An Investigation of Yields and Characteristics of Tars Released During the Thermal Decomposition of Coal

J. D. Freihaut and D. J. Seery

United Technologies Research Center
East Hartford, CT 06108

Introduction

Reported results indicate that tar yields obtained from a wide variety of coals and reactor conditions can represent a significant fraction of the mass of the parent coal.[1-6] Tar yields and characteristics appear to reflect not only the nature of the parent coal but also the experimental conditions of the decomposition process.[1,2, 6-9] The variation in tar yields and characteristics with intrinsic characteristics of the coal and process parameters underscores the possibility of relating such observations to fundamental aspects of the decomposition process.

This report contains some results of an initial investigation of tar yields and properties obtained from eight coals. Results are shown for variations with 1) coal rank characteristics; 2) apparent thermal history; and 3) ambient pressure. Apparent heating rates of 10^2 C/sec to 10^3 C/sec and final temperatures of 500 C to 1780 C were utilized. Ambient pressures were varied from near vacuum to 760 torr. The results indicate that tar yields and characteristics are sensitive functions of intrinsic characteristics of the coal and the process parameters associated with the decomposition process. Prediction of tar yields may involve coal rank characteristics as a basis but the nature of the transforms introduced by the process conditions (ambient pressure, heating rate, final temperature, particle size) are equally important.

Experimental Design

Figure 1 represents schematically the apparatus employed to perform the thermal decomposition experiments. The procedure involves placing small samples (20-50 mg) of finely ground coal (-100+325 mesh) between the folds of a fine (325 mesh) metal screen (stainless steel, molybdenum, tungsten). The grid is then driven to a predetermined temperature via the preset control circuitry. The apparent heating rate is monitored by a thermocouple bead placed between the folds of the grid. For vacuum runs the light gases evolved are immediately vented through a glass wool filter into the infrared cell of a Fourier Transform Infrared Spectrometer (FTIR). The total time for each run is 10 seconds.

For runs conducted with ambient nitrogen present, the reaction chamber is isolated from the infrared cell. The pressure is monitored by a pressure transducer attached to the reaction chamber. In addition, a fine mesh screen cylinder is placed around the grid with a baffle below the grid to prevent recirculation of the aerosol mist to the grid. In both configurations the tar mass is defined as the material which condenses on the room temperature walls, linings and filters.

In the cases where infrared spectra of the overall tar mass was desired a dry KBr pellet was placed in the reaction chamber and exposed to the evolving tar species. The pellets were then removed and scanned using the FTIR. Glass filters placed in the chamber were also removed and examined with a Scanning Electron Microscope (SEMC) to ascertain the nature of the tar release at various ambient pressures.

Infrared Characteristics and Elemental Analysis of Coals

The coals selected for these initial studies represent a wide cross section by rank and geologic province. Elemental analyses of these coals were provided by the institutions supplying the coals but each sample was also subjected to elemental analysis on a Perkin Elmer 240 Elemental Analysis System (EAS). In cases where substantial differences were observed between the reported values and the measured values, samples were sent to an independent laboratory for additional analysis. Table I contains the elemental analysis of the coal samples as well as the calculated H/C and O/C ratios. Figure 2 represents the location of the samples on the coalification band as revealed by the H/C and O/C values. The position of the Western bituminous coals relative to the Eastern bituminous coals reflects the differences in geologic sources.

The variation in chemical structural characteristics with position on the coalification band is reflected in the infrared spectra (Fig. 3) of the coals. The spectra are obtained from KBr pellets of finely ground coal samples and spectra are normalized with respect to 1 mg of coal. Identified mineral matter contributions to the spectra have been substracted. The spectra indicate, although at times indirectly, the manner in which the organic hydrogen and oxygen are distributed throughout the coal matrix. For example, the regions associated with aliphatic hydrogen (2800-3000 cm^{-1}, 1450-1475 cm^{-1}) show absorption increase with hydrogen content. The resolution of the aromatic hydrogen peaks (3020-3050 cm^{-1}, 700-900 cm^{-1}) increases with reductions in the H/C and O/C ratios. The regions associated with oxygen-containing functional groups (1500-1800 cm^{-1}) are more clearly defined for the higher oxygen-containing coals. The variation in infrared structural characteristics with position on the coalification band is clearly reflected in

the differences in the spectra of the bituminous coals from the different geological regions.

