N_2O REDUCTION BY COALS AND CHARS

Wei-Yin Chen and Xia Zhang
Department of Chemical Engineering, Anderson Hall
The University of Mississippi, University, MS 38677

Introduction

The increase in nitrous oxide (N_2O) in the atmosphere upon switching to fluidized bed combustion has caused environmental concerns since it is known to be involved in greenhouse effect and ozone depletion. Recent efforts have revealed that afterburning [1] and reburning [2] are effective routes for in-furnace control of N_2O. Both approaches involve introduction of a secondary fuel where the majority of N_2O is chemically reduced to nitrogen. Afterburning is operated under fuel lean, while reburning is operated under fuel rich conditions. Both have N_2O reduction potential over 90% without adverse effects. The published work, however, lacks information about the utilization of solid fuels, such as coals, for N_2O reduction in reburning. The objective of this study is to explore the potential of N_2O reduction by coals and chars of different origins in a gaseous environment similar to that of the dense phase of a fluidized bed coal combustor or that of reburning. Emphases have been placed on the comparisons of 1) the effectiveness of solid and gaseous fuels, and, 2) the levels of homogeneous and heterogeneous mechanisms.

Experimental

Experiments have been carried out in a alumina flow reactor with a simulated flue gas consisting of 16.8 or 14.8% CO_2, 1.95 or 4.23% O_2 and 150 ppm N_2O in a helium base, which resembles the flue gas of a coal-fired boiler at a stoichiometric ratio 1.1 or 1.25. A detail description of this reactor and experimental setup can be found elsewhere [3, 4]. Pittsburgh #8 bituminous coal and its char, Mississippi lignite and its char, methane and CO have been used as the reburning fuels. Chars have been produced in N_2 by pyrolyzing a coal sample in a alumina-tube furnace from the room temperature to 950°C with two different sets of heating rates and holding times, 0.5°C/s and 0 min, and 6°C/s and 5 min. Blank-tube experiments, i.e., runs with the all the feed components except the reburning fuel, have been conducted to obtain the homogeneous phase, thermal decomposition levels of N_2O at various temperatures, with different gas compositions and gas flowrates. In the subsequent reburning experiments, N_2O has been fed at higher concentrations so that the exit N_2O concentration from the corresponding blank-tube experiments is always maintained at 150 ppm. To evaluate the contributions of the homogeneous and the heterogeneous N_2O reduction mechanisms, reburning with chars has been conducted and the results are compared with those from

reburning with their parent coal/lignite. Furthermore, net N_2O productions from the volatile portion of the coal/lignite during reburning have been experimentally measured with the feed containing all species except N_2O; the overall N_2O reductions contributed by reburning have then been estimated by subtracting the N_2O productions contributed by the coal-derived volatiles from the exit N_2O concentrations in reburning.

Results and Discussion

The reduction efficiencies of these reburning fuels can be ranked based on the exit N_2O concentrations after reburning or after a full three-staged combustion process. If the N_2O concentrations from reburning stage are chosen for comparison, the efficiencies can be further be evaluated resorting to the stoichiometric ratio of reburning stage (SR2), per unit carbon, or per unit energy fed into the reburning. After the N_2O productions contributed by the coal-derived volatiles from the exit N_2O concentrations in reburning, the rank based on SR2 can be listed as following: CO > Mississippi lignite ≥ methane ≈ Pittsburgh #8 bituminous coal > lignite char > bituminous coal char, as shown in Figure 1. Nevertheless, to achieve the same variation in SR2, the required quantity of CO is about 20 times of that of methane due to the 1:1 atomic ratio of carbon to oxygen of CO, the rank of CO based on the amount of carbon becomes lower than that based on SR2. Similarly, lignite has about 16% of oxygen, and its efficiency becomes lower if carbon quantity is adopted in the ranking. The N_2O reduction efficiency based on carbon quantity becomes: methane > lignite ≥ bituminous coal ≥ CO > lignite char > bituminous coal char. When the efficiencies are arranged by the unit heat input of the reburning fuels, the difference between the gaseous fuels and the two solid fuels, coal and lignite becomes very small: methane ≥ CO ≥ lignite ≥ bituminous coal > lignite char > bituminous coal char. The ranking of the two gaseous fuels and coal is consistent with those based on the reburning temperature reported by Rutar et al. [2].

