PARAMETERS, KINETICS AND MECHANISMS OF HETEROGENEOUS REBURNING

Wei-Yin Chen and Lin Tang
Department of Chemical Engineering, Anderson Hall
The University of Mississippi, University, MS 38677-9740

Introduction

Reburning is an emerging three-stage combustion technology designed for the reduction of NO by introducing a small amount of reburning fuel above the primary flame where the majority of NO is chemically reduced to nitrogen in the fuel rich environment. Recently, we have demonstrated that lignites and lignite-derived chars are an effective class of fuels for NO reduction in reburning [1, 2] and the heterogeneous mechanisms contribute greatly to the overall NO reduction [3]. To further research the technological potential of reburning involving char, the objectives of this study focus on the variables, kinetics and mechanisms of heterogeneous reburning. The effects of char origin, pyrolysis severity and gas composition have been studied. Furthermore, the effect of particle size of a bituminous coal before pyrolysis on reburning efficiency have also been examined. Intrinsic rates of NO reduction have been estimated in various gaseous environments; implications of Langmuir-Hinshelwood mechanisms and mass transfer limitations have been examined.

Experimental

Reburning experiments have been conducted with chars in an alumina flow reactor with a simulated flue gas consisting of 16.8% carbon dioxide, 1.95% oxygen, and 0.1% NO in a helium base. The above concentrations have been chosen to be consistent with those of a coal primary flame operated at a stoichiometric ratio of 1.1. The reburning temperatures are from 800°C to 1100°C. The estimated residence time is about 0.2 s. NO has been analyzed by a chemiluminescent NO-NO_x analyzer. CO_2, CO and N_2O have been analyzed by infrared gas analyzers.

Chars derived from the Pittsburgh #8 bituminous coal and the Mississippi lignite have been produced in N_2 by suspending a sample basket in a tube furnace at various temperatures with a low (0.5°C/s) heating rate and a high (6°C/s) heating rate and with different holding times. Most of the chars have been produced in an alumina basket, while selected samples have been produced in a stainless-steel basket. After the furnace reached the set temperature, the sample is kept in the furnace for another pre-determined time period, 0, 5 min or 2 h. For high heating rate, the holding time is 5 min. Quenching is achieved by raising the sample basket to a water-cooled, reversed-nitrogen gas flow section for 25 minutes before removal from the furnace.

Results and Discussion

Parameter study has revealed that the effectiveness of heterogeneous reburning strongly depends on variables in three areas: (1) the origin of char, (2) char devolatilization temperature, time and heating rate, and, (3) the concentrations of CO_2, O_2, and CO. The exit NO concentrations presented in Figure 1 suggest that the pyrolysis holding time is a very significant variable in the determination of char activity, particularly for the lignite char. Long pyrolysis time severely destroys the char reactivities. The lignite chars are substantially more reactive with NO than the bituminous coal chars. Samples which are devolatilized with a higher heating rate have a shorter residence time inside the reactor, and are more reactive than those derived from slow heating (0.5°C/s). Since most published rate data for the NO/char reaction were collected from experiments where chars were prepared with 1 to 3 h pyrolysis time, their rates are expected to be lower than ours. Furthermore, since devolatilization completes within a fraction of a second under rapid heating, shorter pyrolysis time is not expected to significantly affect the devolatization level. Our study implies that future studies on NO/char interactions should focus on "younger" chars derived from rapid heating and shorter residence times.

CO_2 and O_2 are more detrimental to the bituminous coal char than that to the lignite char. Addition of CO enhances the NO reduction by the lignite char, as shown in Figure 2; this enhancement in NO reduction is accompanied with CO_2 production implying the possible role of CO as a scavenger of surface oxygen complexes, i.e., $C(O) + CO \rightarrow C_f + CO_2$. Effect of CO on NO reduction by the bituminous coal char is insignificant. Chars produced from a stainless-steel sample basket during pyrolysis have higher reactivities with NO than those from a alumina basket, indicating the catalytic effects of redeposited metal vapor from the stainless-steel basket. Another interesting observation is that the chars derived from the smaller particles of the bituminous coal before pyrolysis, <78µm, have higher reactivities during reburning than those from the larger particles, even the coked chars have been reground and the particles in the same size range have been used in the reactivity study.

