SECONDARY PYROLYSIS AND COMBUSTION OF COAL VOLATILES

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Keywords: Coal Volatiles, Combustion, Burning Velocity

INTRODUCTION

During the initial stages of pulverized fuel (p.f.) firing devolatilization converts about half of the injected coal mass into gases, including many fuel compounds. The subsequent secondary pyrolysis and combustion of these volatile compounds accounts for large portions of the heat release, pollutant formation, and soot evolution during coal combustion. This study focuses on the combustion of the volatiles. Noncondensible volatiles, without tar or soot, from the pyrolysis of a bituminous coal were mixed with \( \text{O}_2 \) and \( \text{N}_2 \) and burned in a constant volume combustion bomb. The resulting laminar burning velocity determinations provide a means of estimating global combustion rates. Laminar burning velocities are reported as a function of equivalence ratio and unburned gas temperature for a single pyrolysis condition, in which most of the tar had converted to soot.

APPARATUS

As seen in Fig. 1, the volatiles are generated by entraining pulverized coal particles in \( \text{N}_2 \), and passing the suspension through an induction furnace. At the exit of the furnace, a fraction of the \( \text{N}_2 \) volatiles stream is diverted from the main stream of gas and char, and drawn through a heated filter to an evacuated storage tank. The stored gas is then pumped to the combustion bomb, where it is mixed with \( \text{O}_2 \) and \( \text{N}_2 \), and ignited by an electric spark. Design details and performance characteristics of the radiant coal flow reactor are given elsewhere. Briefly, the coal suspension passes through a quartz tube within an inductively heated cylinder of graphite maintained at temperatures from 1000 K to 1850 K. Radiation from the graphite heats the coal particles at \( 10^4 - 16 \) W/sec. The \( \text{N}_2 \) carrier gas is transparent to radiation, and can only be heated by convection from the coal suspension and the quartz tube. Since the coal suspension supplies much of the heat to the carrier gas, the gas temperature can be kept low to minimize secondary reactions among the volatiles by operating with very dilute suspensions (about 100 particles/cc). However, to obtain the flammable mixtures for this study the coal loading was increased to 2400 particles/cc. At this condition, secondary pyrolysis of the volatiles is virtually complete.

Gas concentrations were determined with gas chromatography (for \( \text{H}_2, \text{CO}, \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{C}_4\text{H}_{10}, \text{C}_5\text{H}_{12} \), and light oils) and non-dispersive infrared analysis (for \( \text{CO}_2 \) and \( \text{H}_2\text{O} \)). Hydrogen and CO were sampled with a gas-tight syringe and measured with a thermal conductivity detector after separation on Molecular Sieve 5A. Chromatography for these compounds was conducted immediately after sampling to avoid diffusive loss of \( \text{H}_2 \). Methane, \( \text{C}_2\text{H}_6 \), \( \text{C}_3\text{H}_8 \), \( \text{C}_4\text{H}_{10} \), and \( \text{C}_5\text{H}_{12} \) were sampled into a multiposition valve and measured with a flame ionization detector (FID) after separation on Silicalite. The remaining hydrocarbons in the gas stream were grouped as light oils and measured by direct injection of the gas stream into the FID. The resulting total signal included the signals from \( \text{C}_1 - \text{C}_5 \) hydrocarbons, which were subtracted out; the remainder was then converted to a light oil concentration using the conversion factor for pentane, which has a molecular weight similar to the oils.

The combustion bomb is a spherical pressure vessel (15.24 cm diam.) constructed from 316 stainless steel, and equipped with 10 access ports. Copper electrodes form a 1 mm spark gap at the center of the spherical chamber. Three ionization gages spaced about the chamber wall monitor the arrival time of the flame to check for flame sphericity (an assumption in the data reduction). The transient
pressure rise from combustion is monitored by a water-cooled piezoelectric pressure transducer mounted at the bomb wall. Laminar burning velocities are determined from the transient pressure trace. But this determination is complicated by the fact that the pressure rise is related both to the rate at which volatiles enter the flame, and the rate at which the unburned gas is compressed by the expansion of the products behind the flame. A computational procedure has been adapted to separate these two effects, and is explained elsewhere.

EXPERIMENTAL

An HVA bituminous coal (Illinois #6, IBCSP 105) distributed by the Illinois Basin coal Sample Program was used. The coal was ground under liquid nitrogen and dry-sieved to produce a 75-106 micron size fraction. The 75 micron cutoff was then improved by sedimentation of the coal in water. An ultimate analysis of the sized coal gave 64.8% C, 4.9% H, and 1.4% N on a moisture free basis. Before each use, the coal was dried overnight at 330 K under 15 kPa of N₂.

