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ROLE OF CHAR DURING REBURNING OF NITROGEN OXIDES

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DISCLAIMER

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ABSTRACT

The four major tasks conducted during this quarter include: (1) extensive investigation in pore structures of chars before and after reactions with NO, CO_2, and O_2, (2) effects of pyrolysis time on char reactivities, (3) estimations of rates of NO reduction and mass transfer limitations, and, (4) char reactivities at low feed NO concentrations.

Pore structure analyses include BET-N_2, BET-CO_2, and DR-CO_2 surface areas, pore size distribution, micropore volume, total pore volume, and average pore radius. These studies suggest that neither BET-N2 nor DR-CO_2 surface area is a normalization factor of chars of different origin. Reaction with NO leads to closures of pores, which may be contributed by formation of surface complexes.

Parameter study reveals that the effectiveness of heterogeneous reburning strongly depends on variables in three areas: (1) the origin of char, (2) char devolatilization temperature and time, and, (3) the competitions of NO with CO_2 and O_2 for the active sites on the char surface. Since the chars derived from less severe pyrolysis, 950°C and zero holding time, are significantly more reactive, future studies on NO/char interactions should focus on the "young" chars. Active sites accessible to CO_2 can be destroyed easier than those accessible to NO; however, within certain levels of severities, CO_2 forms stable surface complexes on bituminous coal char. Fundamental understanding of these mechanisms has practical importance to the production of activated carbon for flue gas cleanup.

The studies on pore structure and on parameter screening signify the importance of transient kinetics (TK) and temperature programmed desorption (TPD) in the future research. These two techniques will lead to the direct measurements of both stable and reactive surface oxygen complexes, *reactive* surface area, and the Langmuir-Hinshelwood model which has both importance to both fundamental understanding of reaction mechanisms and to industrial practice.

Estimation of rate of NO reduction has been established to include the conversions in the nonoisothermal and isothermal regions of the flow reactor, and internal mass transfer limitations. Solving a set of equations simultaneously with MathCad gives frequency factor, activation energy, Thiele modulus, and effectiveness factor. The calculated results imply that internal mass transfer limitaions exist only when the temperature is close to 1100°C. External mass transfer rate is of the same order of magnitute of reacion rate at 1100°C. Possible reasons of the higher intrinsic rates obtained from the present study are discussed. The present study also suggests that the gasification rate for char/NO reaction is about the same or even higher than the rate for char/O_2 reaction.

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 NH_3. 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 CH_2 to HCN and amine radicals (NH_i) (Miller and Bowman, 1989). The amine radicals, in turn, can be converted to N_2 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, CO_2 and N_2 (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 H_2, and inhibited by O_2 when the CO_2/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 Fe_2O_3 (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 CO_2 and N_2, Lin *et al.* indicated that CO decreases the NH_3 conversion to NO. Lin *et al.* also claimed that NO may oxidize NH_3 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 CO_2, O_2 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 CO_2 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 CO_2 and O_2, 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. For the chars derived from pyrolysis at 1100°C, conversion of oxygen of feed NO to the gasification products, CO and CO_2, is 100% when feed gas contains only two reactive species, NO and CO_2; additional gasification products form when the feed contains O_2;
8. For the chars derived from pyrolysis at 950°C, conversion of oxygen of feed NO to the gasification products, CO and CO_2, is 100% when feed gas contains only one reactive species, NO; additional gasification products form when the feed contains other oxidants, CO_2 or O_2;
9. The 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;
10. Activation energy of the NO reaction with bituminous coal char changes with temperature implying changes in mechanisms;

11. 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 the variables which are significant to heterogeneous reburning, particularly the effect of pyrolysis time. Product distributions of NO reaction with chars of two different origins have been examined by sequentially adding the three major oxidants in reburning: NO, O_2, and CO_2. Internal pore structures of chars before and after the reactions have been determined to assist the interpretations of experimental results. Rates of NO reduction have estimated; 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. Pore Structure Analyses and Their Implications

The BET-surface areas of eight samples were measured with nitrogen (N_2) as the adsorbate at a temperature of 77 K. Table 1 lists the origin and history of these samples. Measurements were carried out under six different relative pressures, P/P^0, with the multi-point method. The values of P/P^0, ranging from 0.05 to 0.30, comprised the linear region of the multi-point BET equation. The experimental results are summarized in Table 2. This table also lists previously obtained results with

CO_2 as the adsorbate at 273K.

Additional measurements were carried out with nitrogen (N_2) as the adsorbate at a temperature of 77 K to evaluate the micropore volume and total pore volume of the eight samples. Measurements for the micropore volume were carried out under five different levels of P/P^0. The values of P/P^0, ranging from 0.02 to 0.1, comprised the linear region of the Dubinin-Radushkevich (DR) equation. The total pore volume was measured directly when P/P^0 was close to 1. The average pore radius evaluated from the total pore volume and surface area has been computed as follows:

$$r = \frac{2V_T}{S}$$

where V_T is the total pore volume; and S, the surface area. The results are summarized in Table 3. The previously measured micropore volume with adsorbate CO_2 at 273K is also listed in the same table for comparison.

Pore-size distributions were determined from the desorption isotherm. Nitrogen (N_2) served as the adsorbate, and the desorption was conducted at 77K. The results are plotted in the attached figures.

The review by Mahajan and Walker (1978) summarized a number of interesting conclusions concerning the observed discrepancies of pore analyses when N_2 and CO_2 were used as adsorbates. Micropore volume and surface area with N_2 at 77K are always considerably lower than those with CO_2 at 273K. It has been suggested that at 77K the micropore system is not completely accessible to N_2 molecules due to an activated diffusion process and/or shrinkage of pores. Adsorption of N_2 is considered to measure the area of the macropores, mesopores, and the larger micropores in chars. CO_2 adsorption at 273K should always measure essentially the total surface area of chars. These observations will be used in the interpretation of our experimental data discussed below.

Data in Table 1 show that the raw lignite char after pyrolysis has a much higher surface area than bituminous coal char, either by BET/N_2 or by DR/CO_2 method. Since NO reduction by lignite char in the absence of CO_2 and O_2 is less severe than that by bituminous coal char (see data in Figure 1, to be discussed in the subsequent section), this observation confirms our earlier claim (Chen and Ma, 1995) that surface area is not a normalization factor of char reactivity. Indeed, as we will discuss later in this report, the effectiveness of heterogeneous reburning depends on: (1) the origin of char, (2) char devolatilization temperature and time, and (3) the competitions of NO with CO_2 and O_2 for the active sites on the char surface.

When either N_2 or CO_2 is used as adsorbate, micropores (<10Å) volumes of both chars decrease after their reactions with NO, see Table 3. The decrease in micropore volume becomes a prominent feature of lignite char during its reaction with NO, CO_2 and O_2, see samples 4-1L and 4-4L in Table 3. On the contrary, the micropore volume of the bituminous coal char increases during its reaction with NO, CO_2 and O_2, see samples 4-1P and 4-4P in Table 3. Pore volume distributions of these chars are presented in Figures 1 through 8, which clearly suggest that closures of micropores of both chars during their reactions with NO. Both chars have major a peak at about 20Å and a second peak below 15Å in the measured range of pore size distributions, 15 to 70Å. The pore structure of the bituminous coal char, however, is relatively insensitive to the reaction with NO.

The decreases in micropore volumes are likely contributed by formation of surface oxygen complexes at the mouths of micropores. This observation is comparable to a char gasification study by Lizzio *et al.* (1990), in which techniques for the determination of both stable and reactive surface oxygen complexes were developed. Reactive surface complexes was determined by transient kinetics, i.e., by measuring the decay of CO yield after the oxidant in the feed (CO_2) is switched to N_2. The decay had a time scale of the order of minutes. The stable oxygen complex was determined by temperature-programmed desorption (TPD) of quenched char after the reactive complex were removed. It was shown that the lignite char has higher stable and reactive oxygen complexes than those of bituminous coal char. In our study, char sample undergoes rapid quenching at the exit of the flow reactor, and both stable and reactive surface oxygen complexes are expected to remain on the char. Therefore, due to the formation of both reactive and stable surface complexes and closures of pores, neither the surface area before the reaction nor the surface area after the reaction can be a good normalization factor for the reactivity of a specific char. For the calculations to be discussed in the subsequent sections, we will report rate constants based on the surface areas of chars before their reaction with NO.

Transient kinetics and TPD experiments should be a potentially important approach for the correction of the aforementioned problem. Surface areas of chars after these experiments should give discerning quantities of reactive surface areas and the surface areas occupied by complexes. Furthermore, these experiments should assist the construction of a Langmuir-Hinshelwood model which is, in turn, a critical missing element in the evaluation of boiler performance when heterogeneous reburning is to be incorporated.

B. Effects of Pyrolysis Time on Char Reactivity

During the last quarter (Chen *et al.*, 1996), we studied the reactivities of chars derived from two conditions: 950°C and zero holding time, and 1100°C and 5 min holding time. The Arrhenius rates of NO/char reaction obtained were consistently higher than the data reported in the literature. After extensive review of the experimental procedures adopted by various groups, we noted that most literature values have been reported by using char produced with 1 to 3 h holding time. Although devolatilization of coal completes within a fraction of second (see, e.g., Howard, 1981), our chars were significantly "younger" than chars produced by others. Since devolatilization severity has been demonstrated to be detrimental to char gasification in carbon dioxide (see, e.g., Radovic *et al.*, 1983a), the finding about the difference in holding time prompted our decision to measure the rate of "older" chars: 1100°C and 2 h holding time. Chars derived from the Mississippi lignite and the Pittsburgh #8 bituminous coal have been tested in three different gaseous environments: NO+char, NO+char+CO_2, and NO+char+CO_2+O_2. Detailed experimental procedures have been discussed in the last quarterly report (Chen *et al.*, 1996).

The results from the experiments with the older chars are compared with data reported earlier, Figures 9 through 11. The exit NO concentrations presented in Figure 9 suggest that the holding time is indeed a very significant variable in the determination of char activity. Long pyrolysis time severely destroies the char reactivities, particularly the reactivities of bituminous coal char. Since most published rate data of NO/char reaction were collected from experiments where chars were prepared with 1 to 3 h pyrolysis time, their rates are expected to be higher than ours. Furthermore, since devolatilization completes within a fraction of a second, our study implies that future studies on NO/char interactions should focus on "young" chars.

The observed dependence of char reactivity on pyrolysis severity is certainly related to the physical and chemical structure of the chars. We are currently investigating the pore structure of chars produced with long pyrolysis time. As we discussed in the last quarter (Chen *et al.*, 1996), the loss of reactivity of high severity 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 H_2 (<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, CO_2 and O_2, and direct reduction of NO. The ultimate analyses shown in the last quarter, 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 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 does have higher CO_2 surface area, but lower N_2 surface area, than those of the high temperature lignite char (Chen *et al.*, 1996).

