

ROLE OF CHAR DURING REBURNING OF NITROGEN OXIDES

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ABSTRACT

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. While coal, in general, has not been considered an effective reburning fuel, our recent research suggested that lignite has a reburning efficiency even higher than that of methane. The objectives of this research are to investigate 1) the relative importance of heterogeneous and homogeneous phase reactions, and, 2) the role of CaO in the catalysis of char gasification by NO in reburning environment. Experiments have been performed with a flow reactor with a simulated flue gas at a stoichiometric ratio (SR) 1.1. Reburning fuels in this study include methane, Pittsburgh #8 bituminous coal, Mississippi lignite, North Dakota lignite, chars derived from the coal and lignites, and the bituminous coal char impregnated with CaO. Chars were produced in N_2 by suspending a sample basket in a 3" tube furnace. The impregnation technique follows that developed for the catalysis of carbon oxidation. Results of reburning with chars indicate that heterogeneous mechanisms are more important than the homogeneous phase mechanisms during reburning with lignite. On the contrary, the bituminous coal char produces little activities at stoichiometric ratios above 0.75, and NO reduction is mainly contributed by homogeneous-phase mechanisms. These data also suggest that lignite char can be an even more effective reburning fuel than the parent lignite. Bituminous coal char impregnated with CaO demonstrates higher NO reduction efficiency than the original char. This observation suggests that the CaO-catalyzed char oxidation may be an important contributor to NO reduction during reburning with lignite, and the

reactivity of a bituminous coal char may be improved by impregnation. These results seem to have opened a new avenue of research, as well as the reburning practice.

I. INTRODUCTION

According to our previous studies (Burch *et al.*, 1991a,b; 1994), lignite char can be an active reburning fuel than methane. This observation is based on simulated reburning tests of two lignites on reactors of two scales. The two lignites tested were selected from Mississippi and North Dakota. Based on the initial screening tests with the North Dakota lignite, it has been demonstrated 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.

A critical review of the recent literature indicates that NO participates in two types of reactions; both are potentially significant to NO reduction in the reburning environment. It has been shown that the carbon in the char may be gasified by NO to form CO, CO₂ and N₂ (e.g., Furusawa, 1980). Recent lab-scale investigations of fluidized bed combustion (FBC) and circulating FBC (CFBC) have also shown that calcium sulfide (Hansen *et al.*, 1992), CaO (Allen, 1991; Hansen *et al.*, 1992; Hansen and Dam-Johansen, 1993; Shimizu *et al.*, 1993; Lin *et al.*, 1993) and Fe₂O₃ (Allen, 1991) serve as catalysts for NO reduction. While most of these researchers claimed that these catalysts enhanced the reaction NO + CO → CO₂ + ½N₂, Lin *et al.* indicated that the presence of CO decreases the NH₃ to NO. Lin *et al.* also claimed that, since CO oxidizes NH₃ to N₂, NO may oxidizes NH₃ through homogeneous and heterogeneous mechanisms in FBC or CFBC. It should be mentioned that the CaS catalyzes NO reduction (Hansen *et al.*, 1992) even with the presence of CO₂. These char gasification and mineral-catalyzed reactions in reburning environment have not been investigated, but can certainly be enhanced by the highly porous nature of lignite char.

The role of calcium during oxidation of various solid carbonaceous materials has also been examined through an class of impregnation/ion-exchange technique (e.g., Hengel and Walker, 1984). For the investigation of the roles of Ca and Mg in lignite during oxidation, Hengel and Walker discovered that gasification (by air, CO_2 , or steam) of exchanged lignites was strongly catalyzed by Ca. Bartholomew *et al.* (1991) and Gopalakrishnan *et al.* (1994) used the same ion-exchange/impregnation procedure for the studies of catalytic oxidation of chars. The char was produced in the presence of oxygen to induce the formation of oxygen complexes for the subsequent ion-exchange with calcium. Their kinetic study included lignite char, demineralized lignite char, demineralized lignite char impregnated with calcium, synthetic char, and synthetic char impregnated with calcium. Since calcium can be transformed into various compounds, including hydroxide, carbonate, oxide, sulfate, and chloride etc., during coal combustion, their impregnated calcium compounds include CaO , CaCO_3 , and CaSO_4 . The results indicate significant catalytic effects - up to 160-fold increase for CaCO_3 catalysis, 290-fold increase for CaSO_4 , and up to 2700 times for CaO . While most of the studies in the literature have been centered around the Ca-catalyzed char oxidation by oxygen, Wojtowicz *et al.* (1991) reported that oxidation of a peat char by N_2O during fluidized bed combustion can be catalyzed by impregnating the char by CaO . Recently, Illan-Gomez *et al.* (1995) reported the effect of calcium as catalyst of the NO-carbon reaction in a fixed-bed flow reactor at 300-600° C. Calcium was found to catalyze NO-carbon reaction through the formation of intermediate $\text{CaO}(\text{O})$ surface species which transfers oxygen to the carbon surface.

The objectives of this research are to investigate the relative importance of heterogeneous and homogeneous phase NO reactions of different coals, the effectiveness of NO reduction by using chars as reburning fuels, and the effectiveness of a bituminous coal char impregnated with CaO .

II. EXPERIMENTAL

The detailed flow reactor system for reburning and experimental procedure have been discussed by Burch *et al.* (1991a,b). The reactor simulates reburning stage and has feed gas consisting of 16.8% CO₂, 1.95% O₂, and 0.1% NO in a helium base. These concentrations of CO₂, O₂, and NO were chosen to be consistent with those of a coal primary flame operated at a stoichiometric ratio of 1.1. The ultimate analysis results of the lignites and coal were reported by Huffman Laboratory, and are listed in Table 1.