The radiant coal flow reactor was operated at 1640 K and a nominal residence time of 200 msec. The large amounts of soot observed at the furnace exit confirmed extensive secondary pyrolysis of the volatiles. Soot and condensed volatiles were removed on a glass fiber filter maintained at 330 K. The filtered noncondensible volatiles were stored at 450 K, and pumped to the combustion bomb through lines heated to 380 K.

The combustion bomb was operated at an initial pressure of 0.07 MPa, which is sufficiently low to keep inordinate uncertainties in the initial section of the pressure trace from obscuring the behaviour at 0.1 MPa. The bomb was preheated to the two initial temperatures of 493 K (5 runs) and 579 K (4 runs). Compression heats the unburned gases to 540 K and 635 K, respectively, by the time the bomb pressure has reached 0.1 MPa. Oxygen was added to the volatiles to obtain fuel lean equivalence ratios (defined in terms of fuel/O₂ ratios) from 0.5 to 0.9, where the fuel comprises H₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀, light oils, and CO. Nitrogen was also added to maintain a constant diluent/O₂ ratio of 4.3 +/- 0.25 on a mole/mole basis; N₂, CO₂, and H₂O are the diluents.

RESULTS

Table I gives the measured species concentrations for two fills of the storage tank. The first mixture provided the results at 540 K, while the second mixture was used at 635 K. While H₂, CH₄, and CO are the most abundant fuel species, the remaining hydrocarbons contribute about half of the heat release of combustion. In fact, the light oils alone contribute about a quarter of the heat release. Because of their higher molecular weights, very small mole fractions of these higher hydrocarbons contribute significant amounts of energy release.

Fig. 2 shows the volatiles burning velocities measured for two unburned gas temperatures. The magnitude of the measured velocities is much smaller than that for H₂/air combustion at similar conditions (Sₐ = 720 cm/sec in air at an equivalence ratio of 0.9 and an unburned gas temperature of 635 K), but similar to that for CH₄/air (see correlations in Fig. 2). Note, however, that the correlations are for air, which has a diluent/O₂ ratio of 3.76, while the volatiles measurements are for a diluent/O₂ ratio of 4.3; CH₄ burning velocities for the same diluent ratio would tend to be 10 to 20 % lower. While CH₄ and volatiles burning velocities compare favorably for the conditions of this study, this result cannot be generalized. Further secondary pyrolysis leads to higher levels of H₂ and CO than observed here and lower levels of heavy hydrocarbons, so that such volatiles mixtures might be expected to burn faster. Also, lower rank coals produce more H₂O, CO₂, and CO than observed here, and these species can be expected to play more important roles in the combustion of volatiles from these coals. Finally, the condensible tars absent from this study can contribute more than half of the heat release of combustion, and can be expected to introduce additional rank effects into the combustion rates of volatiles.

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SUMMARY

A facility has been constructed to study the effects of primary and secondary pyrolysis on the combustion rates of the volatiles from coal. Concentration measurements for an HVA bituminous coal show that under significant secondary pyrolysis H2, CH4, and CO are the most abundant noncondensible fuel species; but other hydrocarbons, especially light oils, contribute significantly to the heat release. For the conditions of this study, the measured burning velocities are similar to those of methane. However, we do not anticipate this similarity in subsequent studies in which coal rank and extent of secondary pyrolysis are varied, and tar is left in the volatile fuel mixture.

ACKNOWLEDGEMENT

Support for this program is provided by the United States Department of Energy's Morgantown Energy Technology Center under Grant DE-FG22-86PC90511.

REFERENCES


Table I: Measured Species Concentrations of Stored Volatiles.

<table>
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<tr>
<th>Mole % of Stored Volatiles</th>
<th>H2</th>
<th>CH4</th>
<th>C2H6</th>
<th>C3H6</th>
<th>C2H2</th>
<th>C3H8</th>
<th>Light Oil</th>
<th>CO</th>
<th>CO2</th>
<th>H2O</th>
<th>N2#</th>
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<td>1</td>
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<td>0.079</td>
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<tr>
<td>2</td>
<td>4.6</td>
<td>1.9</td>
<td>0.050</td>
<td>0.49</td>
<td>0.55</td>
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<td>1.88</td>
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<td>3.0</td>
<td>86.6</td>
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* Estimated. Not measured.
# By difference.
Fig 1: Schematic of the radiant coal flow reactor, the means of transporting volatiles, and the constant volume combustion bomb.

Fig 2: Burning Velocities, $S_u$, for the noncondensable volatiles of Table 1 as a function of stoichiometry for unburned gas temperatures of 540 K(○), and 635 K(●). The burning velocities for CH$_4$/air combustion are indicated by 540 K, and 635 K. Schematic of the radiant coal flow reactor, the means of transporting volatiles, and the constant volume combustion bomb.