

COAL STRUCTURE VS. FLASH PYROLYSIS PRODUCTS

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The fast pyrolysis of coal produces tar, char and a range of low molecular weight gases in various proportions and amounts depending on the pyrolysis conditions (temperature, pressure) and the coal being pyrolyzed. Much research effort has been devoted to study of the reaction kinetics and effect of process variables, attempting thereby to elucidate the pyrolysis mechanism⁽¹⁾. Less effort has been focused on coal chemical structure and its relationship to the pyrolysis reactions and pyrolysis products. It was to attempt to better understand coal structure and its influence on pyrolysis products and pyrolysis mechanisms that this project was undertaken. This paper will report only on that portion of the work concerned with the aliphatic hydrocarbon products and particularly the light olefins.

A continuous bench-scale pyrolysis apparatus (Fig. 1) was constructed similar to the design of Tyler⁽²⁾. The coal entrained in a nitrogen stream was injected into a sand bed fluidized with nitrogen and heated in a split furnace to the temperature desired. Volatiles emitted from the sand bed were passed into two cold traps in series containing cellulose thimbles to filter out the tar and char from the off-gas. Gas exiting the cold traps was vented through a wet-test meter with a side stream entering a Perkin-Elmer Sigma One computer-controlled gas chromatograph which analyzed for some 16 components. At the end of a pyrolysis run, the tar and char caught in the two thimbles were extracted in a soxhlet extractor with methylene chloride and methanol to obtain the weight of tar and char produced.

Figure 2 shows tar yields vs. temperature for a Texas Lignite. Figure 3 shows how the quantity and composition of the pyrolysis gas from the same coal varies with temperature. Only the major gases are shown. These curves are typical of many coals although the actual quantities vary⁽³⁾. From these two figures, it is apparent that the tar produced goes through a maximum at about 600°C and up to that temperature relatively small amounts of gases are evolved. Above 600°C, the production of the various gases increases rapidly while at the same time, the tar yield drops off. The inference can be drawn that the gas is coming from tar pyrolysis. That this is so, can be shown by pyrolyzing tar which has been produced at 600°C, at higher temperatures. Similar gaseous products are produced and in similar ratio as when coal is pyrolyzed at the higher temperature⁽⁴⁾.

The yields of the hydrocarbon gases produced on coal pyrolysis vary greatly depending on the particular coal. This is shown for ethylene, one of the major products, in the first two columns of Table 1. The ethylene yield is related to the propylene

yield as shown by Figure 4. Similarly, the ethylene yield is related to the butadiene yield, suggesting that these gases have a common precursor. The methane and benzene, however, show no obvious relation to the ethylene yields. These products are apparently derived mainly from other components in the coal.

Coal Structure vs. Pyrolysis Products

To try to relate these yield differences to structural differences in the coals themselves, each coal whose pyrolysis behavior was studied was examined by ^{13}C NMR (with cross polarization and magic angle spinning). This work was done by E. A. Hagaman and H. Zeldes of Oak Ridge National Laboratory in a cooperative program with Du Pont. Typical pattern differences between a high ethylene-producing coal (PSOC 124), a low ethylene-producing bituminous coal (Sewickley) and two intermediate coals (Con Paso Blue 2 and PSOC 181), are shown in Figure 5. While the PSOC 124 coal shows high aliphatic character and the Sewickley shows the expected higher aromaticity, various other evidence suggests that aliphatic character alone is not the determining factor. The fractional area representing a chemical shift at 31 ppm, however, which is associated with methylene chains greater than 5 or 6 segments long, appears to correlate with the ethylene yield results. This peak which occurs at a chemical shift of 29 ppm in substances in solution is apparently shifted slightly to 30-32 ppm in solid coal. This was shown by running stearic acid in solution, and impregnated on to anthracite coal. The 29 ppm peak was shifted up field and broadened on the coal.

A plot of ethylene yield vs. the area fraction of the ^{13}C NMR spectrum at a chemical shift of 31 ppm, times the weight fraction of carbon in the coal is shown in Figure 6. The line is the least-squares fit to the points shown. While there is scatter in the data, a correlation is apparent (Correlation coefficient = .92).

Tar Structure Studies

Low temperature (600°C or less) pyrolysis of coal produces high yields of tar which on further pyrolysis produces the volatile hydrocarbon products we observe on high-temperature pyrolysis of coal. This shows that this tar contains the aliphatic precursors we observe in the coal itself, although they may be changed somewhat from the form in which they are in the coal. A number of tars were therefore produced by pyrolysis of several different coals at 600°C in the laboratory coal pyrolysis unit for further study.

A ^{13}C NMR pattern for a solution of Millmerran tar (10% in CDCl_3) from 600°C pyrolysis is shown in Figure 7. It shows a very strong peak at a chemical shift of 29 ppm. The ^1H NMR spectrum was run on the same tar in CDCl_3 solution (Figure 8). It shows a strong peak at 1.2 ppm known to be due to methylene chains over 5 units long. By using a Dow Corning silicone DC200 fluid ($\% \text{H} = 8.06$) internal standard in the CDCl_3 solvent, quantitative determination of the $(\text{CH}_2)_n$ peak by ratio of its area to that of the 0 ppm silicone peak was possible. This showed 33.6 wt. % $(\text{CH}_2)_n$ in the tar. Similar patterns are shown by tars of other coals.

To quantify the assignment of the 1.2 peak in the proton NMR spectrum, a series of model compounds having long methylene chains was dissolved in CDCl_3 containing the silicone internal standard. In all cases, the 1.2-1.3 peak was very large and clearly detectable. Weight % $(\text{CH}_2)_n$ calculated for each compound are shown in Table 2. As can be seen from the Table, not all methylene groups appear in the proton NMR spectrum at 1.2-1.3 ppm. Only those (CH_2) groups shown in brackets in the structural formulas show up at that place. Those CH_2 groups conjugated with or close to the carboxyl groups or benzene rings appear at higher chemical shifts, and methyl groups appear at 0.7-0.8 ppm. This clearly identifies the 1.2-1.3 ppm peak as due to $(\text{CH}_2)_n$ but at the same time indicates that any analysis based on this method will not include all of the (CH_2) groups in coal. If the chains are long, however, most of the methylene will be included.

Table 3 shows the distribution of types of protons in 600°C pyrolysis tars from four different coals representing a wide range of olefin yields on pyrolysis. The Table shows that roughly 35% of the protons in the tar are polymethylene protons, the rest are divided between methyl groups, hydroaromatic hydrogens, hydrogens attached to aromatic carbons, and a small number of olefinic and some unidentified protons.

Table 4 shows the distribution of protons in tar from Texas Lignite pyrolyzed at various temperatures from 600°C to 920°C. This clearly shows that as the pyrolysis temperature is increased, the content of polymethylene in the tar decreases as do the hydroaromatic hydrogens. The aromatic hydrogens on the other hand increase rapidly to become the predominant species. This provides a convenient measure of the completeness of pyrolysis.

To try to isolate and purify larger quantities of the hydrocarbon precursors, a separation was made of the Millmerran tar by Preparative Liquid Chromatography. A number of fractions across the chromatogram were analyzed by FTIR and ^1H NMR and fraction 21 representing 38% of the original sample turned out to be high in $(\text{CH}_2)_n$ (concentration 68%). An Infrared spectrum of that fraction (Figure 9) showed a well resolved peak at 720cm^{-1} , known to be characteristic of long methylene chains. This peak has a low extinction coefficient and is rarely discernible above background in coals themselves. A GC/MS pattern of that fraction (Figure 10) shows olefin/paraffin pairs of peaks from C_{17} to C_{24} .