Chars were prepared in a ceramic tube electrically heated by a split tube furnace (Thermcraft Model # 23-18-12H). A 50 mesh stainless steel screen was installed as the distributor which was located at 6" high from the bottom of the furnace. To provide an effective heat transfer to the gas, a silicon sand layer was placed on the distributor. The coal/char basket assembly consisted of a stainless steel handle (1/4 inch stainless steel tubing) and a stainless steel basket (serving as the coal/char container 2.2 cm O.D. \times 15 cm height). The basket is equipped with a mesh screen cover. During the pyrolysis, the sample basket, with only two third of its volume filled with the sample (about 20g), was lowered into the ceramic tube just above the sand bed. The volatile products were carried away by nitrogen. The set temperature of the furnace was then raised from the room temperature to 1050°C with a 0.45°C/s heating rate. After the furnace reached the set temperature, the sample was kept in the furnace for another 5 minutes. Quenching was achieved by raising the sample basket to a water-cooled, reversed-nitrogen gas flow section. The sample was kept in the quenching zone for about 20 minutes before removed from the furnace. The char samples were stored in glass bottles sealed with caps. This procedure generates char with a weight percentage (on

dry basis) of 49.6% of the Mississippi lignite, 55.7% of the North Dakota lignite, and 61.8% of Pittsburgh #8 bituminous coal.

The impregnation and ion-exchange techniques were developed for the verification of calcium's catalytic role during lignite combustion in the early 1980s (Radovic *et al.*, 1983, 1985), and has been implemented in the last decade in the catalytic oxidation of chars derived from synthetic carbon, bituminous coal, lignite and peat with oxygen, N_2O , and NO. Char derived from bituminous coal was used for impregnation. Furthermore, partially oxidized char was also used to enhance the possible char-Ca interaction (Figure 1). Slurry of 10 g char and 250 ml of 1.5 M calcium acetate aqueous solution was kept at room temperature for 24 hours. The pH of the solution was kept at 8.5 using a 0.01 N solution of $Ca(OH)_2$ to enhance the possible ion-exchange with the oxygen-containing complexes in the char. The solution is then filtered, washed with 200 ml deionized water, and dried at 105°C for 12 hours. Before reburning, the impregnated char is thermally treated to 900°C in nitrogen with the same furnace for the char production for about 5 min. With this treatment, the incorporated calcium acetate converts to $CaCO_3$ at 450°C, and then $CaCO_3$ converts to CaO at 775°C (Bartholomew *et al.*, 1991). Reburning was conducted within one hour after the thermal treatment to avoid formation of $CaCO_3$ through recombination of CaO with CO_2 . For the preparation of partially oxidized char, the Pittsburgh #8 bituminous coal char was placed in a furnace at 300°C for five hours before impregnation. The furnace was flushed with air during treatment. Assuming the char has the same CaO content as the coal (2.97%, on an ash basis), the impregnated CaO loading is about 2.24% on an ash basis, or 0.43% on the char basis.

III. WORK ACCOMPLISHED

A. Reburning with Coals and Their Chars

Figure 2 shows the effectiveness of various reburning fuels on exit NO concentrations. These results indicate that lignites and lignite chars are the most effective reburning fuels in our studies. Furthermore, the chars derived from the Mississippi lignite and North Dakota lignite are even more effective than their parent coals over a wide range of reburning stoichiometric ratios (SR2). Both lignites and their chars have much higher NO reduction efficiency than that of methane and Pittsburgh #8 bituminous coal. Pittsburgh #8 bituminous coal is the poorest reburning fuel among all the reburning fuels studied.

Since lignite in reburning environment does not produce more hydrocarbon free radicals than methane, gas phase kinetics (e.g., Miller and Bowman, 1989), which have been well adopted in the interpretation of NO reduction in many systems, can not be the dominant mechanisms for NO reduction for systems involving lignite. In other words, heterogeneous mechanisms contribute more NO reduction than homogeneous mechanisms over a wide range of stoichiometric ratios when Mississippi and North Dakota lignites are used as reburning fuels. The heterogeneous NO/char reactions during reburning with Pittsburgh #8 bituminous coal are essentially negligible when SR2 is greater than 0.75.

Figure 2 also shows that the Pittsburgh #8 coal char impregnated with CaO demonstrates higher NO reduction potential than its parent char. This result indicates that NO reduction in reburning can be enhanced, though not to the levels of lignite, by impregnation. Since the Mississippi

and North Dakota lignite ash are usually rich in calcium oxide, the observation also suggests that 1) the CaO-catalyzed char oxidation may be an important contributor to NO reduction during reburning with lignites, and 2) the reactivity of a bituminous coal char may be improved by impregnation with CaO. These results seem to have opened a new avenue of research, as well as reburning practice.

HCN and NH₃ are the two major intermediate compounds during the conversion of NO to N₂ (Chen *et al.*, 1991; Miller and Bowman, 1989). Figure 3 shows the effects of reburning fuels on exit HCN concentrations. Figure 4 shows the effects of reburning fuels on exit NH₃ concentrations. Figure 5 shows the effects of reburning fuels on yields of total fixed nitrogen (TFN, the summation of NO, NH₃, and HCN). Since the HCN and NH₃ yields are extremely low during reburning with chars while their yields during reburning with coal, lignites and methane are not negligible, lignite chars exhibit exceedingly superior effectiveness in terms of the total fixed nitrogen yields. For example, as shown in Figure 2, Mississippi lignite char offers the same effectiveness at SR2 = 0.95 as the Mississippi lignite at SR2 = 0.90. Figure 5 also shows that the TFN yields from reburning with Mississippi lignite is about the same as those with the North Dakota lignite over a wide range of stoichiometric ratios.