The yields of gasification products, CO and CO_2, presented in Figure 10 suggest a number of interesting phenomena. First, pyrolysis severity, in terms of time and temperature, reduces the rates of gasification of both chars with, NO, CO_2 and O_2. Second, only the chars derived from the least severe conditions (series C and F), i.e., 950°C and zero holding time, is reactive with CO_2. The chars derived at the next level of severity (series B and E), i.e., 1100°C and 5 min holding time, however, produce very low levels of gasification products when CO_2 is present in the reactive gas stream. Figure 11 presents the total oxygen in the gasification products normalized to the converted NO, which indicates the competitions of various oxidants and the levels of active sites accessible to NO, CO_2 and O_2. Third, exit NO data in Figure 9 suggests that increasing pyrolysis time from 5 min to 2 h seriously destroies the reactivities of both chars with NO. Fourth, both CO_2 and O_2 are detrimental to NO reduction, for chars produced under all severities. Fifth, the effects of CO_2 on NO reduction is less serious for younger lignite char. These observations seem to imply that there are two, not quite mutually exclusive, kinds of active sites: one is more accessible to NO and the other is more accessible to CO_2. Active sites accessible to CO_2 can be destroyed easier than those accessible to NO; however, at the first two levels of severities, CO_2 forms stable surface complexes on bituminous coal char. Fundamental understanding of these mechanisms has practical importance to the production of activated carbon for flue gas cleanup.

The studies on pore structure and on parameter screening signify the importance of transient kinetics (TK) and temperature programmed desorption (TPD) (Lizzio *et al.*, 1990) in the future research. These two techniques will lead to the direct measurements of both stable and reactive surface oxygen complexes, *reactive* surface area, and the Langmuir-Hinshelwood model which has both importance to both fundamental understanding of reaction mechanisms and to industrial practice.

Our investigation discussed above reveals that the effectiveness of heterogeneous reburning depends on variables in three areas: (1) the origin of char, (2) char devolatilization temperature and time, and, (3) the competitions of NO with CO_2 and O_2 for the active sites on the char surface.

C. Rates of NO Reactions with Chars

1. Experiments

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 pint 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.

Two series of experiments with two different chars have been conducted with feed NO at 200 ppm and in the temperature range 800 and 1100°C. To be consistent with the experiments conducted in the last few quarters, the two chars were produced from the Pittsburgh #8 bituminous coal and Mississippi lignite at 1100°C and 5 min holding time. No oxidants are included in the feed during their reactions with NO. 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 12 and 13 present the exit NO concentrations observed in these two 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, 800, 600, and 400 ppm, and those with feed containing oxidants.

2. Rate Constants and Internal Mass Transfer Limitations

The calculation conducted in this quarter included estimation of mass transfer limitations. 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.

$$\ln(1 - X) - 733.6 \left(\int \frac{0.765}{T} W_1 A k_0 e^{-\frac{E_a}{RT}} dT - t_h W_1 A k_0 e^{-\frac{E_a}{RT}} - \int - \frac{0.765}{T} W_1 A k_0 e^{-\frac{E_a}{RT}} dT \right) \tag{1}$$

where X is the NO conversion,
W_1 is the char feeding rate, in g s^{-1},
A is the specific, internal surface area of char, in m^2 g^{-1},
k_0 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.,

$$\ln(1 - X) = 733.6\ \Big(\int \frac{0.765}{T} W_1 A \eta k_0 e^{-\frac{E_a}{RT}} dT - t_h W_1 A \eta k_0 e^{-\frac{E_a}{RT}} - \int - \frac{0.765}{T} W_1 A \eta k_0 e^{-\frac{E_a}{RT}} dT \Big) \qquad (2)$$

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

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

where the Thiele modulus is defined as

$$\phi = R\left[\frac{a\ k\ A\ \rho_P}{D_{eff}}\right]^{0.5} \qquad (4)$$

where R is the radius of char particles, in cm,
k is the rate constant, in mole s^{-1} m^{-2} atm^{-1},
a is the ideal gas conversion constant, 2.445×10^4 cm^3 $mole^{-1}$,
D_{eff} is the effective diffusion coefficient, in cm^2 s^{-1}, and,
ρ_p is the bulk density of char, in g cm^{-3}.

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),

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

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

$$D_{12,\,eff} = \frac{0.001858\,T^{1.5}\left[\dfrac{M_1 + M_2}{M_1 M_2}\right]^{0.5}}{P\,\sigma_{12}^{\,2}\,\Omega_D} \tag{7}$$

where $D_{k,\,eff}$ is the Knudsen diffusion coefficient for a porous solid, in $cm^2\ s^{-1}$,
$D_{12,\,eff}$ is the bulk diffusion coefficient of species 1 in species 2, in $cm^2\ s^{-1}$,
θ is the particle void fraction,
τ_m is the tortuosity factor based on the mean pore radius, assumed 2,
M, M_1 are the molecular weights of diffusing molecules, $M_{NO} = 30$, $M_{HE} = 4$,
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 $g\ cm^2\ s^{-2}$, σ in Å, and,
k_B is the Boltzmann constant, $1.38 \times 10^{-16}\ g\ cm^2\ s^{-2}\ K^{-1}$.

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 2, and obtained the average pore volumes for the MS lignite char and the Pitt#8 coal char, $0.07\ cm^3/g$ and $0.0065\ cm^3/g$, respectively. By water displacement method, the bulk densities of the lignite char and bituminous coal char have been measured, 1.2 and $1.4\ g/cm^3$, respectively. Based on these values, we obtain the pore fraction

θ = pore volume × density
= 0.084 for the MS lignite char and 0.0091 for the Pitt#8 char.

From Bird *et al.* (1960),

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

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

$D_{k,\,eff} = 3.98 \times 10^{-5}\ cm^2\ s^{-1}$ for lignite char at 1100°C,
$D_{12,\,eff} = 8.127\ cm^2\ s^{-1}$,

$D_{eff} = 3.98 \times 10^{-5}$ cm^2 s^{-1} for lignite char at 1100°C.

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, k_0, and E_a. Since there are four unknowns, Eq. 2 is used twice for two experimental data in each calculation. For reactions with varying activation energy in the temperature range 800 to 1100°C, such as the rate of bituminous coal char with NO, calculations have been conducted stepwise from lower temperatures to the higher temperatures, and the new sets of η, ϕ, k_0, and E_a are recovered stepwisely. As discussed in the last section, formation of both stable and reactive surface complexes cause closures of pores during the reaction, and neither the BET N_2 nor the DR CO_2 surface area provides a good measure of the actual reactive surface area. In the present calculations, surface ares of raw chars have been used in the estimation of rate constants. The results of these calculations are shown in Tables 4 and 5.

As shown in Tables 4 and 5, internal mass transfer limitations are not serious for most cases except for experiments at high temperatures. The intrinsic rates are illustrated in Figures 13 through 16. For comparison, a number of published rates are also included in these figures. Our data are higher than most of the published results; there are a number of possible reasons. First, our chars are "younger" than all published data presented in these figures where chars were prepared with 1 to 3 h pyrolysis time. In section II.A, we have shown the remarkable difference in their reactivities between the young and the old chars. Second, possible mass transfer limitations have not been discussed in a number of studies. For example, rate measurement by TGA usually uses a sizeable amount of sample where internal mass transfer limitations may exist (Aarna and Suuberg, 1996). Third, gas/solid mixing and temperature history of the various experimental setups can also play an important role in rate estimations. Specifically, our reactor tube has an 1.91 cm i.d., and particles have been injected into the reactor from an 1/4" o.d. tube. This design should provide better mixing than injecting particles from an 1/16" o.d. tube to a 2" i.d. reactor (Song, 1978). Fourth, our reactor measures the rate of NO/char reaction in the first 0.2 s, while a fixed bed reactor measures rates after the stable surface oxygen complexes are formed.

3. External Mass Transfer Limitations

The high activation energies shown in Table 4 and 5 suggest that external mass transfer should not a limitaing factor in the detrmination of rate constant. The following calculation provides justifications to the estimation.

Under steady state conditions, the mass transfer rate of NO through the gaseous boundary layer equals to the surafce reaction rate, i.e.,

$$k_c\, S\, (C_g - C_s) = (-r)\, W_p \qquad (8)$$

where
C_g = NO concentration in the mainstream of gas flow, moles cm^{-3}
C_s = NO concentration at the particles surface, moles cm^{-3}
k_c = mass transfer coefficient, cm s^{-1}
S = external surface area of a single particle, cm^2
- r = reaction rate, moles g^{-1} s^{-1}, and,
W_p = weight of a single particle, g

The NO reduction on the char surface has been expressed in the following form

$$-r = \eta\, k\, A\, P_{NO} \qquad (9)$$

The concentration gradient,

$$F = (C_g - C_s) / C_s \qquad (10)$$

is an index of mass tranfer limitations; that is, large concentration difference indicates large mass transfer resistance. Assume the gas follows idea gas law, i.e.,

$$P_{NO} = C_s\, R\, T \qquad (11)$$

then

$$W_p - \rho_p \frac{1}{6} \Pi d_p^3 \qquad (12)$$

Substituting Eqs. 8, 9, 11 and 12 into 10, we obtain

$$F - \frac{C_g - C_s}{C_s} - \frac{\eta k A R T \rho_p \Pi d_p^3}{6 k_c S} \qquad (13)$$

The mass transfer coefficient has been estimated based on the Frossling correlation with Sherwood number (Sh) = 2, i.e.,

$$k_c = D_{AB}\, Sh / d_p = 2\, D_{AB} / d_p \qquad (14)$$

The diffusivity, D_{AB}, at 1100°C has been estimated by the Chapman-Enskog equation, i.e., Eq. 7 on p.15 of this report,

$$D_{AB} = 13.7\ cm^2\ s^{-1}$$

We have been using particles with mean diameter 0.0128 cm, therefore, from Eq. 14,

$$k_c = 2.14 \times 10^3\ cm\ s^{-1} \qquad (15)$$

Substituting the highest rate constant shown in Table 4 and 5, i.e., the rate of the bituminous coal char derived from pyrolysis at 1100°C and 5 min holding time followed by reaction with NO at 1100°C,

$$F = 1.62$$

This value suggests that external mass transfer rate is of the same order of magnitude of the reaction rate at the highest reaction temperature of this investigation. Rates higher than what we have obtained may be distorted by mass transfer limitations.

4. Competition of NO/Char and O_2/Char Reactions

One frequently discussed question in the combustion literature is that if the rate of oxidation of char by oxygen higher than that by NO. The rate of char oxidation reported by Smith (1982) has been well-referenced.

$$k_{oxygen} = 305 \exp(-42{,}850 \text{ cal}/RT) \quad \text{in } g_c\ cm^{-2}\ s^{-1}\ atm^{-1}$$

At 1100°C, this equation gives

$$k_{oxygen,\ 1100C} = 4.6 \times 10^{-5}\ g_c\ cm^{-2}\ s^{-1}\ atm^{-1}$$

After converting the unit of the rates in Tables 4 and 5 to that used by Smith, our measured rates for char/NO reaction based on CO_2 surface area give

$$k_{NO,\ 1100C} = 3.5 \times 10^{-5}\ g_c\ cm^{-2}\ s^{-1}\ atm^{-1} \text{ for the lignite char}$$

$$k_{NO,\ 1100C} = 6.68 \times 10^{-4}\ g_c\ cm^{-2}\ s^{-1}\ atm^{-1} \text{ for the bituminous coal char}$$

These results suggest that the gasification rate for char/NO reaction is about the same or even higher than the rate for char/O_2 reaction. This is a conclusion consistent with that Chu and Schmidt (1993) if we extrapolate their rates 700 to 1100°C. However, Song (1978) reported that the rate for char/O_2 reaction is about two orders of magnitude higher than the rate for char/NO reaction.

IV. WORK FORECAST

In the succeeding quarter, we will continue the investigation of (1) rates of NO reduction in various gaseous environments, (2) the role of surface oxygen complexes by TK and TPD techniques, and (3) the changes in pore structure during reaction.

