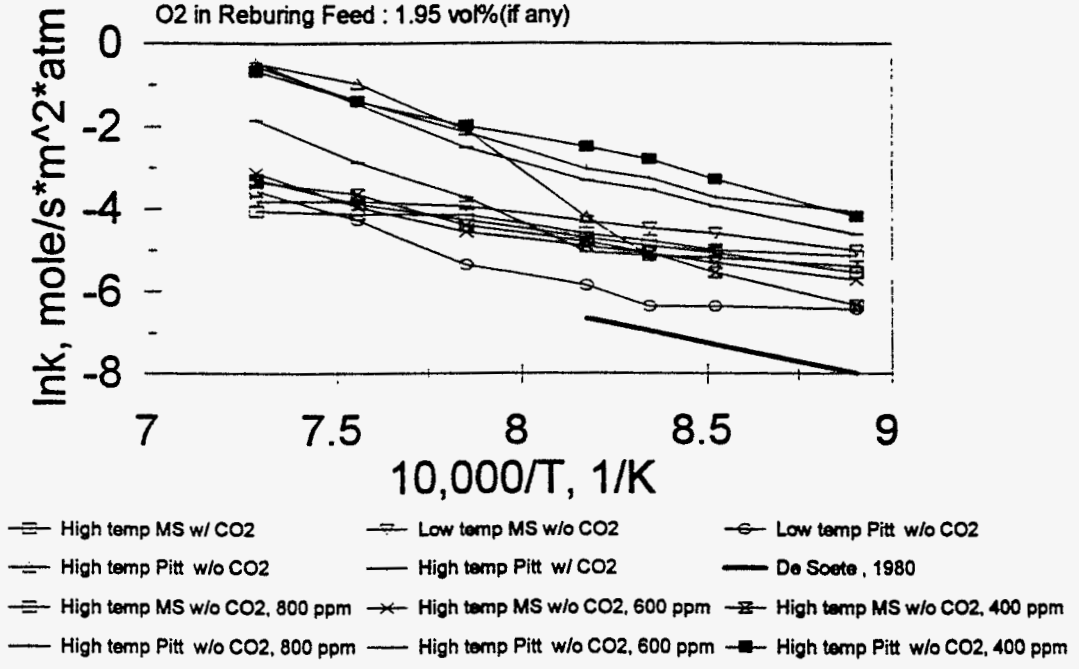


Figure 9. Arrhenius plots of NO reactions with chars of different origins and with different feed compositions. The solid line represents the rates reported by De Soete (1980) for a West Virginia bituminous coal.