The polymethylene compounds in pyrolysis tars are mainly present as linear paraffins or olefins, however, there are indications of lesser amounts of branched paraffins and olefins and alkylaryl compounds as well in the unfractionated tars. The form the polymethylene compounds have in the coal itself is not known, but extraction of various coals with methylene chloride for several days failed to remove more than 1% of the material, suggesting that the major part of the polymethylene compounds may be either chemically combined in the coal structure or else trapped.

Model Compound Pyrolysis

While it seemed likely on the basis of petroleum experience that polymethylene compounds would pyrolyze to form the low molecular

weight aliphatic hydrocarbons we observe on coal pyrolysis, known compounds as models of polymethylene and other structures in coal were pyrolyzed at similar temperatures and contact times as the coal.

Table 5 summarizes the results of pyrolysis of 7 model compounds. Products are only shown as major and minor. As can be seen by referring to the Table, under the pyrolysis conditions used, compounds containing methylene chains such as dodecane, octadecane, stearic acid, ethylbenzene, propylbenzene, butylbenzene, and phenyl-dodecane on cracking give substantial quantities of ethylene along with butadiene, propylene and other hydrocarbons in amounts roughly comparable to what we observe in coal pyrolysis. The aromatic portion in alkylaryl compounds appears to go mainly to toluene although small amounts of benzene and some styrene are produced as well. Some methane is also produced along with minor amounts of ethane, butane and other hydrocarbon. These results are quite consistent with what we find in coal pyrolysis and with petroleum cracking technology.

Interestingly, the methylaryl compounds investigated thus far do not produce methane on pyrolysis under the conditions we used. Toluene and the three xylene isomers apparently are only slightly converted at 850°C and 0.5 to 1.0 second contact time in the sand bed. 9-Methylantracene and 3,6-dimethylphenanthrene produced no methane or other gaseous products, although they appeared to form tar or coke. This is consistent with the observations of Lang et al on methyl-naphthalenes(5) which form condensation products but not gases under pyrolysis conditions.

Analysis for Polymethylene in Coal Itself

With ^{13}C NMR indication of the $(\text{CH}_2)_n$ moiety in coal and evidence of $(\text{CH}_2)_n$ in low and high temperatureⁿ pyrolysis tars, as well as model compound pyrolysis information, it seemed important to devise a quantitative analytical method for $(\text{CH}_2)_n$ in coal itself. This raised the question whether coal could be liquefied under generally accepted solvent refining conditions and still retain undecomposed the polymethylene component? Also, if the $(\text{CH}_2)_n$ is liberated but not destroyed, can it be detected and quantitatively determined by proton NMR?

Figure 11 shows the proton NMR pattern of the liquefaction product of PSOC 124, a high ethylene yielding coal which was liquefied using 3 grams of coal, 3 grams of tetralin as donor solvent, 0.1 gram each of sodium sulfide and ferrous sulfide as liquefaction catalysts and 2000 psi pressure (cold) of hydrogen in a 10 ml shaker bomb. The liquefaction was run at 425°C for 2 hours in a sand bath with vertical shaking. The product liquid was washed out of the shaker tube with methylene chloride and filtered to remove the solids (ash, unconverted coal and catalysts). After removal of the CH_2Cl_2 by distillation, a weighed sample of the liquid was dissolved in deuterio-chloroform containing a known amount of DC200 silicone fluid as internal standard. Examination of the NMR pattern clearly shows the $(\text{CH}_2)_n$ peak at 1.2 ppm and the CH_3 peak at about 0.8 ppm indicating that the polymethylene component of the coal is released from the coal matrix but not destroyed in the liquefaction process.

The rest of the NMR pattern (beyond 1.3 ppm) is heavily affected by the presence of the donor solvent and its dehydrogenation products so that this method is only useful for detecting the $(\text{CH}_2)_n$.

To develop a routine analysis based on coal liquefaction, first a series of batch shaker tube liquefaction runs were made in 10 ml shaker tubes using the same recipe as previously but varying the time, temperature and donor solvent. Tests were made with three different donor solvents [tetralin, dihydrophenanthrene (DHP), and tetrahydroquinoline (THQ)]. The $(\text{CH}_2)_n$ figures on the right hand 5 columns of Table 6 were obtained by separating the liquid from the solid by extraction with CH_2Cl_2 , filtration to remove the solids, and distilling off the solvent (CH_2Cl_2). The $(\text{CH}_2)_n$ content of the liquid was determined by dissolving a weighed sample of liquid into a volumetric flask and making up to the line with CCl_3D containing a known quantity of DC-200 silicone internal standard. All conversions were 85% or more and usually above 90%.

In most cases, all three donor solvents gave similar results, but in a few cases the tetrahydroquinoline gave higher values. THQ was, therefore, selected for further investigation. Liquefactions were run, varying temperature and contact time. These results are shown in the three right-hand columns of Table 6 where results were reported for 400°C and 1.65 hours and 435°C for 4 hours. The lower temperature short contact time liquids were viscous and hard to work up. The high temperature longer time reactions showed little change over the 425°C/2 hour samples, so the latter conditions were selected as optimum.

The values obtained for $(\text{CH}_2)_n$ content of coals from coal liquefaction are reasonable based on the amount of ethylene produced in pyrolysis shown in column 1 and ethylene plus other hydrocarbons believed to come from the same source shown in column 2 of Table 6. These should represent minimum amounts in the coal. Column 3 shows the $(\text{CH}_2)_n$ found in pyrolysis tars calculated on the basis of the original coal which should also be a minimum since not all the tar is driven out of the coal at 0.5 seconds pyrolysis contact time.

For a number of reasons, it was desirable to be able to run this liquefaction analysis on a micro (<10 mg) scale. This would be much simpler to do if no added catalyst was required and hydrogen pressure was not needed. Experiments were, therefore, tried to see whether such an analysis could be developed under those conditions. Liquefactions were run in 3" long 3 mm pyrex glass tubes. Approx. 5 mg of (-200 mesh) coal samples (weighed to .01 mg) were charged to the tubes along with 10 mg of calcined clean sand, 1.1 times the weight of coal of the donor solvent and a 1 cm long 2 mm glass rod (for agitation) and the tubes purged with nitrogen and sealed.

Two such tubes were packed into each 10 ml shaker tube with steel wool packed around them. They were then subjected to 425°C for 2 hours in a sand bath with rapid vertical agitation with approximately 5 minutes heat up time to temperature and rapid cool down in a cold air stream.

The tubes were worked up by breaking in the middle and rinsing repeatedly with CCl_3D containing a weighed amount of DC-200 fluid, through a glass wool plug filter into a 1 ml volumetric flask. The contents of the flask were put into an NMR tube and run on the IBM NR-80 Fourier Transform NMR Spectrometer. The area of the 1.2 ppm peak was determined relative to the silicone peak and the weight % $(\text{CH}_2)_n$ calculated using the area ratio.

The results of these experiments are shown in columns 1, 2 and 3 in Table 7. They clearly show that low results are obtained with tetralin and dihydrophenanthrene under these conditions. This may be due in part to lower donor activity, but more likely due to low hydrogen content of the donor in the absence of a hydrogen atmosphere. The results with tetrahydroquinoline, however, appear to be about the same whether in the micro mode without hydrogen pressure or catalyst or in the macro mode with both. This system was, therefore, adopted as being simple, rapid and giving results equivalent to the macro system. Analysis of pairs of samples from some 40 coals by this method ranging in % $(\text{CH}_2)_n$ content by weight of from 0 to 17% (MF) showed a standard deviation of 0.59%. Table 1 column 3 shows these values for the coals previously discussed together with the ethylene yields. In view of the sampling problems with a heterogeneous material like coal and the small sample size, analyses were normally run in pairs. The coal was ground fine (-200 mesh) and well blended. Where greater accuracy is desired, more replicates can be easily run and the ^1H NMR can be run with more scans.