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Table 1. Char preparation conditions

4-1L	lignite char pyrolyzed at 1100°C and 5 min holding time
4-2L	lignite char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 1100°C
4-3L	lignite char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 800°C
4-4L	lignite char pyrolyzed at 1100°C and 5 min holding time followed by reaction with $(NO+CO_2+O_2)$ at 1100°C
4-1P	bituminous coal char pyrolyzed at 1100°C and 5 min holding time
4-2P	bituminous coal char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 1100°C
4-3P	bituminous coal char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 800°C
4-4P	bituminous coal char pyrolyzed at 1100°C and 5 min holding time followed by reaction with $(NO+CO_2+O_2)$ at 1100°C

Table 2. Comparison of surface areas measured by various methods

Sample	N_2-BET[a] 77 K (m^2/g)	CO_2-BET[b] 273 K (m^2/g)	CO_2-DR[c] 273 K (m^2/g)
4-1L	86.86	136	255
4-2L	12.18	125	235
4-3L	9.37	124.5	245.5
4-4L	16.48	26.4	49.9
4-1P	4.18	31.2	36.2
4-2P	4.65	N/A	24.6
4-3P	4.15	24.2	22.1
4-4P	69.19	137	270.7

[a] measured volumetrically and evaluated with multi-point BET equation.
[b] measured volumetrically and evaluated with multi-point BET equation.
[c] measured volumetrically and evaluated with DR equation for micro-pore surface area.

Table 3. Micropore volume, total pore volume, and average pore radius with adsorbate N_2 at 77 K

sample	micro[a] pore volume (cc/g)	total[b] pore volume (cc/g)	volume ratio of micro pore to total pore (%)	average[c] pore radius (A)	micro[d] pore volume (cc/g)
4-1L	0.0418	0.0715	58.46	16.46	0.093
4-2L	0.0049	0.0286	17.13	46.96	0.086
4-3L	0.0036	0.0180	20.00	38.42	0.089
4-4L	0.0065	0.0332	19.58	40.29	0.018
4-1P	0.0012	0.0065	18.46	31.10	0.013
4-2P	0.0011	0.0061	18.03	26.24	0.009
4-3P	0.0010	0.0062	16.13	29.88	0.008
4-4P	0.0335	0.0483	69.36	13.96	0.098

[a] measured volumetrically and evaluated with DR equation.
[b] volume measured directly when P/P^0 is close to 1.
[c] evaluated from total pore volume and surface area, $r=2V_T/S$.
[d] with adsorbate CO_2 at 273 K.

Table 4. Summary of Arrhenius' constants and mass transfer limitations of NO reaction with two different chars at various temperatures based on CO_2 surface areas. (reaction time about 0.2s)

Reactants	Temp. Range, °C	k_0, mole/(s m^2 atm)	E_a, Kcal/mole	ϕ	η
MS Lignite Char (1100C,5min)+NO $[NO]_{in}$ = 1000 ppm w/ CO_2	800-850	13.752	15.9	1.458	0.882
	850-900			1.781	0.837
	900-925			1.922	0.817
	925-950			1.965	0.811
	950-1000			2.480	0.739
	1000-1050			2.622	0.720
	1050-1100			2.547	0.730
MS Lignite Char (1100C,5min)+NO $[NO]_{in}$ = 800 ppm w/o CO_2	800-850	1.52×10^3	28.8	0.891	0.958
	850-900			1.191	0.916
	900-925			1.353	0.896
	925-950			1.406	0.889
	950-1000			1.739	0.843
	1000-1050			2.155	0.784
	1050-1100			3.121	0.657
Pitt #8 Coal Char (1100C,5min)+NO $[NO]_{in}$ = 1000 ppm w/ CO_2	800-925	1.53×10^{-1}	7.68	0.159	0.998
	925-1000	5.45×10^6	49.25	0.284	0.995
	1000-1100	8.33×10^{12}	84.43	0.929	0.947
Pitt #8 Coal Char (1100C,5min)+NO $[NO]_{in}$ = 800 ppm w/o CO_2	800-925	1.87×10^3	25.76	0.416	0.989
	925-1000	3.1×10^6	43.38	0.687	0.970
	1000-1100	2.88×10^9	60.61	1.613	0.861

* The feeding rate of Mississippi lignite char w/o CO_2 at $[NO]_{in}$ = 1000 ppm is 0.064 g/min.
† The feeding rate of Pitt #8 bituminous coal char at $[NO]_{in}$ = 1000 ppm is 0.0446 g/min.

Table 5. Summary of Arrhenius' constants and mass transfer limitations of NO reaction with two different chars at various temperatures based on N_2 surface areas. (reaction time about 0.2s)

Reactants	Temp Range, °C	k_0, mole/(s m^2 atm)	E_a, Kcal/mol	ϕ	η
MS Lignite Char (1100C,5min)+NO w/ CO_2 $[NO]_{in}$ = 1000 ppm	800-850 850-900 900-925 925-950 950-1000 1000-1050 1050-1100	17.1	14.20	0.674 0.709 0.776 0.829 1.036 1.010 1.036	0.958 0.941 0.934 0.931 0.902 0.893 0.898
MS Lignite Char (1100C,5min)+NO w/ CO_2 $[NO]_{in}$ = 800 ppm	800-850 850-900 900-925 925-950 950-1000 1000-1050 1050-1100	1.355×10^3	26.16	0.556 0.686 0.732 0.787 0.965 1.164 1.589	0.980 0.970 0.966 0.961 0.943 0.920 0.864
Pitt #8 Coal Char (1100C,5min)+NO $[NO]_{in}$ = 1000 ppm w/ CO_2	800-925 925-1000 1000-1100	1.18 2.46×10^7 1.64×10^{13}	7.08 47.60 80.95	0.053 0.105 0.545	1 0.999 0.981
Pitt #8 Coal Char (1100C,5min)+NO $[NO]_{in}$ = 800 ppm w/o CO_2	800-925 925-1000 1000-1100	1.31×10^4 1.66×10^7 4.82×10^9	25.578 42.548 56.831	0.150 0.245 0.545	0.999 0.996 0.981

* The feeding rate of Mississippi lignite char w/o CO_2 at $[NO]_{in}$ = 1000 ppm 0.064 g/min.

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

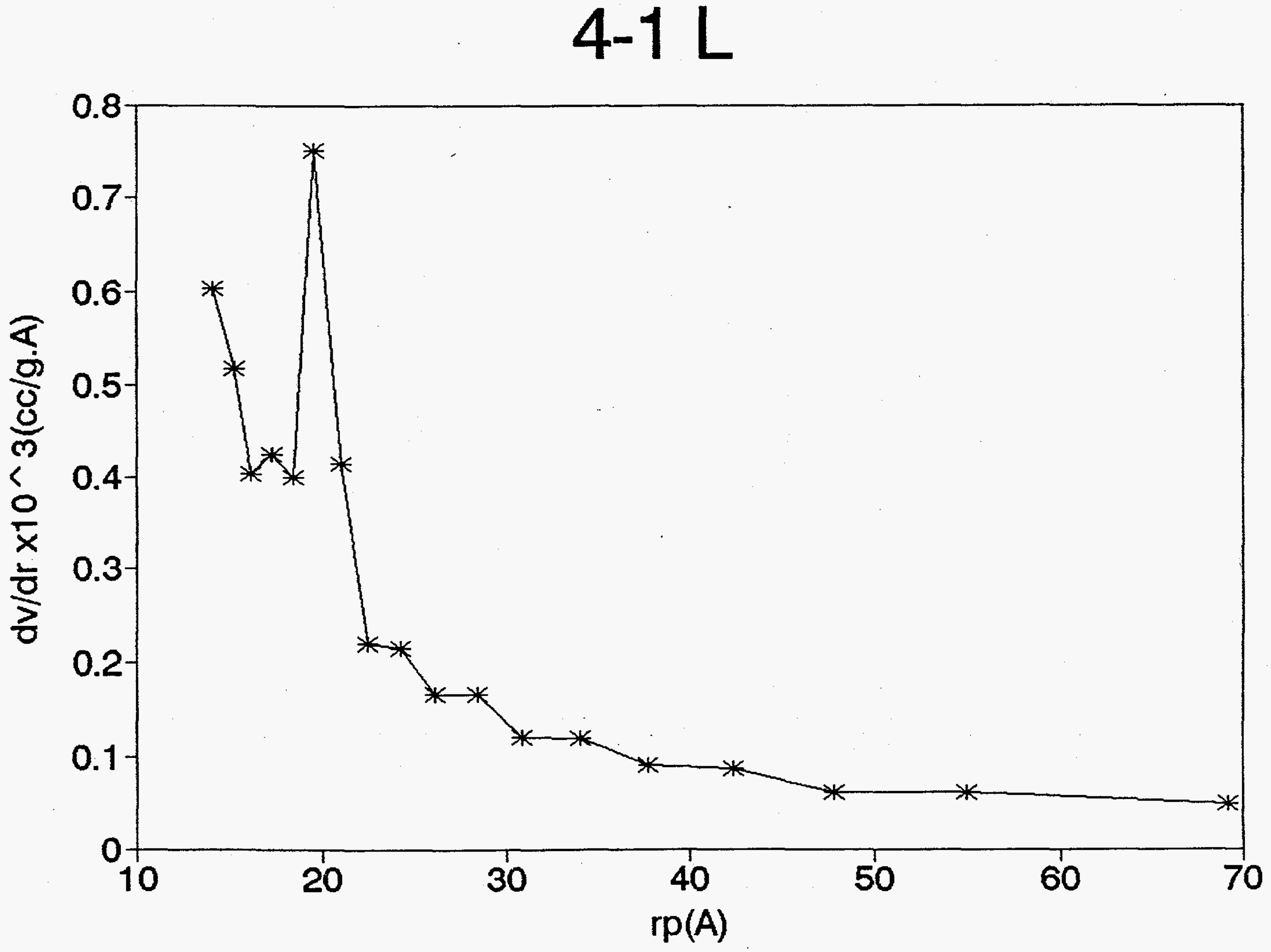


Figure 1. Pore size distribution of lignite char pyrolyzed at 1100°C and 5 min holding time.

