Variables, Kinetics and Mechanisms of Heterogeneous Reburning

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The variables, kinetics, and mechanisms of heterogeneous reburning were studied in a flow reactor with a simulated flue gas. The efficiency of heterogeneous reburning depends on the origin of the char, char preparation history and the presence of oxidants, CO_2 and O_2, and the reducing agent CO, in reburning. Estimated intrinsic rate constants for surface NO reduction in various gaseous environments were compared with those published. In addition to its large surface area, the effectiveness of lignite char appears to be due to its ability to promote two consecutive reactions: (1) the gasification of char by CO_2 and O_2 for production of CO; (2) the removal of surface oxygen complexes, including those formed after adsorption of NO, by gaseous CO, for the regeneration of reactive sites. Moreover, lignite ash also catalyzes the decomposition of HCN, a major intermediate of NO conversion during gas reburning. These observations suggest that reburning by a mixed fuel containing natural gas and lignite char can be a potentially attractive route for the in−furnance control of nitrogen oxide.

Introduction

Reburning is a three-stage combustion technology designed for the reduction of NO by introducing a small amount of reburning fuel aft of the primary flame where the majority of NO is chemically reduced to nitrogen. Recent research suggested that lignites from Mississippi and North Dakota have reburning efficiencies comparable to that of methane (Burch et al., 1991b, 1994). It has been demonstrated that in contrast to the findings related to the bituminous coals, heterogeneous reactions on the lignite char surface contribute higher NO reduction than the corresponding gas-phase NO reactions (Chen and Ma, 1996). The effectiveness of lignite during reburning has also been demonstrated in a 1.0 and a 0.1 MBtu pilot-scale combustion facilities (Payne et al., 1995; Pershing, 1995).

The effectiveness of lignite and lignite char in reburning is potentially attractive to the utilities and industries which are striving to seek economical means to meet the stringent regulations enforced by the Clean Air Amendments of 1990. While there are a number of ongoing projects targeted at demonstrating reburning with low rank coals, there is also an eminent need of base line data for evaluation and further development in the future, particularly in the areas of its variables, kinetics, and mechanisms of heterogeneous reburning. As stated in a recent review by Smoot et al. (1998), "Some test results show low-rank coal chars to be particularly effective reburning fuels, but much remains to be done to clarify the differences in reburning fuels and associated causes."

Char gasification by CO_2 and O_2 has been an active research topic in the last half of the century (Laurendeau, 1978; Essenhigh, 1981; Lahaye and Ehrburger, 1991). The catalytic nature of lignite char during the oxidation by CO_2 and O_2 has been recognized (Radovic et al., 1983a; Lizzio et al., 1990). The reaction of NO with char has also been a subject of intensive studies in the last two decades (De Soete, 1990; Aarna and Suuberg, 1997). The interactions of NO, char, CO_2, O_2, and other species in a reburning environment, including the reaction intermediates, however, consist of a complex reaction network and remain a challenging area of research. Indeed, heterogeneous reburning is governed by a large number of potentially important variables. In addition to the reaction mechanisms in reburning, char's origin (Chen and Ma, 1996) and its production history may also affect its efficiency of NO reduction. For instance, for the chars prepared in an inert gas, heating rate, peak temperature, and holding time during pyrolysis have been demonstrated to be important variables of char gasification by CO_2 and O_2; nevertheless,

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the extent of their influences on reburning effectiveness have not been studied.

Published work of the (NO + char) reaction revealed significant variations in their rates (De Soete, 1990; Aarna and Suuberg, 1997). These discrepancies may have been attributed at least partially, to the char preparation history discussed above. The characteristics of the various measurement methods adopted by various groups may have also contributed to these differences. Conversion data from reactors of different characteristics, in turn, often give rise to new insights concerning the reaction mechanisms. Moreover, the rate of NO reduction in the presence of other oxidants, CO_2 and O_2, has not been the focus of a systematic study. Cross comparison of the rates of NO reduction by chars of different origins, and preparation procedure in various gaseous environments are expected to yield mechanistic understandings.

This article presents our study of two areas of heterogeneous reburning, its variables and kinetics. Mechanistic implications from these studies are postulated and the potential of using a mixed fuel for reburning is assessed.

Experimental Studies

Brief description of reburning apparatus

Reburning experiments were carried out in a ceramic flow reactor (Burch et al., 1991b, 1994, Chen and Ma, 1996) with a simulated flue gas consisting of 16.8% CO_2, 1.95% O_2, and 0.1% NO in a helium base. These concentrations of CO_2, O_2, and NO were chosen to be consistent with those of a coal primary flame operated at a stoichiometric ratio of 1.1. Helium was used, instead of nitrogen, as the base gas to minimize the heatup time after the gas enters the reactor at room temperature. The flow reactor was an alumina tube (Coors Ceramics Co.) with an inside diameter of 1.91 cm and an overall length of 64 cm. The central portion of the reactor tube was enclosed in a 30-cm long, electrically heated furnace (Lindberg Model 55035), which provided tube temperatures up to 1,150°C. A particle feeder, which utilized controlled aerodynamic stripping of the powder surface by passing a carrier gas through a narrow, concentric space between a cylindrical piston and the inner wall of particle reservoir to affect the feed rate, was designed, fabricated, utilized (Burch et al., 1991a) and modified (Tang and Chen, 1999) for delivering coal, char, and catalyst particles at low and steady rates.

Most of the experiments were conducted in the temperature range of 800–1,100°C. Chars were usually fed at 0.0640 and 0.0446 g/min for the lignite and bituminous coal chars, respectively, which corresponded to the char feeding rates at stoichiometric ratio of reburning, or SR2, at about 0.9. The gas residence time in isothermal zone is about 0.2 s (Burch et al., 1991b).

Fixed gas species of interest was monitored by an online instrument package. The analysis included NO_x (chemiluminescence, Thermoelectron Model 10A), CO and CO_2 (infrared, California Analytical Instruments Model ZRH), and N_2O (infrared, Horiba Model VIA-510). Differences between the base gas used for the calibration gas and sample gas were found to produce significant instrument error. This is particularly true for chemiluminescent NO_x measurement, which relies on a constant gas flow through capillary tubes. Therefore, each of these instruments was calibrated with a gas mixture representative of the feed gas composition.

The reaction intermediates HCN and NH_3 were collected by diverting the reactor effluent through a straight tube impinger filled with 0.5 L of 0.1N HNO_3 aqueous solution for a specified time interval. The captured solutions were pH adjusted with NaOH and analyzed for CN^- and dissolved ammonia with specific ion electrodes (Orion Research). Poisoning of the cyanide electrode by sulfur ions was prevented by adding an aqueous solution to $Pb(NO_3)_2$ prior to adding the NaOH. Sulfide ions were precipitated as PbS. Due to the acidic nature of the impinger solution, recovery of HCN and NH_3 by this method was tested using known standards and found to be near quantitative for NH_3, but only 22% for HCN in the range of 100 to 700 ppm of HCN. Therefore, NH_3 values have been presented as measured, while HCN values reported have been corrected for collection efficiency.

Char particles after reburning were collected by a 10.16 cm I.D. × 20.32 cm height stainless-steel unit below the flow reactor which was designed based on inertia and gravity separation principles. A sharp change of the flow direction from downward to upward, and a decrease in gas velocity due to expansion, facilitated settling the particles on a Teflon plate sitting on a stainless-steel flange designed for easy opening and cleaning. About 70 wt. % of char particles was recovered by this procedure, and the remaining char particles were collected by an in-line filter in the downstream. Char particles removed from the collection unit, not from the in-line filter,

Table 1. Ultimate Analysis of Coals and Chars

Content %	MS Lignite	Pitt No 8 bituminous Coal	MS Lignite Char (950°C)	Pitt No. 8 Coal Char (950°C)	Ms Lignite Char (1,000°C)	Pitt No. 8 Coal Char (1,100°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	16.32*	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	9.00

*By difference.

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

Analyses were conducted by the Huffman Laboratories, Inc., Golden, CO.

were subject to elemental, surface area, and pore volume analyses. Gas residence time in the transfer lines, including that in the char/ash collection unit, is about 12 min.

Sample preparation and designation of sample code

A Mississippi lignite and a Pittsburgh No. 8 bituminous coal were ground, and particles in the range 100 to 140 mesh were used for the preparation of chars. Table 1 shows their elemental analysis. For the preparation of char, coal particles were pyrolyzed in N_2 by suspending a sample basket containing 12 g of coal into a 6.35 cm I.D. alumina tube electrically heated by a split-tube furnace (Thermcraft Model 23-18-12H), which has been discussed in an earlier article (Chen and Ma, 1996). Most of the chars were produced in an alumina basket, while selected samples were produced in a stainless-steel basket. Materials of the basket affect the reactivity of the char derived from the bituminous coal in reburning, and was a subject of our study.

To examine the effects of pyrolysis severity, chars were prepared using various procedures representing the combinations of two different heating rates, two peak temperatures, and three holding times. The two heating rates 0.45°C/s and 6°C/s were achieved by adopting two different experimental procedures. For the preparation of chars at high heating rate 6°C/s, the sample basket was placed into the preheated furnace for 5 min, which allowed the sample to reach the maximal temperature in 3 min and then remain at that temperature for about 2 min. The maximum sample temperature 950°C is about 50°C lower than the set temperature 1,000°C. This temperature profile was measured by a thermocouple immersed in the sample basket with sand particles. Quenching was achieved by raising the sample basket to a water-cooled, reversed-nitrogen gas-flow section for 25 min before removing it from the furnace.

For the preparation of char under the low heating rate 0.45°C/s, the sample basket was suspended into the furnace before the furnace power was turned on. The furnace temperature was raised from the room temperature to the peak temperatures, about 50°C lower than the set temperatures 1,000 or 1,150°C, in about 40 min. After the furnace reached the set temperature, the sample quenched immediately or kept in the furnace for another 5 min., or 2h. Quenching was achieved by the same procedure discussed above.

The pyrolysis procedure, including heating rate, final temperature, and holding time, did not generate noticeable affects on the weight-loss and elemental compositions of the chars; the procedure discussed above generated 45.0 wt. % and 61.8 wt % of chars from the lignite and the bituminous coal, respectively. Caked bituminous coal chars were ground and sieved again to the size range 100 to 140 mesh for simulated reburning experiments. Lignite chars do not agglomerate and do not require further grinding before reburning. Char samples were stored in sealed vials to minimize its contact with moisture and air.