While the Eastern bituminous and Western bituminous coals are different structurally, the infrared spectra of the Utah and Colorado bituminous coals are similar. The two subbituminous coals also display infrared spectra similar to each other. On the basis of the infrared spectra and the elemental analysis, the Alabama bituminous coal appears more aromatic than the Pittsburgh bituminous coal. If thermal decomposition behavior is related to infrared structural characteristics, the behavior of the Western bituminous coals should be similar to each other, but measurably different than that of the Eastern bituminous coals. The Alabama bituminous coal should in turn exhibit thermal decomposition behavior different than the Pittsburgh bituminous coal. The Western subbituminous coals would be expected to be similar to each other in their thermal decomposition behavior.

Variations in Tar Yields/Characteristics with Coal

The maximum tar yields obtained from the vacuum devolatilization experiments are listed in Table I and displayed in Fig. 2. The results indicate that the fractional conversion of the parent coal to tar is not a simple linear function of the H/C ratio, O/C ratio, hydrogen or oxygen percentages. For example, the Pittsburgh bituminous coal has a maximum tar yield 40-60% greater than the other bituminous coals. The hydrogen content of the Pittsburgh coal is ~ 3% lower than the Western coals and ~ 15% greater than the Alabama coal. The Alabama coal has a hydrogen content approximately 15% lower than the Western bituminous coals but has a maximum tar yield only 4% lower than the Colorado bituminous coal and about 9% less than the Utah coal. Differences in H/C ratios show a similar pattern.

Inspection of the infrared spectra of the parent coals also reveals no simple relationship between infrared spectral characteristics of a coal and its maximum tar yield. For example, the Pittsburgh bituminous coal has weaker absorption in the aliphatic hydrogen regions than either of the Western bituminous coals. The Alabama coal on the other hand gives a tar yield nearly the same as the Western coals, though it also displays weaker aliphatic absorption than these coals. The tar yields from the Western subbituminous coals are very nearly equal as are the tar yields from the two Western bituminous coals. As noted above, these pairs of coals have similar infrared spectra in the regions of interest - aliphatic type H, aromatic H, and oxygen - containing functional groups. The coals of similar infrared spectra do produce similar tar yields, but a coal with a dissimilar spectra can also produce comparable tar amounts.

The variations of maximum tar yield with elemental composition and infrared spectral characteristics both indicate the multi-parameter nature of the yield dependence. As a path from the low rank side of the coalification band is followed the tar-producing potential of a coal reaches a maximum in the H/C-O/C region near that of the Pittsburgh bituminous coal. It is interesting to note that this is not a point of maximum H/C nor does the infrared spectra of the coal show more aliphatic-type H than the other, lower rank coals. Beyond the Pittsburgh coal the tar yield drops with further decreases in H/C and O/C ratios. In this region the H/C ratio is changing more rapidly than the O/C ratio. The infrared spectra of these coals show well-defined aromatic hydrogen regions, reduced aliphatic hydrogen absorption and a reduction in oxygen-containing functional group absorption. Tar yields are increased as the O/C ratio is decreased from the low rank side of the coalification band. They are also increased as H/C ratios are increased from the high rank side of the band. Inspection of the infrared spectra indicates that tar yields do not vary directly with change in absorption characteristics associated with a particular structural characteristic. Such a relationship may be valid for samples from a limited region on Fig. 2. It appears that tar yields are related to a mix of structural characteristics present in the parent coal and as revealed by infrared and elemental analysis.

Tar Yields and Apparent Thermal History

Figures 4-6 show plots of tar yields obtained for various final temperatures. Figure 4 contains the results for the two Western subbituminous coals. Figure 5 displays the Western bituminous coal, and Fig. 6 the Eastern bituminous coals as well as the anthracite and lignite.

The tar yields obtained from the two Western subbituminous coals show a close resemblance both with respect to magnitude and final temperature dependence (Fig. 4). The Western bituminous coals also show a close resemblance to each other with respect to magnitude and final temperature dependence of the tar yields (Fig. 5). As noted above, these coals have similar infrared spectra. Both the subbituminous and Western bituminous coals show a maximum in tar yield at low final temperatures. This maximum occurs at approximately 775 C for the subbituminous coals but at a slightly lower temperature for the bituminous coals. The reduction in tar yield at final temperatures greater than the maximum is not as sharp as the rise to the maximum yield.

