



Project Summary

Bench-Scale Evaluation of Non-U.S. Coals for NO_x Formation Under Excess Air and Staged Combustion Conditions

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This report summarizes results of bench-scale fuel screening experiments. Twenty non-U.S. coals (including lignite, subbituminous, and bituminous) were tested in a 21-kWt refractory-lined tunnel furnace. NO_x emissions were measured as a function of coal composition and initial fuel/air contacting rate under excess air conditions. In addition, inflame measurements were made to quantify the influence of stoichiometry and temperature on the fate of fuel nitrogen species under staged combustion conditions.

The results show that NO_x emissions are generally correlated to fuel nitrogen content; however, such factors as hydrocarbon volatile content and the partition of fuel nitrogen between char and volatile fractions are also important. Moreover, coals with high volatile contents give high NO_x emissions under well mixed or excess air conditions, but give low NO_x emissions under staged conditions or with long axial flames. Both increasing flame temperature and decreasing particle size decrease NO_x emissions in staged combustion but increase it in well mixed combustion. Increasing the rate of heat extraction from staged combustion, however, generally reduces NO_x emissions via a complex mechanism.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Background -- NO_x Formation

During the combustion of coal, nitrogen oxides (NO_x) are formed by at least two fundamentally different chemical mechanisms: high temperature fixation of atmospheric nitrogen (leading to thermal NO_x), and the oxidation of nitrogen chemically bound in the fuel (leading to fuel NO_x). The formation of thermal NO_x in gas systems has been studied extensively and is usually described using a modified Zeldovich mechanism.

At least 70% of the NO_x formed during the combustion of pulverized coal are due to the oxidation of coal-bound nitrogen. Therefore, it is of major importance in the development of low emission systems to understand the phenomena which control the fate of this fuel-bound nitrogen. The current hypothesis concerning the fate of coal nitrogen during pulverized coal combustion can be simplified to include the following three processes:

- *Thermal Decomposition* - As the coal particle is heated, it decomposes. Volatiles are evolved, and the nitrogen is split between the volatile and solid fractions. The nitrogen remaining in the solid, char nitrogen, is a function of the temperature attained by the particle and the time at that temperature.
- *Gas-Phase Reactions* - The gas-phase nitrogen produced from the volatile coal fractions can react to form NO, NH₃, HCN, or N₂. The

formation of NO is favored under fuel-lean conditions, and the formation of N₂ is favored under fuel-rich conditions.

- **Char Burnout** - The char nitrogen associated with the solid, either as a pyrolysis product of tars or as the original coal char, can also be oxidized to form NO during char burnout. Char nitrogen conversion efficiency is usually assumed to be low.

This simplified hypothesis provides a basis to understand the potential fuel effects involved in NO formation during pulverized coal combustion as well as to recognize the steps involved in the optimization of a staged combustion system.

Control Technology

Most NO_x control technology is based on the use of combustion modification techniques because they have proven cost-effective compared to stack gas scrubbing. The most successful combustion modification technique for coal has been staged combustion: through external staging (biased firing, over-fire air ports, off-stoichiometric combustion), burner modifications (staging via delayed mixing), or compartmentalization (primary combustion furnace). In all of the concepts a portion of the combustion air is removed from the normal burner air and added at some distance downstream. Field testing and pilot-scale studies have demonstrated the potential of external staged combustion.

During the past 10 years, the U.S. EPA has devoted considerable effort to understanding the mechanisms involved in the formation of NO_x during the combustion of pulverized coal. This understanding has led to the development of a low-NO_x pulverized-coal burner (the Distributed Mixing Burner, DMB) which is suitable for retrofit to coal-fired boilers. EPA's DMB uses a combination of proper fuel injector and distributed air addition to create conditions which minimize fuel NO_x production and yet provide a combined heat-release zone which is compatible with current boiler combustion chambers.

Purpose and Scope

A problem associated with applying the DMB to coal-fired boilers is the impact of the fuel type on burner performance. In this instance, performance refers not only to pollutant emissions but also to ignition stability, combustion efficiency, and the necessity to reoptimize burnout to account for differences in coal properties.

The purpose of this program is to assess the application of low NO_x coal combus-

tion technology to non-U.S. coals. The overall objectives are to define the level of NO_x control likely to be achieved with non-U.S. coals and to determine the performance of the DMB on non-U.S. coals. The overall effort consists of bench-scale fuel screening studies and pilot-scale burner evaluation. Goals of the bench-scale investigation are to determine the NO_x formation characteristics of non-U.S. coals under both excess air and staged combustion conditions, and to provide a basis for comparison with U.S. coals and for the selection of fuels to be tested in the pilot-scale investigations.