For the convenience of our discussion, char were labeled by including the key variables used in preparing the samples. For example, the code L950/5F/C//NO/CO_2/O_2/1100 denotes that the lignite char was produced in a ceramic basket by fast heating to 950°C with a total pyrolysis time (5 min) followed by reburning in $(NO + CO_2 + O_2)$ at 1,100°C. The code B1100/5/S//NO/1100 denotes that the bituminous coal char was produced in a stainless-steel basket by slow heating to 1,100°C with a 5 min holding time, followed by reburning with NO at 1,100°C. All the temperatures stated are sample peak temperatures, which are approximately 50°C lower than the set temperatures.

Reactivities of chars produced from four different pyrolysis procedures have been investigated in the present study; in the order of pyrolysis severity, they are 950/5F, 950/0, 1,100/5, and 1,100/120. In the subsequent discussion, chars produced from less severe conditions such as 950/5F, will be referred to as the "young" chars, and those from the high severity such as 1,100/120 will be referred to as the "old" chars.

Surface area and pore volume analysis

Surface area and pore volume of char were determined before and after the experiments, with Quantachrome NOVA-1200 by both the N_2 BET method and the CO_2 Dubinin-Radushkevich (D-R) method (1947). The BET-surface areas of samples were measured with nitrogen 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 is P/P_0. Measurements were carried out under six different relative pressures P/P_0 with the multipoint method. The values of P/P_0, ranging from 0.05 to 0.30. comprised the linear region of the multipoint BET equation.

The CO_2 D−R method was carried out with carbon dioxide as the adsorbate at a temperature of 273 K. The P/P_0 ranging from 0.001 and 0.010 was within the region of the adsorption isotherm. The P/P_0 is small compared to that of the above measurements, because the adsorbate saturation vapor pressure P_0, at 273 K, is much larger than the atmospheric pressure. Measurements were carried out under eleven different levels of P/P_0 with the multipoint method. The surface area of each sample has been estimated by both the BET and D−R equations. Furthermore, the micropore volume and micropore surface area of each sample have been calculated with the D−R equation (Lowell, 1979). For a few selected samples, CO_2 D-R analyses were also conducted at 195 and 228 K.

Additional measurements were carried out to evaluate the micropore volume and total pore volume of the eight samples; nitrogen served as the adsorbate, and the desorption was conducted at 77 K. The micropore volume has been evaluated with the D−R equation, and the total pore volume, directly at P/P_0 close to 1. The average pore radius has been computed from the total pore volume and surface area as follows

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

where V_T is the total pore volume; and S is the surface area. Pore-size distributions were determined from the desorption isotherm. Detailed procedures for these analyses have been documented by Chen et al. (1997).

Summary of experiments

In order to study the effects of char preparation history on NO reduction, simulated reburning experiments were conducted with chars prepared under four sets of pyrolysis conditions: (a) 6°C/s heating rate, 950°C peak temperature, and 5 min total pyrolysis time; (b) 0.45°C/s heating rate, 950°C peak temperature, and zero holding time; (c) 0.45°C/s heating rate, 1,100°C peak temperature, and 5 min holding time; and (d) 0.45°C/s heating rate, 1,100°C peak temperature, and 2 h holding time. To investigate the effects of oxidants CO_2 and O_2, all four types of chars prepared by these procedures were subject to reactions at 1,100°C in three types of gaseous environments, NO, $NO + CO_2$, and $NO + CO_2 + O_2$.

The effects of grinding the bituminous coal before pyrolysis were investigated by examining the reburning activity of chars produced from three particle sizes: -140 mesh, $+140$ and -100 mesh, and 3 mm particles selected by hand. These particles were pyrolyzed with a heating rate of 0.45°C/s to 950°C and with a zero holding time. These caked chars were ground and sieved to $+140$ and -100 mesh before reburning with NO at 1,100°C.

To study the effects of NO concentration level in the feed, reburning experiments were conducted with feed NO at 400 and 1,000 ppm and in the temperature range from 800 to 1,100°C, with char feeding rates at 0.0640 and 0.0446 g/min for the lignite and bituminous coal chars, respectively.

To investigate the role of CO in heterogeneous reburning, additional CO was introduced in the feed with its concentration varied from 0 to 1,540 ppm. Since the alumina reactor wall has previously been demonstrated to be catalytic for NO reduction during the startup operation of a flow reactor involving CO, NO, and char (Levy et al., 1981), a series of "blank-tube" experiments, that is, runs with all the gas components but without char, were also conducted. To ensure that there are no interactions between the gas components in the transfer line under our steady-state experiments, experiments were performed at room temperature with known feed compositions: 1,000 ppm NO, 16.8% CO_2, 1.95% O_2 and CO, varying from 0 to 1,540 ppm. As expected, under steady state, the measured gas compositions were very consistent with the feed composition, indicating undetectable catalytic reactions.

During the course of this study, the data continued to reveal the significance of the role of char in the catalytic (NO + CO) reaction. Therefore, a novel concept for reburning, involving mixed fuels containing both a natural gas for NO reduction and a lignite ash for catalyzing the (NO + CO) reaction was postulated, and a set of experiments was designed and conducted. Simulated reburning was conducted at SR2 = 0.85 and 1,100°C. Mississippi and North Dakota lignite ashes were produced in a crucible over a Benson burner at 1 atm and with a 40 min oxidation time. During the reburning, lignite ash was fed at 0.005 g/min, a rate comparable to the amount of ash feeding rate when char is used as reburning fuel. For the comparison of catalytic activities, CaO was also used as a catalyst, and was fed at 0.01 g/min during reburning.

A few char/O_2 experiments were designed and conducted for two different reasons. First, the present study generated higher rate constants for the (NO + char) reaction than those published, and it was anticipated that a comparison of our char/O_2 rate with the widely accepted char/O_2 rate can give us some clues about the source of the discrepancies. Second, the literature contains conflicting conclusions concerning the relative rates of (NO + char) and (char + O_2) reaction. Experiments of char/O_2 reaction were conducted with 1.95 vol. % of O_2 in the feed at 1,100°C, and with the similar char feeding rates mentioned before.

Estimation of Rate Constants

A significant part of the current study is devoted to the estimation of rate constants of the (NO + char) reaction by resorting to the conversion data under various experimental conditions. Although electrically-heated tubular flow reactors, such as those used in the current study, have been commonly used for rate measurement in research laboratories, questions often arise concerning the effects of velocity profile, axial, and radial molecular diffusions, and axial temperature distribution on the measured conversion and estimated rate constants. These problems have recently been analyzed in detail through two examples involving the data collected from this study (Chen, 1999). In the first example, the Taylor-Aris criterions (Taylor, 1953, 1954; Aris, 1956), along with those established by Wehner and Wilhelm (1956), Wissler (1969), and Hunt (1977), were adopted in the justifications of estimating the rate constants based on the conversion data from our laminar flow reactor and a plug-flow reactor model. The second example addressed the effects of axial temperature distribution on the estimation of rate constants, including the Arrhenius rate constants and internal and external mass-transfer limitations. These justifications and algorithms form the basis of subsequent discussions of estimated intrinsic rates.

Implications of Surface Area Analysis

Surface areas of selected chars have been analyzed to gain better understandings about (1) the variations in surface area during pyrolysis, (2) the effects of the N_2 BET and CO_2 D–R methods on the conclusions derived from the measured rate constants, and, (3) the variations in surface area during heterogeneous reburning.

Figures 1 and 2 present the CO_2 D–R and N_2 BET surface areas, respectively, of raw chars derived from two different origins and various pyrolysis conditions. Note that samples 1 and 6 in these two figures denote chars derived from fast heating, while others are derived from slow heating. Under slow heating, the surface area of char, regardless of its origin, passes a maximum value during pyrolysis. This trend is particularly distinct for the N_2 BET surface area of lignite char. These results imply that the surface of the chars derived from zero holding time are covered by a small amount of products, or intermediates, of pyrolysis which seal the pores, but can be driven away by further heat treatment. The observed decrease in surface area of chars after a certain pyrolysis severity is likely due to a structural ordering of carbon, or graphitization, taking place at elevated temperatures (Radovic et al., 1983a,b; Sahu et al., 1988; Wong et al., 1995). The structural reorganization of the carbon matrix at higher pyrolysis temperature, up to 1,300°C, leads to closure of pore

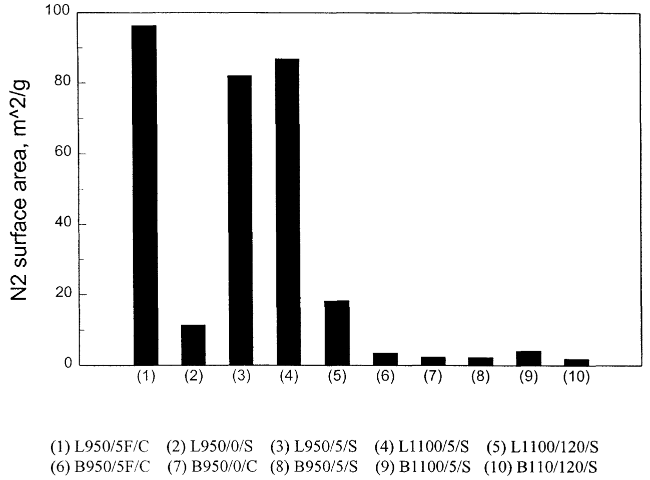


Figure 1. CO_2 D-R surface areas of chars derived from different origins and pyrolysis histories.

mouths and pore coalescence, thus reducing surface area. Recently, Thomas (1997) found that the surface area decreases very rapidly with increasing temperature of pyrolysis between 1,273 and 1,773 K.

The high CO_2 D−R surface areas of chars derived from fast heating are likely caused by the vigorous transport of a large amount of volatiles out of the char matrix during a short pyrolysis time. Under fast heating, the majority of the volatile products is driven out of coal within a fraction of a second (Howard, 1981), leaving pores with relatively large openings in the char matrix. Since these chars have the shortest residence time in the furnace during pyrolysis, the char surface is least ordered in structure and may retain a large amount of reactive products, or hydrocarbon intermediates. We will demonstrate that the chars derived from fast heating have the highest reactivity for NO reduction.