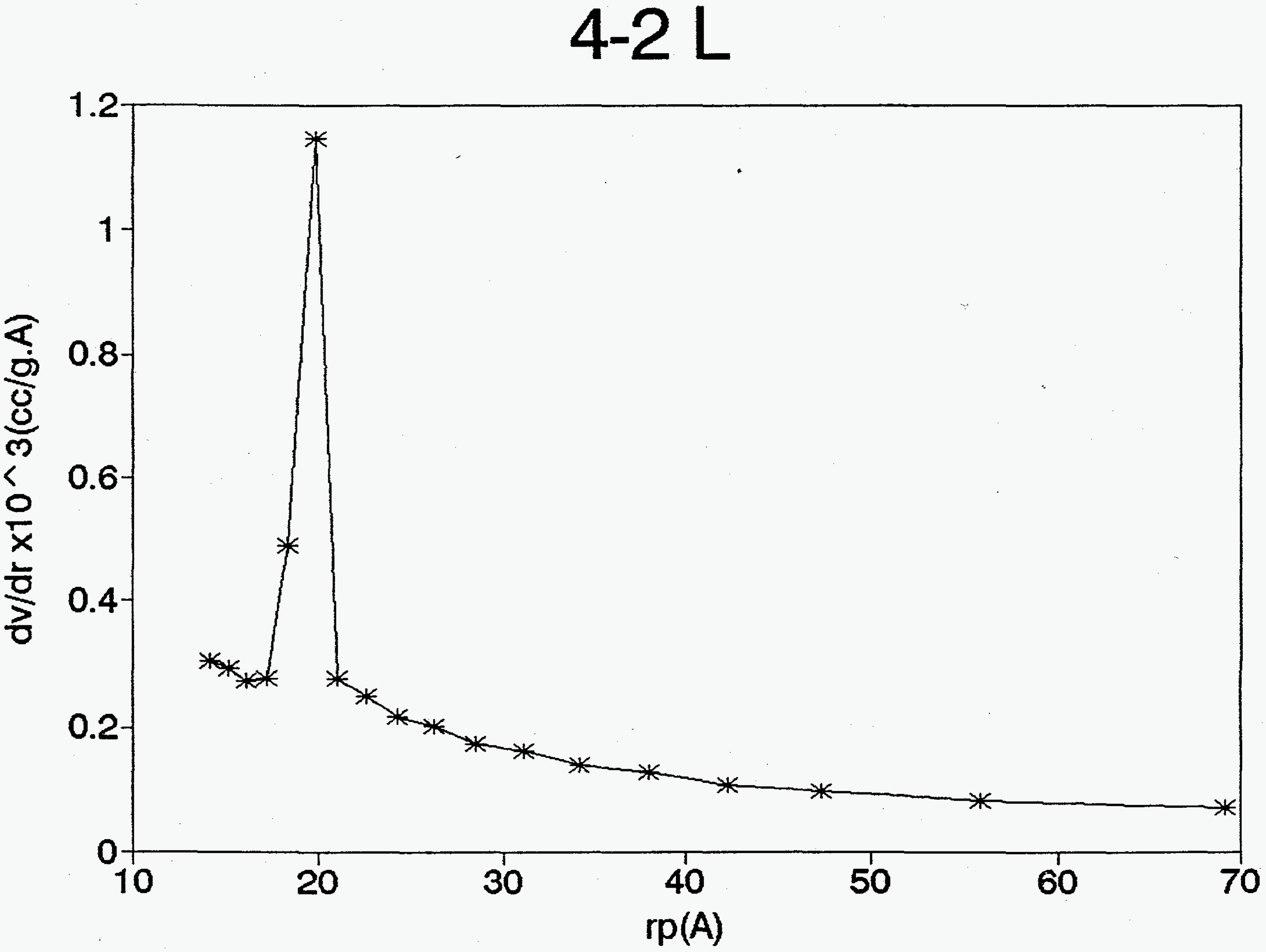


Figure 2. Pore size distribution of lignite char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 1100°C.

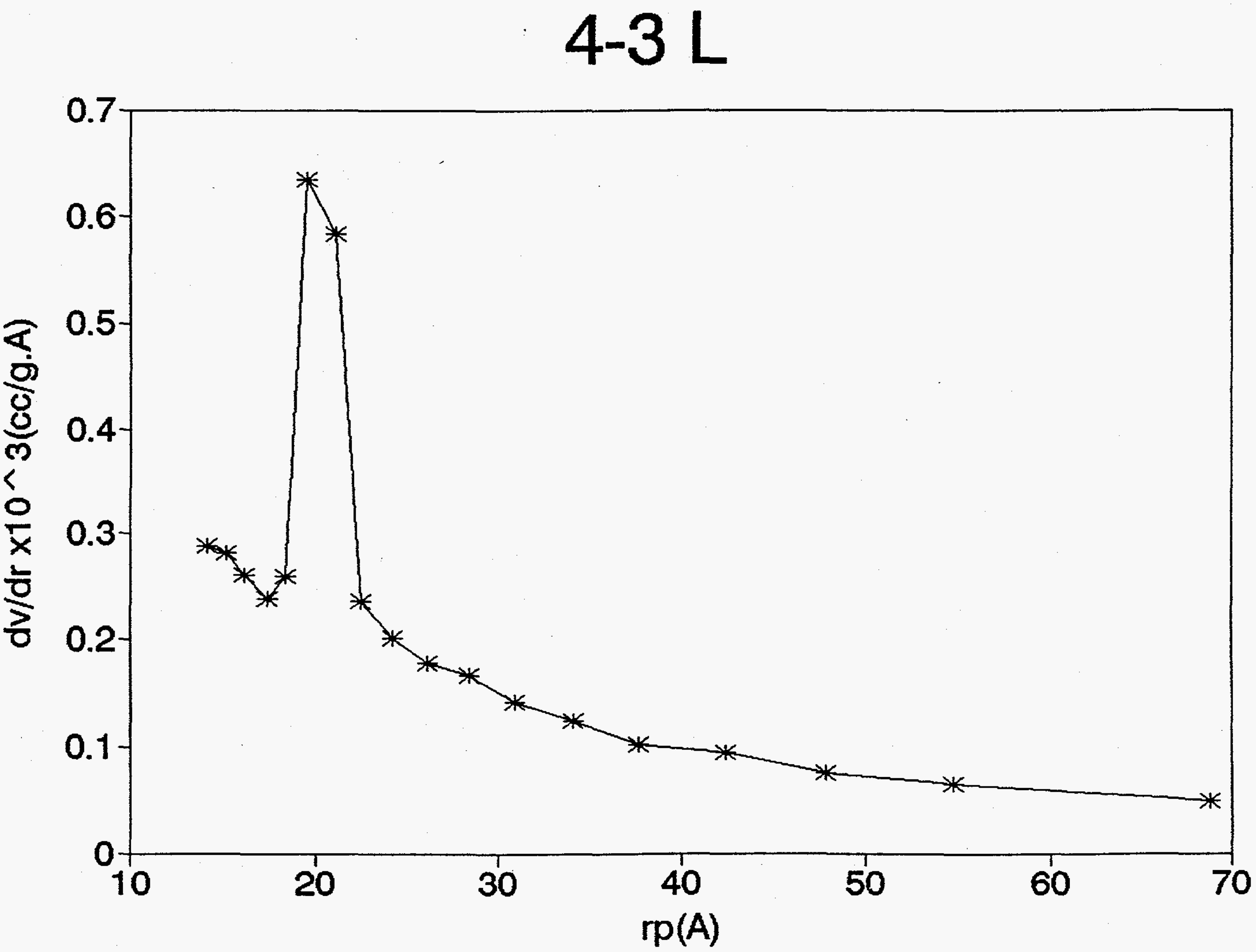


Figure 3. Pore size distribution of lignite char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 800°C

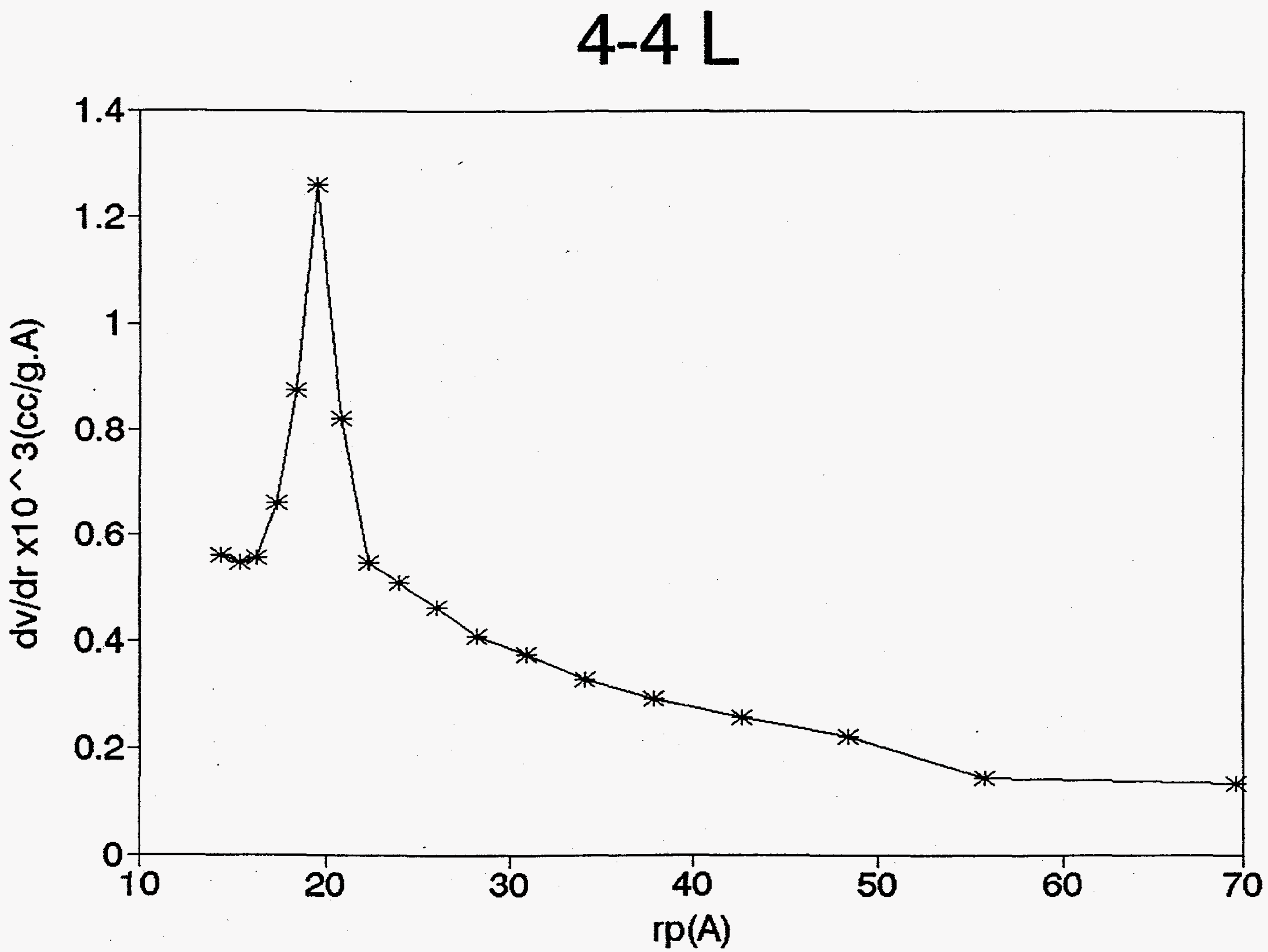


Figure 4. Pore size distribution of lignite char pyrolyzed at 1100°C and 5 min holding time followed by reaction with (NO+CO_2+O_2) at 1100°C.

