

FINAL TECHNICAL REPORT
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Project Title: Reactivity and Combustion Properties of Coal-derived Solid Fuels

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ABSTRACT

The objective of this research was to supply a broad range of combustion characterization data on coal-derived solid fuels. Three size fractions of an Illinois coal (IBC-101, VM=43.9%), three chars with volatile matter contents of 6, 12, and 15%, and a clean coal were studied.

Fuel analyses showed that removal of volatile matter lowered sulfur emissions (lb SO₂/MMBtu) of the resulting chars. Chars appeared to be nonporous and had significantly lower N₂-BET surface areas and slightly higher CO₂ surface areas than the raw coal. Chars were also more difficult to grind than the coal.

Ignition temperatures of fuels increased with decreasing volatile matter. However, the dependence of ignition temperatures on particle size was not strong. Burning profiles and reactivity data were obtained using a thermogravimetric analyzer. The results showed that the smaller size fractions and higher volatile fuels were easier to burn. However, the 200x270 and 270x400 mesh size fractions burned similarly. Chars had seven times higher reactivity in steam than in CO₂. Gasification reactions were much slower than the combustion reaction.

Combustion efficiencies and ash deposition behaviors of fuels were obtained in an entrained flow reactor under conditions representative of coal-fired boilers. Combustion efficiencies increased with increasing temperature, volatile matter and residence time and decreasing particle size. The effects of residence time and particle size were more pronounced for lower volatile fuels. Oxygen concentrations between 3 and 6% did not affect combustion efficiencies.

Ash deposition studies showed that clean coal produced a deposit that grew at a faster rate than the original coal. However, the deposit strength of the clean coal was less than that of coal. Deposits of the 6% char grew fastest and were the strongest deposits of the fuels tested.

EXECUTIVE SUMMARY

The reduction in volatile matter that accompanies most thermal and chemical coal-desulfurization processes influences combustion characteristics such as ignition temperature, flame stability, and carbon burnout. The goal of this research was to supply a broad range of combustion characterization data on low volatile chars and a physically cleaned coal.

The project had four tasks. In the first task, three chars with volatile matter contents ranging between 5 and 15% and a medium cleaned coal were prepared. In task two, physical and chemical properties of chars and coals were obtained to help explain combustion properties. In task three, reactivities of the coal and those of three size fractions of each char were measured in air, steam, and carbon dioxide with a thermogravimetric analyzer (TGA). An ignitability apparatus was used to measure the relative temperature of ignition of fuels. Carbon combustion efficiencies were determined in a drop tube furnace under conditions representative of coal-fired boilers. In task four, ash deposition behaviors of the coal, clean coal and the lowest volatile char were studied. A summary of each task is given below.

Task 1. Acquisition and preparation of fuels

The sample used for char production was 28x100 mesh size fraction of IBC-101 coal (VM=43.8%, dry basis). Chars with volatile matter contents of 6.4%, 12.2% and 15.3% were prepared in a 2-inch ID batch fluidized-bed reactor under mild gasification conditions. Pyrolysis temperature and soak times for the low, medium, and high volatile chars were: 600°C, 60 mins; 505°C, 30 mins; and 475°C, 10 mins. Original coal and chars were subjected to a series of sieving and grinding steps to prepare 100x150, 200x270 and 270x400 mesh size samples. Grinding behavior of the fuels showed that chars were more difficult to grind and that 40% more grinding time was required to grind the chars to 70% minus 200 mesh than for the coal.

The clean coal was prepared from a 200x400 mesh size fraction of IBC-101 coal in a batch flotation system. The ash content of the clean coal was 5.6% compared to 9.6% for the original coal.

Task 2. Physical and Chemical Characterization

Coal and chars were subjected to a complete fuel analysis to determine changes that occurred during pyrolysis and the effect they might have on the combustibility of the fuels. Volatile matter contents of the three chars increased slightly with decreasing particle size range and averaged about $15.7 \pm 0.7\%$, $11.9 \pm 0.1\%$ and $6.4 \pm 0.2\%$. Devolatilization profiles of chars were obtained using a TGA and showed that char samples were homogeneous and were not mixtures of coal and highly devolatilized chars.

Devolatilization reduced sulfur emissions from 6.9 lb SO₂/MMBtu for coal to 5.4, 5.0 and 4.6 lb SO₂/MMBtu for 15%, 12% and 6% volatile fuels. The sulfur emissions of the clean coal was 5.9 lb SO₂/MMBtu since 72% of the sulfur in the original coal was in the form of organic sulfur which was not efficiently removed by flotation.