Ethylene yields (850°C) vs. $(\text{CH}_2)_n$ concentration for these coals are plotted in Figure 12 with the linear regression line shown. A correlation coefficient of 0.952 and a 0 intercept shows a good correlation.

Similarly plots of propylene and butadiene yields for the same coals, vs. $(\text{CH}_2)_n$ content also show strong correlations.

Conclusions

We conclude from the experiments described that the low molecular weight aliphatic hydrocarbons produced by flash pyrolysis of coal at temperatures of 700°C and over, result primarily from the cracking of long methylene chains which are part of the coal structure or trapped in it. Low temperature (600°C) pyrolysis of the coal drives off a portion of the coal as tar which contains these polymethylene moieties, primarily in the form of normal paraffins and olefins from C_{17} to C_{24} and higher. This polymethylene precursor(s) in coal is apparently destroyed during coalification, as it is essentially absent in anthracite and is much higher in lignite and subbituminous coals. However, even in low rank coals the concentration of the polymethylene moiety varies widely, probably determined by the types of plants from which the coals are derived. Cannel coals generally contain fairly large amounts of $(\text{CH}_2)_n$ (up to 17% or more). Some lignites and subbituminous coals contain as much as 10% $(\text{CH}_2)_n$.

Several other investigators (6-15) have reported the presence of aliphatic hydrocarbons in coal based mainly on solvent extractions. The amounts reported, however, have been generally much less than was found in this work. The difference presumably is that most of the polymethylene is chemically bound or trapped and non-extractable. Deno⁽¹⁶⁾ reported the presence of long chain methylene compounds by chemical degradation of the coal, however, no quantitative conclusions could be drawn from that work.

The liquefaction method for estimation of $(CH_2)_n$ content of coals is being used to determine the $(CH_2)_n$ content of coal macerals and to explore the geochemical origins of the polymethylene components in coal.

Acknowledgements

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REFERENCES

1. Howard, J. B., Chemistry of Coal Utilization, second supplement, Wiley Interscience, pps. 665-783
2. Tyler, Ralph J., "Flash Pyrolysis of Coals - 1", Fuel, 59, 218 (1980)
3. Tyler, Ralph J., "Flash Pyrolysis of Coals - 2", Fuel, 59, 218 (1980).
4. Tyler, Ralph J., "The Chemistry of Flash Pyrolysis; Secondary Cracking", 6th Anstradian Workshop on Coal Hydrogenation, November 13, 1981.
5. Lang, K. F. et al, Chem. B 89 2866 (1956).
6. Vahrman, M., Fuel 49 5 (1970).
7. Spence, J. A. and Vahrman, M., Fuel 49 395 (1970).
8. Rahman, A and Vahrman, M., Fuel 50 318 (1971).
9. Birkofer, L. et al, Brennstoff Chemie 50 376 (1969).
10. Chauvin et al, Bull de la Soc. de France 11 3916 (1969).
11. Bartle, K. D. et al, J. Appl. Chem. 20 197 (1970).
12. Bartle, K. D. et al, Fuel 54 226 (1975).
13. Bartle, K. D. et al, Fuel 58 410 (1979).
14. Bartle, K. D. et al, Nature 277 184 (1979).
15. Zilm, K. N. et al, Fuel 58 11 (1972).
16. Deno, N. et al, Fuel 60 210 (1981).

FIGURE 1
 -1 GM/HR COAL PYROLYSIS UNIT

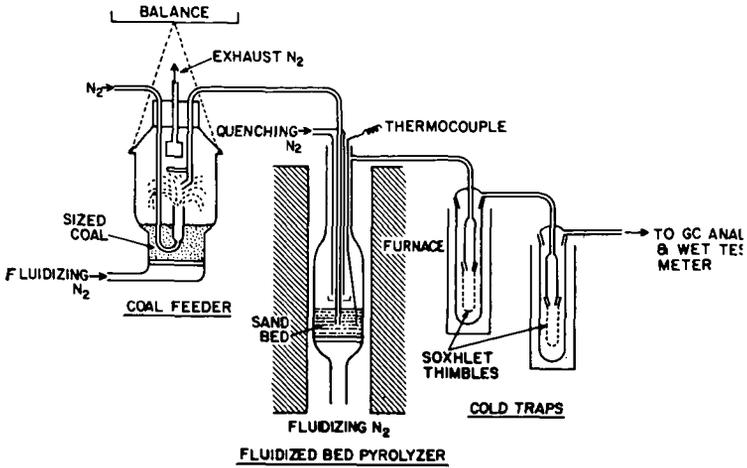


FIGURE 2

PRODUCT YIELDS FROM THE FLASH PYROLYSIS
 OF TEXAS LIGNITE

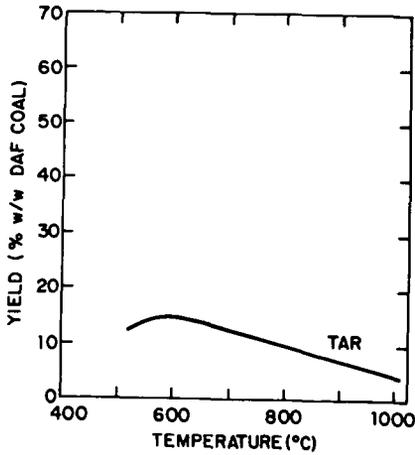


FIGURE 3
 PYROLYSIS OF TEXAS LIGNITE
 YIELDS OF PRINCIPAL GASES

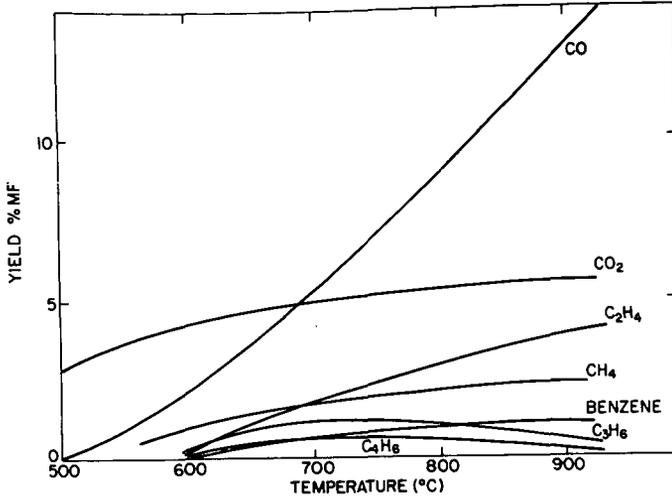
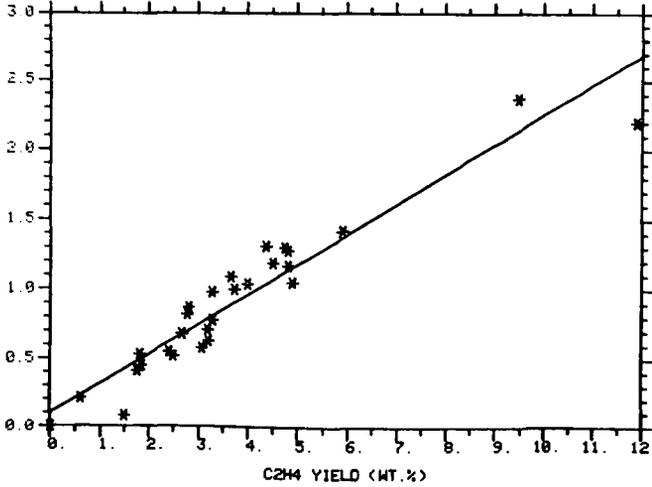