The surface areas generated from the N_2 BET and CO_2 D−R methods in Figures 1 and 2 are in good accord with those of Mahajan and Walker (1978) such that the micropores are not completely accessible to the nitrogen molecules at 77 K due to an activated diffusion process and/or shrinkage of pores. Adsorption of N_2 measures the area of the macropores, mesopores, and large micropores. However, CO_2 adsorption at relative higher temperatures, such as 273 K, measures the total surface area of chars, including that of the micropores.

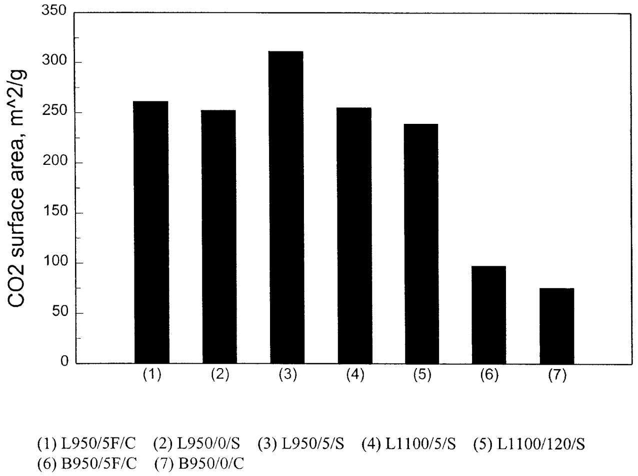


Figure 2. N_2 BET surface areas of chars derived from different origins and pyrolysis histories.

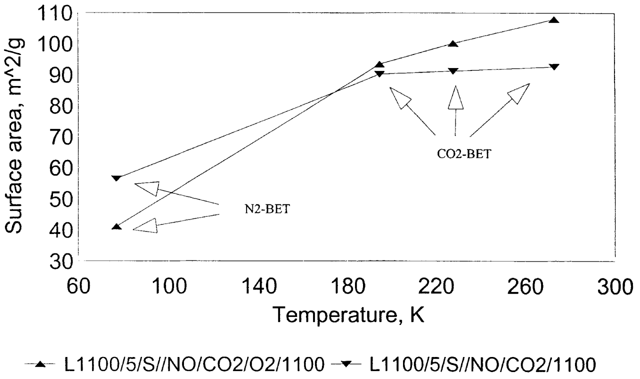


Figure 3. Adsorption temperature effects on the surface area of two lignite chars derived from two reburning environments.

To further examine the effects of adsorption temperature on the measured surface areas and micropore volumes of samples, two lignite chars after reburning, L1100/5/S//NO/CO_2/O_2/1100 and L1100/5/S//NO/CO_2/1100, were analyzed with adsorbate CO_2 at three different temperatures, 195, 228, and 273 K. Results in Figures 3 and 4 illustrate that the effects of adsorption temperature on the micropore volume and surface area are significant, especially for the lignite char. In comparison with the surface area obtained from the CO_2 D−R analysis at 273 K, it appears that 46 and 75.8% of the micropores are inaccessible to the adsorbates in CO_2 D−R analysis at 195 K and in N_2 BET analysis at 77 K, respectively.

Lignite chars usually have higher surface areas than bituminous-coal chars derived from the same pyrolysis condition.

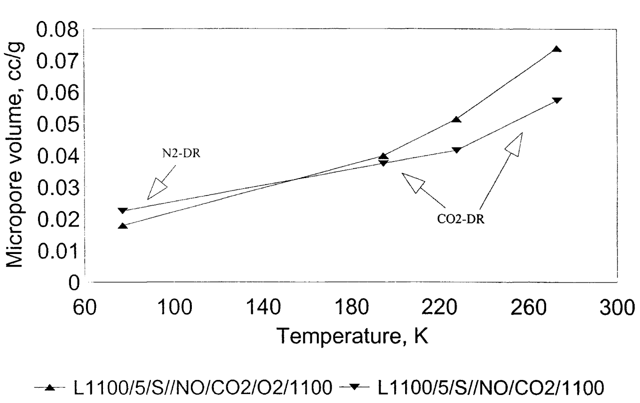


Figure 4. Adsorption temperature effect on the micropore volume of two lignite chars derived from two reburning environments.

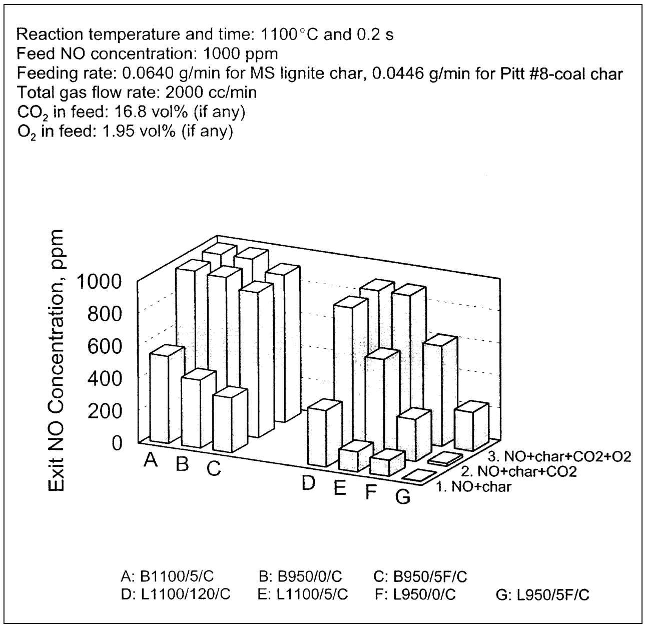


Figure 5. Char origins effects, char history, and oxidants on the exit NO concentration.

The feed composition corresponds to reburning at SR = 0.9 with either lignite char or bituminous-coal char.

After the chars are exposed to NO, CO_2 and O_2 in a simulated reburning environment for 0.2 s, the surface area of a lignite char notably decreases (such as from 261.3 to 209.9 m^2/g CO_2 D–R), while the surface area of a bituminous-coal char usually remains essentially the same (at about 73.0 m^2/g CO_2 D–R). It is possible that the decrease in internal surface area is due to the closure of micropores by forming oxygen complexes at the pore mouths. Using various desorption techniques, Lizzio et al. (1990) observed that there is a greater number of oxygen complexes formed on the lignite char surface than that on the bituminous coal char surface during gasification with CO_2. If the formation of these oxygen complexes indeed causes pore closure, the surface area data revels above represent a reduction of about 20% of the surface area during reburning. Due of the possibility of pore closures, CO_2 D–R surface area after reburning is used in the estimation of rate constants in the current study.

Char samples prepared by stainless-steel and alumina baskets during pyrolysis were selected for surface area analysis and no notable differences were observed.

Parameter Studies

Effects of char origin, char preparation history, and presence of CO_2 and O_2

Figure 5 depicts the effects of char origin, char preparation history, and presence of oxidants CO_2 and O_2 on NO reduction. The two groups of data presented in this figure, one for the lignite chars and, the other, for the bituminous-coal chars, are approximately based on the same reburning stoichiometric ratio. Therefore, NO reductions are compared based on approximately the same carbon content. Since NO has contact only with the exposed carbon surfaces during reburning, the reactivity based on unit surface area is also estimated, which is the focus of our kinetic study discussed later in this article.

Figure 5 illustrates, that, in the presence of CO_2 and O_2, the lignite chars are substantially more reactive than the bituminous-coal chars prepared under the same conditions. The presence of oxidants, CO_2 alone or CO_2 and O_2, at concentrations representative to those in reburning environments, is detrimental to NO reduction; however, its effects on the bituminous-coal chars are more severe than those on the lignite chars. Moreover, chars produced from pyrolysis either at a higher temperature or with a longer residence time have lower reactivities for NO reduction.

It has been reported that partially devolatilized coals possess higher reactivities for NO reduction and it is attributable to the bound hydrogen in the partially devolatilized coals (De Soete, 1990). Hydrogen evolution during coal pyrolysis is a slow process, and it takes place after hydrocarbons are driven out of the char (Howard, 1981). Radovic et al. (1983a) observed that the commonly-observed deactivation of char with increasing severity of pyrolysis conditions was correlated with their active surface areas, which, in turn, were determined by isothermal thermogravimetric analysis. The data in Figure 5 reveal the significant loss of char reactivity during pyrolysis and, from the standpoint of reburning by coal chars, the reactivities of "young" chars in typical flame conditions should be the focus of future studies. Most of the published works of NO/char reaction have been conducted with "old," or "clean," chars prepared from pyrolysis of high severity; 1 to 3 h pyrolysis time has been commonly employed.

The remarkable NO reburning efficiency of lignite char was demonstrated by Chen and Ma (1996). However, the differences of the lignite and bituminous-coal chars in reburning efficiencies observed by Chen and Ma (1996) appeared to be much larger than those published on the NO/char reactions in the absence of oxidants CO_2 and O_2. Although increasing pyrolysis severity, as discussed earlier, narrows the reactivity of chars of two different origins in a reburning environment without oxidants, questions also arose concerning the roles of the oxidants typically existing in reburning during the course of the current study. Data in Figure 5 demonstrate that CO_2 and O_2 are more detrimental to the bituminous-coal char than that to the lignite char. Therefore, the presence of CO_2 has only a minimum effect on the reactivity of the youngest lignite char (see experiment G in Figure 5).

Interesting trends are observed when the exit NO concentrations in Figure 5 are compared with the net yields of gasification products CO and CO_2, presented in Figure 6, which was generated based on data from the same set of reburning experiments. Introducing a 16.8 vol. % of CO_2 in the feed in experiment G results in a high yield of CO, 2.6 vol. %, and a net consumption of CO_2 which is apparently due to conversion of CO_2 to CO (see data set G5 in Figure 6). However, the presence of CO_2 causes only nominal increases in CO yields during reburning with the bituminous-coal charts. The high reactivity of lignite chars with CO_2 is likely due to the fast turnover of the reactive surface oxygen complexes (Lizzio et al., 1990), which, in turn, have been demonstrated to be catalytic in nature (Illan-Gomez et al., 1996a). Further examination of data in Figures 5 and 6 suggests that the high yields of CO are always accompanied with high NO reductions within the operating range of these experiments. Thus, correlation between these two compounds may be possible. Specifically, we speculate as to whether the catalytic (CO + NO) reaction plays a pivotal role in heterogeneous reburning.