The effect of the laminar flow pattern on the rate resorting to a plug flow reactor model has been shown to be small. To begin this analysis, the flow region based on the Peclet number has been determined, and an axial dispersion model is selected for the subsequent analysis. The extent of external and internal mass transfer limitations have also been estimated. Solving a set of equations simultaneously with MathCad gives the frequency factor, activation energy, Thiele modulus, and effectiveness factor. The calculated results imply that the internal mass transfer limitations exist only for the lignite. External mass transfer rate is in the same order of magnitude as the intrinsic reaction rate at 1100°C indicating minimal external mass transfer limitations. As expected, the younger chars have higher reaction rates than older chars, and the rates of the older chars are favorably compared with the data in the literature. The present study also suggests that the intrinsic gasification rate of char/NO reaction is about the same as, or even higher than, the rate of char/O_2 reaction at 1100°C.

Conclusions

The results from this program reveal that heterogeneous reburning is a potentially significant approach for NO control. 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.

1. Efficiency of heterogeneous reburning is governed by origin of char, pyrolysis time, temperature and heating rate, and the concentrations of CO, CO_2 and O_2 in reburning.
2. NO reduction efficiency of a bituminous coal char can be enhanced by using smaller coal particles (<78μm) before pyrolysis.
3. CO appears to serve as a surface oxygen complex scavenger during reburning with lignite char.
4. Internal mass transfer limitations exist only for the lignite. External mass transfer limitation appears insignificant.
5. The intrinsic gasification rate of char/NO reaction has the same order of magnitude as the rate of char/O_2 reaction at 1100°C.

Acknowledgments

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References

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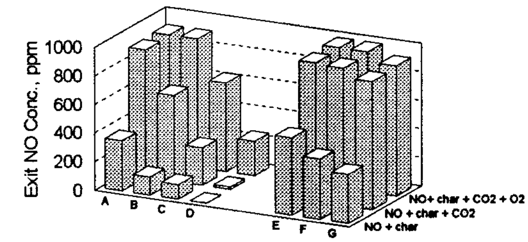
Reaction Temperature and Time: 1100°C and 0.2 s
Feed NO Conc.: 1000 ppm
Feeding Rate: 0.0640 g/min for MS lignite char
Feeding Rate: 0.0446 g/min for Pitt #8 coal char
Total Gas Flow Rate: 2000 cc/min
CO_2 in Feed: 16.8 vol% (if any)
O_2 in Feed: 1.59 vol% (if any)



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

Figure 1. Effects of char origins, history, and oxidants on exit NO concentration. The NO to char ratios correspond to agent used in reburning at SR2 = 0.95 and 0.90 for the lignite char and bituminous coal char, respectively.

Pyrolysis History: 950°C, 0 holding time, low heating rate
Reaction Temperature and Time: 1100°C and 0.2 s
Feeding Rate: 0.0640 g/min for MS lignite char
Feeding Rate: 0.0446 g/min for Pitt #8 coal char
Total Gas Flow Rate: 2000 cc/min
Feed Composition: 16.8 vol% CO_2, 1.95 vol% O_2, and 1000 ppm NO

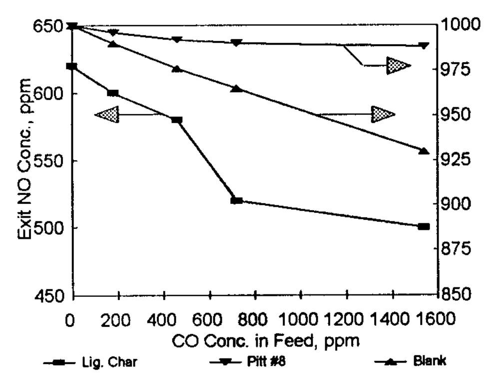


Figure 2. The effects of addition of CO on NO reduction during reburning with chars of two different origins. Experiments with all the gaseous species except the char are labeled "blank."