FIGURE 4

C₃H₆ (WT. %)

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ETHYLENE VS PROPYLENE YIELDS (WT. %)



C2H4 YLD (WT. %)

FIGURE 6

08:19 8-MAR-63

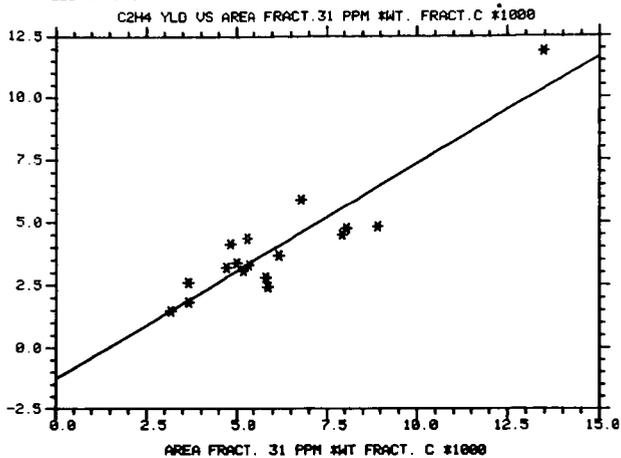


FIGURE 5
¹³C NMR SPECTRA OF COALS PRODUCING DIFFERENT ETHYLENE YIELDS ON PYROLYSIS (850°C 4sec. CT)

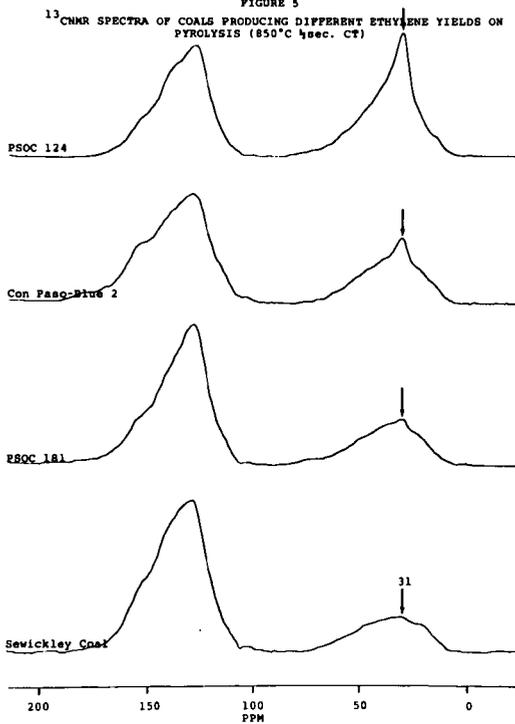


FIGURE 9

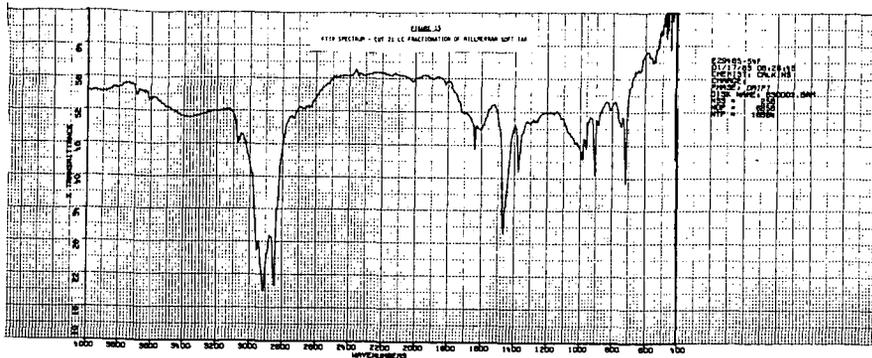
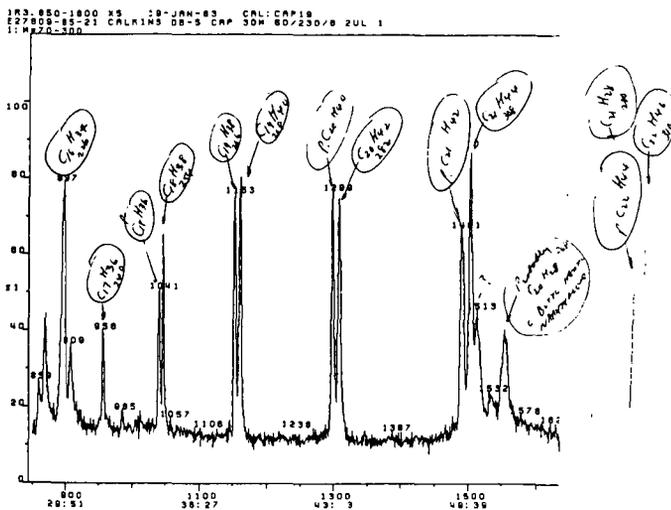


FIGURE 10

GC/MS SPECTRUM - CUT 21 LC FRACTIONATION OF MILLERRAN SOFT TAR



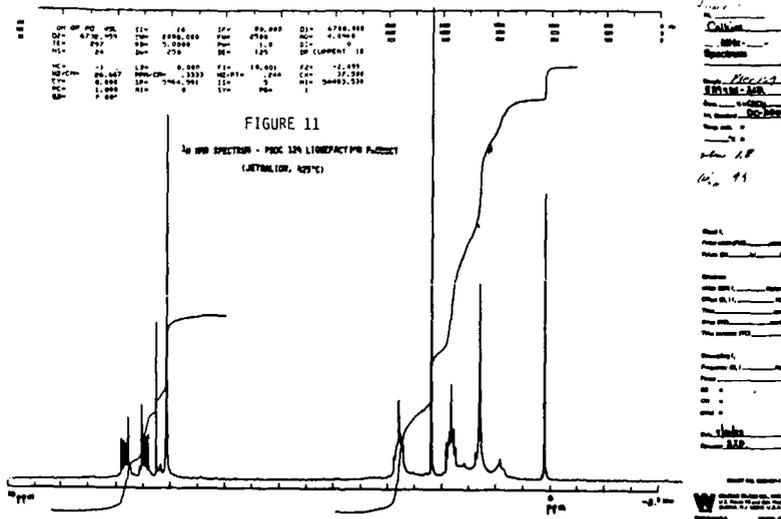


FIGURE 12

C2H4 YIELD (WT.%)

08:58 19-JAN-83

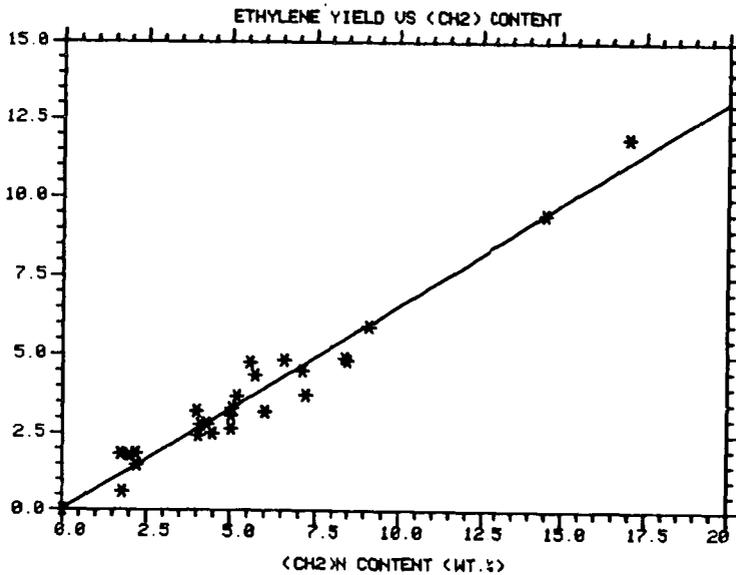


TABLE 1

ETHYLENE YIELDS IN COAL PYROLYSIS AND (CH₂)_n CONTENT (WT. %)

(850°C 0.5 sec. CT.)