The Eastern bituminous coals also show a low temperature maximum in tar yield (Fig. 6). The Pittsburgh seam bituminous coal gives a maximum tar yield around 600 C whereas the Alabama bituminous coal shows a maximum around 700 C. The reduction in tar yields with final temperatures greater than these is not as sharp as

that of the Western subbituminous and bituminous coals. However, these coals do display the same steep gradient for the change in tar yield with final temperature on the low temperature side of the tar maximum.

Figure 7 shows typical char yields obtained during the runs. The char yield decreases sharply with final temperature in the 500-800 C range, the temperature range of greatest increase in tar yields. At final temperatures from 800 C to 1000 C, production is not as sensitive to changes in final temperature. The tar yields are decreasing significantly in this final temperature regime. For final temperatures greater than 1000 C total volatile yields do not increase appreciably. Tar yields continue to decrease to final temperatures of 1400 C at which point a high temperature asymptote is nearly achieved.

Examination of the thermocouple data for a decomposition run associated with a particular final temperature indicates that the apparent heating run did vary with final temperature setting. The initial slopes of the temperature-time data are taken as the apparent heating rate. The variation in apparent heating rate with final temperature is shown in Fig. 8. A final temperature setting of 500 C corresponds to an initial apparent rate of ~ 100 C/sec whereas a setting of 1000 C corresponds to an apparent rate of ~ 600 C/sec. Thus, the coal particles experience slightly different thermal conditions with variations in final temperature setting. The tar yields for the two Western bituminous coals and the Alabama coal are maximimzed under conditions of an apparent heating rate of approximately 200 C/sec and a final temperature temperature of ~ 700 C. The Western subbituminous coals on the other hand show tar maximums at a heating rate of ~ 250 C/sec to a final temperature of 775 C. The Pittsburgh bituminous coal has a tar maximum at 150 C/sec and ~ 625 C. The lignite and anthracite show no clearly defined maximum.

In light of these results and those of other investigations[8,9] it is obvious that further investigation of tar yields from bituminous coals under a wider range of thermal drive conditions is needed.

Tar Characteristics and Apparent Thermal History

Figure 9 illustrates the changes in the infrared spectral characteristics of tars collected for different final temperatures. As has been reported elsewhere[10,11,12], low temperature vacuum tars give infrared spectra similar to that of the parent coal but with enhanced absorption in regions associated with aliphatic hydrogen. As indicated, however, the high temperature tars show considerable reduction in absorption in regions associated with functional groups attached to aromatic rings. The low temperature tars apparently thermally decompose when subjected to

the longer times at higher temperatures that accompany the increase in thermal drive with final temperature. The condensed high temperature tars are noticeably darker than the low temperature tars, indicating a more aromatic nature.

Figure 10 shows typical paths followed by evolved chars in a H/C vs. O/C plot for different final temperatures. As reported elsewhere[13] the char shows a rapid decline in H/C and O/C values as volatiles are evolved. The low-temperature tars have H/C and O/C ratios greater than those of parent coal whereas the high temperature tars have values below those of the parent coal.

The nitrogen content of the evolved tars is of particular interest. Figure 11 shows fractions of parent coal mass evolved as tar vs. the fraction of parent coal nitrogen evolved as tar nitrogen. The fraction of fuel nitrogen evolved as tar is directly proportional to the fraction of coal mass evolved as tar.

Infrared spectra of the light gases evolved reveal that HCN is the principal nitrogen-containing gas species that is observed. Figure 12 is a plot of the fuel nitrogen distribution in the gaseous, tar and char species as observed for the Utah bituminous coal. The distribution pattern for the other subbituminous and bituminous coals were similar although the magnitudes of the distribution varied with rank characteristics of the coal. The main chracteristics of these nitrogen distribution plots are:

1. A low temperature evolution of fuel N as HCN-usually about 10% of the coal nitrogen to the point of maximum tar evolution.

2. The fuel nitrogen evolved as a tar component is directly proportional to the coal mass evolved as tar.

3. HCN is observed to be the major nitrogen-containing light gas.

4. As the tar fraction is reduced with higher final temperatures, HCN is a principal nitrogen-containing by-product.

5. Around 1100 C nitrogen is evolved from the char product as HCN. Little increase in total volatiles is observed at those temperatures but a substantial increase in nitrogen evolution as HCN is observed.