In the previous reburning studies (Chen *et al.*, 1991), it was demonstrated that the lignite char surface participates in heterogeneous/ catalytic NO reductions to HCN, NH₃, and N₂. It seems to be highly desirable, from both technological and scientific aspects, to acquire knowledge concerning the relative importance of the heterogeneous to the homogeneous phase NO reduction in reburning environment, particularly when lignite is used as reburning fuel. Since coal or lignite produces only about 50% of the volatile carbons of that which methane produces during reburning, the effectiveness of lignite over methane suggests that heterogeneous mechanisms must have contributed NO reduction

levels similar to, or even higher than, the homogeneous mechanisms when lignite is used as a reburning fuel. The results of reburning with chars have also been examined for their heterogeneous contributions. In the calculation, it was assumed that the coal or lignite consists of both char and volatile; thus, the NO reduction during reburning with lignite or coal is considered to be contributed by both char and volatile matters. Volatile matters contributed to homogeneous phase NO reduction during reburning, while reburning with char provides no homogeneous phase NO reduction. Therefore, when the NO reductions from char reburning are compared with those from coal and lignite reburning of equivalent char feeding rate, the contribution of heterogeneous mechanisms is elucidated.

Figure 6 presents the comparison of NO yields from reburning with Mississippi lignite and its char at various reburning stoichiometric ratios (respect to Mississippi lignite, not its char). Similarly, Figure 7 presents the comparison of NO yields from reburning with North Dakota lignite and its char at various reburning stoichiometric ratios. These results indicate that the heterogeneous mechanisms have contributed more NO reductions than the homogeneous mechanisms over a wide range of stoichiometries during reburning with Mississippi lignite and North Dakota lignite. For instance, at stoichiometric ratio of 0.88 (respect to lignite), NO reduction contributed by Mississippi lignite char is 66%. Considering the additional NH_3 and HCN yields produced from reburning with lignite or coal, the lignite chars are even better reburning fuels in terms of TFN yields. Figure 8 illustrates the heterogeneous NO reductions contributed by the char produced from the bituminous coal. The results indicate that the heterogeneous contributions are essentially negligible when SR is greater than 0.75. This Figure again illustrates the benefits, although it is limited, of the impregnation of CaO with bituminous coal char.

The Clean Coal Technology Program sponsored by the U.S. Department of Energy (DOE) include two programs on reburning with coals (Yagiela *et al.*, 1993; Bradshaw *et al.*, 1993). Although Yagiela *et al.* observed that subbituminous coal is a better reburning fuel than the bituminous coal, no lignite reburning has been demonstrated on any larger scale units. Our observation of the heterogeneous mechanisms along with the impregnation approach discussed herein may have profound impacts on the practice of coal-fired boilers in utilities and industries. First, if high NO reduction can be achieved by reburning with char at higher oxidant/fuel stoichiometric ratios, less unburned carbon will enter the burnout stage. This observation along with the demonstrated catalytic activity of calcium compounds in char oxidation, in turn, could lead to lower residual carbon and CO emissions which are typical concerns for a number of advanced NO control technologies. Second, the impregnation/ion-exchange technique is expected to increase the value of bituminous coal as a reburning fuel. Third, the presence of calcium compounds may also enhance sulfur capture, both in the reburning and in the burnout stages. Although SO₂ may compete with NO in the reburning zone for CaO, it has been established that CaS and CaSO₄ also catalyze the oxidation of char (Gopalakrishnan *et al.*, 1994, Hansen *et al.*, 1992). Finally, the boiler behavior, such as the slagging and fouling problems, may change when lignite is used as reburning fuel or CaO is added into the system.

B. Measurements of the Surface Fractal Dimension

The BET-surface areas of six samples [(MS Lignite Char 1,100 °C: SR₂=0.99, SR₂=0.95, SR₂=0.93, SR₂=0.90), (Mississippi Lignite Char: No. 1), and (Mississippi Lignite Ash/Char No.2)]

were measured with nitrogen (N_2) and argon (Ar) as the adsorbates at a temperature of 77 K.

Measurements were carried out under four different relative pressures with the multi-point method.

The volume of gas adsorbed, V , at pressure P can be described by the BET equation (see, e.g., Lowell, 1979)

$$\frac{P/P_0}{V[1-(P/P_0)]} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C} \right] \frac{P}{P_0} \quad (1)$$

where P_0 is the vapor pressure of liquified gas at the adsorbing temperature; V_m , the volume of gas required to form an adsorbed monomolecular layer; and C , a constant related to the energy of adsorption. Moreover, V_m is related to V and P through the Langmuir equation for the type- I isotherms given below (see, e.g., Lowell, 1979).

$$\frac{P}{V} = \frac{1}{KV_m} + \frac{P}{V_m} \quad (2)$$

The values of V and V_m are measured at the standard temperature and pressure, STP. With V_m given, the surface area, A , of an individual sample is evaluated as follows (see, e.g., Lowell, 1979):

$$A = \frac{V_m N_0 \sigma}{M} \quad (3)$$

where N_0 is the Avogadro number; σ , the effective cross-sectional area of an adsorbate molecule; and M , the molar volume of the gas.

The surface fractal dimension, d_{FS} , can be determined by probing the surface of a char sample with adsorbates whose molecules vary in size but are similar in shape. Since carbon dioxide and krypton are inappropriate from the stand-points of size and/or shape in obtaining d_{FS} of our char samples on the basis the BET data, only nitrogen and argon served as adsorbates. The apparent

surface area, A , as measured by an adsorbate can be expressed by

$$A = N_0 n \sigma \quad (4)$$

where n is the number of molecules of adsorbate required to completely cover the surface of the sample; n is related to σ through the power law (see, e.g., Fan *et al.*, 1991),

$$\log n = \left(-\frac{d_{fs}}{2}\right) \log \sigma + \text{constant} \quad (5)$$

where d_{fs} is the surface fractal dimension. The two expressions given above lead to

$$\log A = \left(\frac{2-d_{fs}}{2}\right) \log \sigma + \text{constant}', \quad 2 \leq d_{fs} < 3 \quad (6)$$

from which d_{fs} can be recovered. If the surface is smooth or nonfractal, d_{fs} is equal to two; otherwise, the value of d_{fs} is greater than two but less than three. In fact, the more rugged the surface, the larger the value of d_{fs} .

