

THE ANALYSIS OF VOLATILE COMPONENTS FROM
PYROLYZED GASIFIER CARBON-RICH SOLID SAMPLES

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ABSTRACT

Samples of carbon-rich solid products, taken during the processing of coal in a Texaco Coal Gasifier, have been analyzed by flash-pyrolysis using the electrically-heated grid technique. Gas chromatography and mass spectrometry data were obtained on the composition of the gases and tars evolved.

SAMPLE PREPARATION

The coal gasifier solid products, consisting approximately of 51.2% carbonaceous material, 47.1% ash, and 1.7% water by weight, were pyrolyzed using a heated grid apparatus, which was similar to a procedure used by other workers.(1,2) The pyrolyzer consisted basically of two layers of wire mesh mounted between two electrodes, with a thin uniform layer of gasifier solid sample weighing about 50 mg placed between the two wire mesh screens. The sample was heated under vacuum for six seconds to a peak temperature of 1350°C. The heating rate was estimated to be in the order to 2000°C/s. The reaction products, consisting of gases, tars, and char were collected.

The gases were analyzed on-line by gas chromatography. The gases consisted of 0.5% hydrogen, 1.8% methane, 1.7% water, 0.2% ethylene, 1.0% carbon monoxide, 0.6% ethane, 0.3% propylene, 0.9% carbon dioxide, and 0.7% other olefins based upon the weight relative to the initial sample.

The tars, materials collected on filter paper at the reactor exit or condensed on other reactor surfaces at room temperature, were analyzed by mass spectrometry.

ANALYSIS OF TARS BY MASS SPECTROMETRY

The tar samples were analyzed by both direct insertion probe and direct exposure probe mass spectrometry, using a VG Analytical 7070HS instrument. The mass spectrometer was operated under the following electron impact conditions: 200 uA trap current, 70 eV electron energy, 4 kV accelerating voltage, 1200 resolution (10% valley), and a 250°C source temperature. Masses were magnetically scanned from 20 to 800 daltons, and subsequently from 25 to 300 daltons every four seconds.

For the direct insertion probe analysis, a 100 ug sample of tar was fractionally sublimed from a shallow (4 mm) quartz cup which was attached to the probe and positioned in the source just short of the electron beam. The probe temperature was controlled by both a water cooling line and an electrical heating element. The sample was initially heated from 20°C to 50°C in the first minute, and then increased by 50°C every 30 seconds, to a final temperature of 450°C for five minutes.

During the direct exposure probe analysis, the tar was dissolved in methylene chloride and then deposited onto a platinum emitter filament. After the evaporation of the solvent, the direct exposure probe was positioned in the source so that the sample was in actual contact with the electron beam. A current was ramped from 0 to 1.2 A in 50 seconds to flash vaporize the sample.

MASS SPECTROMETRY RESULTS

Approximately 75% of the tar sublimed from the quartz direct insertion probe cup into the mass spectrometer source. This was determined by weighing the probe cup after the analysis. Although the initial mass scanning range was from 25 to 800 daltons, few ions were observed above a mass of 250 daltons, even at the higher probe temperatures. The upper mass limit was then reduced to 300 daltons.

When using the second introduction technique, the emitter coil on the direct exposure probe was burnt clean. Although this technique generally allows better detection for high molecular weight molecules, again only an upper mass range of approximately 250 daltons was observed.(3)

A total ion chromatogram for a tar sublimation reveals that the tar was composed of a fairly uniform distribution of materials over the entire temperature range. (Figure 1) Each time the temperature was incremented by 50°C, there was a corresponding increase in total ion intensity which would then fall off after about 15 seconds. This periodic tendency continued even at the highest probe temperature of 450°C. There was still about 15% of the tar remaining after about five minutes at this temperature, although the ion intensity dropped off to only a few percent of this maximum level.