6. The nitrogen retained in the high temperature chars is a function of coal rank. Higher coal ranks retain a greater fraction of the coal nitrogen in the char product.

The nitrogen distribution in the thermal decomposition products reflects both the coal type and the conditions of thermal decomposition in a manner similar to the tar yields and properties.

Tar Yields and Ambient Pressure

Figure 13 displays the tar and char yields obtained from the bituminous coals as a function of ambient nitrogen pressure. The two Eastern bituminous coals and one Western bituminous coal produced tar yields as low as 50% of the vacuum value. The other Western bituminous coal gave an approximately 25% reduction in tar yield upon increasing the ambient pressure from near vacuum to one atmosphere of nitrogen. This coal showed a gradual reduction in tar yield with increases in pressure throughout this range. The other coals however showed much greater changes in tar yield per unit of pressure change in the range from near vacuum to 190 torr of nitrogen than from 190 torr to 760 torr.

The decrease in tar yield with increase in ambient pressure did not result in a proportionate reduction in total volatiles yield for any of the coals investigated (Fig. 13). The Pittsburgh bituminous coal produced about a 20% reduction in total volatiles yield while the tar yield dropped by 50%. Two other bituminous coals displayed only 10% reductions in total yield. The coal giving the gradual reduction in tar yield over the entire pressure range showed no significant decrease in total yield as the tar yield decreased.

There has been no direct measurement of the gas species produced at various ambient pressures while the tar yield is being reduced. However, the decrease in tar yield per unit mass of coal is accompanied by a proportionate increase in internal pressure within the reactor above the initial pressure. Thus, there appears to be a significant increase in light gas yield as the tar yield is decreased due to ambient pressure effects.

Apparently the ambient pressure serves to decrease the rate of escape of the large tar species from the devolatilizing coal mass. Such effects have been reported elsewhere.[3,6] The increased contact time of the large hydrocarbon species with the hot coal mass promotes further cracking of these species to lighter gases. As a result more light gas species are produced per unit of total yield. The thermal degradation of the tar mass in contact with the coal/char results in some secondary deposition of carbon on the devolatilizing particles. The amount of secondary deposition seems to be dependent upon the specific coal and its properties during the decomposition process.

Tar Characteristics and Ambient Pressure

In order to determine if any overall changes in the chemical nature of the tars released occurred due to changes in ambient pressure, dried KBr pellets were placed above the grid within the reaction chamber. After a run the pellets were removed and scanned with the FTIR. The infrared spectra of the tars formed in vacuo closely resemble the spectra of the parent coal from which it was derived. However, the infrared spectra of the tars formed under pressure showed reduced absorption in the regions associated with functional groups of vacuum tars. The greatest reductions occur in the near vacuum to 190 torr region, corresponding to the greatest reducing in tar yield per unit change of ambient pressure. As pressures are increased beyond 190 torr further reductions in absorption due to functional groups are slight. The Utah bituminous coal showing the least change in tar yield per unit pressure increase also displays the least change in functional group absorption per unit pressure increase.

The tar pellets from the pressure runs scattered the infrared beam considerably, where as the pellets from the vacuum runs did not. It is believed that the scatter is due to the physical form of the tars condensed on the pellets. In the case of the devolatilization runs performed with an ambient pressure, the tars released immediately form an aerosol mist. It is these mists which condense on the KBr pellets. The particle-like nature of the condensed tar mass on the pellets scatters the infrared signal. No mist is observed in the case of the vacuum runs. The vacuum tars apparently coat the KBr pellets in more of a molecular-layering like condensation. Scanning Electron Microscope photographs of the tars condensed on glass fiber filters placed in the reaction vessel reveal crystallite-like structure formed on the filters from the vacuum runs. The filters from the pressure runs displayed particle-like droplets coating the filters. Tar droplet formation similar to this has been observed elsewhere but under different devolatilization conditions.[9,14]

In order to demonstrate the propensity of the tar mass to form aerosol mists when released in ambient pressure conditions high speed films were made of the devolatilizing Pittsburgh bituminous coal. A cross flow of nitrogen across the heating grid immediately swept any released volatiles from the grid so that a clear view of the decomposing coal mass could be maintained. The plasticizing Pittsburgh coal was selected for the initial film study since the release of volatile matter during the plastic stage of decomposition can be observed to occur via bubble rupture. By means of a framing projector one can obtain a rough estimate of the time interval between the rupture of a specific bubble and the formation of a visible aerosol mist in the flow stream around the grid. Examination of such films

reveals that the aerosol mist formation in a one atmosphere cold flow is rapid, taking place during the first few milliseconds of the bubble rupture.