The surface area, A , of each sample was determined as follows. First, four values of the volume of gas adsorbed, V , were generated at four different pressures. Then, the volume of gas for monomolecular layer, V_m , was calculated from Eq. 2. Subsequently, A was evaluated from Eq. 3 or 4; the resultant A 's depend on the effective cross-sectional area, σ , of the adsorbate, N_2 or Ar . In the present work, two A 's of each sample were obtained and plotted in Figure 9. The surface fractal dimension, d_{fs} , of the sample can be evaluated from the slope of the plot in the light of Eq. 6. The fractal dimensions, d_{fs} 's, obtained are summarized in Table 2. Note that we have failed to recover the fractal dimensions of some of the samples in spite of repeated measurements. It is highly probable that the char characteristics of the original coal for these samples and/or combustion conditions were

such that the samples' surfaces are no longer fractal. Additional measurements will be carried out with a new BET apparatus to be installed in the near future in our laboratory.

IV. WORK FORECAST

In the succeeding quarter, we will measure the rates of reactions involving NO, chars and CO in isolated environments. Chars derived from Pittsburgh #8 bituminous coal and Mississippi lignite will be used in this kinetic study. Emphases will be placed on the char gasification by NO and CO+NO reaction. The catalytic roles of lignite char and ash will also be examined. Following the reburning experiments, the surface area of char collected will be measured by BET method and the rates of surface reaction will be corrected by fractal dimension of char.

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Table 1. Ultimate Analysis of Coals*

Contents (%)	MS lignite	ND lignite	Pittsburgh #8 bituminous coal
Moisture	0.29	14.39	2.02
Carbon	53.07	60.63	70.48
Hydrogen	5.34	4.44	4.66
Oxygen, by Difference	16.32	22.63	8.53
Nitrogen	0.58	0.86	1.44
Sulfur	0.94	1.19	3.35
Ash	23.75	10.25	11.54

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

Table 2. Surface fractal dimension of coal char.

Sample	N_2 [cm ² /g]	Ar [cm ² /g]	d_{FS} [-]
MS Lignite Char			
SR ₂ =0.90	102.2	108.5	2.98
SR ₂ =0.93	126.5	148.6	N/A
SR ₂ =0.95	105.3	113.0	N/A
SR ₂ =0.99	91.6	92.8	2.19
Mississippi Lignite Char No.1			
	51.2	32.7	N/A
Mississippi Lignite Ash/Char No.2			
	84.9	86.6	2.28

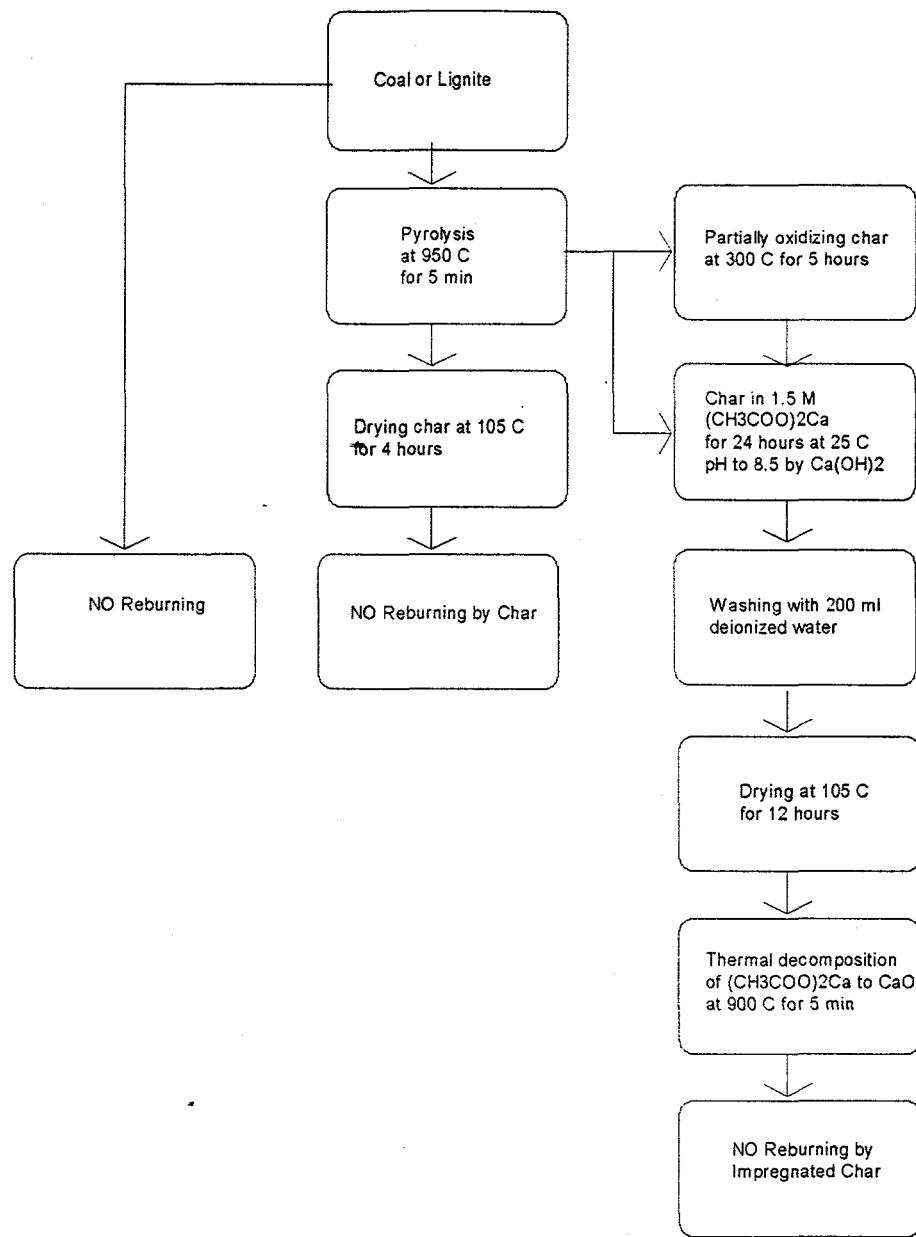


Figure 1. Experimental Flow Chart.