<u>Coal</u>	<u>MF*</u>	<u>MAF**</u>	<u>(CH₂)_n (MF)*</u>
PSOC 124	11.9	13.1	17.0
King Cannel	9.47	11.04	14.5
Millmerran	6.08	7.01	9.65
Lovelady-L-2	5.91	7.94	9.11
Lovelady Y-4	4.90	6.68	8.40
Lovelady 81 VLL-92	4.82	7.00	8.48
Blind Canyon	4.82	5.07	6.56
PSOC 435	4.75	4.98	8.86
Emery	4.50	4.95	7.12
Con Paso-Blue 3	4.36	4.88	5.72
Con Paso-Blue 2	3.73	4.78	7.21
Con Paso-Yellow 4	3.67	4.17	5.18
Upper Hiawatha	3.30	3.65	5.03
Wyodak	3.21	3.52	4.0
<u>Texas Lignite</u>	3.20	3.59	6.01
PSOC 181	3.07	3.33	5.02
Con Paso-Yellow 6	2.80	3.05	4.31
PSOC 464	2.78	3.06	4.12
Lower Hiawatha	2.66	2.85	5.00
Pittsburgh 8	2.50	2.98	4.47
PSOC 1106	2.42	2.53	4.04
PSOC 657	1.85	2.28	2.18
Illinois 6-Burning Star	1.83	2.18	1.75
PSOC 833	1.77	2.01	2.00
Sewickley	1.48	1.75	2.20
Ohio 9-Egypt Valley	.61	.68	1.78
Anthracite	0.0	0.0	0.0

*Moisture Free

**Moisture and Ash Free

TABLE 2

(CH₂)_n ANALYSIS OF KNOWN COMPOUNDS
(Proton NMR)

	<u>Theory</u>	<u>Found</u>
CH ₃ [(CH ₂) ₁₄]CH ₂ CH ₂ - $\overset{\text{O}}{\underset{\text{ }}{\text{C}}}$ -OH	64.0	62.6
CH ₃ [(CH ₂) ₁₀]CH ₃	82.0	77.7
CH ₃ [(CH ₂) ₁₃]CH ₃	85.8	81.8
CH ₃ [(CH ₂) ₁₇]CH ₃	88.8	84.6
CH ₃ [(CH ₂) ₂₂]CH ₃	91.1	91.7
CH ₃ [(CH ₂) ₂₃]CH ₃	91.5	92.5
 CH ₂ CH ₂ [(CH ₂) ₉]CH ₃	51.2	49.1

TABLE 3

600°C. PYROLYSIS TARS - DISTRIBUTION OF TYPES OF H ATOMS

PPM	0.8	1.3	1.6-1.7	1.7-3.0	5.2	7.2
H TYPE	CH ₃	(CH ₂) _n		hydroaromatic or benzylic	olefinic	aromatic
<u>COAL TYPE</u>						
Texas Lignite	.085	.352	.077	.300	--	.187
Emery	.099	.331	.064	.263	.016	.232
PSOC 124	.110	.349	.170	.190	.010	.175
PSOC 435	.113	.220	.113	.267	.003	.166

TABLE 4

PYROLYSIS TARS - DISTRIBUTION OF H ATOMS
TEXAS LIGNITE PYROLYSIS VS. TEMPERATURE

H TYPE	PPM	.3 - .5	.8	1.3	1.6 - 1.7	1.7 - 3.0	5.2	6.5 - 8.0
			CH ₃	(CH ₂) _N		HYDROAROMATIC	OLEFINIC	AROMATIC
600		=	.110	.320	.048	.259	.044	.141
700		=	.100	.254	.036	.258	.048	.250
825		=	.067	.189	.027	.208	.053	.414
850		.009	.035	.078	.106	.159	.009	.566
920		.027	.018	.099	.117	.072	-	.577

TABLE 5

PYROLYSIS OF MODEL COMPOUNDS (LIQUIDS)
 (0.3 ml/hr Liquid Feed in ca 2.1 l/min. N₂)
 850°C 0.5-1.0 Sec. Contact Time

<u>Model Compound</u>	<u>Gaseous or Volatile Products</u>	
	<u>Principal Products</u>	<u>Minor Products</u>
Stearic Acid	C ₂ H ₄ C ₃ H ₆ C ₄ H ₆ CH ₄ CO ₂	Benzene C ₂ H ₆
Dodecane	C ₂ H ₄ C ₃ H ₆ CH ₄	C ₄ H ₆ C ₂ H ₆
Octadecane	C ₂ H ₄ CH ₄ C ₃ H ₆	C ₄ H ₆ C ₂ H ₆
Ethyl Benzene	Styrene Toluene Methane	C ₂ H ₆ Benzene C ₂ H ₄
Propyl Benzene	Toluene Ethylene Styrene	Benzene Methane Ethyl Benzene
n-Butyl Benzene	Ethylene Toluene Ethyl Benzene Methane Styrene	C ₂ H ₆ C ₃ H ₆ Benzene
Phenyl Dodecane	Ethylene Propylene Methane Toluene Styrene	C ₄ H ₆ C ₂ H ₆ Benzene

TABLE 6

ESTIMATES OF $(CH_2)_N$ IN COAL (WT.%)

COAL	COAL FROM		FROM 600°C		FROM COAL	
	$\frac{\%C_2H_4}{850^\circ C}$	$\frac{C_2H_4}{plus other hydrocarbons}$	PYROLYSIS TAR	$\frac{\% (CH_2)_N}{925^\circ C/2 hrs}$	LIQUEFACTIONS (MACRO) 2000 PSI H_2 ($Na_2S, FeSO_4$ CATALYSTS) *	THQ *****
PITTSBURGH 8	2.5	4.2	-	2.38	1.91	4.10 4.36 5.2
TEXAS LIGNITE	3.2	5.3	3.3	5.49	-	6.59 6.45
WYODAK	3.21	5.3	-	-	4.84	5.06 6.42
EMERY	4.5	7.5	5.2	7.77	-	8.77 7.3 8.60
PSOC 435	4.75	7.9	3.5	9.02	8.39	9.57 7.14 7.39
MILLMERRAN	6.10	10.2	4.4	-	-	9.65 12.35
PSOC 124	11.90	17.3	9.2	16.47	17.6	13.9 16.4 17.7

* ASSUMES 100% CONVERSION OF ORGANIC PORTION

** LOW CONVERSION, VERY VISCOUS PRODUCT

*** DIHYDROPHENANTHRENE

**** TETRAHYDROQUINOLINE

TABLE 7

COAL LIQUEFACTION ANALYSIS FOR (CH₂)_n IN COAL (WT.%)

<u>Coal</u>	<u>Liquefactions(Micro) 425°C/2 hr.</u>			<u>Liquefactions(Macro) 2000 psi H₂</u>	
	<u>Tetralin</u>	<u>DHP</u>	<u>IHQ</u>	<u>IHQ</u>	<u>425°C/2 hr.</u>
Pittsburgh 8	1.81	1.72	4.63		4.36
Texas Lignite	3.07	3.88	6.02		6.59
Wyodak			6.3		5.06
Emery	6.99	-	7.12		7.3
PSOC 435	4.82	5.19	7.73		7.14
Millmerran	4.31	6.57	9.13		9.65
PSOC 124	9.02	9.32	16.58		16.4

FLASH PYROLYSIS OF COAL IN REACTIVE AND
NON-REACTIVE GASEOUS ENVIRONMENTS

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ABSTRACT

The objective is to obtain process chemistry for the rapid pyrolysis of coal with reactive and non-reactive gases for the production of liquid and gaseous fuels and chemical feedstocks. The gaseous products were analyzed via an on-line GC and the heavy liquids were characterized by HPLC, IR and GC/MS. The total carbon conversion was higher in the presence of reactive gases than in the presence of non-reactive gases. The heat-up rate of the coal particles in non-reactive gasifying media followed the order $\text{He} > \text{N}_2 > \text{Ar}$. The total carbon conversion from New Mexico sub-bituminous coal in the presence of these gases also followed the same order. Experiments were performed in a down-flow, entrained tubular reactor under a wide range of process conditions: 700° to 1000°C, 20-1000 psi, 0.5 - 5 sec. coal particle residence time. The effects of these process variables and the physical properties of the pyrolyzing gases on the yield and the quality of products from the pyrolysis of New Mexico sub-bituminous coal will be discussed.