Furusawa et al. (1982) discovered that, in the presence of H_2 and CO, char catalyzes the NO reduction, and the consumption of carbon in the char is nearly negligible. Tsujimura et al. (1983) found that CaO catalyzes the following (NO + CO) reaction at a rate higher than those of catalytic and noncatalytic NO reduction through char gasification

$$NO + CO \Rightarrow 1/2N_2 + CO_2 \tag{1}$$

The role of CO and rates of the catalytic reaction of (NO + CO) on various surfaces, including char, ash, and soot, have been critically reviewed by De Soete (1990). Levy et al. (1981), Chan et al. (1983), and De Soete (1990) suggested that upon increasing the concentration of NO in the gas phase, NO reduction on carbon shifts from the carbon gasification by NO toward the carbon-catalyzed (NO + CO) reaction. Therefore, during the carbon-catalyzed (NO + CO) reaction, CO appears to serve as a scavenger of surface oxygen complexes

$$C(O) + CO \Rightarrow C_f + CO_2 \tag{2}$$

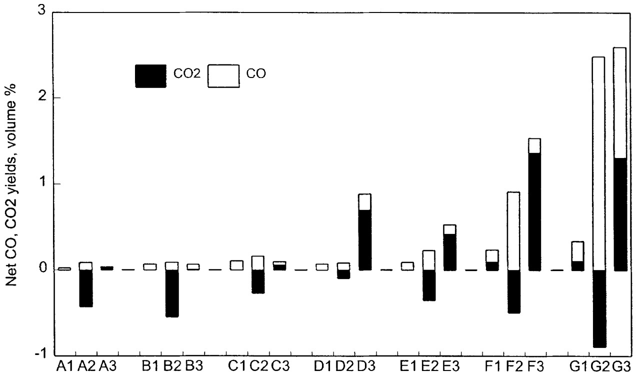
where the subscript f represents an unoccupied reactive site. Since desorption of surface oxygen to gaseous CO is usually considered a rate limiting step in NO reduction by char, the above reaction is a highly desirable alternate for freeing the reactive sites. The role of CO as a surface oxide scavenger was postulated by Semechkova and Frank-Kamenetzky in 1940, and it has been included in the interpretations of many combustion works in the last six decades (Reif, 1952; Blackwood and Ingeme, 1960; Laurendeau, 1978; Calo and Hall, 1991; Chen et al., 1993); nevertheless, the quantitative impact of this scavenging role of CO on NO reduction in reburning has not been systematically assessed. To further verify the role of CO in heterogeneous reburning, experiments have been designed and conducted with added CO, which is the subject of discussion in the latter subsection Role of CO.

When both O_2 and CO_2 are added in the feed at concentrations representative of reburning conditions, the exit NO concentration increases (Figure 5) and the yields of gasification products CO and CO_2 notably increase (Figure 6). Oxygen inhibits NO reduction because it competes with NO and CO_2 for reactive sites on the char surface, and consumes reducing agents, such as CO, in the system. Data in Figure 6 show that the yields of CO decrease and the yields of CO_2 increase after O_2 are introduced in the systems containing char/NO/CO_2. However, in the absence of CO_2 in the feed, char/O_2 reaction produces CO, and oxygen atoms are capable of gasifying surface C(O) thus producing additional reactive sites for NO adsorption. Both promote NO reduction. Indeed, published works contain conflicting results concerning the effects of oxygen on NO reduction. For instance, it has been shown that oxygen promotes NO reduction during NO/char reactions (Smith et al., 1959; Tucker, 1972; Suzuki et al., 1994; Aarna and Suuberg, 1997).

After critically reviewing various published works, De Soete (1990) concluded that oxygen inhibits NO reduction when the CO_2/CO ratio in the oxidation products is greater than one, and it promotes NO reduction when the ratio is smaller than one. High oxygen concentrations in the feed usually results in high CO_2/CO ratios. Moreover, since a fixed-bed reactor at the same feed oxygen concentration usually has a higher carbon-to-gas ratio than a flow reactor, such as that used in the present study, the former is expected to generate a lower CO_2/CO ratio than the latter. Indeed, data from our char/O_2 study, discussed in the Kinetics Studies section, indicate that the CO_2/CO ratios vary from 39 to 150 for chars derived from different origins and severity. Also, we have observed the detrimental effects of CO_2 and O_2, an observation, which is very different from that of fixed-bed studies (Aarna and Suuberg, 1997). In simulated reburning environments involving NO, CO_2 and O_2, the CO_2/CO ratios are even higher than that stated above, due to the presence of additional oxidants. Although the oxygen effects are not clearly understood, De Soete (1990) speculated that the (CO + NO) reaction, or the first reaction stated above, may be controlling at low CO_2 concentrations, and oxygen stripping of chemisorbed CO upon oxidation may be invoked.

Effects of reburning temperature and initial NO concentration

Figures 7 and 8 exhibit the temperature effects on the exit NO concentrations from reburning with lignite chars and bituminous-coal, respectively. Chars were prepared by different pyrolysis conditions. The effects of feed concentrations were studied by feeding NO at either 400 or 1,000 ppm. Results suggest that the effects of char origin and preparation history discussed in the preceding section are generally valid in the temperature range between 800 to 1,100°C. All these data sets are used for the estimation of rate constants, which will be discussed later.



A: B1100/5/C B: B950/0/C C: B950/5F/C
D: L1100/120/C E: L1100/5/C F: L950/0/C G: L950/5F/C
1: NO+char 2: NO+char+CO_2 3: NO+char+CO_2+O_2

Figure 6. Effects of char origins, char history, and oxidants on the net yields of carbon oxides (feed contains 16.8% CO_2, if any) from the reactions of NO with the chars.

Experimental conditions are identical to those in Figure 5.

Effects of particle size of a bituminous coal before pyrolysis

Particles of bituminous coal soften, swell, form volatiles-filled bubbles, and agglomerate during pyrolysis (Howard, 1981). The caked char has to be ground again before reburning and grinding, either before or after pyrolysis, and is likely to generate a higher fraction of the less crystalline, high reactivity carbons. Although particle size before pyrolysis is not usually considered an important variable in the laboratory studies of char reactivity after secondary grinding, it is included as a parameter here because grinding is a time-consuming step in the laboratory and we would like to know if the careful grinding and sieving are necessary before pyrolysis.

A Pittsburgh No. 8 coal was ground and sieved; two fractions after sieving, < 104 μm, 104 to 150 μm, and hand-picked 3 mm particles, were subject to pyrolysis and reburning study. These three char samples have essentially the same volatile matters, measured by weight loss during pyrolysis, and ash contents, measured by burning the samples in a Bunsen burner. The agglomerated chars were again ground and sieved. The fraction used in all other experiments, 104 to 150 μm, was used in the NO reduction studies at 1,100°C, in the absence of O_2 and CO_2. Exit NO concentrations from these experiments, (Figure 9) indicate that NO reduction of a bituminous coal are enhanced by using finer coal particles before devolatilization. However, it is not clear if the enhanced reactivity is caused by the increased fraction of the less crystalline carbons.

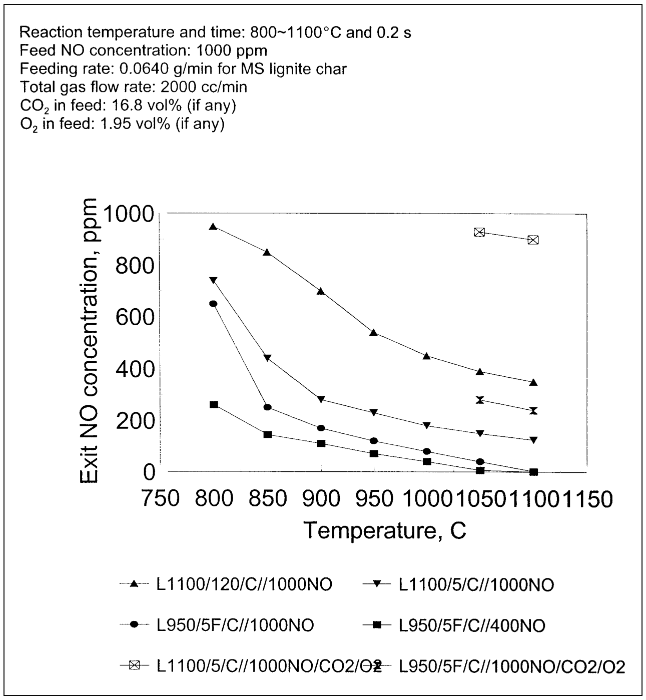


Figure 7. Effects of preparation history of lignite char, NO concentration in the feed, and gas composition on the exit NO concentration over a wide temperature range.

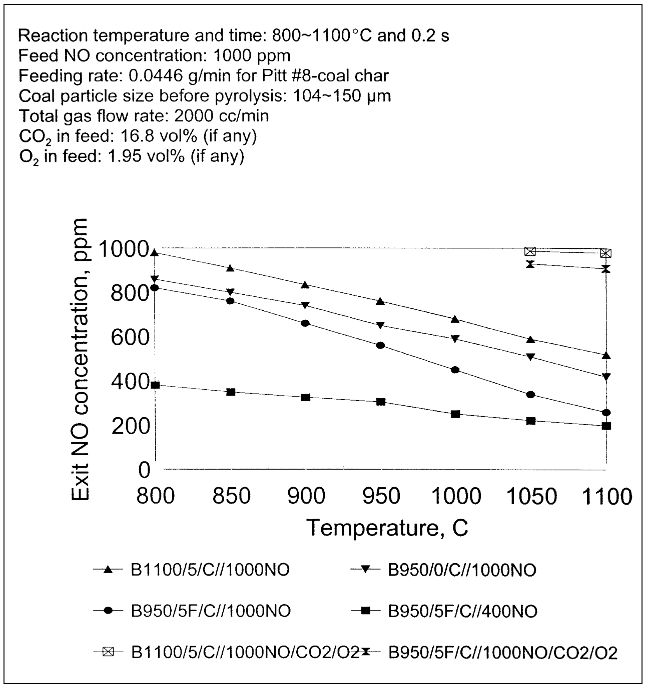


Figure 8. Effects of preparation history of bituminous-coal char, NO concentration in the feed, and gas composition on the exit NO concentration over a wide temperature range.

Effects of contact material in pyrolysis

Since different materials have been used in various research laboratories for the production of chars, reactivities of the chars produced from a stainless-steel sample basket and those from an alumina basket were compared (Figure 10). NO reductions by these chars were investigated without the presence of O_2 and CO_2. The chars derived from the stainless-steel basket, regardless of their origin, have notably lower NO reduction efficiencies below 950°C. This observation extends to temperatures greater than 950°C for the lignite char. Nevertheless, the reactivity of the bituminous-coal char derived from a stainless-steel basket dramatically increases above 950°C. Although the reason for this observation is not known, metal vapors from the stainless-steel basket during pyrolysis are likely to form deposits on the char surface which either promote or inhibit NO reduction.