Primary Zone Stoichiometric Ratio: 1.10
Feed NO Concentration: 1000 ppm
Reaction Time: 0.20 Sec
Temperature: 1100 C

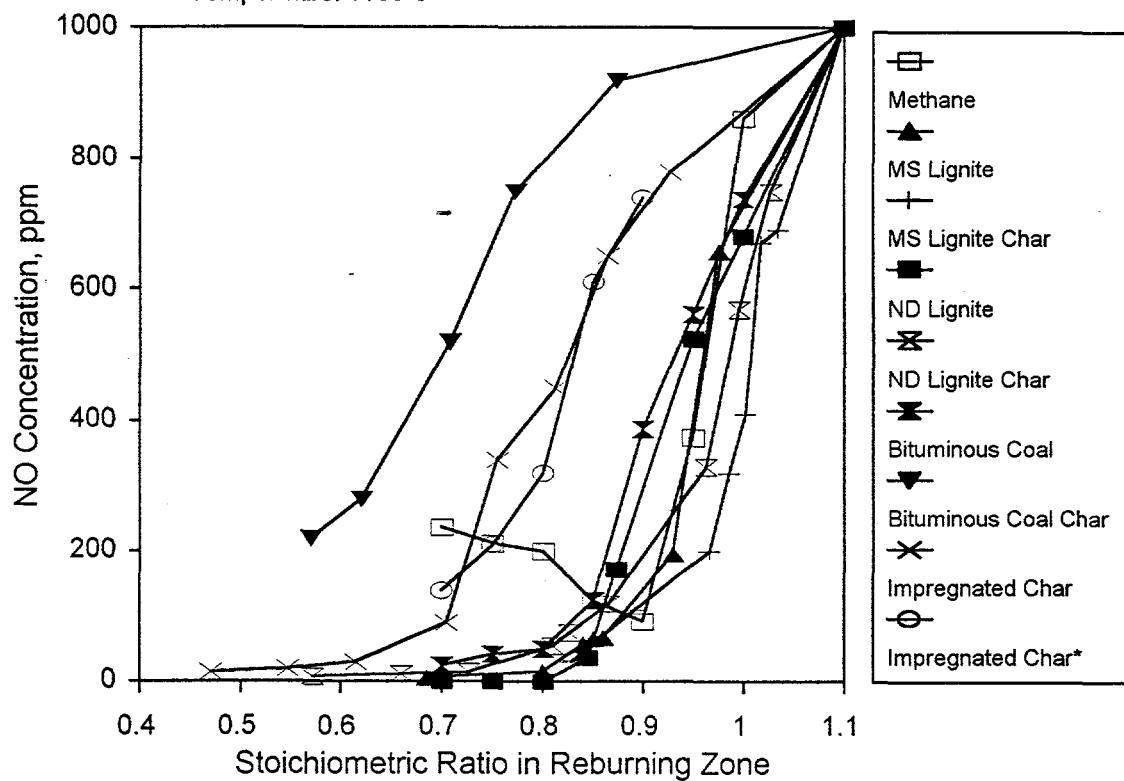


Figure 2. Effects of Reburning Fuels on Exit NO Concentrations.

(* Partially oxidized char before impregnation.)

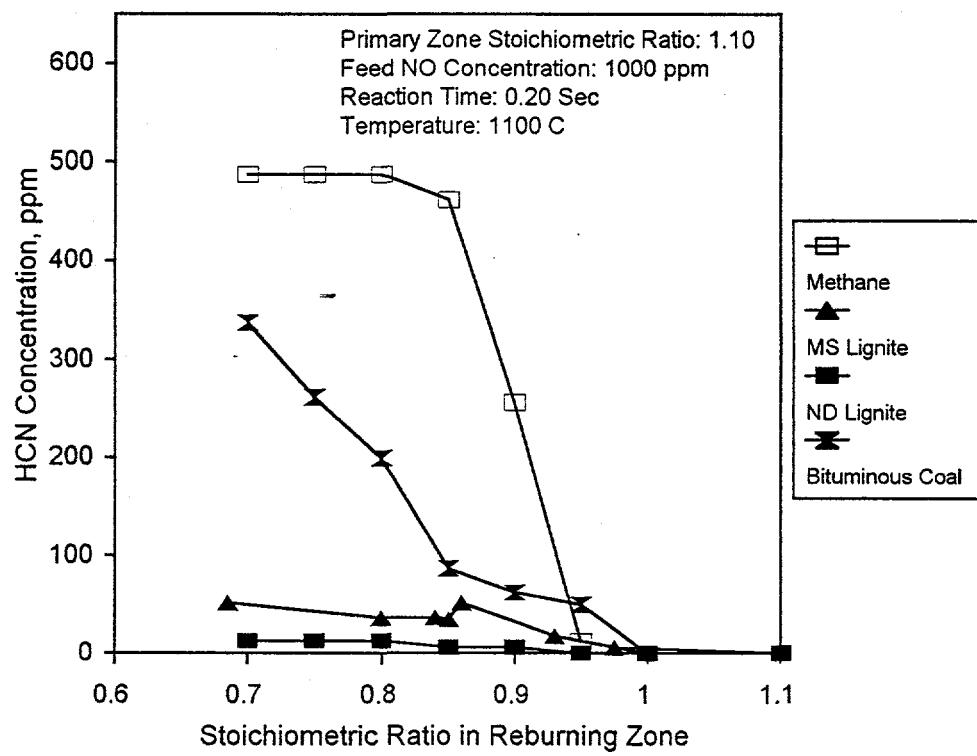


Figure 3. The Effects of Reburning Fuels on Exit HCN Concentrations.