Summary and Conclusions

Based on these initial investigations the following general observations can be formulated:

1. In vacuo tar yields can be related to structural characteristics of the parent coal:

   a. For coals with O/C values less than ~ 0.09 the tar yield appears to be proportional to the H/C parameter. In this region as previously reported,[15] the maximum tar yield appears to be proportional to the aliphatic-type functional groups of the parent coal as revealed by infrared analysis of the coal.

   b. For coals with O/C values greater than 0.1 the tar yield is inversely proportional to the O/C values of the coal. In this region the tar yield appears to be proportional to a mix of aliphatic and oxygen-containing functional groups as revealed by infrared analysis.

   b. Consequently, predictive equations for in vacuo tar yields which are to be valid for a range of coals along the coal-lification band must consider the multi-parameter nature of the dependence of tar yield on intrinsic coal structural paramters.

2. In vacuo tar yields are dependent on the thermal drive experienced by the coal particles. Subbituminous and bituminous coals produce a maximum tar yield when heated to a final temperature in the 600 C to 800 C range with an apparent heating rate of ~ 100-200 C/sec. Coals with higher O/C ratios display a sharper reduction in tar yields with an increase in thermal drive characteristics beyond these values.

3. Tar yields for bituminous coals are sensitive functions of ambient pressure in the near vacuum to one atmosphere region. Reduction in tar yields up to 50% of the in vacuo value are observed. Total volatile yields are not proportionately reduced.

4. Physiochemical characteristics of tar species are dependent on parent coal structural characteristics as well as the conditions of devolatilization. Vacuum formed low temperature tars closely resemble the parent coal in structural characteristics. Changes in apparent thermal drive and ambient conditions produce changes in tar characteristics. In general, functional group characteristics are reduced with increases in thermal drive and ambient pressure. HCN appears to be a principal nitrogen-containing light gas species released as tar yields are reduced with an increase in thermal drive.

Since tar yields and characteristics are sensitive functions of coal characteristics and devolatilization conditions, predictive relationships are of necessity multi-parameter in nature. Both intrinsic and process parameters must be considered as the tar yields and characteristics are shown to be sensitive functions of both. The sensitivity of yields and characteristics to parameter changes for a wide variety of coals is indicative of the coupled chemical kinetic-transport nature of coal devolatilization.

ACKNOWLEDGMENTS

The authors would like to express gratitude to David Santos and Gerald Wagner for their technical assistance and to Marty Zabielski for assistance in the grid temperature measurements and interpretations. We are grateful for the financial support of the Department of Energy under Contract ET-78-C-01-3167, Energy and Environmental Research Corporation under Contract EER-8318-8, and United Technologies Corporation financial support under its Chemistry of Coal Gasification project.

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TABLE I

ELEMENTAL ANALYSIS (DMMF) AND TAR YIELDS

	Mon Lig(L)	WY Sub(S1)	WY Sub(S2)	Utah Bit(UB)	Col Bit(CB)	Pitt Bit(PB)	Ala Bit(AB)	Anth. (AN)
C	0.6827	0.7540	0.7550	0.7818	0.8100	0.8197	0.8497	0.9369
H	0.0457	0.0490	0.0517	0.0552	0.0553	0.0536	0.0463	0.0259
O	0.2547	0.1807	0.1699	0.1386	0.1119	0.0936	0.0818	0.0189
N	0.0102	0.0128	0.0171	0.0169	0.0163	0.0142	0.0173	0.0108
S_o	0.0067	0.0035	0.0063	0.0076	0.0064	0.1089	0.0052	0.0072
H/C	0.803	0.780	0.822	0.847	0.819	0.785	0.654	0.332
O/C	0.280	0.180	0.169	0.133	0.104	0.086	0.072	0.015
Max Tar%	18	20	21	27	26	39	25	2
T_{max} tar (^oC)	-----	750-800	750-800	675-725	675-725	600-650	700-750	-----