Role of CO

To further verify the correlation between CO yield and NO reduction, CO was introduced incrementally into the feed of three series of experiments of simulated reburning: with a lignite char, with a bituminous-coal char, and with a "blank tube." The "blank-tube" experiments were conducted with all the components in the simulated flue gas, except, char. They were conducted to examine the extent of the wall-catalyzed (NO + CO) reaction, which was observed by Levy et al. (1981) in an unsteady-state flow reactor operation. The exit NO concentrations from these experiments are shown in Figure

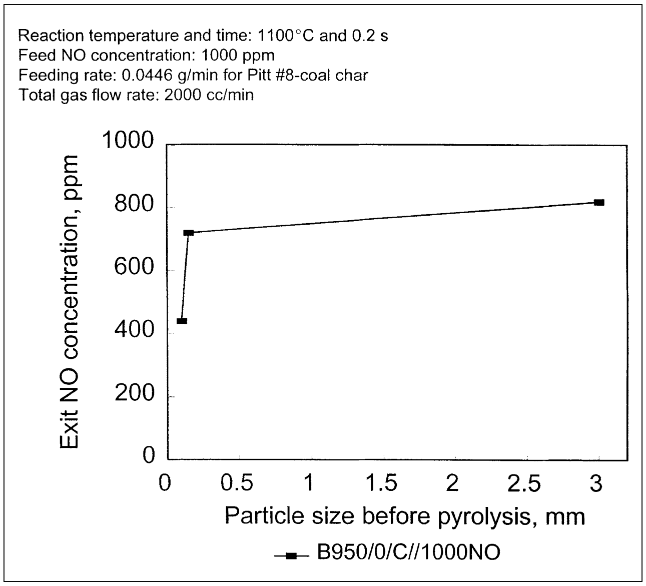


Figure 9. Effect of the particle size of bituminous coal before pyrolysis on the subsequent tests on NO reduction:

Three fractions of particles were tested: < 104 μm, 104 ~ 150 μm, and 3 mm.

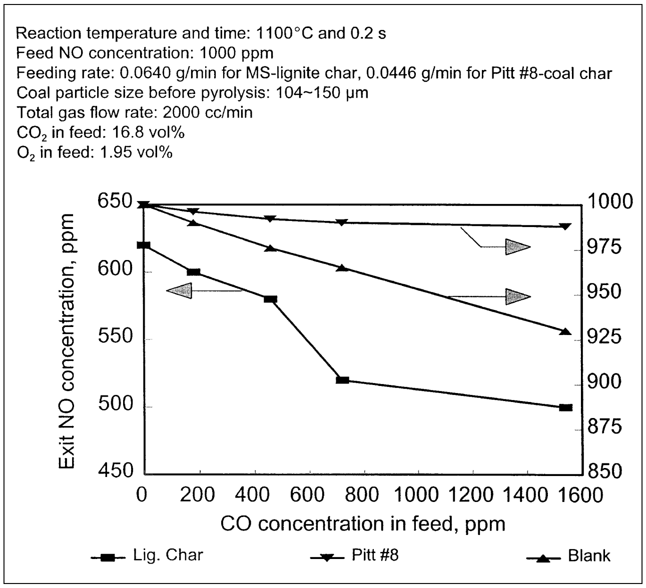


Figure 11. Effects of introducing additional CO on NO reduction during reburning with chars of two different origins L950/0/C//1100NO/CO_2/O_2 and B950/0/C//1100NO/CO_2/O_2.

Experiments with all the gaseous species expect char are labeled "blank."

11, and the net yields of CO and CO_2 that is, the feed concentrations subtracted from their exit concentrations, are presented in Figure 12.

Addition of CO in the reburning feed effectively enhances NO reduction on the lignite char, but it produces little effects on the reduction of NO on the bituminous-coal char. The data from the blank-tube experiments shown in Figure 11 imply that the wall-catalyzed (NO + CO) reactions are not negligible. Unexpectedly, however, the exit NO concentrations from reburning with bituminous-coal char are even higher

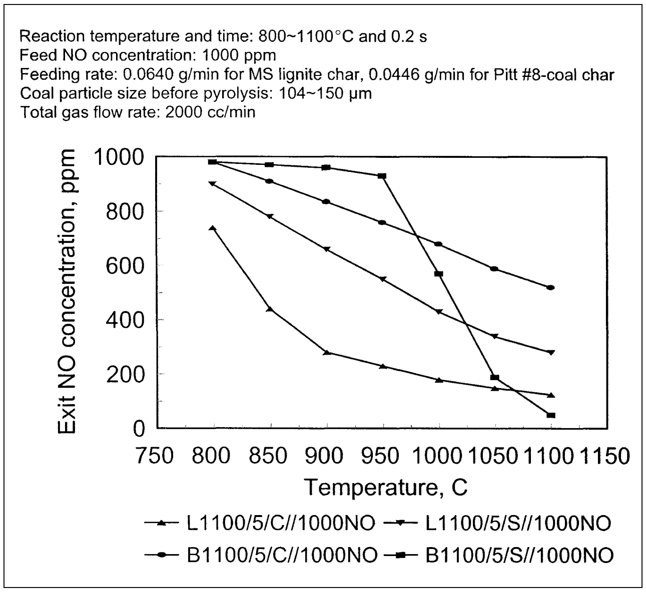


Figure 10. Effects of the basket material in pyrolysis on NO reduction.

C: ceramic, S; stainless steel.

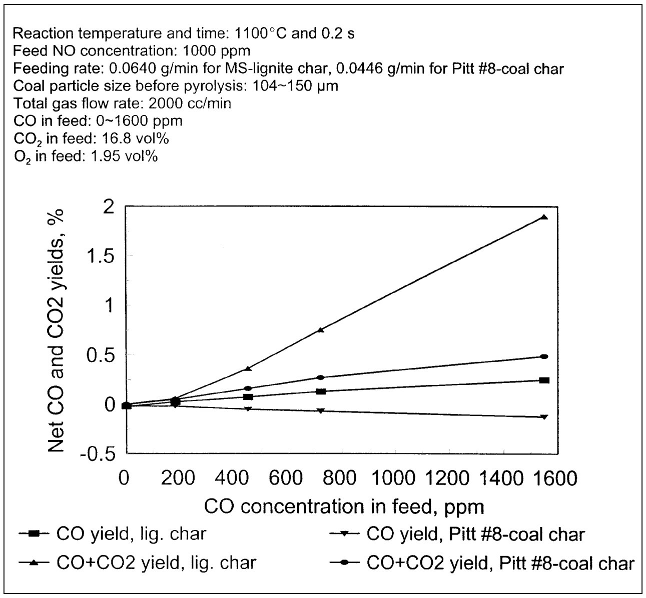


Figure 12. Net CO and CO_2 yields from reburning when additional CO is introduced in the reburning feed with lignite and bituminous-coal char, L950/0/C//1100NO/CO_2/O_2 and B950/0/C//1100NO/CO_2/O_2.

than those from the blank-tube experiments. The cause of this difference is not clear, but it is possible that the presence of char reduces the collisions of gas molecules with the catalytic reactor wall.

Data in Figure 12 suggest that the NO reductions contributed by the additional CO during reburning with the lignite char in Figure 11 are accompanied with sizable increases in CO_2 yields. Examination of the oxygen budget implies that these increases in CO_2 are attributable to the char oxidation by both NO and O_2. During reburning with the bituminous-coal char, addition of CO in the feed results in a small consumption of CO and a small increase in CO_2, (Figure 12) which is apparently due to the oxidation of CO to CO_2. However, during reburning with the lignite char, the net yield of CO increases slightly when additional CO is introduced (Figure 12). The sizable, absolute production of CO during reburning with lignite char, about 1% by volume (see the CO yield from the experiment F2 in Figure 6) seems to warrant a high NO reduction efficiency, even when CO is simultaneously consumed through scavenging surface C(O) in a NO reduction mechanism. The relation between CO and NO observed in Figures 11 and 12 are consistent with the postulate that CO serves as a scavenger of surface oxygen complexes during reburning with lignite char (Eq. 15) discussed above. The scavenging role of CO appears to be a pivotal reaction step in the overall heterogeneous reburning mechanism, which is discussed below.

For the (NO + char) reaction, or the char gasification by NO, a number of Langmuir-Hinselwood models have been postulated (De Soete, 1990; Teng et al., 1992; Illan-Gomez et al., 1996b). It is generally believed that char gasification by NO, similar to char gasification by CO_2 and O_2, involves the following kinetically-controlled elementary steps: (a) chemisorption of NO on the catalyst; (b) transfer of oxygen from the catalytically active sites to the carbon reactive sites; (c) desorption of oxygen from the carbon surface. Chars with a high content of metals such as Ca and K are expected to promote reactions steps a and b above, leaving the desorption step (c), a rate controlling step.

Desorption of surface oxygen complexes is not the only possible route for the production of reactive sites. In a reburning environment, NO, CO_2 and O_2 are the principle oxidizing agents and are potentially competitive for the reactive, or catalytic, sites for adsorption. Nevertheless, if their common oxidation product CO is capable of scavenging surface C(O), the reactive site will be regenerated and the barrier in an overall NO reduction mechanism discussed above is effectively reduced. Moreover, scavenging surface C(O) by CO(reaction 15) does not consume carbon in the char; therefore, unlike the desorption reaction, the oxygen surface complexes formed after dissociative adsorption of NO can be repeatedly removed by CO in a shuttling process of oxygen atoms. In other words, char serves as a catalyst in this step of the process.

In the overall NO reburning scheme, the effectiveness of lignite char appears to be its ability to minimize a number of reaction barriers: (1) it comprises catalytic components for chemisorption of both NO and O_2; (2) it contains a large amount of reactive sites for desorption of surface oxygen complexes and, therefore, the production of CO (Lizzio et al., 1990); (3) CO, in turn, serves as a scavenger of surface C(O) and liberates the reactive site. These reaction steps are potential rate-controlling for reburning with carbonaceous materials, such as bituminous-coal char; however, the catalytic features discussed above seem to render lignite char uniquely effective in reburning.