INTRODUCTION

The flash pyrolysis of coal is a fast, gas-phase, non-catalytic, direct coal conversion technique for the production of gaseous hydrocarbons and significant quantities of aromatic liquid hydrocarbons for distillate fuels and chemical feedstocks. Pyrolysis is a complex process during which several chemical reactions occur simultaneously. A general concept of the pyrolysis process is shown in Figure 1.

Considerable amount of work has been done in the past on pyrolysis of coal which was summarized recently in a classic review by Howard (1). The experimental techniques, reaction conditions and the coal used were so diversified that the information available is of limited value in a process point of view. We have, therefore, undertaken a systematic generalized study to methodically develop and build a reliable data base on the flash pyrolysis of coals with reactive and non-reactive gases. The choice of inert gas is based on covering a range of physical property effects, i.e., heat capacity, thermal conductivity and diffusivity etc. The choice of reactive gas is based on the type of gases usually formed in the pyrolytic reactions of coal. The results obtained from the pyrolysis of New Mexico sub-bituminous coal in H₂, CH₄, He, N₂ and Ar atmospheres are presented in this paper.

EXPERIMENTAL

New Mexico sub-bituminous coal ground to less than 100 mesh and vacuum dried at 70°C was used in all pyrolysis experiments. The ultimate analysis of the coal is given in Table 1.

The experimental equipment used in these studies (Figure 2) is a highly instrumented 1-in.-i.d. by 8-ft-long entrained downflow tubular reactor system, which has been described in detail (2). Coal particles 150 micrometers or less in diameter are fed by gravity into the top of the reactor from a coal feeder enclosed in a high pressure vessel. The pyrolysis gas enters through a preheater, contacting the coal particles at the

top of the 8-ft reactor. The heat transfer, pyrolysis, and secondary reactions take place as the coal and entraining gas meet and flow concurrently down the reactor. Below the reactor is a 3-ft forced air cooling section in which the product-laden gases are cooled to 250° to 300°C. The char is removed from the effluent gas in a high pressure vessel which is maintained at 250° to 300°C to prevent liquid product condensation. The heavy liquid products in the effluent gas are removed in two condensers, one water cooled (15°C) and the other Freon cooled (-40°C). The remaining gases are then reduced to atmospheric pressure, measured via a positive displacement meter, and vented to the atmosphere.

The velocity of the coal particle through the reactor is calculated by adding its free-fall velocity based on Stoke's law to the down-flow gas velocity. The residence time is determined from the length of the reactor and the total coal particle velocity.

Product yields, as a function of coal particle residence time, are determined by sampling from taps located at 2-ft intervals along the length of the reactor. The product analysis is accomplished via an on-line, programmable gas chromatograph (GC) which determines CO, CO₂, CH₄, C₂H₄, C₂H₆, and BTX (benzene, toluene, and xylene) concentrations every 8 minutes. Products heavier than BTX (>C₉) can not be measured on-line because of condensation in the sample lines and the temperature limit (230°C) of the gas chromatograph. These products are collected in the condensers and analyzed at the end of each experiment. Selected liquid samples are subjected to elemental analysis and GC/MS studies.

The duration of an experiment is at least one hour and steady state is achieved in 3 to 4 minutes. Coal feed rates are usually about 500 g/hr. To facilitate uniform flow, 10% by wt Cab-0-Sil, a silica flour, is added to the coal. The non-reactive gases used were the inert gases, argon, helium and nitrogen. The reactive gases included hydrogen, methane and carbon monoxide. Yields are based on the percent of the carbon in the feed coal which is converted to products and determined as follows:

$$\% \text{ Carbon converted to product} = \frac{\text{Carbon in Product, g} \times 100}{\text{Carbon in Feed, g}}$$

A sum of the gaseous and liquid product yields, expressed as % carbon converted, will give the total carbon conversion due to pyrolysis. From feed rates, product yields, and an elemental analysis of the feed coal and char produced, a complete material balance can be made.

RESULTS AND DISCUSSION

Coal particles entering the reactor are heated to reaction temperature by convection from the preheated gas and by radiant heat from the reactor wall. In calculating the coal particle heat-up rate due to convection, a number of experimental configurations were considered for which heat transfer coefficients had been determined. These included heat and mass transfer from a falling water droplet (3), heat transfer to a fluidized-bed of particles (4), heat transfer to particles at Reynolds numbers greater than 500 (5), heat transfer in a distended bed of particles (6), and the theoretical heat transfer between a particle and a stagnant fluid. Since the Reynolds number for the coal particles falling through the gas in our work is very low, less than 10, neither the fluidized-bed nor the high Reynolds number work seemed appropriate. Also, the fluidized-bed work gave very low heat transfer coefficients, which were attributed to excessive bypassing of gas through the bed during the experiments (7). Since the work on distended beds showed good correlation of data from void fractions of 0.45 to 0.78, this appeared to provide the closest approach to our experimental conditions. The expression used is as follows (6):

$$Nu = 2.06 N_{RE}^{0.425} N_{PR}^{1/3}$$

where $Nu = \text{Nusselt number} = \frac{h_g D_p}{k_g}$ (1)

$$N_{RE} = \text{Reynolds number} = \frac{D_p V \rho_g}{\mu_g}$$

$$N_{PR} = \text{Prandtl number} = \frac{C_p \mu_g}{k_g}$$

h_g = heat transfer coefficient for gas film,
 D_p = diameter of particle,
 K_g = thermal conductivity of gas,
 V = velocity of particle through gas (free fall),
 ρ_g = density of gas,
 μ_g = viscosity of gas, and
 C_{p_g} = heat capacity of gas.

By substitution

$$h_g = \left(\frac{2.06 K_g}{D_p} \right) \left(\frac{D_p V \rho_g}{\mu_g} \right)^{0.425} \left(\frac{C_{p_g} \mu_g}{K_g} \right)^{1/3} \quad (2)$$

and

$$M C_{p_s} \frac{dT_s}{dt} = h_g A_s (T_g - T_s), \quad (3)$$

$$dT_s = \frac{h_g A_s}{M C_{p_s}} (T_g - T_s) dt,$$

$$t = \frac{M C_{p_s}}{h_g A_s} \ln \left(\frac{T_g - T_i}{T_g - T_s} \right), \quad (4)$$

Where

C_{p_s} = heat capacity of coal
 M = mass of coal particle
 A_s = area of coal particle
 T_g = temperature of gas
 T_s = temperature of coal particle
 T_i = initial temperature of coal particle
 t = time to raise the particle temperature from T_i to T_s

Equation (2) was used to calculate the gas-film heat transfer coefficient between the coal particle and the preheated gases hydrogen, methane, carbon monoxide, helium, nitrogen, and argon. The values of gas-film heat transfer coefficient for various pyrolyzing gases under a set of arbitrarily chosen conditions are given in Table 2. Table 2 shows that for reactive gases, the heat transfer coefficient decreased in the following order: $H_2 > CH_4 > CO$; for non-reactive gases the order is found to be $He > N_2 > Ar$. Equation (4) was used to calculate the coal particle

temperature as a function of time and is plotted in Figure 3. Figure 3 shows that hydrogen gives the highest heat-up rate and argon the lowest; among the non-reactive gases, helium gives the highest rate. Although calculations of the final temperature of the coal particle were made, these should be considered as limiting values because chemical energy exchange and devolatilization also take place.

