

Soot Formation during Coal Pyrolysis

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Introduction

Soot can be found in almost all combustion and pyrolysis systems. In a coal system, the impact of soot on coal combustion can be identified in two ways. First, soot particles suspended in the combustion flame significantly enhance radiative heat transfer near the burner due to their large surface area, small size and spectrally continuous radiation characteristics [1]. Second, part of the nitrogen released from coal during devolatilization will be reincorporated into soot, which complicates nitrogen transformations and NO_x production.

The study of the chemical structure of soot is also important for many environmental and health reasons. Soot, formed by condensation of polyaromatic hydrocarbons (PAH), poses a health hazard, since many PAH produced in pyrolysis or combustion processes are carcinogenic and mutagenic materials [2]. Soot has also been found in the unburned carbon in flyash [3].

Experimental

Apparatus and operation

A flat flame burner (FFB) was used in this study to provide a high temperature (1150 to 2000 K) fuel-rich laminar flow environment [4]. CO-air (with small amounts of H₂) flames were used due to their broader flammability limits and low steam concentrations (steam interferes with FTIR spectra). An FTIR gas analysis system was added and used in connection with the suction probe in the FFB system to allow on-line measurements of the pyrolysis gases during experiments. Samples were collected at residence times of approximately 50 ms [see reference 4 for more details]. An electrically-heated drop tube reactor was also used to perform pyrolysis experiments for selected coals in nitrogen. The drop tube reactor can be operated from 900 K to 1250 K [5].

Product Characterization

The elemental compositions of the condensed products were determined on a dry basis using an elemental analyzer. For the pyrolysis experiments performed in the FFB with a CO flame, the noncondensable hydrocarbon gases were quantified by an FTIR spectrometer, coupled with an unheated 10 m multi-reflection gas cell. All spectra were acquired with a resolution of 1 cm⁻¹ and spectral range of 500-4000 cm⁻¹. With a liquid N₂-cooled MCT detector, the detection limit of the FTIR can be as low as 50 ppb for certain gases (including NH₃, C₂H₄ and C₂H₂) [4].

The average chemical features of the parent coal and the tar or soot samples were characterized by solid-state ¹³C NMR spectroscopic techniques at the University of Utah. Three different NMR experiments were used to determine the carbon skeletal structure of a sample, including a standard cross-polarization and magic angle spinning (CP/MAS) experiment, a variable contact time experiment, and a dipolar dephasing experiment [6].

Results and Discussion

Soot Formation from Coal Tar

The number of side chains per aromatic cluster for the tars and soots for the Pittsburgh #8, Illinois #6, and South Banko coal experiments are plotted in Figure 1a. The number of side chains per cluster decreased with temperature for all of the three coals. At about 1300 K, the numbers of side chains per cluster in the tar or soot had dropped by 88% for the Pittsburgh #8 coal, 80% for the Illinois #6 coal, and by more than 95% for the South Banko coal. A loss of oxygen-containing groups was observed in the tars/soots in a manner similar to decrease in the number of side chains per cluster.

Major structural changes occurred between 1280 K and 1410 K, as indicated in Figure 1b. A dramatic increase of the bridges and loops per cluster was noticed beginning at about 1250 K. For the Pittsburgh #8 coal, the bridges and loops per cluster increased almost 60% from 1100 K to 1250 K. For the Illinois #6 coal, a 50% increase of the bridges and loops per cluster was observed between 1280 K and 1410 K. Such a dramatic increase of the number of bridges and loops per cluster, which is a measure of potential cross-linking sites, clearly showed that the clusters in the tars are more interconnected, a sign of soot initiation.

Ring opening reactions seemed to occur between 1300 K and 1500 K, although this is not obvious from the chemical structure analysis. However, the analysis of the decay of the tar nitrogen content strongly suggests that ring opening reactions occurred at approximately the same temperature as the early ring growth process [4]. Between 1300 K and 1500 K, the dramatic decrease of the nitrogen in the tar suggests that significant ring opening reactions have taken place, since most of the coal nitrogen is incorporated into heterocyclic ring structures. Therefore, it is reasonable to believe that ring opening and ring growth are competitive reactions during the early stages of soot formation [6].