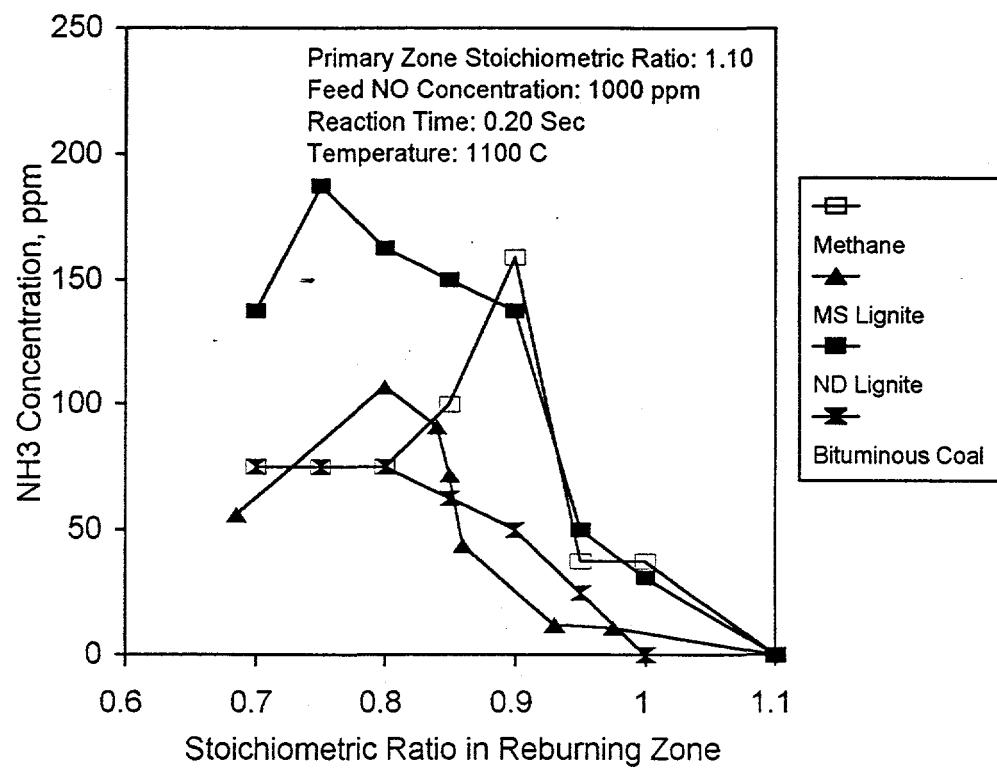


Figure 4. The Effects of Reburning Fuels on Exit NH_3 Concentrations.

Primary Zone Stoichiometric Ratio: 1.10
 Feed NO Concentration: 1000 ppm
 Reaction Time: 0.20 sec
 Temperature: 1100 C

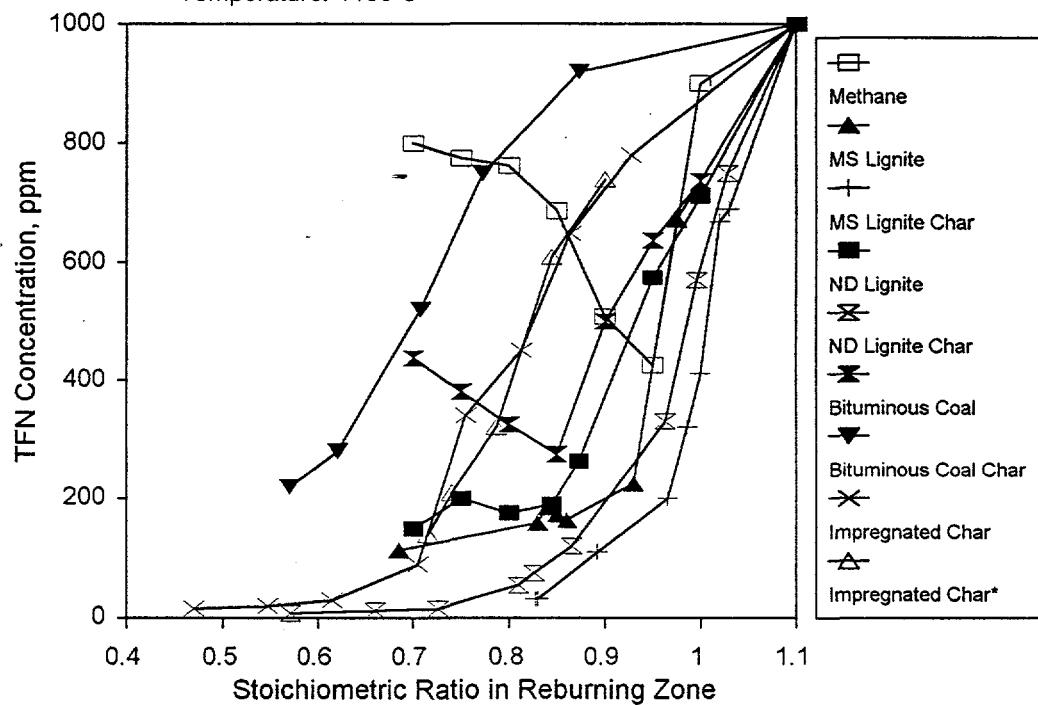


Figure 5. Effects of Reburning Fuels on Total Fixed Nitrogen Concentrations.

(* Partially oxidized char before impregnation.)