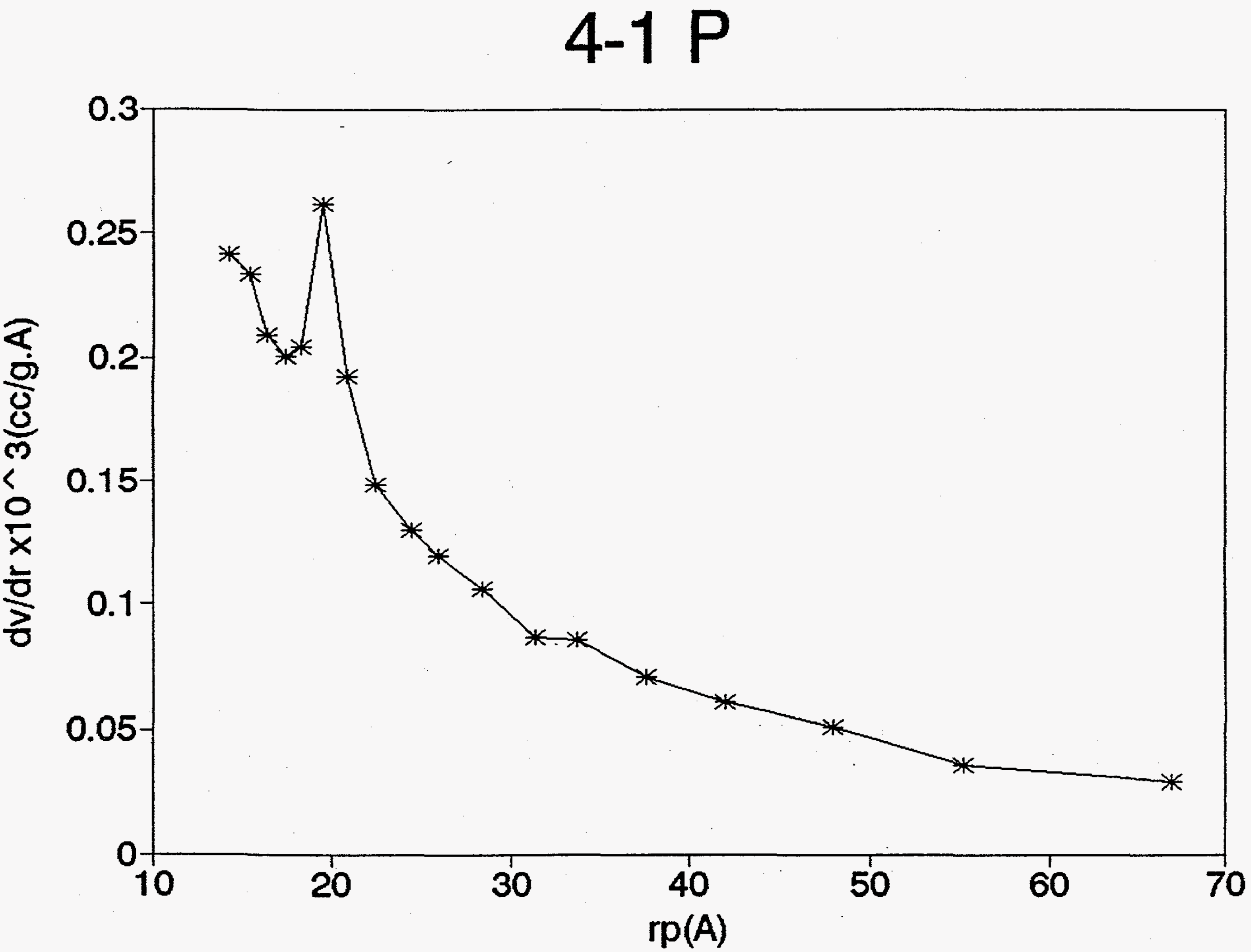


Figure 5. Pore size distribution of bituminous coal char pyrolyzed at 1100°C and 5 min holding time.

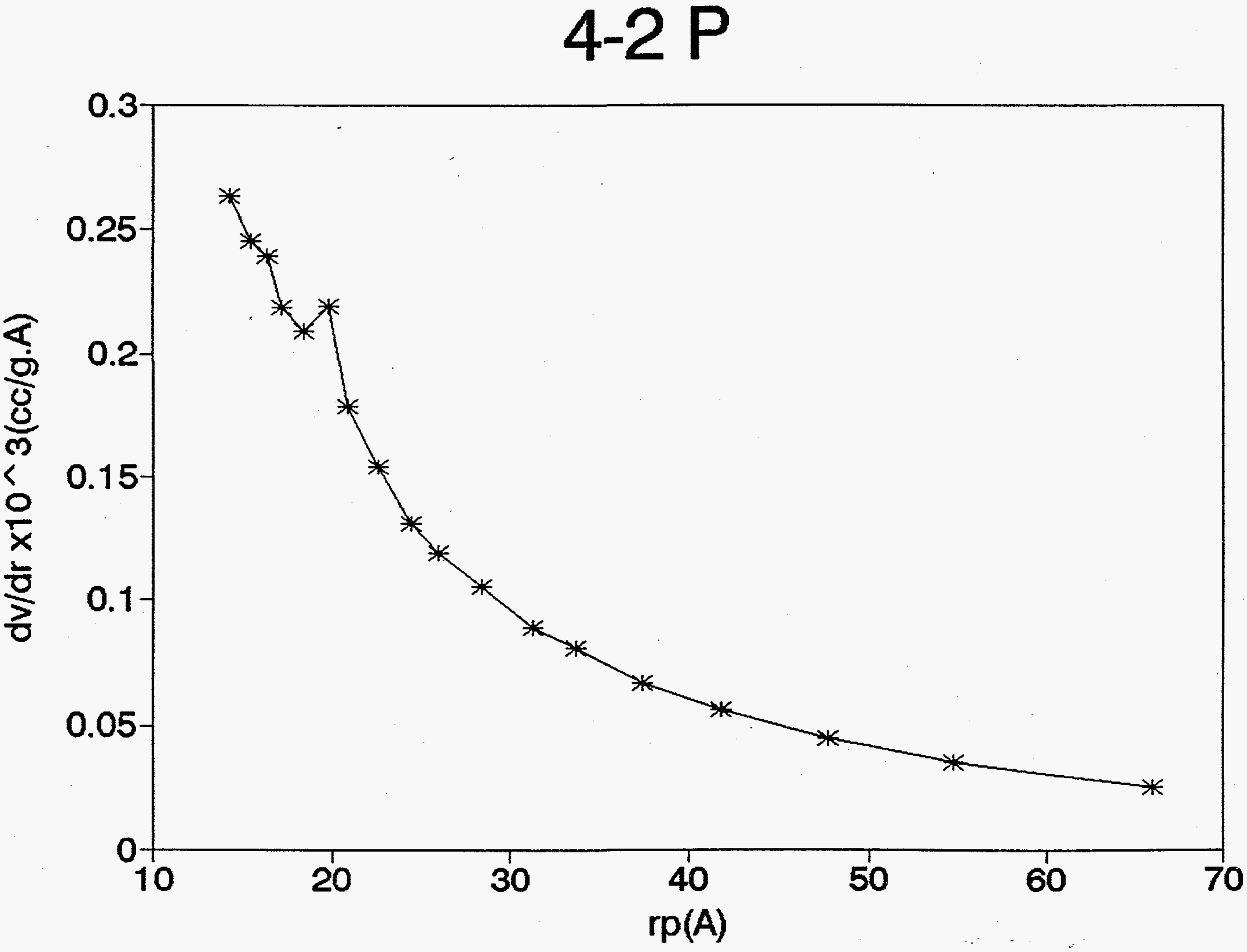


Figure 6. Pore size distribution of bituminous coal char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 1100°C.

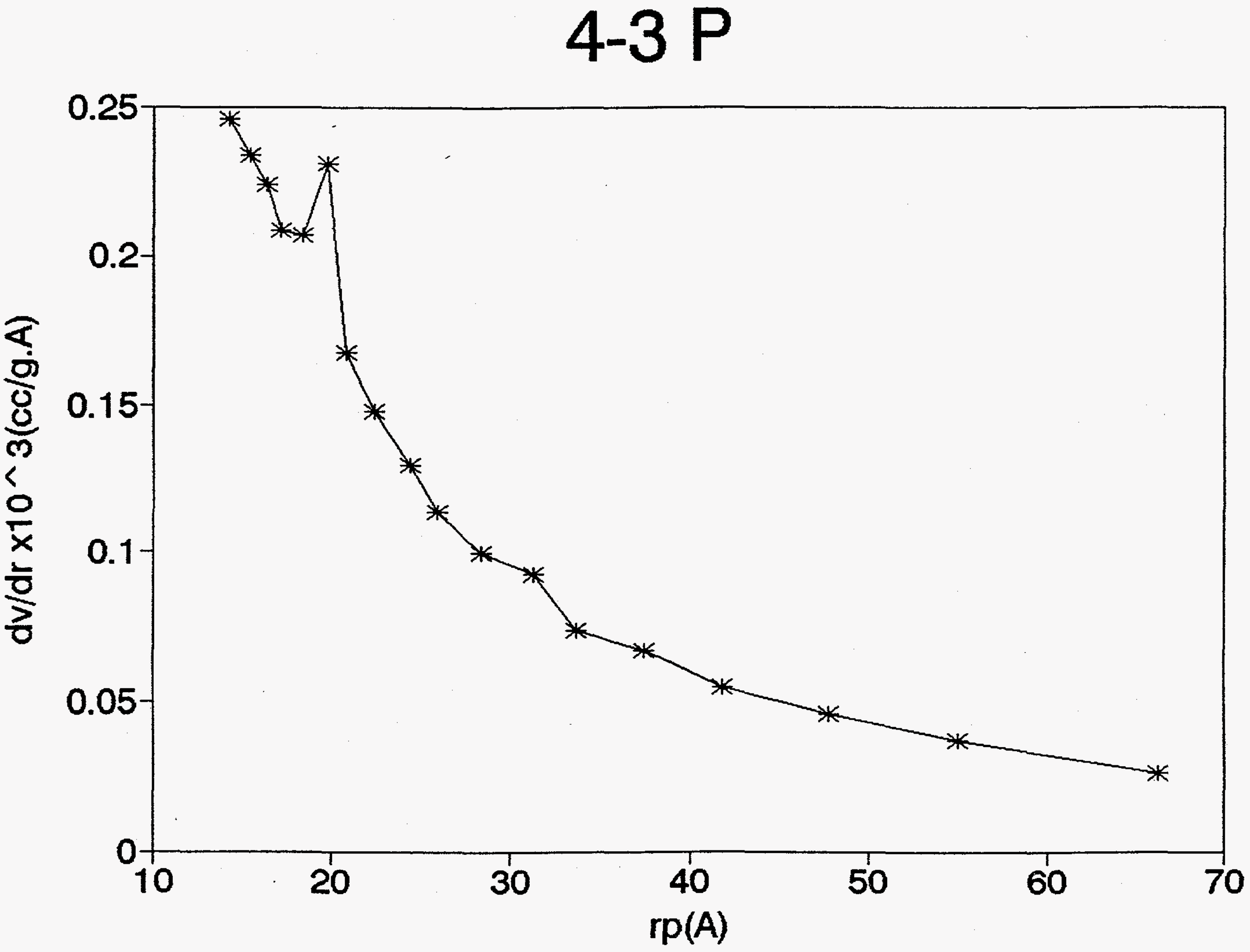


Figure 7. Pore size distribution of bituminous coal char pyrolyzed at 1100°C and 5 min holding time followed by reaction with NO at 800°C