Ring growth reactions are accelerated between 1400 K and 1600 K, as evidenced by a rapid increase of the molecular weight per cluster from 200 amu at 1280 K to about 320 amu at 1410 K, then to a remarkable 1190 amu at 1530 K for the Illinois #6 coal (see Figure 2). The large aromatic clusters are also very interconnected. These aromatic clusters continue to grow at temperatures above 1500 K, leading to a very large and interconnected network of clusters. Experimental data showed that ring opening reactions become negligible above 1600 K, which means that ring condensation reactions are favored at high temperatures [4].

Additional Soot Growth from Hydrocarbons in the Gas Phase

Direct addition of low molecular weight hydrocarbon species to the soot surface is thought to be a major soot growth mechanism at high temperatures [7]. The participation of hydrocarbons in the growth of coal-derived soot can be justified by the carbon balance in this study. The carbon fractions in the tars and soots are plotted in Figure 3 for the four coals used in the FFB pyrolysis tests. During secondary reactions, primary tars lose carbons due to the release of light hydrocarbons (loss of side chains). When heteroatoms (mainly oxygen) in tar are expelled during the ring opening reactions, additional carbons are lost since oxygen is mainly released from tar as CO [8] and nitrogen as HCN [9]. In Figure 3, the fraction of coal carbon in the sum of tar plus soot at 1858 K is higher than that at 1159 K. This means that the carbon loss during tar decomposition was compensated by gains in carbon from other sources. Previous studies have shown that the CO yield always increases with increasing temperature during secondary reactions [8,9]. CO is therefore not considered to be a source of carbon

for the soot growth. The only source of carbon that contributed to soot growth would be hydrocarbons in the gas phase, generated either from tar cracking or thermal decomposition of char at elevated temperatures.

FTIR measurements of light hydrocarbon species were examined to determine which species contributed to soot growth. Figure 4 shows the distribution of hydrocarbons with residence time at 1618 K for the Black Thunder coal in the FFB. Apparently, acetylene is the dominant light hydrocarbon species in the flame at temperatures higher than 1600 K. Benzene and other low molecular weight gas species were rapidly consumed at high temperatures, and hence do not make significant contributions to soot surface growth. Similar results were obtained for other coals [4].

Conclusions

1. Soot formation mechanisms are similar for tars from different coal types. The coal-derived soot first exhibited loss of side chains and oxygen functional groups at temperatures below 1300 K, followed by ring opening reactions at 1300-1500 K, finally experiencing substantial ring growth at temperatures above 1400 K.

2. Ring opening and ring growth reactions are competitive reactions during soot formation. Ring growth reactions are favored at higher temperatures (above 1500 K).

3. Direct addition of low molecular weight hydrocarbon species to the soot surface appears to be a significant soot growth mechanism at high temperatures.

4. In this coal system, C_2H_2 is the predominant hydrocarbon that participates in soot growth at high temperatures. The contribution from aromatic hydrocarbons is insignificant at the higher temperatures (above 1500 K).

References:

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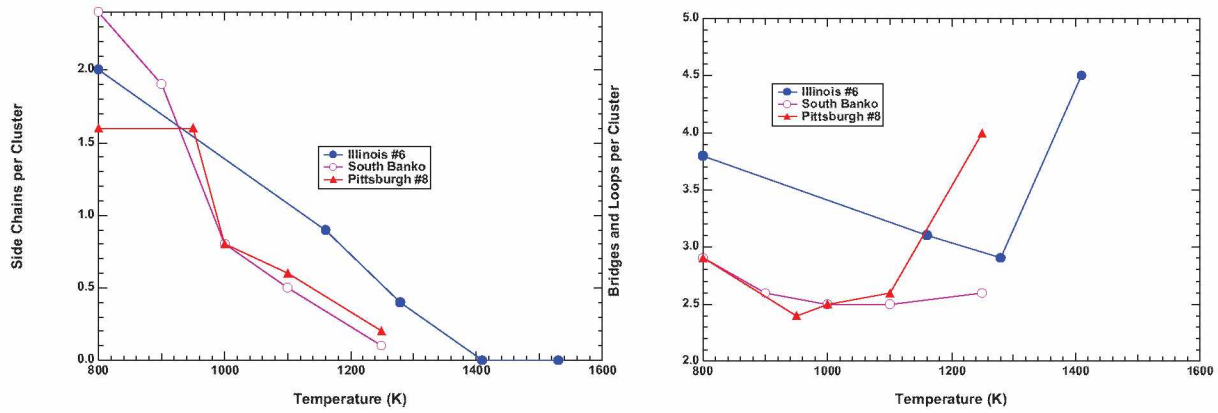