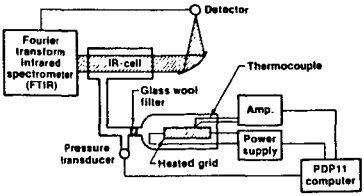

Figure 1: Heated Grid Pyrolysis Apparatus

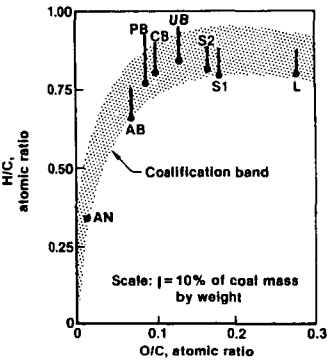

Figure 2: Tar Yields and Coalification Band Position (See Table I for Abbreviation Key) Tar Yields Are Maximum Tar Yields Obtained in Vacuo

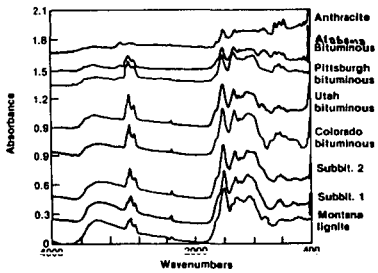

Figure 3: IR Spectra of Coals

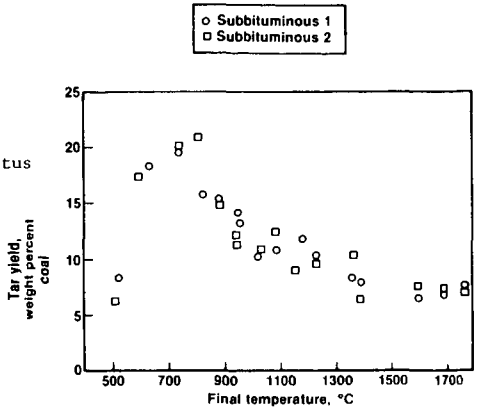

Figure 4: Tar Yields as a Function of Final Temperature for Western Sub-bituminous Coals

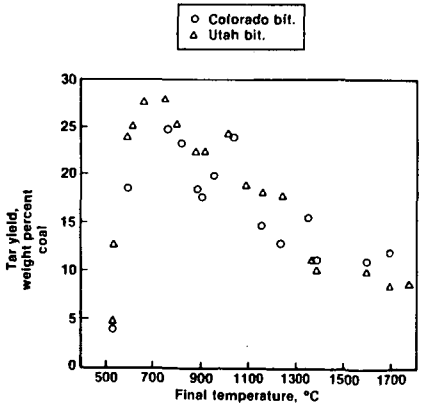

Figure 5: Tar Yields as a Function of Final Temperature for Western Bituminous Coals

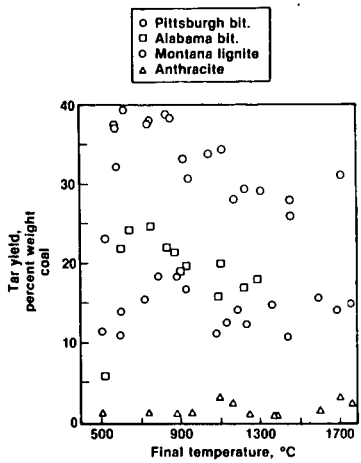

Figure 6: Tar Yields as a Function of Final Temperature for Eastern Coals and Montana Lignite

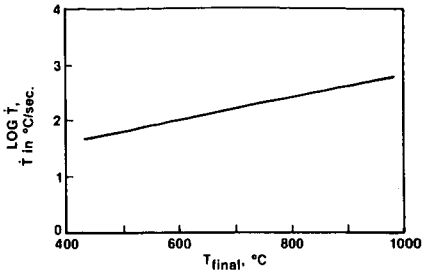

Figure 8: Temperature - Heating Rate Correlation: 75 μm Thermocouple Bead Placed Between Folds of Grid