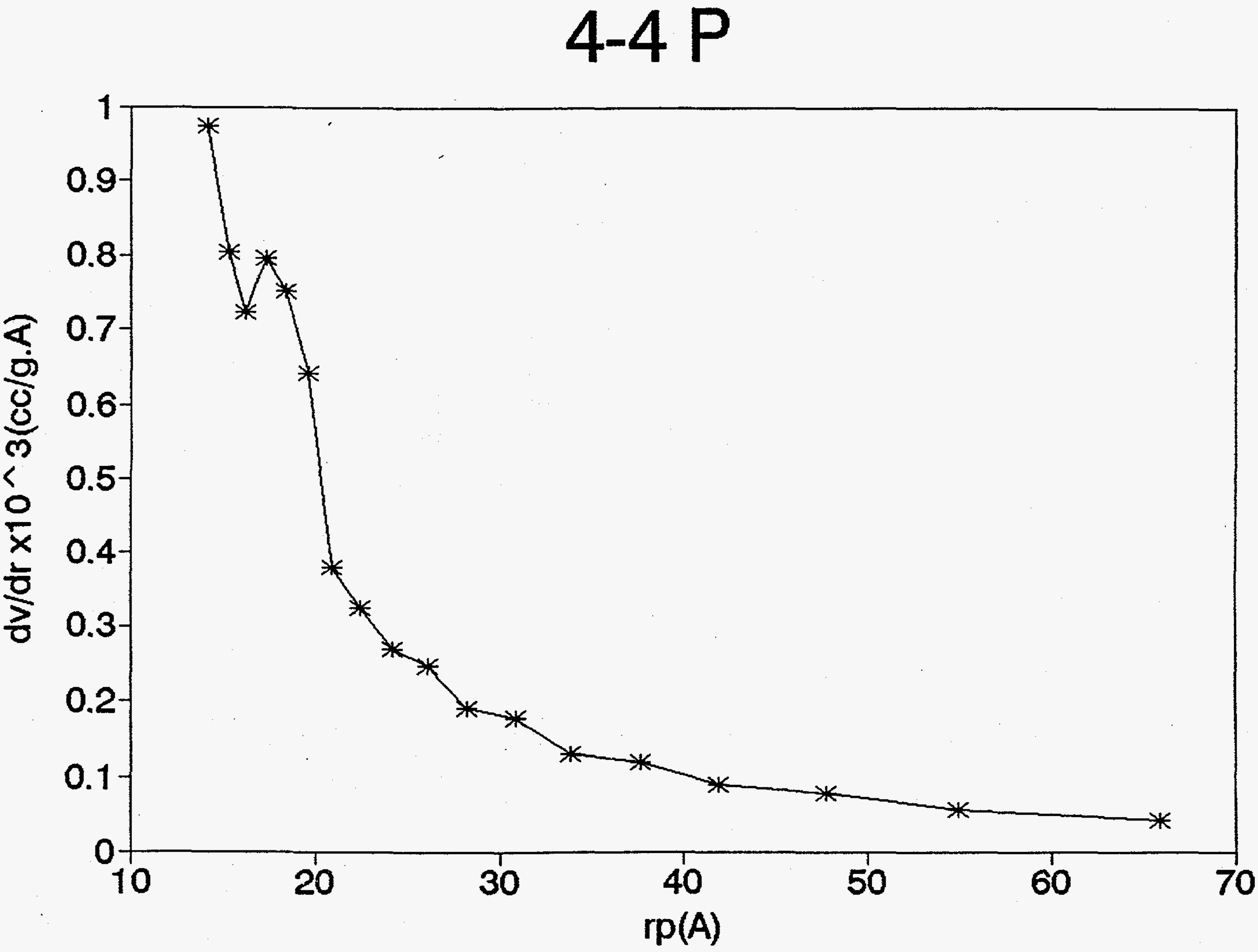
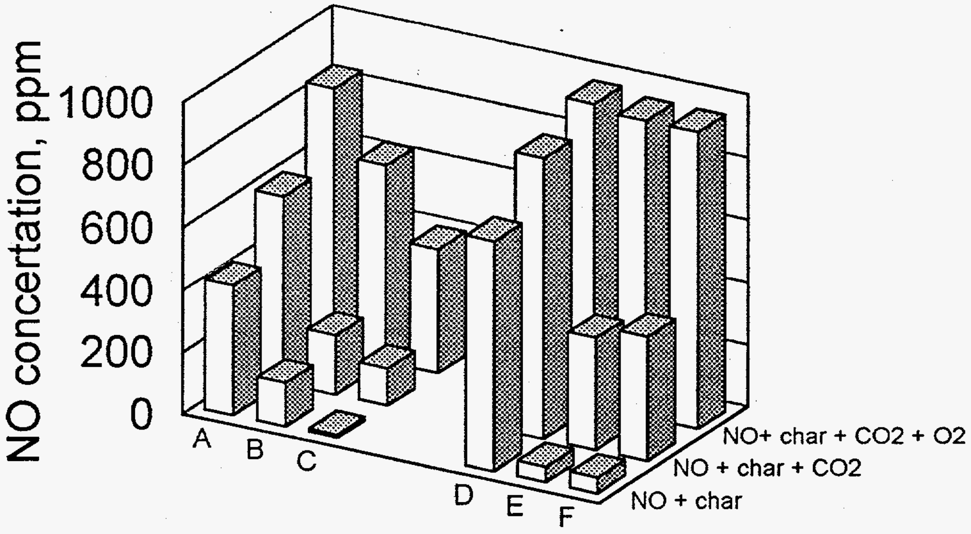


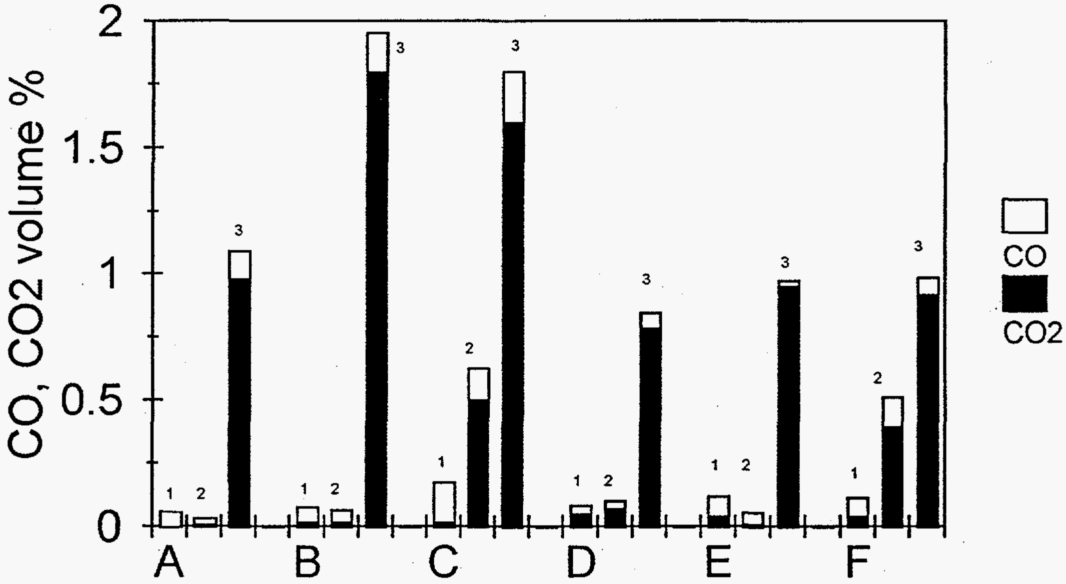
Figure 8. Pore size distribution of bituminous coal char pyrolyzed at 1100°C and 5 min holding time followed by reaction with $(NO+CO_2+O_2)$ at 1100°C.

Reburing Tempperature: 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 Rebúring Feed: 16.8 vol% (if any)
O2 in Reburing Feed: 1.95 vol% (if any)



A : MS lignite char, py. temp. 1100 C, 2 h holding time
B : MS lignite char, py. temp. 1100 C, 5 min holding time
C : MS lignite char, py. temp. 950 C, 0 holding time
D : Pitt # 8 coal char, py. temp. 1100 C, 2 h holding time
E : Pitt # 8 coal char, py. temp. 1100 C, 5 min holding time
F : Pitt # 8 coal char, py. temp. 950 C, 0 holding time

Figure 9. Effects char origins, char history, and oxidants on exit NO concentrations. The NO to char ratios correspond to that used in reburning at SR = 0.95 and 0.90 for the lignite char and bituminous coal char, respectively.

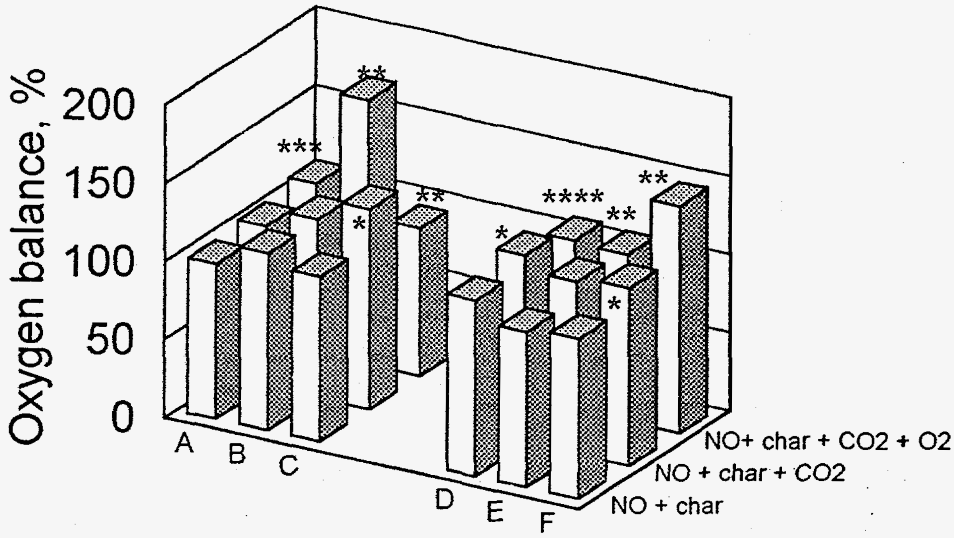


Reburing Tempperature: 1100 C
Feed NO Conc. in reburing: 1000 ppm
Reburing Residence Time: 0.2 s
Feeding Rate: 0.0640 g/min for MS lingite char
0.0446 g/min for Pitt # 8 coal char
Total Gas Flow Rate: 2000 cc/min
CO2 in Reburing Feed: 16.8 vol% (if any)
O2 in Reburing Feed: 1.95 vol% (if any)

1 : NO+char reaction, 2 : NO+char+CO2 reaction, 3 : NO+char+CO2+O2 rea
A : MS lignite char py. temp. 1100 C, 2 h holding time
B : MS lignite char py. temp. 1100 C, 5 min holding time.
C : MS lignite char py. temp. 950 C, 0 holding time.
D : Pitt #8 coal char py. temp 1100 C, 2 h holding time
E : Pitt #8 coal char py. temp 1100 C, 5 min holding time
F : Pitt #8 coal char py. temp 950 C, 0 holding time.

Figure 10. Effects char origins, char history, and oxidants on yields of carbon oxides (in volume percentage) from the reactions of NO with the chars. The NO to char ratios correspond to that used in reburning at SR = 0.95 and 0.90 for the lignite char and bituminous coal char, respectively.

Reburing Tempperature: 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)



A : MS lignite char, py. temp. 1100 C, 2 h holding time
B : MS lignite char, py. temp. 1100 C, 5 min holding time
C : MS lignite char, py. temp. 950 C, 0 holding time
D : Pitt # 8 coal char, py. temp. 1100 C, 2 h holding time
E : Pitt # 8 coal char, py. temp. 1100 C, 5 min holding time
F : Pitt # 8 coal char, py. temp. 950 C, 0 holding time
* : value/16
** : value/60
*** : value/120
**** : value/600

Figure 11. Effects char origins, char history, and oxidants on percentage conversion of oxygen in feed NO to the gasification products, CO and CO_2. The NO to char ratios correspond to that used in reburning at SR = 0.95 and 0.90 for the lignite char and bituminous coal char, respectively.