The CO₂ and N₂-BET surface areas of clean coal and the size-graded coal were similar and ranged from 235 to 259 m²/g and 55 to 61 m²/g. Chars had comparable CO₂ surface areas, but significantly lower N₂-BET areas (2-5 m²/g). It appears that during devolatilization, a large fraction of the macropores in the coal were partially plugged. Scanning electron micrographs showed that chars appear to be nonporous.

Standard ASTM techniques were used to determine ash fusability temperatures and compositions of coal, clean coal and 6% volatile char. Analyses of the ash showed only small differences between coal and 6% volatile char. The cleaning process removed only soluble sulfate minerals and about half the calcite. Silica and base-acid ratios of fuels were about 68 and 0.40, respectively. However, the initial deformation temperature of 6% volatile char was 60°F higher than that of the original coal (2055°F). Slagging indices for the fuels fell in the medium range, while the fouling index was high for coal and char and medium for the clean coal.

Task 3. Reactivity and Combustion Studies

TGA Studies

Burning profiles of the fuels were obtained by heating the fuels in 10% O₂-90% N₂ at 20°C/min. Fuels exhibited single burn profiles. In general, the profiles shifted to higher temperatures with decreasing volatile matter and increasing particle size indicating that smaller size fraction and higher volatile fuels were easier to burn. For a given fuel, however, the 200x270 and 270x400 mesh size fraction burned similarly. The profiles for coal and clean coal were also similar. The results of the burning profiles indicated that coal and clean coal were the most reactive fuels followed by 15%, 12% and 6% fuels.

Isothermal experiments were conducted in air at 400, 440 and 480°C to determine the activation energies for the oxidation of chars. The apparent activation energy was 33 kcal/mole for the 6, 12, and 15% chars. The chars were an order of magnitude more reactive than chars prepared in pilot-scale pyrolysis reactors.

Reactivities of chars in steam and CO₂ were measured at temperatures between 880 and 960°C. Reactivities were independent of the type of char. However, the reactivity of char in steam was seven times higher than in CO₂. The activation energies for steam and CO₂ gasification were 62 and 52 kcal/mole, respectively.

Drop Tube Tests

Combustion efficiencies of the fuels were determined in a laminar flow reactor, referred to as a drop tube furnace (DTF), under conditions representative of coal-fired boilers. These tests were conducted at UNDEMRC. Combustion efficiencies of the 6, 12, and 15% volatile chars were determined under the following conditions: oxygen concentrations of 3 and 6%; residence times of 0.1, 0.4 and 0.8; gas temperatures of 900 and 1300°C; and particle size of 100x150 and 270x400 mesh. The coal was tested at only one oxygen concentration (3%) and at 900 and 1300°C. The clean coal was tested at only one particle size (200x400 mesh), 3% oxygen and 900°C.

The results of the DTF tests showed chars with lower volatile matter content required higher combustion temperatures and longer residence times to achieve acceptable levels of carbon conversion. The 6% char showed essentially no conversion at 900°C and showed high carbon conversion only at the longest (0.8 sec) residence time at 1300°C. The 12% and 15% volatile chars showed higher conversions than 6% char at 900°C, but the conversion was only 20% to 30%. At 1300°C, these chars showed 80% or greater conversion after 0.4 seconds residence time. The raw coal and clean coal burned similarly and gave rapid high conversions even at 900°C. The effects of particle size and residence time were most pronounced with lower volatile matter chars. The high reactivity of the coals appeared to mask any effect of particle size.

Task 4. Ash Deposition Studies

Ash deposition tests were conducted in the DTF at the UNDEMRC using the raw coal, clean coal and the 6% volatile char. Three to five individual tests were performed on each sample. The tests were at times between 5 and 30 minutes. The tests were run at 1500°C with an oxygen concentration of 20%. Sample was fed at a rate of 0.2-0.3 g/min.

The results of the ash deposition study showed that the clean coal produced a larger deposit that grew at a faster rate than the original coal. However, the deposit strength of the clean coal was slightly softer than coal and did not show evidence of partial melting. The deposits for char grew much faster than either coal or char. Due to extensive melting, the deposit strength of char was much greater than either coal or clean coal.