Results

Fuel NO formed during the combustion of pulverized coal can be isolated by replacing the combustion air with an artificial oxidant mixture containing CO₂, Ar, and O₂. It appears that under conditions typical of commercial practice, oxidation of nitrogen chemically bound in the coal is the major source of NO_x emissions. Tests with 20 non-U.S. coals under excess air conditions indicated that, although the nitrogen content of these coals ranged from 0.8 to 2.5% (DAF), the emissions correlated generally with those obtained from 28 U.S. coals with a smaller range of nitrogen content. Fuel NO emissions were reduced as the rate of fuel/air mixing was reduced. In general, fuel NO emissions increased with increasing fuel nitrogen content; however, fuel properties such as hydrocarbon volatile content and the partition of nitrogen between the char and volatile fractions were also found to be important. In general, coals which evolve large amounts of reactive volatile nitrogen under inert-pyrolysis conditions give high exhaust emissions with rapidly mixing burners and relatively low exhaust emissions with long axial flames. Conversely, those coals which tend to retain a large fraction of their nitrogen in the solid-phase until the char burnout regime, tend to produce relatively low NO under well-mixed conditions. It was found that the exhaust emissions could be correlated in terms of total fuel-nitrogen content, reactive volatile nitrogen content as determined by inert-pyrolysis, and nitrogen content of the ASTM char.

Increasing flame temperature and decreasing particle size both increased NO_x emissions with rapidly mixed flames because both changes enhanced the evolution of fuel-nitrogen from the coal particle. Conversely, with axial diffusion flames, increasing temperature or decreasing particle size was found to be beneficial because both changes promote the evolution

of fuel nitrogen species within a fuel-rich flame core.

Detailed measurements of first-stage and exhaust species concentrations suggest that a staged combustion system must be optimized with respect to first-stage stoichiometry and residence time, fuel properties, and heat extraction rate. As first-stage stoichiometry is decreased, the NO formed in the fuel-rich zone decreases, but other oxidizable gaseous nitrogen species increase as does nitrogen retention in the solid-phase material exiting the first stage. Total fixed-nitrogen (TFN = NO+NH₃+HCN) generally increases with increasing fuel nitrogen and correlates well with fuel-nitrogen. Increasing the residence time in the fuel-rich stage allows TFN species to decay toward low equilibrium values and thus reduces NO emissions.

The distribution of the TFN species leaving the first-stage is strongly dependent on the coal composition. Of the nine coals tested in detail, none produced the high HCN concentrations previously observed with the Utah and Texas lignite coals from the U.S. The medium volatile Line Creek bituminous coal formed essentially no NH₃, and very little HCN, even under extremely fuel-rich conditions. This behavior was directly analogous to that observed previously with a low-volatile Pennsylvania anthracite and with coal chars. In general, the first-stage NO percentage decreased significantly with decreasing coal rank from bituminous to lignite. Conversely, the relative importance of NH₃ grew with decreasing rank. In general, HCN was greater than NH₃ with bituminous coals, but less than NH₃ with all of the subbituminous and lignite coals.

Second-stage TFN conversion decreases as the TFN distribution shifts in favor of HCN and NH₃, and as the hydrocarbon content of the second-stage reactants increases. The percentage conversion of char nitrogen to NO in the second stage is low (less than 20%) and appears to be inversely proportional to the first-stage stoichiometric ratio. Exhaust emissions can be correlated in terms of the gas-phase TFN, and the char nitrogen entering the second stage.

Increasing the rate of heat extraction from a staged combustion system generally reduces exhaust NO emissions via a complex mechanism. Reduced second-stage flame temperatures have little effect on solid-phase nitrogen conversion, but they dramatically decrease gas-phase TFN conversion due to a shift in controlling flame chemistry. If the reactants are cooled suf-

ficiently to bring the bulk gas temperature at the first-stage exit to approximately 1200 K, it is possible to obtain selective NO reduction (by NH₃) in the second-stage flame zone and, therefore, reduce the exhaust NO emissions. However, the effectiveness of this concept is strongly dependent on the combustor design (first-stage temperature profile and residence time) and fuel chemistry. Increasing heat extraction appears to be most favorable with low-rank coals, because they produce large amounts of NH₃ and relatively less first-stage NO. Conversely, high-rank coals (e.g., Russia) may be less influenced by the cooling in the first stage because they produce relatively little NH₃. Additionally, first-stage cooling may decrease the rate of TFN decay in the fuel-rich zone and, hence, increase both the TFN and char nitrogen carry-through into the second stage. Finally, because of the extremely low temperatures required for the selective NO + NH₃ reaction, carbon burnout in the second stage may be a significant problem.

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The complete report, entitled "Bench-Scale Evaluation of Non-U.S. Coals for NO_x Formation Under Excess Air and Staged Combustion Conditions," (Order No. PB 83-196 014; Cost: \$14.50, subject to change) will be available only from:

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