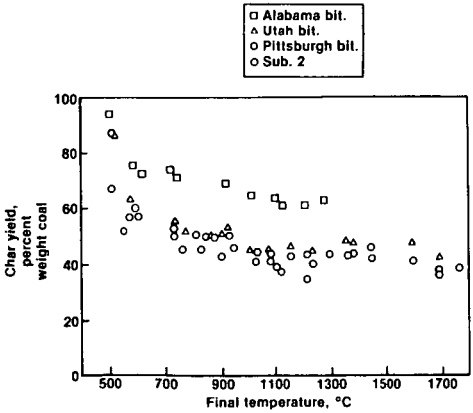

Figure 7: Char Yields as a Function of Final Temperature

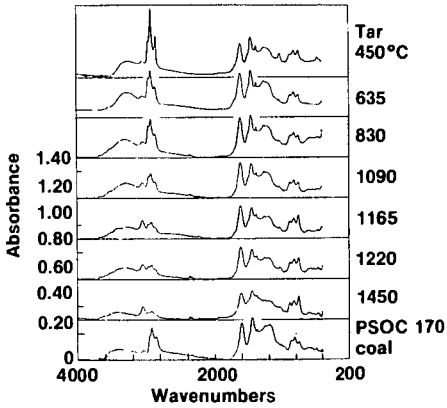

Figure 9: IR Spectra of Tars from Pittsburgh Bituminous Coal Tars from 10 Sec Vacuum Pyrolysis at the Indicated Final Temperature

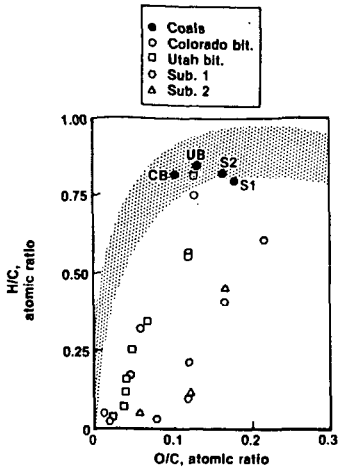

Figure 10: H/C - O/C Paths During Thermal Decomposition Process

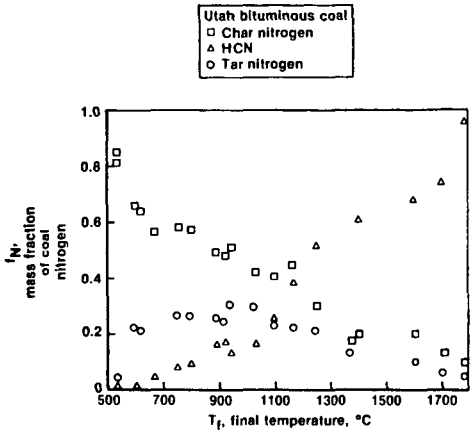

Figure 12: Nitrogen Distribution in Thermal Decomposition Products of The Utah Bituminous Coal

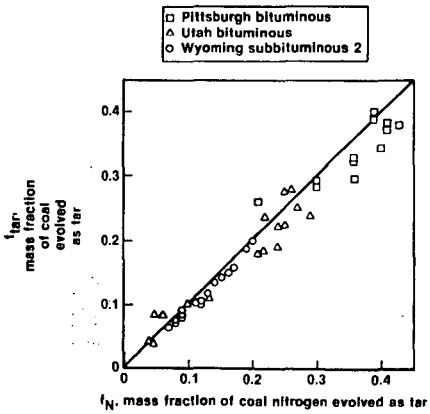

Figure 11: Mass Fraction of Coal Mass Vs. Mass Fraction of Coal Nitrogen

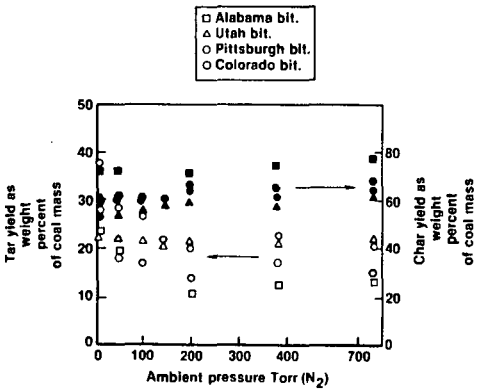

Figure 13: Tar and Char Yield Variation with Ambient Pressure Open Symbols → Tar; Closed Symbols → Char: Final Temperature - 635°C, Thermocouple Heating Rate ≈ 150°C/sec