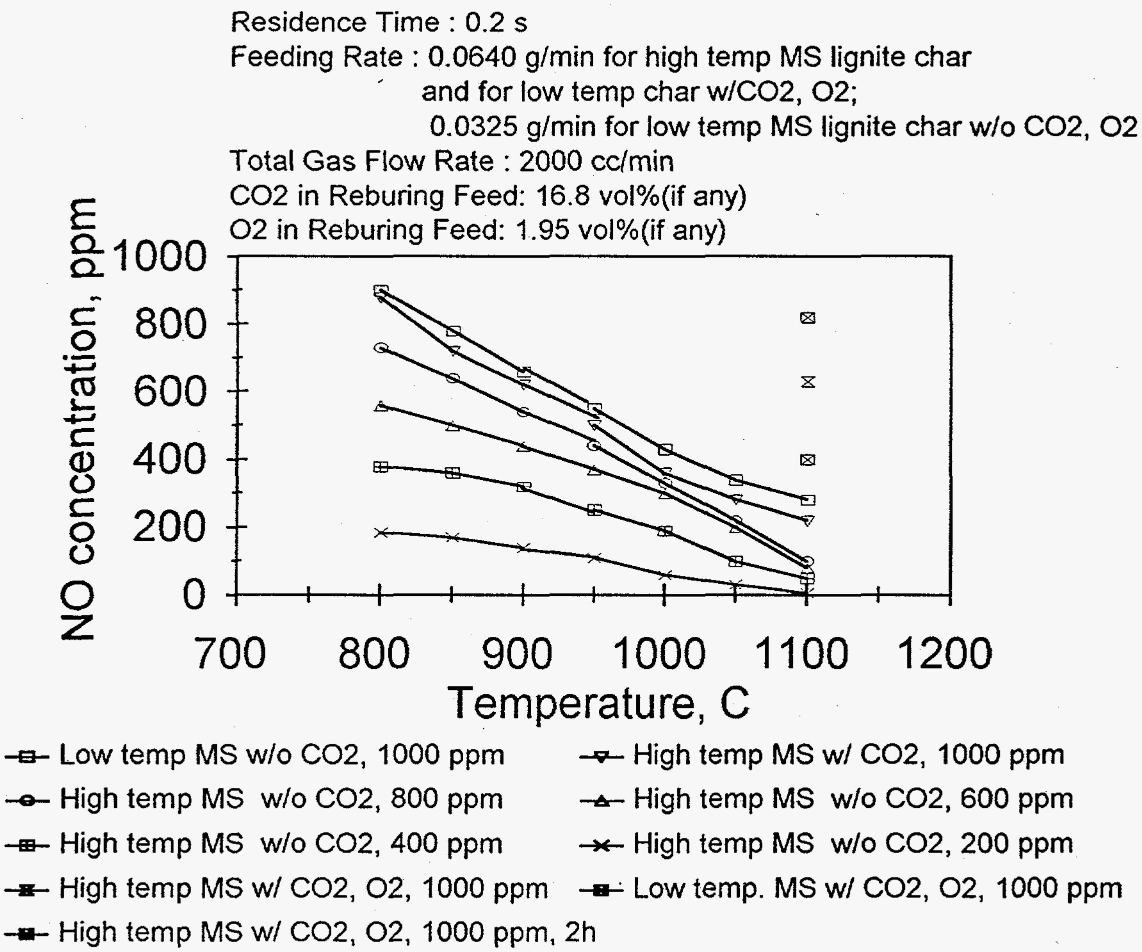

Residence Time : 0.2 s
Feeding Rate : 0.0640 g/min for high temp MS lignite char
and for low temp char w/CO2, O2;
0.0325 g/min for low temp MS lignite char w/o CO2, O2
Total Gas Flow Rate : 2000 cc/min
CO2 in Reburing Feed: 16.8 vol%(if any)
O2 in Reburing Feed: 1.95 vol%(if any)

Figure 12. Exit NO concentrations from reburning 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 reburning at SR = 0.97 and 0.93 for the high and low temperature chars.

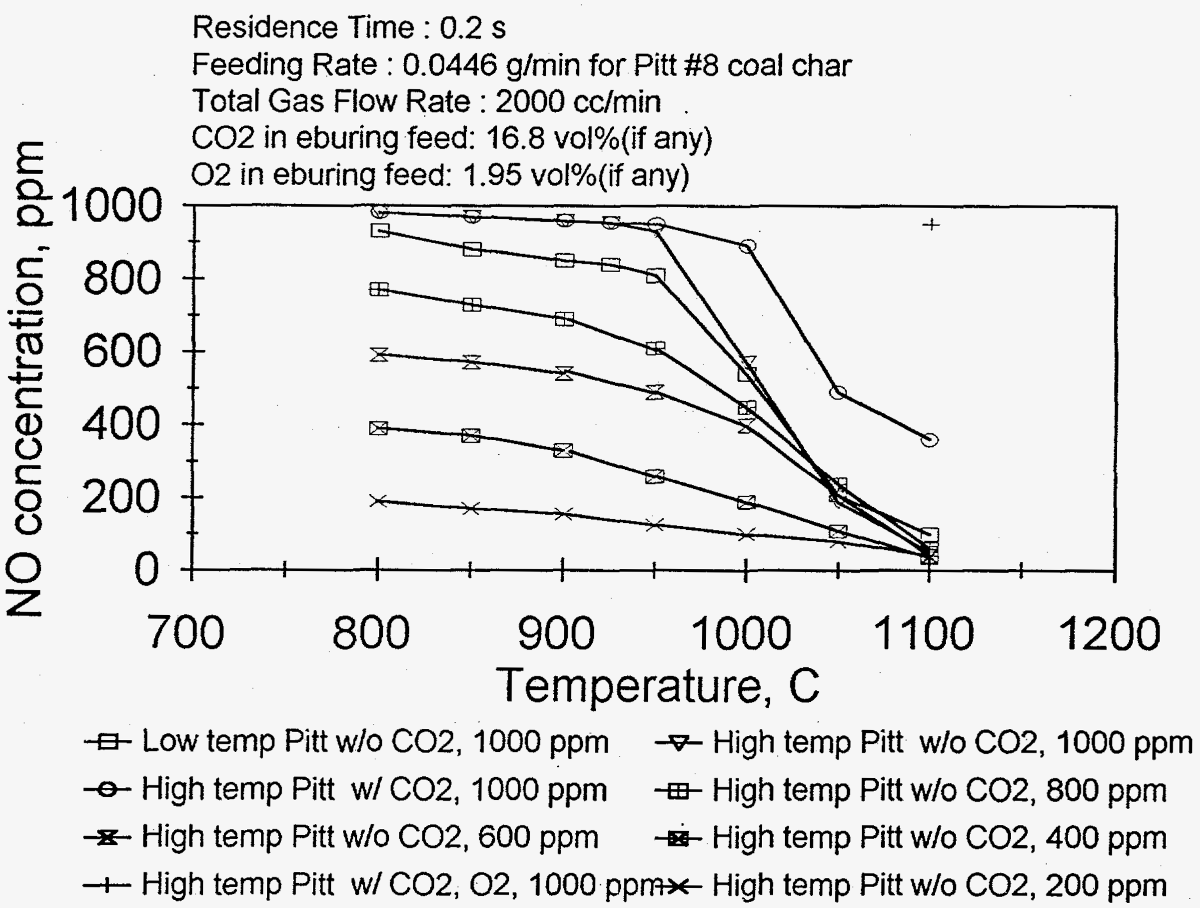
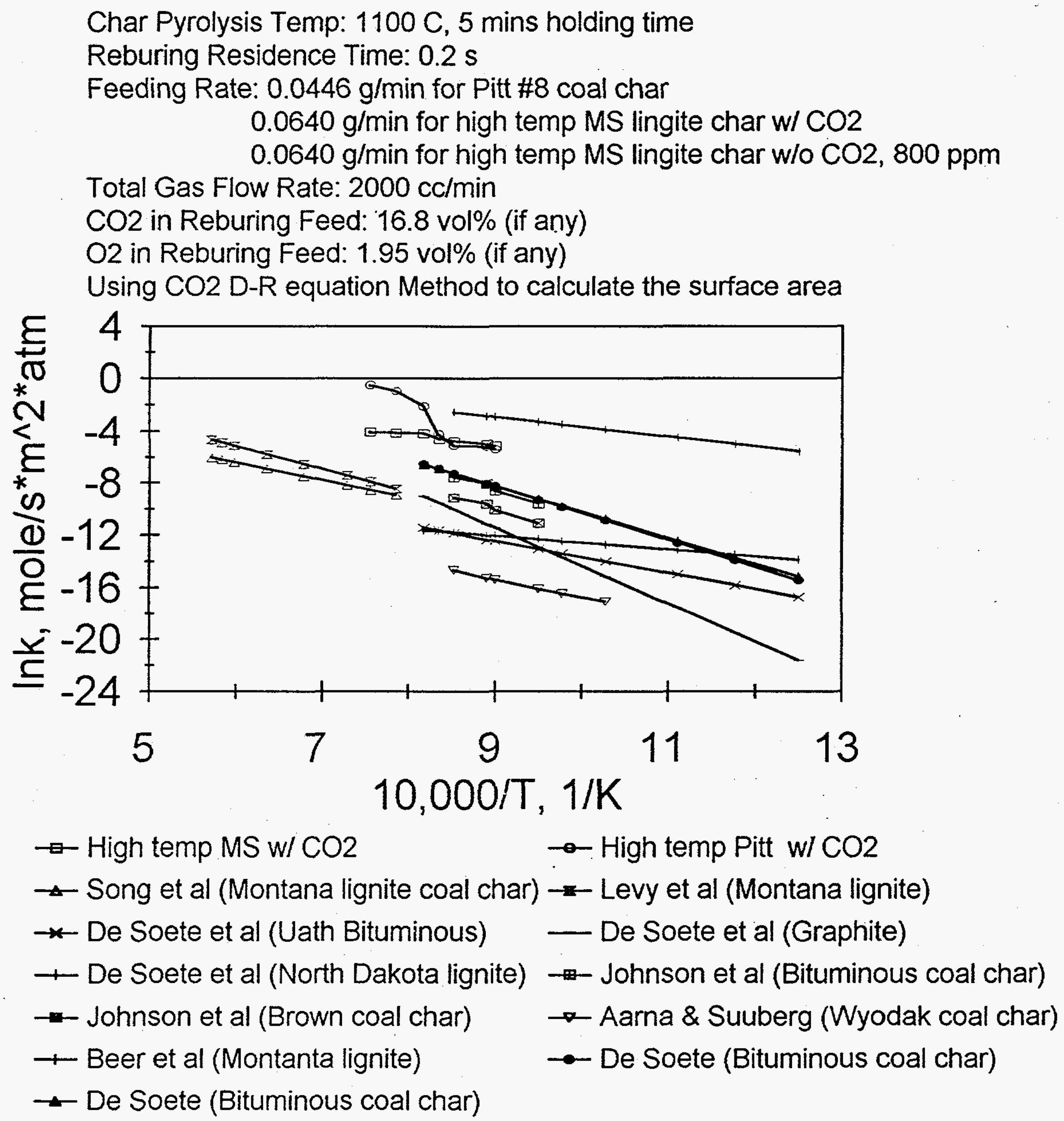


Figure 13. Exit NO concentrations from reburning with the bituminous coal chars as functions of temperature, char pyrolysis temperature, and feed compositions. The NO to char ratios correspond to those used in reburning at SR = 0.9 and 0.88 for the high and temperature chars, respectively.



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
0.0640 g/min for high temp MS lingite char w/o CO2, 800 ppm
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)
Using CO2 D-R equation Method to calculate the surface area

Figure 14. Arrhenius plots of NO reactions with chars of two different origins in the presence of CO_2 based on CO_2 surface areas. Published data in the literature are included for comparison.