Figure 1. (a) Side chains per cluster and (b) bridges and loops per cluster measured for tar/soots in the FFB (Illinois #6 data) [4] and in the drop tube reactor [5].

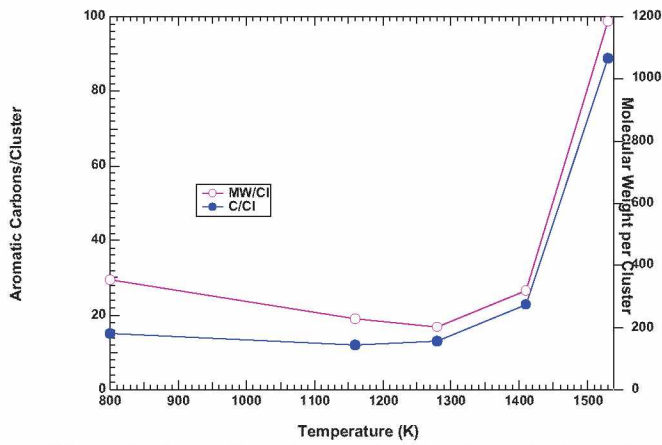


Figure 2. Aromatic carbons and molecular weight per cluster measured for tar/soots in the FFB for the Illinois #6 coal [4]. Data at 800 K represent the parent coal.

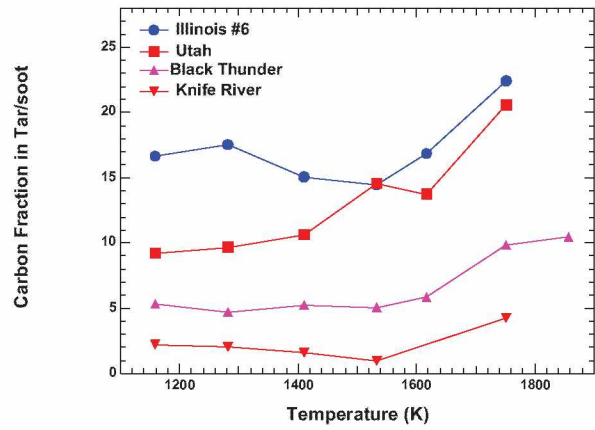


Figure 3. Fraction of coal carbon incorporated into tar and soot

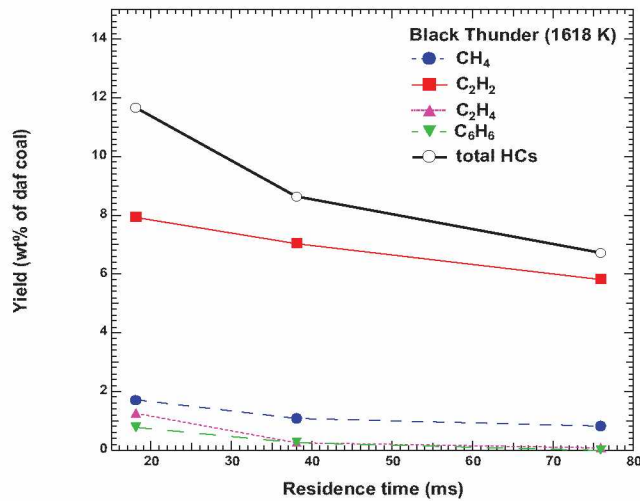


Figure 4. Yields of light hydrocarbons from the Black Thunder coal during pyrolysis at 1618 K in the FFB.