Calculations of the radiant heat transfer from the hot reactor wall to the coal particles indicate this contribution to be about 5 to 10% of the total heat transfer. Since these calculations are probably not accurate to better than $\pm 10\%$, radiant heat transfer was not included in the coal particle heating rate or the temperature estimates.

When pyrolysis took place in the presence of non-reactive gases, the total carbon conversion followed the order: $\text{He} > \text{N}_2 > \text{Ar}$. For example, at 900°C and 200 psi pressure of He, N_2 and Ar, the total carbon conversions were: 21.0%, 20.1% and 14.5%, respectively (Table 3). This includes the yields due to hydrocarbon gases, oxides of carbon, BTX and heavy liquids. In runs using N_2 or Ar as the pyrolyzing gas, difficulties were experienced in measuring the CO produced which arose as a result of inadequate resolution of this component from the solvent peak (N_2 or Ar). Hence, the CO yields from helium pyrolysis runs under identical conditions were used to determine the total carbon conversion in these cases. This could introduce some error in the total carbon conversion data for N_2 and Ar pyrolysis runs. In the case of reactive gases, the total carbon conversions were 37.6%, 30.4% and 17.5% respectively for H_2 , CH_4 and CO atmospheres. There is a significant increase in total conversion in hydrogen and methane atmospheres over other inert gases. Though CO is a reactive gas, no enhancement in pyrolysis yields were noticed under the conditions investigated. The decrease in the gas film heat transfer coefficient for reactive and non-reactive gases and the total conversion both follow the same trend within each category. Thus, there appears to be a relationship between the heat transfer coefficient (or the heat-up rate of the coal particles) and total carbon conversion (Figure 4).

The effect of gas pressure on total carbon conversion was also investigated (Figure 5). As expected, hydrogen gave the highest carbon conversion. However, increasing the hydrogen pressure from 100 psi to 500 psi had little influence on the total conversion. The effect of pressure on total conversion was marked for all other gases. The maximum in the total carbon conversion and the pressure at which it occurs clearly seem to be dependent on the pyrolysis temperature. These differences indicate that a strong relationship exists between coal devolatilization and the transport properties of the pyrolyzing gases. More experiments are planned to understand these effects on coal pyrolysis in greater detail.

The flash pyrolysis of coal produces a wide range of gaseous and liquid products. The gas stream is mostly made up of methane, ethane, ethylene, CO and CO₂ besides the entraining gas. A typical pyrolysis product distribution is shown in Figure 6. Similar product distributions were obtained for other pyrolysis atmospheres and other conditions (8). Among these pyrolysis products, ethylene showed greatest variation in its yield. This is shown in Figure 7. Under all conditions, ethylene was produced in characteristically higher quantities in methane atmosphere (which we term "flash methanolysis") than in the presence of any other gas used. As high as 10.5% carbon in the feed coal was converted to ethylene at 825°C and 50 psi CH₄ pressure. This is approximately two times higher than that with the inert gases under similar conditions (10.5% with methane and 4.9% with helium). From several blank experiments, in the absence of coal, it was determined that homogeneous decomposition of methane does not occur in the reactor (8). A free-radical mechanism for the enhanced yield of ethylene during flash methanolysis of Douglas Fir wood, in the same pyrolysis reactor, was recently proposed (9). Figure 7 also reveals that in all cases, the ethylene yield decreased with gas pressure.

As expected, high yields of gaseous hydrocarbons were obtained when pyrolysis took place in hydrogen atmosphere. The total gaseous hydrocarbon yield ranged from 8.9% C at 800°C and 50 psi to 28.0% C at 900°C and 500 psi. The yields of both ethane and ethylene decreased with

increase in the pressure of hydrogen. In non-reactive gas media, no ethane was produced in measurable quantities in most instances. Among non-reactive gases, the yield structure was comparable between helium and nitrogen atmospheres and a representative case is shown in Table 3 in which the product yields from the pyrolysis of New Mexico coal in various gasifying media, under identical conditions, are compared. From the same table, it could be seen that in argon atmosphere, the yield of gaseous hydrocarbons and other products are considerably low.

The yield of CO₂ was about 1-2% C under all conditions in the presence of all gases with the exception of CO. Higher yields of CO₂ were obtained (7-9% C) when the pyrolyzing gas was CO. This is believed to be due to disproportionation of CO under the reaction conditions.

The liquid products (excluding process water) consist of two fractions: the "light oil" fraction, boiling between 60° and 150°C, and the "heavy liquid" fraction, boiling above 150°C. This classification is arbitrary, and various distillation ranges are used by different workers. In the BNL work, usually more than 90% by weight of the "light oil" is made up of benzene, toluene, and xylene, and the "heavy liquids" or "tars" contain condensed ring aromatic structures and high molecular weight compounds with high aromaticity (10).

"Light Oil" from coal is a potential source of some key chemicals such as benzene-toluene-xylene (BTX). Even though the exact mechanism of their production is not known, it is generally thought to consist largely of secondary pyrolytic reactions. Prolonged heating of the primary devolatilization products induces cracking and if hydrogen is available, stable lighter products are formed. Thus, the yield of light oil depends on the residence time of the tar vapor in the pyrolysis reactor and on the temperature. With longer residence times, more light oil is formed at the expense of the heavy liquids (tar). Too high a temperature (>900°C) results in an increased yield of gases at the expense of both light oil and tar.

BTX yield ranged 1-3% C in the case of CO and non-reactive gases; up to 7% carbon in the feed was converted to BTX during flash hydrolysis and flash methanolysis experiments. The IR spectra of light oils, free from process water, obtained from a series of flash hydrolysis experiments with New Mexico sub-bituminous coal show (i) strong absorption in the low frequency range between 900 and 675 cm^{-1} , typical of aromatic ring C-H out-of-plane bending, (ii) strong absorption in the medium frequency range between 1600 and 1580 cm^{-1} due to C=C stretching, and (iii) moderate absorption between 3100 and 3000 cm^{-1} characteristic of the aromatic C-H stretch. Weak absorptions at 2926, and 2853 cm^{-1} ($\nu_{\text{C-HCH}_3}$, $\nu_{\text{as CH}_2}$, and $\nu_{\text{s CH}_2}$, respectively) indicate that the extent of alkyl substitution is small.

Phenols, if any, were present only in very small amounts in the light oils produced from the flash pyrolysis of New Mexico sub-bituminous coal. The IR spectra of light oils produced at 900°C at 20, 60, and 200 psi showed absorption due to -OH groups to be present only in the 20 psi sample, and this spectrum was similar to the one obtained at 800°C and 200 psi. An increase in the hydrogen pressure or residence time of the volatiles tends to decrease the amount of phenols in the product stream, and temperatures above 900°C and hydrogen pressures above 50 psi favor the dehydroxylation/decomposition reactions of phenols. The light oil from the inert helium pyrolysis at 900°C and 50 psi had a composition qualitatively similar to that from flash hydrolysis under the same conditions, but for different reasons: In the presence of external hydrogen, the phenols initially formed undergo decomposition, but during inert gas pyrolysis the conditions are not favorable for initial phenol formation.