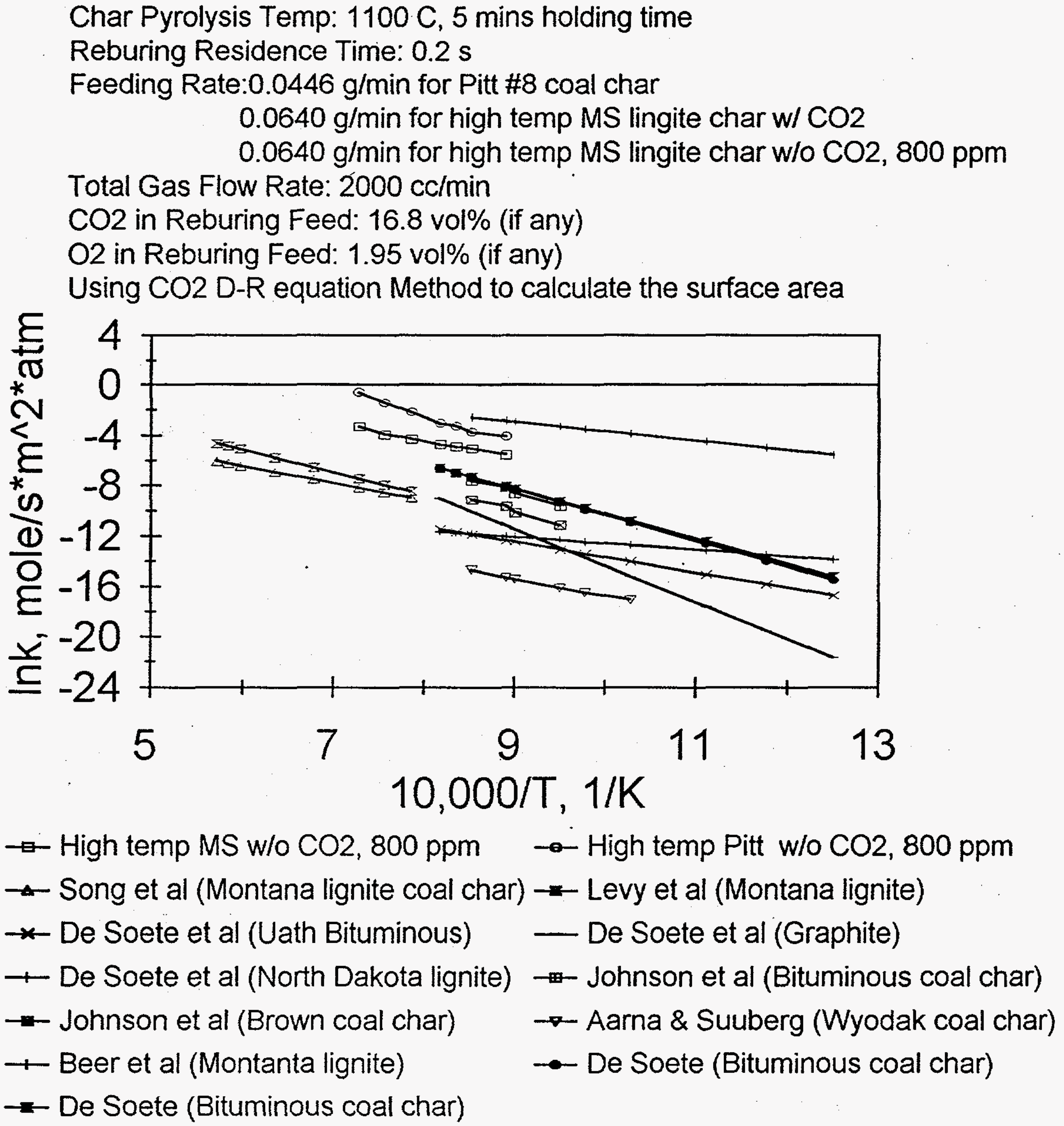
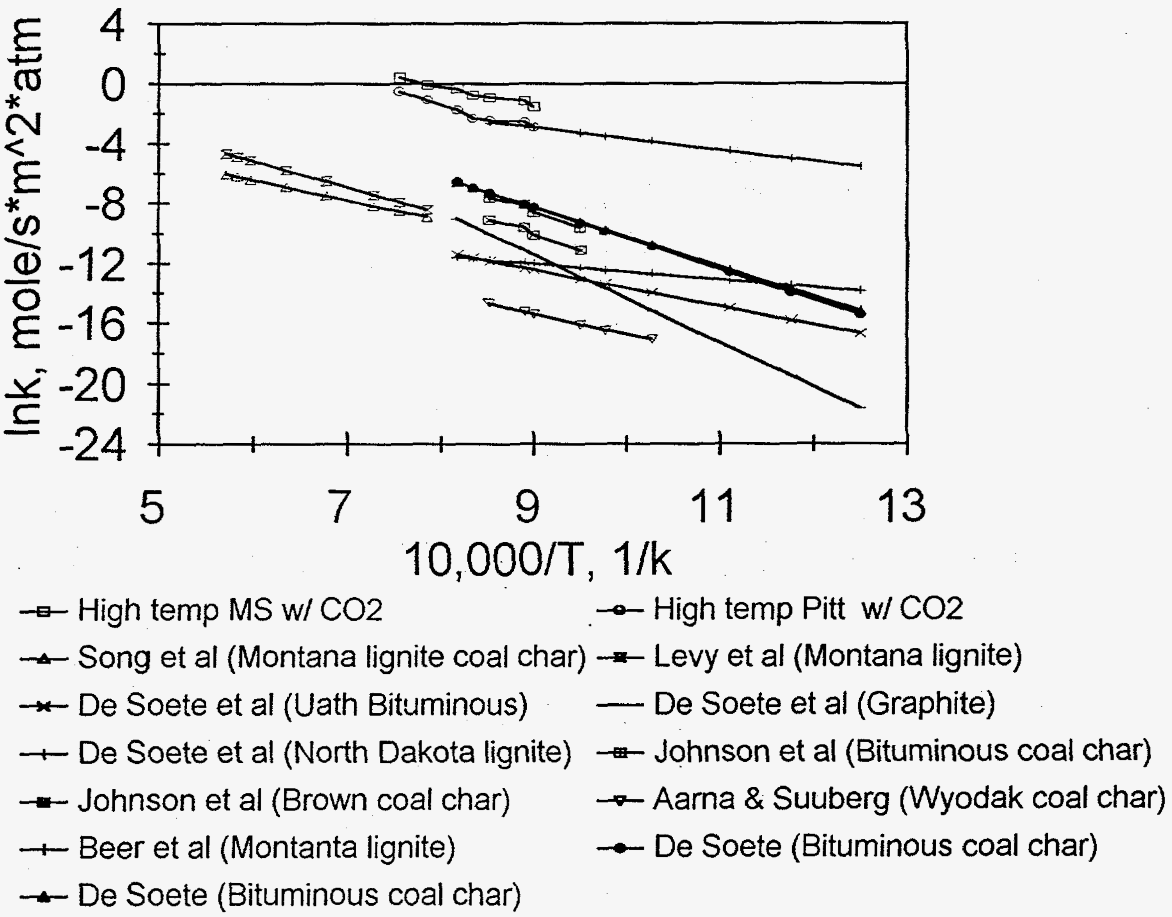


Figure 15. Arrhenius plots of NO reactions with chars of two different origins in the absence of CO_2 based on CO_2 surface areas. Published data in the literature are included for comparison.



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
0.0640 g/min for high temp MS lingite char w/o CO2, 800 ppm
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)
Using N2 BET Method to calculate the surface area

Figure 16. Arrhenius plots of NO reactions with chars of two different origins in the presence of CO_2 based on N_2 surface areas. Published data in the literature are included for comparison.

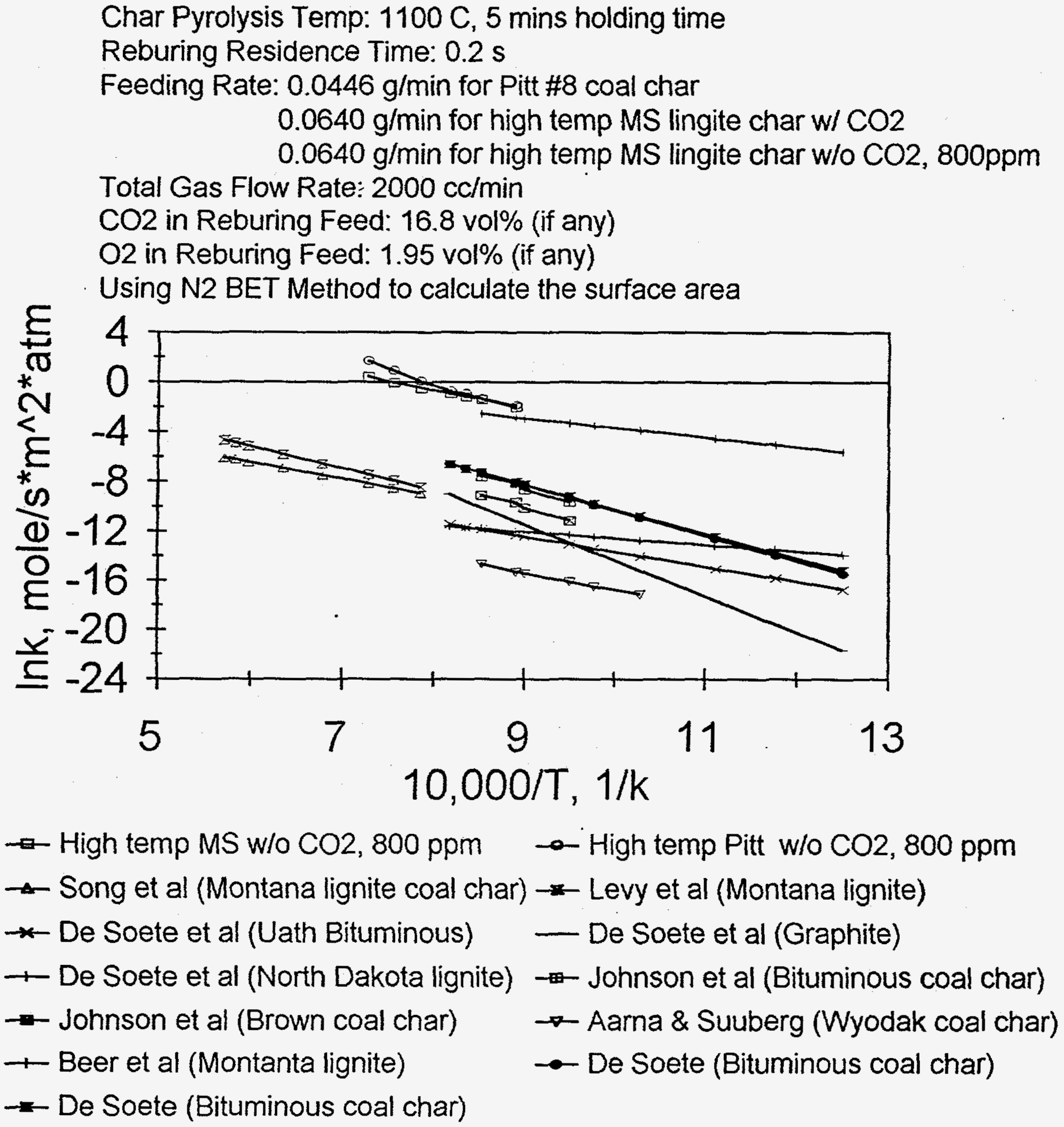


Figure 17. Arrhenius plots of NO reactions with chars of two different origins in the absence of CO_2 based on N_2 surface areas. Published data in the literature are included for comparison.