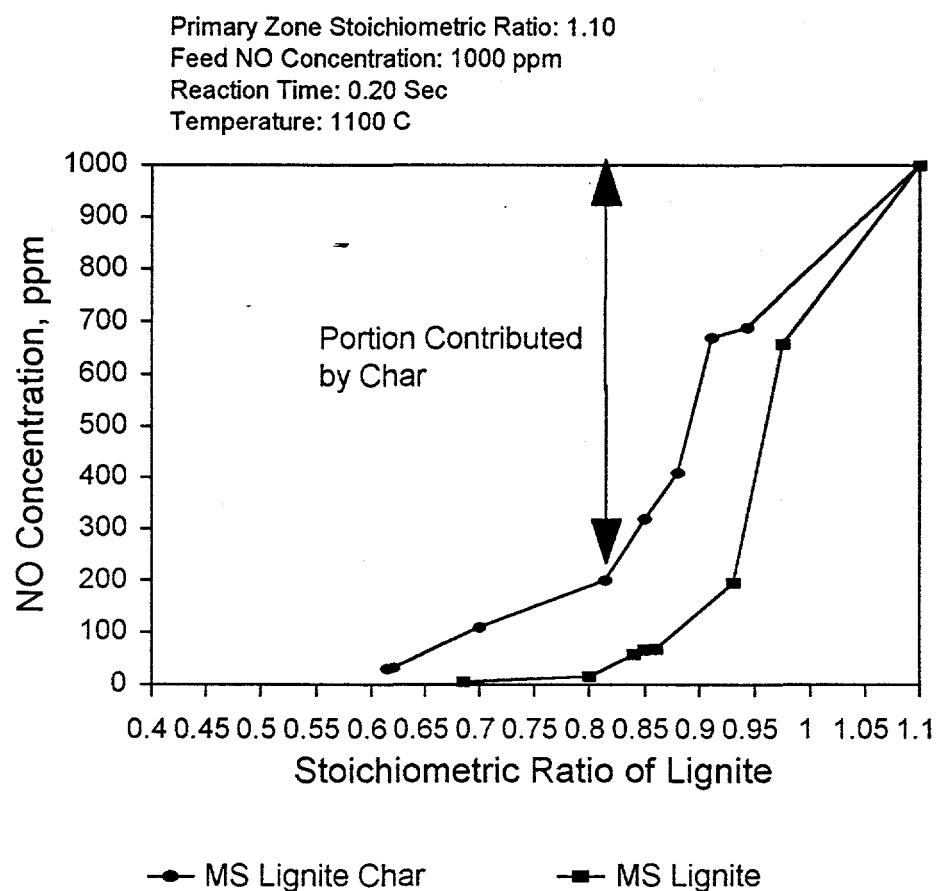


Figure 6. Heterogeneous vs. Homogeneous Reaction Mechanisms during Reburning with Mississippi Lignite.

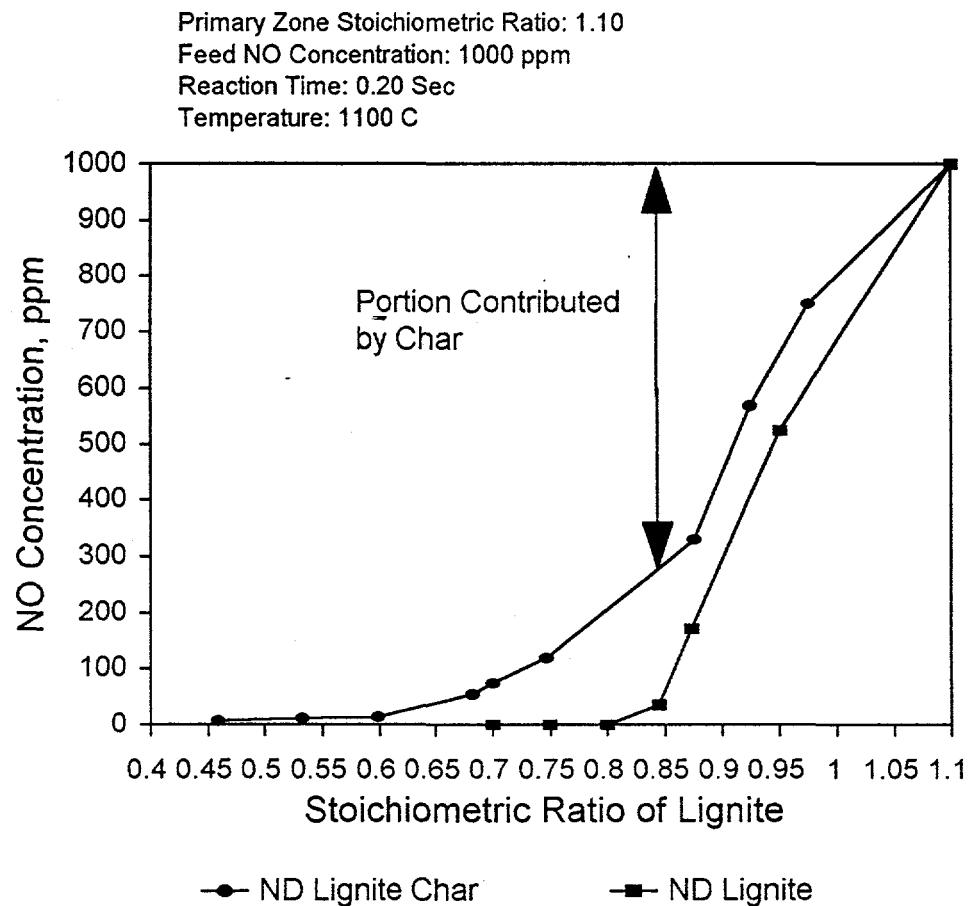


Figure 7. Heterogeneous vs. Homogeneous Reaction Mechanisms during Reburning with North Dakota Lignite.