The role of CO in scavenging surface oxides may play an important, if not principal, role in a number of well documented combustion phenomena involving low NO productions. For instance, the commonly observed low conversions of lignite nitrogen in primary flames in comparison with that of a bituminous coal is likely due to the rapid, catalytic production of CO followed by CO scavenging of surface oxides during lignite combustion. It is also known that the flue gas of fluidized-bed combustion of lignite has lower NO concentrations than those from the pulverized coal combustion, and the interactions among NO, CO, and lignite char in the dense phase of the bed may have contributed to the low-NO production in the former.

At the present time, it is not certain if the utilities are willing to use a large amount of solid fuel in reburning. Nevertheless, if char serves as a catalyst in reburning, a mixed fuel containing a gaseous fuel and lignite char can be a potentially efficient substitute for heterogeneous reburning. A volatile fuel, such as methane, burns much faster than char; moreover, it depletes O_2, produces CO, and reduces NO on the char surface. To demonstrate this potentially attractive concept, reburning with mixed fuels has been investigated, which is discussed next.

Reburning with a mixed fuel

A set of experiments has been conducted to examine the feasibility of using natural gas as the primary fuel for reburning and lignite ashes as the catalyst. Figure 13 shows the yields of three major nitrogen species from heterogeneous reburning: NO, HCN, and NH_3. While NO is the reactant at 1,000 ppm in feed, HCN and NH_3 are two major intermediates

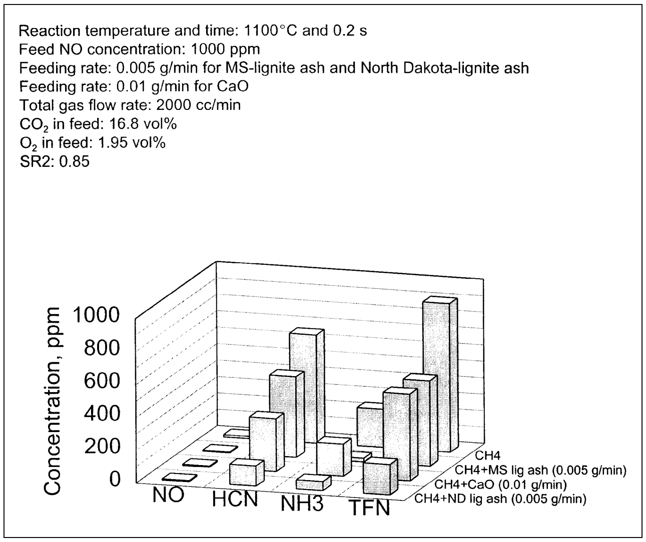


Figure 13. Reburning with a mixed fuel containing methane and lignite ash, or CaO.

before NH_3 is oxidized to N_2. The total yield of these nitrogenous compounds is called total fixed nitrogen, or TFN in short. Reburning with natural gas, or methane, has been adopted in utilities due to its effectiveness in NO reduction, and easy handling. However, reburning with methane produces a large amount of HCN, and a significant portion of this HCN will eventually be oxidized to form NO in the subsequent burnout stage of a full reburning process. Recycling of NH_3 to NO is relatively low, therefore, NH_3 is a more preferred intermediate than HCN. When lignite ash or calcium oxide is introduced in the reburning feed, the following results are observed (Figure 13):

(1) The ashes of Mississippi lignite and North Dakota lignite effectively catalyze the conversion of HCN to NH_3 and lower the TFN yields.

(2) CaO is a less effective catalyst than lignite ashes for the conversion of HCN, implying that CaO is not the only catalyst in lignite char.

(3) The ash of North Dakota lignite is more effective for the reduction of TFN than the ash of Mississippi lignite.

These observations reveal that the catalyst activities of lignite ash and char effectively reduce the yield of TFN. Specifically, reburning of 1,000 ppm of NO with a mixed fuel containing methane at $SR2 = 0.85$, and lignite ash at a feeding rate equivalent to ash concentration at $SR2 = 0.85$, generates only about 185 ppm TFN. With methane alone, reburning at the same condition generates about 900 ppm TFN.

The ashes and chars used in the current study were produced from straightforward burning and pyrolysis procedures in a laboratory; no attempts have been made either to maximize the surface areas and reactivities of these lignite products, or to investigate the effects of burnout level of lignite on reburning efficiency. Nevertheless, it is anticipated that reburning with a mixed fuel containing methane and lignite char can result in a TFN yield similar to, or better than, that from reburning with methane and lignite ash. Burch et al. (1991a) demonstrated that the presence of a lignite char contributes to a higher NO reduction in reburning with methane, which, in fact, supports the possible role of CO discussed in the proceeding section and the technological potential of using a mixed fuel in reburning. More importantly, it is anticipated that low level of TFN yield can be obtained at a higher SR2 because reburning with methane at a moderately fuel-rich condition, that is, $SR2 = 0.97$, produces 1% CO which is sufficient for scanvenging surface C(O) (Figures 5 and 6), and for provoking the cyclic oxygen turnover process on the char surface required for effective NO reduction. Present reburning technology is operated at a SR2 between 0.8 to 0.9. From the standpoint of reburning practice, higher SR2 implies a number of advantages: less reburning fuel is required, and less unburned carbon and nitrogen will enter the burnout stage. It should be noted that, in actual practice of reburning, maximum NO reduction can also be achieved by exercising various feeding options such as the feeding sequence and feeding geometry of the volatile and solid fuels.

Yield of Nitrous Oxide

The possibility of NO conversion to N_2O in reburning was first discussed by Kramlich et al. (1989). Therefore, the concentration of N_2O was routinely monitored during this study. The yields of nitrous oxide (N_2O) from the experiments of the present study have always been very low. For instance, reburning with the chars of two different origins and with the NO initial concentration at 1,000 ppm, the yields of N_2O vary between 7 and 10 ppm in the temperature range 800 to 1,100°C. Higher temperature favors lower yields of N_2O.

Kinetics Study

In the preceeding section, the efficiencies of the lignite and bituminous-coal chars have been compared based on the same stoichiometric ratio, that is, the same amount of carbon in reburning. Since not all the carbon atoms in the chars are exposed to the gases, rate of NO reduction based on unit surface area is estimated.

Table 2. Arrehenius' Constants and Mass-Transfer Limitations of NO ($[NO]_{in} = 1{,}000$ ppm) Reaction with Mississippi Lignite-Char and Pitt No. 8 Bituminous-Coal Char Based on CO_2 Surface Areas*

Reactants	$\ln k$ Mol/(s·m^2·atm)	$-k_0$ mol/(s·m^2·atm)	E_a kcal/mol	ϕ	η	Ω
L1100/120/C//NO 4-Equation model	−4.43	0.069	4.72	2.7	0.7	N/A
L1100/5/C//NO 4-Equation model	−3.27	0.116	2.99	6.3	0.4	N/A
L1100/5/C/NO 5-Equation model	−1.96	0.430	2.99	12	0.2	0.1
L950/5F/C//NO 4-equation model	−0.16	1.434×10^7	44.6	29	0.1	N/A
B950/5F/C//NO 4-equation model	0.2	269	14.4	55	0.1	N/A
B950/0/C//NO 4-equation model	−0.524	320	16.9	39	0.1	N/A
B1100/5/C//NO 4-equation model	−1.193	53.07	13.8	27.8	0.1	N/A
B950/5F/C//NO/CO_2/O_2 4-equation model	−3.683	1.359×10^4	35.4	7.9	0.3	N/A
B1100/5/C//NO/CO_2/O_2 4-equation model	−6.467	1.337×10^4	4.29×10^4	2.0	0.8	N/A

*Reaction time about 0.2s, temperature range 1,050-1,100°C.

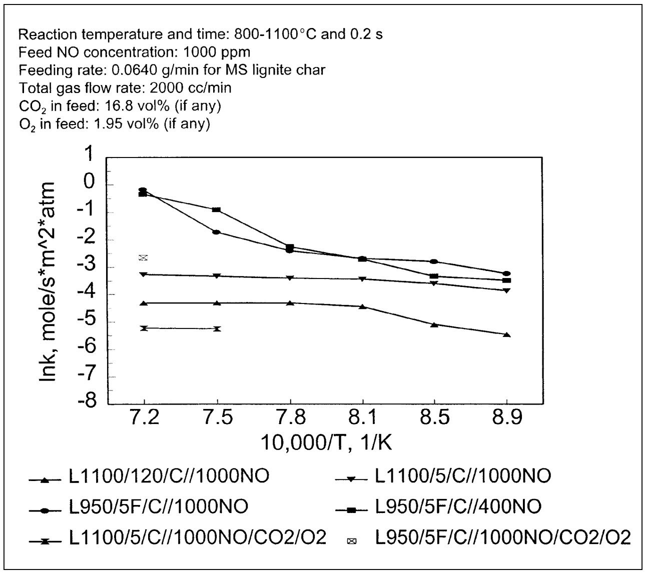


Figure 14. Arrhenius-plots for the NO reduction by lignite chars of varying age in various gaseous environments:

Surface areas were determined by CO_2 at 273 K with the D-R equation.

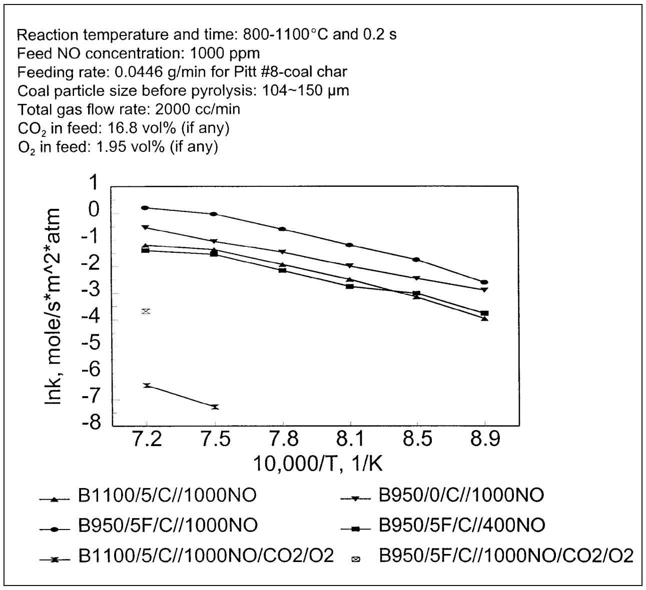


Figure 15. Arrhenius plots for the NO reduction by bituminous-coal chars of varying age in various gaseous environments.