The mass spectra indicate mainly the presence of relatively simple hydrocarbons. The most prominent types of hydrocarbons observed were alkenes, dienes and some alkylated phenols. No substituted cycloalkanes, benzenes, polynuclear aromatics, or common biomarkers such as dicyclic terpanes, were observed. The major fragmentation series at 27, 41, 55, 69, 83, 97, and 111, having the empirical formula C_nH_{2n-1} , and the relative abundance of these peaks, represents the strong presence of alkenes. The fragmentation series 67, 81, 95, 109, 123, 137, 151, and 165,

having the empirical formula C_nH_{2n-3} , and the relative abundance of these peaks, represents the presence of dienes. Alkenes and dienes were prominent throughout the entire chromatogram, especially being dominant below 150°C. (Figure 2) The alkylated phenol fragmentation was represented in the 135, 149, and 163 series. The alkylphenols were most intense at about 250°C. (Figure 3) Peaks representing paraffinic molecules, having an empirical formula C_nH_{2n+1} , end very quickly at about 85 daltons indicating that this series probably only represents the alkylated regions in the parent molecules.

CONCLUSION

Overall the mass spectra indicate that the tars generally contained only relatively light alkenes, dienes, and alkylphenols. These components are somewhat less complex than materials typically associated with coal pyrolysis.(4) This simpler distribution is actually the result of a double pyrolysis. The coal was first pyrolyzed in a coal gasifier, and then the selected carbon-rich products were pyrolyzed in the screen-heater reactor.

REFERENCES

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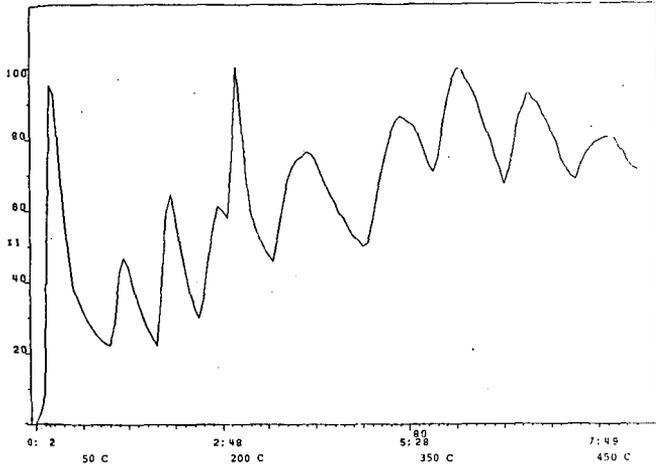


FIGURE 1. Total Ion Chromatogram of Tar

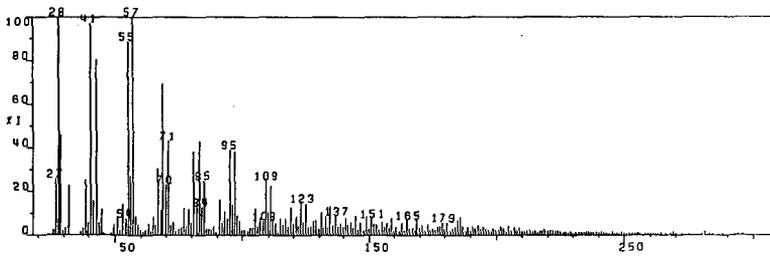


FIGURE 2. Mass Spectrum at 100°C

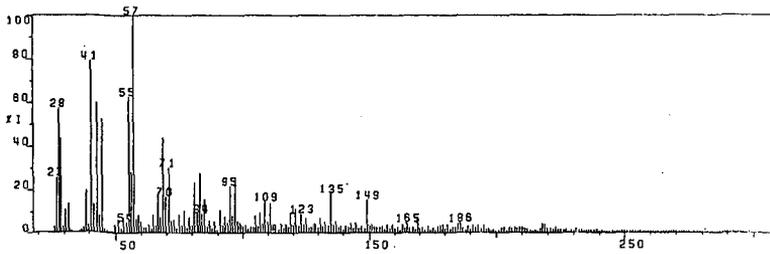


FIGURE 3. Mass Spectrum at 250°C