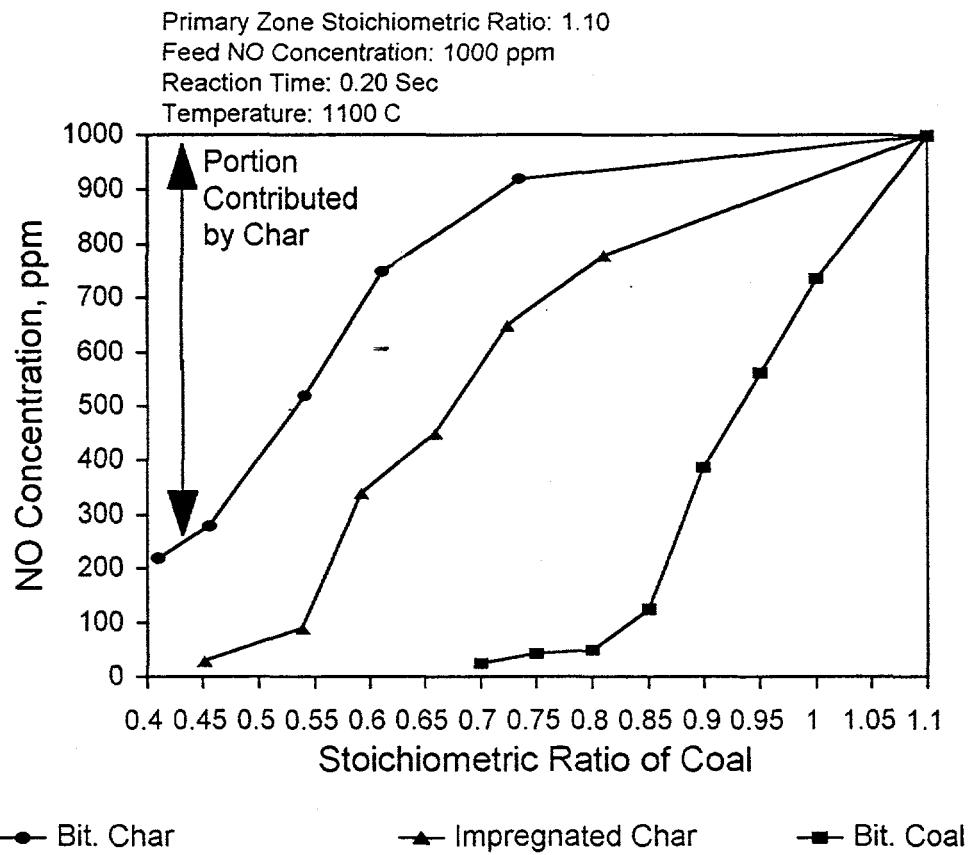


Figure 8. Heterogeneous vs. Homogeneous Reaction Mechanisms during Reburning with Bituminous Coal.

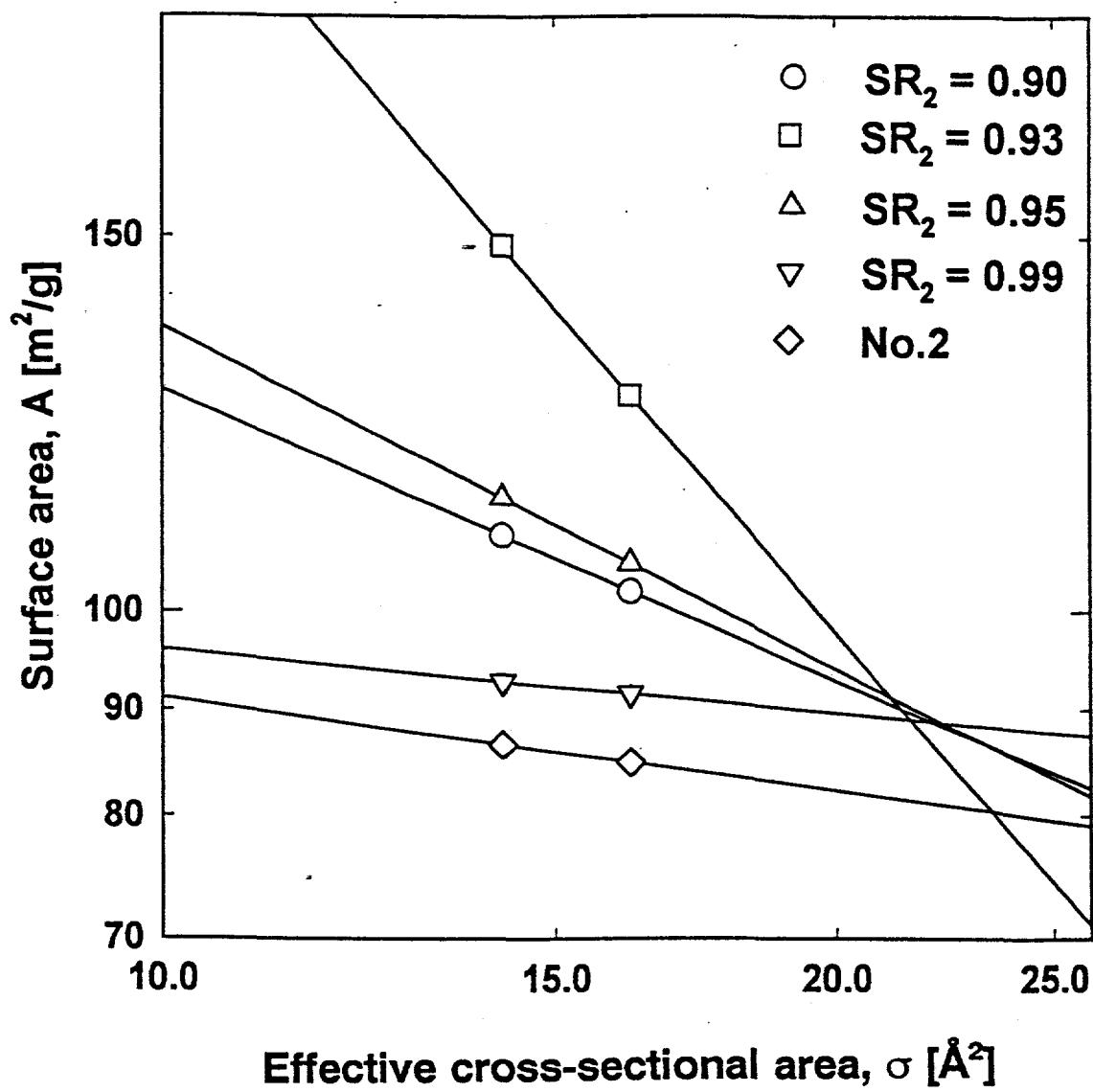


Figure 9. Surface Areas Obtained with the Adsorbate Molecules of N_2 and Ar .