Surface area determined by CO_2 at 273 K with the D-R equation.

Rate of NO reduction

The procedure presented earlier, including that shown in Figures 7 and 8, constitute the basis for the estimation of rate constants (see Tables 2 and 3), and Figures 14 and 15. CO_2 surface area of chars after simulated reburning are used in the rate calculation.

On the unit surface area basis, the "young" lignite char (see data labeled L950/5F/C//1100NO in Figure 14) has slightly lower rates for NO reduction than the bituminous-coal char produced from the identical pyrolysis conditions (see data labeled B950/5F/C//1100NO in Figure 15). The rate constants for both lignite and bituminous-coal chars decrease with increasing pyrolysis severity.

The results in Figure 14 suggest that the pyrolysis severity profoundly changes the activation energy for the reaction of (NO + lignite char), signifying the change in reaction mechanisms. However, its influence on the bituminous-coal char is minimal as depicted in Figure 15. The "old" lignite char has a very low activation energy for NO reduction, particularly at temperatures above 900°C. As a consequence, at temperatures about 800°C, the relatively "old" bituminous-coal char (see data labeled B1100/5/C//1000NO in Figure 15) has approximately the same rate constant as its lignite counterpart (see data labeled L1100/5/C/1000NO in Figure 14). This observation is consistent with those reported earlier, that old chars derived from low rank coals and bituminous coal have about the same reactivity for NO reduction (Teng et al., 1992). Nevertheless, at 1,100°C, the bituminous-coal char has a rate constant about two orders of magnitude in the natural logarithmic scale higher than that of the lignite char. This result

Table 3. Arrhenius' Constants and Mass-Transfer Limitations of O_2 ($[O_2]_{in}$ = 1.95 Vol %) Reaction with Mississippi Lignite-Char and Pitt No. 8 Bituminous-Coal Char Based on CO_2 Surface Areas*

Reactants	ln$k$ Mol/(s·m^2·atm)	k_0 mol (s·m^2·atm)	E_a kcal/Mol	Φ	η	Ω
L1100/5/C//O_2 4-Equation model	−2.76	696	24.9	8.2	0.32	N/A
L1100/5/C//O_2 5-equation model	−2.46	935	24.9	3.5	0.61	0.22
L950/5F/C//O_2 4-equation model	−3.93	16.1	18.0	1.7	0.85	N/A
L950/5F/C//O_2 5-equation model	−2.86	47.0	18.0	2.9	0.68	0.29
B950/5F/C//O_2 4-equation model	−2.80	0.128	2.0	12.4	0.22	N/A
B950/5F/C//O_2 5-equation model	−2.58	0.408	2.0	22.2	0.13	0.07
B1100/5/C//O_2 4-equation model	1.90	0.932	4.89	19.6	0.15	N/A

*Reaction time about 0.2 s, temperature range 1,050-1,100°C.

is unexpected, and the reason for this large difference is not clear. However, these observations imply the importance of preserving the char's reactivity by reducing the pyrolysis severity.

Although fine char powders between 104 μm and 150 μm are used in the experiments, the effectiveness factors estimated for these experiments are less than one (see Table 2) indicating that the transport limitations are not negligible. Lower effectiveness factors factors are observed when younger chars are used due to higher conversion of NO.

The effects of the feed NO concentration, at 400 and 1,000 ppm, are depicted in Figures 14 and 15. Recent development of low-NO_x burners has lowered the NO production in a primary flame to about 400 ppm. For the lignite char, the rate constants for the two series of experiments fall into essentially the same line implying the same reaction mechanisms. Linear regression of these two sets of data yields the following Arrhenius expression for the rate constant of NO reduction by the "youngest" lignite char produced in the current study, L950/5F/C.

$$k = 56{,}079 \exp\left(\frac{-32{,}335 \text{ call mol}}{RT}\right), \quad \text{in mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\text{atm}^{-1} \qquad (3)$$

For the bituminous-coal char shown in Figure 15, the rate constants for the two series of experiments indicate that the rate constant for the feed with 1,000 ppm of NO is about one order of magnitude higher than that for the feed at 400 ppm, but they have approximately the same activation energy. Linear regression of these two sets of data yields the following Arrhenius expression for the rate constant of reaction of 1,000 ppm NO and the "youngest"bituminous-coal char B950/5F/C

$$k = 515{,}725 \exp\left(\frac{-34{,}918 \text{ call mol}}{RT}\right), \quad \text{in mol } m^{-2}\cdot\text{s}^{-1}\cdot\text{atm}^{-1} \qquad (4)$$

Figures 14 and 15 also illustrate the effects of the presence of CO_2 and O_2 in reburning on the intrinsic rate of NO reduction. The rate constant for the "young" lignite char (see data labeled L950/5F/C in Figure 14) at 1,100°C decreases about two orders to magnitudes in the natural logarithmic scale after these oxidizing agents are introduced. The effect of these oxidizing agents on the reburning with the "young" bituminous-coal char (see data labeled B950/5F/C in Figure 15), however, results in a four-orders of magnitude decrease in its rate constant. Since the "young"lignite char has only a slightly lower reactivity than the "young" bituminous-coal char in the absence of CO_2 and O_2, the addition of these oxidants results in a higher reactivity of lignite char (see Figures 14 and 15). Although the reactivity of the "old" lignite char, as mentioned earlier, is much lower than that of the "old"bituminous-coal char, the effects of CO_2 and O_2 on the bituminous-coal char are so substantial that it results in a notably higher reactivity for the lignite char (see Figures 14 and 15). These findings evidently suggest that CO_2 and O_2 play a pivotal role in reburning with the lignite char. Interestingly, they are in good accord with the mechanisms discussed earlier that the oxidation product CO significantly promotes the NO reduction when lignite char is used.

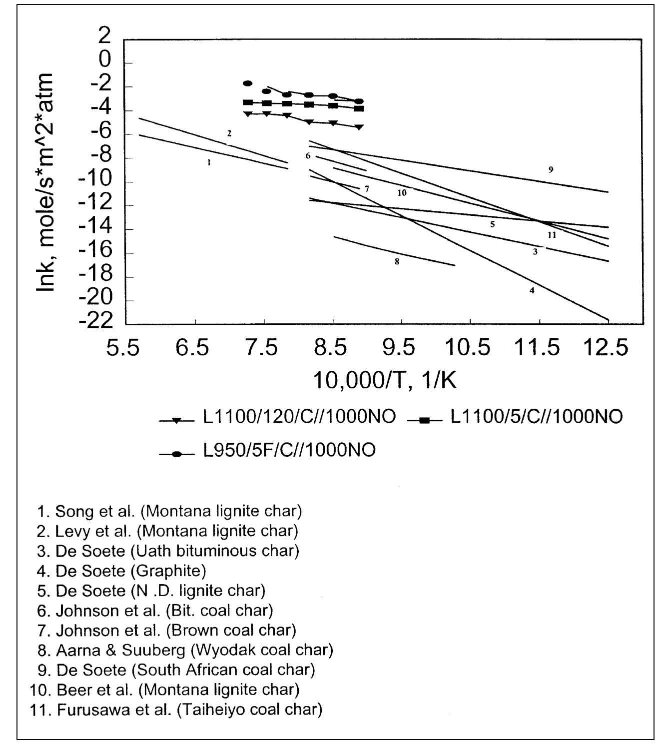


Figure 16. Arrhenius plots for the (NO + lignite char) reaction with published works.

Surface-areas of the current work were determined by CO_2 at 273 K with the D-R equation.

Comparison with published data

The rate of (NO + char) reaction has been subject of many studies. Large variations, about 10 orders of magnitude difference, have been reported in the literature. The rate constants calculated from the current study are even higher than those published (see Figures 16 and 17). However, these differences appear to imply the influences of a number of reactor and mechanistic characteristics which are discussed below.

It is noted that the rates estimated based on conversion data in various differential, fixed-bed reactors, and thermogravimetric analyzers, (Aarna, and Suuberg, 1997) are usually lower than those based on the conversions in entrained-flow reactors, (Song 1978; Levy et al., 1981; and the current study). The residence time used in a flow reactor is typically about two orders of magnitude higher than that used in a differential fixed-bed reactor. Moreover, the gaseous products of a gas/solid reaction have continuous contact with the solid particles before exiting a flow reactor. Therefore, it is speculated that secondary reactions may have contributed to the high rates of NO reduction in flow reactors. Interestingly, this speculation appears to be in good accord with the role of CO discussed above. The secondary reaction involving CO also implies the complexities of applying laboratory data to the

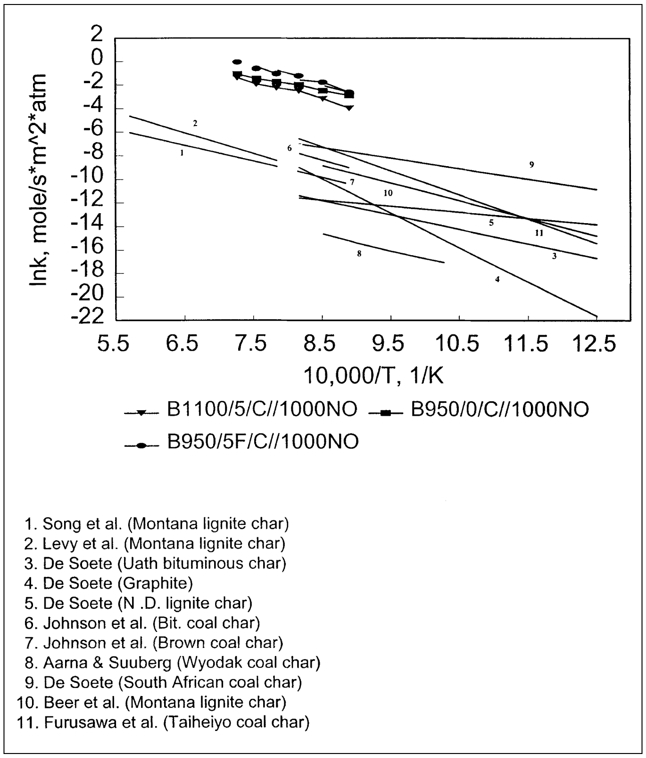


Figure 17. Arrhenius plots for the (NO + bituminous-coal char) reaction with published works:

Surface areas of the current work were determined by CO_2 at 273 K with the D-R equation.

prediction of NO reduction in a flame, because many published works have been conducted under the conditions of minimal influences of the secondary reactions.