The conversions of volatile-nitrogen of coal and lignite to N_2O are less than 20 ppm, or less than 10%, above SR2=0.9; therefore, in this SR2 region, the volatile-nitrogen conversions to N_2O during reburning with coal/lignite do not affect the ranking discussed above. Coal and lignite are much more effective N_2O reduction agents than their chars at 850°C. Due to the high conversion of volatile-nitrogen to N_2O at lower stoichiometric ratios, the optimal exit N_2O yield occurs at about

SR2=0.9 for bituminous coal reburning and above 0.95 for lignite reburning. At these conditions, the exit N_2O concentrations are minimal, and about 70% of N_2O reductions has been achieved. Reburning with chars results in little N_2O reduction when the SR2 is above 0.9. In Figure 2, the efficiencies of reburning with the lignite char are compared with those of reburning with the lignite under the equivalent char feeding rates; i.e., the char data presented in Figure 1 have been corrected for the examination of volatiles-contributions at a specific SR2 of lignite reburning. It is found that the effectiveness of reburning of N_2O by coal/lignite is mainly contributed by homogeneous phase mechanisms through free radical reactions. Lignite is more reactive than the bituminous coal probably due to the high content of volatiles of lignite. Lignite char has higher reactivities than the bituminous coal char, which is probably attributable to the catalytic reactions of minerals, such as calcium. Chars produced under less severe devolatilization conditions have only slightly higher reactivities than the older chars.

Sizeable amounts of NH_3 and HCN are formed during reburning when coal or lignite is used as reburning fuel. Therefore, to evaluate the efficiencies of various fuels based on the N_2O emissions from a full three-stage process, additional factors have to be considered: char-nitrogen, HCN and NH_3 conversions to N_2O in the burnout stage. Nevertheless, the char-nitrogen [5], NH_3 [6] and HCN [7] conversions to N_2O in the burnout stage are known to be very low, and they are not expected to change the ranking of coal and lignite discussed above.

Acknowledgments

References

1. Gustavsson, L., Glarborg, P. and Leckner, B., *Combustion and Flame*, 1996, **106**, 345.
2. Rutar, T., Kramlich, J.C. and Malte, P.C., *Combustion and Flame*, 1996, **107**, 453.
3. Burch, T.E., Conway, R.B. and Chen, W.Y., *Rev. Sci. Instrum.*, 1991, **62**, 480.
4. Burch, T.E., Tillman, F.R., Chen, W.Y., Lester, T.W., Conway, R.B. and Sterling, A.M., *Energy & Fuels*, 1991b, **5**, 231.
5. Pels, J.R., Wójtowicz, M.A. and Moulijn, J.A., *Fuel*, 1992, **72**, 373.
6. Lin, W., Johnsson, J.E., Dam-Johansen, K. and Van der Bleek, C.M., *Fuel*, 1994, **73**, 1202.
7. Jensen, A., Johnsson, J.E. and Dam-Johansen, K., *Proc. 12th Int'l Conf Fluidized Bed Combustion*, ASME, 1993, 447.

Char Pyrolysis History: 950°C, 0 Holding Time
Primary Zone Stoichiometric Ratio: 1.1 for solid fuels
1.25 for gas fuels
Feed N_2O 150 ppm
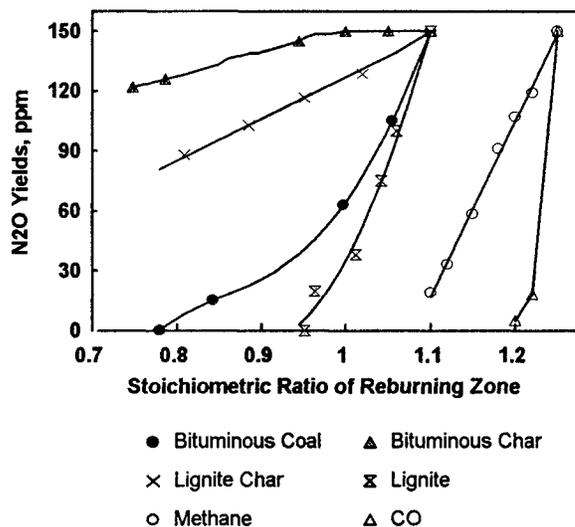Temperature: 850°C
Reaction Time: 0.2 S

Figure 1. Efficiency of reburning fuels based on stoichiometric ratio of reburning zone. Contributions of volatile-nitrogen to N_2O, if any, have been subtracted from the exit N_2O concentraions.

Char Pyrolysis History: 950°C, 0 Holding Time
Primary Zone Stoichiometric Ratio: 1.1
Feed N_2O 150 ppm
Temperature: 850°C
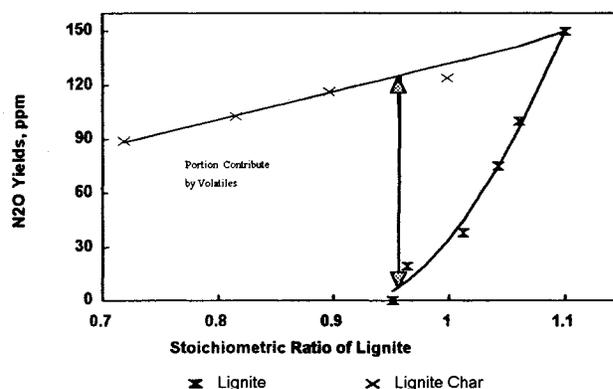Reaction Time: 0.2 S
Total Gas Flow Rate: 2000 cc/min

Figure 2. Homogeneous and heterogeneous reaction mechanisms during reburning Mississippi lignite.