Chars for the measurement of the rate of (NO + char) reaction have often been "cleaned" at high temperature for 1 to 3 h to minimize the influences of the volatile products of pyrolysis remaining on the char surface and those adsorbed on the char after pyrolysis. As illustrated in Figure 16, this cleaning procedure reduces the reactivity of lignite char produced by the current procedure by 4 orders of magnitudes on the natural logarithmic scale at 1,100°C. It should be noted that the youngest char was produced under fast heating and with a holding time about 5 min in the current study. Since most of the volatile hydrocarbons have evolved from the char (Howard, 1981) within a fraction of a second, it is therefore anticipated that lignite chars with even higher reactivities can be produced with shorter residence times in pyrolysis. For the bituminous-coal char, pyrolysis severity reduces the char's reactivity by about 2 orders of magnitude on the natural logarithmic scale. Literature contains limited quantitative information concerning char deactivation during pyrolysis; yet, many reactions in coal combustors rely on it.

Internal and external mass-transfer limitations are not negligible for all the cases (see Tables 2 and 3). Nevertheless, they are not always included in the estimation of rate constant of (NO + char) reaction in the published works, and may be a source of discrepancies shown in Figures 16 and 17.

The current study measures the rate constant of (NO + char) reaction in the first 0.6 s in a flow reactor, while the rate constants in a fixed-bed reactor are estimated based on conversions after the NO readings are stabilized, which usually takes a few minutes. Stable surface oxygen complexes may have formed during this period of time. For instance, Lizzio et al. (1990) have demonstrated the formation of relatively stable surface oxygen complexes during the reaction of char and CO_2, and the estimated rate constants may be retarded by the formation of these complexes.

Solid mixing and the temperature history of the various experimental setups can also play an important role in rate estimation. Specifically, our reactor tube has a 1.91 cm ID, and char particles have been injected into the reactor from a 0.635 cm O.D. tube. The ratio of the sizes of these tubes is much smaller than that used by Song (1978), a 0.159 cm O.D. tube for feeding particles at high velocity along the centerline into a 5.08 cm ID reactor. Moreover, one-half of the total gas flow in the current study is fed through a horizontal side tube with a 90-degree angle from the vertical stream to induce swirl and better mixing before the mixture enters the heated section of the furnace. Better mixing results in better particle distribution in the flow reactor, and higher rate constants than those which are less well mixed.

Rate Constants: NO/Char and O_2/char reactions

Experiments for the estimation of the rate constants of the (char + O_2) reaction have been conducted for two independent purposes. First, the rate constant of the (char + O_2) reaction has often been compared with that of the (char + NO) reaction in the literature, and conflicting results have been reported. Chars produced from severe pyrolysis conditions have often been the focuses of those studies. Thus, further comparison of their rate constants appears necessary, especially for the chars produced from relatively less severe pyrolysis conditions. Second, since the rate constants of the (char + NO) reaction generated from the current study are consistently higher than that of those published, it is anticipated that a comparison of the published rate of the (char + O_2) reaction with those generated from the current study will verify that the calculation algorithm established above and provide additional insights, especially those concerning the characteristics of various reacting systems.

Oxidation was conducted with either 1.95 vol. % of O_2 or 0.1 vol. % of NO at 1,100°C, and char of two different origins, lignite and bituminous coal, and of two levels of pyrolysis severity, one from fast heating and the other from slow heating to 1,100°C for 5 min. To compare the rate constants of the (NO + char) reaction with that of the (O_2 + char) reaction, Eq. 8 was adopted. The rates of both reactions are assumed to be first order with respect to the oxidant partial pressure. The conversion of oxygen X for the (O_2 + char) reaction, is defined as

$$x_{\text{oxygen}} = \frac{\text{exit conc. of } CO_2 + \dfrac{\text{exit conc. of CO}}{2}}{\text{oxygen conc. in feed}}. \qquad (5)$$

Equations 8 through 10 and Eq. 13 have been solved simultaneously by MathCad and the results are shown in Table 3.

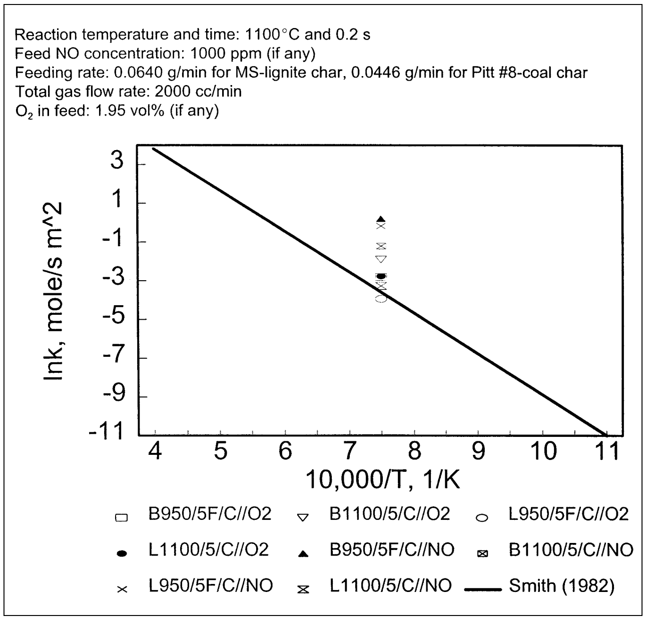


Figure 18. Arrhenius rates of (NO + char) and (O_2 + char) reactions of the current work with the Arrhenius rate of char oxidation, (O_2 + char), reported by Smith (1982).

The Arrhenius rate expression of (O_2 + char) reaction of Smith (1982), the straight line in the figure, is

$$k = 2.54 \times 10^5 \exp\left(\frac{-42{,}850 \text{ cal/mol}}{RT} \right),$$

$$\text{in mol} \cdot m^{-2} \cdot s^{-1} \cdot atm^{-1}$$

Smith (1982) critically reviewed the published rate of the (char + O_2) reaction and found that the data scattered around the following Arrhenius expression for the intrinsic rate constant

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

or

$$k_{\text{oxygen}} = 2.54 \times 10^5 \exp(-42{,}850 \text{ cal}/RT) \text{ in mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}.$$

At 1,100°C, these expressions give the following values

$$k_{\text{oxygen,1,100C}} = 4.6 \times 10^{-5} \text{g}_c \cdot \text{cm}^{-2} \cdot \text{s}^{-1},$$

or

$$k_{\text{oxygen,1,100C}} = 3.83 \times 10^{-2} \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}.$$

Note that the intrinsic rates of chars of two different origins from the current study fall well within the fluctuation range of the rate of (char + O_2) reaction recommended by Smith (1982) (see Figure 18). This observed consistency in the rate constant of the (char + O_2) reaction assures the quality of the data and estimation algorithm. More importantly, it also assures the quality of the rate constants of the (NO + char) reactions, as the same algorithm has also been adopted. Thus, the observed high rates of NO reduction in a flow reactor, discussed in the proceeding section, is likely attributable to the secondary reations, such as the char catalyzed (NO + CO) reaction, and the differences in reactor characteristics, as discussed in proceeding section. Data in Figure 18 also demonstrate that the chars derived from less severe conditions in pyrolysis also exhibit higher rates of (char + O_2) reaction, an expected result of char deactivation.

Although the contribution of a secondary reaction to NO reduction can be substantial in a flow reactor, the rates of (NO + char) reaction at 1,100°C are also plotted in Figure 18 for comparison, and data for chars of two different origins and those derived from two different pyrolysis severities are included. These rates of reaction are one or two orders of magnitudes in the logarithmic scale higher than that of Smith suggested for the (char + O_2) reaction. Similar findings have also been observed by Chu and Schmidt (1993) for char oxidation at temperatures below 700°C. Interesingly, Song (1978) and Teng et al. (1992) reported that the rate of (char + O_2) reaction is about two orders of magnitude higher than the rate for (char + NO) reaction. As mentioned in the preceding section, direct comparison is difficult due to the various reactor and char characteristics. Moreover, breaking point often appears in the Arrhenius plot for the (NO + char) reaction (Teng et al., 1992), which prohibits extrapolation for comparison.

Conclusions

The process potential of heterogeneous reburning has been evaluated by investigation its variables and kinetics. Evidence suggests that, in the absence of CO_2 and O_2, the intrinsic rate of NO reduction by a lignite char is comparable to that of a bituminous-coal char. However, in a reburning environment the intrinsic rate of NO reduction by lignite char is much higher than those by bituminous coal coal char due to lignite's ability to promote two consectuive reactions: (1) the catalytic gasification of char by CO_2 and O_2 for production of CO; (2) the removal of surface oxygen complexes, including those formed after adsorption of NO, by gaseous CO, for the regeneration of reactive sites. Lignite char, particularly that from the less severe pyrolysis, reacts vigorously with CO_2 and O_2 during reburning, and produces CO at a concentration as high as 1%. Carbon monoxide effectively scavenges the oxygen complexes on the char surface and liberates the reactive sites, thus, resulting in sustained shuttling of oxygen atoms and substantial reduction of NO. This role of CO is supported by the following observations.

(1) Within the experimental ranges of the current study, high NO reduction is always accompanied with high CO production in the isolated reburning stage.

(2) Introducing additional CO in the feed of the simulated reburning with lignite char promotes further NO reduction; the additional NO reduction is accompanied with a noticeable CO_2 production.

(3) Effective NO reduction has been observed when a mixed fuel, containing methane and a lignite char, is used for reburning.

(4) The intrinsic rates of NO reduction estimated by resorting to the conversion in a flow reactor are usually higher than those from fixed-bed reactors, signifying the possible role of secondary reactions between the volatile products and the entrained char, such as scanvenging of surface oxygen complexes by CO.

The role of CO discussed above implies that the use of a mixed fuel, containing a volatile fuel and lignite char or lignite ash, can be a potentially very attractive technology for NO reduction. Moreover, lignite char or ash catalyzes the conversion of HCN to NH_3; HCN is an important intermediate which has a higher recycle ratio to NO than NH_3 in the burnout stage. These characteristics of lignite char render the possibility of operating the advanced reburning at stoichiometric ratios much higher than those normally used $SR2 = 0.8$ to 0.9 for effective NO reduction, and, therefore, warrants minimum production of CO and unburned hydrocarbons in the burnout stage.

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