Heavy liquid or tar is an inherent product of coal devolatilization. Its composition is much more complex than that of light oils. Tar accounts for only a small amount of the carbon in the feed coal that is converted (0-5% C). Tars from selected runs were subjected to detailed investigation, but the data available at present are limited.

A basic problem in identifying the individual components in a tar is that compounds of widely varying polarities are present, precluding GC/MS analysis of the tar as such. By fractionating the tars on the basis of solubility in selected solvents and analyzing the fractions for individual compounds, valuable information could be obtained.

In one scheme of solvent fractionation, the tar is separated into oil (hexane soluble), asphaltenes (hexane insoluble but benzene soluble), and pre-asphaltenes (benzene insoluble). The yields of total tar and tar fractions from selected pyrolysis runs are shown in Table 4. The pre-asphaltenes, which include compounds of high polarity, comprise only a very small part of the tar. Except when the pyrolysis gas is methane, an increase in tar yield is accompanied by an increase in oil yield. The tar yield from flash methanolysis is between those from helium pyrolysis and from hydroxyrolysis. In the case of helium pyrolysis, the tar yield tends to increase with increasing pressure.

The individual components in an oil sample from the flash hydroxyrolysis of New Mexico sub-bituminous coal at 1000°C and 25 psi hydrogen pressure were identified with capillary GC/MS which is shown in Figure 8. The peaks are identified in Table 5. Naphthalene is the most abundant product in this tar; higher-ring aromatic compounds and heteroatom containing specie account for less than 10% of the total. No sulfur containing compounds were detected. The reason for the presence of relatively large amount of acenaphthylene in this tar is not known at present.

CONCLUSIONS

The conclusions which can be drawn from this work thus far are as follows:

1. Under the same conditions, the total carbon conversion was higher in the presence of reactive gases than in the presence of non-reactive gases. Among the reactive gases, the total carbon conversion followed the order: $H_2 > CH_4 > CO$. Among the non-reactive gases, the total carbon conversion followed the order: $He > N_2 > Ar$.

2. Pyrolysis in methane was characterized by high yields of ethylene and liquid products. As high as 10.5% carbon in the feed coal was converted to ethylene at 825°C and 50 psi. The ethylene yield during pyrolysis of coal with methane was approximately two times higher than that with the inert gases under similar conditions (10.5% CH₄ vs 4.9% with He at 825° and 850°C and 50 psi).

3. Phenols, if any, were present only in very small amounts in the light oil fraction of the liquid products. In the presence of external hydrogen, the phenols formed undergo decomposition, but during the inert gas pyrolysis the conditions are not favorable for initial phenol formation. An increase in the hydrogen pressure or residence time of the volatiles tends to reduce the amount of phenols in the product stream, and temperatures above 900°C and hydrogen pressures above 50 psi favor the dehydroxylation/decomposition reactions of phenols.

4. In the case of helium pyrolysis, the tar yield tends to increase with increasing pressure. The tar yield from methane pyrolysis is between those from helium pyrolysis and from hydrolysis.

5. The pre-asphaltenes, which include compounds of high polarity, comprise only a very small part of the tar. Except when the pyrolysis gas is methane, an increase in tar yield is accompanied by an increase in oil yield.

6. A correlation appears to exist between the total carbon conversion to gaseous and liquid products and the heat-up rate of coal particles for inert gases in the order of He > N₂ > Ar. Uncovering other effects of heat-up rate of coal particles on the pyrolytic behavior of coals require further investigation.

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REFERENCES

1. J. B. Howard, Fundamentals of Coal Pyrolysis and Hydropyrolysis, Chapter No. 12 in Chemistry of Coal Utilization, Ed. Elliot, M.A., John Wiley and Sons, New York, NY, p. 665-784 (1981).
2. P. Fallon and M. Steinberg, Flash Hydropyrolysis of Coal, The Design, Construction, Operation and Initial Results of a Flash Hydropyrolysis Experimental Unit, BNL 50698, Jan. 1977.
3. R.B. Bird, W.E. Steward, and E.N. Lightfoot, Transport Phenomena, Wiley, New York, 1960.
4. W.W. Wamsley and L.N. Johanson, Chem. Eng. Prog. 50, 347 (1954).
5. H.F. Johnstone, R.L. Pigford, and J.H. Chapin, Trans. AIChE 37, 95 (1941).
6. A. Sen Gupta and G. Thodos, AIChE J. 9, 751 (1963).
7. F. A. Zenz, and D. F. Othmer, "Heat Transfer in Particle-Fluid System", Chapter No. 13 in Fluidization and Fluid-Particle Systems, Reinhold Pub. Co., New York, NY, p. 421 (1960).
8. M. Steinberg, P. Fallon, and M. S. Sundaram, "Flash Pyrolysis of Coal with Reactive and Non-reactive Gases", Progress Report for October 1, 1981-Septemehr 30, 1982, To be published by Departemnt of Energy, Morgantown Energy Technology Center, Morgantown, W. Va.
9. M. S. Sundaram, Steinberg, M., and Fallon, P.T., "Flash Pyrolysis of Biomass with Reactive and Non-Reactive Gases", presented at International Conference on Fundamentals of Thermochemical Biomass Conversion, Estes Park, CO, BNL 32280 (October 1982).
10. M. S. Sundaram, M. Steinberg, and P. Fallon, "Flash Hydropyrolysis of Coals for Conversion to Liquid and Gaseous Fuels", BNL 51537, DOE/METC/82-48, (1982).

Table 1

Ultimate Analysis (Wt % Dry) of New Mexico Sub-Bituminous Coal
Used in Pyrolysis Experiments

Carbon	59.3
Hydrogen	4.2
Oxygen ^a	16.8
Nitrogen	1.2
Sulfur	0.8
Ash	17.7

a) By difference.

Table 2

Calculation of Gas Film Heat Transfer Coefficients
for Various Pyrolyzing Gases

Coal Particle Size - 100 micrometers
Coal Particle Initial Temp. - 20°C
Gas Conditions - 900°C and 1000 psi

Gas	h_g (Cal/cm ² -K ⁰ -sec)
Hydrogen	2.21×10^{-1}
Methane	2.02×10^{-1}
Helium	1.73×10^{-1}
Carbon Dioxide	9.9×10^{-2}
Carbon Monoxide	7.7×10^{-2}
Nitrogen	7.16×10^{-2}
Argon	4.96×10^{-2}

Table 3

Product Yields from the Flash Pyrolysis of New Mexico Sub-bituminous Coal at 900°C and 200 psi Coal Residence Time: 2.4-4.6 sec.			
Entraining Gas	He	N ₂	Ar
<u>% Carbon Conv. to Prod.</u>			
CH ₄	8.1	10.2	2.6
C ₂ H ₄	3.5	0	3.3
C ₂ H ₆	0	0.7	0
Total Gaseous H.C.	<u>11.6</u>	<u>10.9</u>	<u>5.9</u>
BTX	1.8	2.7	2.0
>C ₉	1.2	0.4	0.8
Total Liquid H.C.	<u>3.0</u>	<u>3.1</u>	<u>2.8</u>
CO	4.4	(4.4)	(4.4)
CO ₂	2.0	1.7	1.4
Total CO _x	<u>6.4</u>	<u>6.1</u>	<u>5.8</u>
Total Carbon Converted	<u>21.0</u>	<u>20.1</u>	<u>14.5</u>

() CO could not be resolved from N₂ or Ar on the on-line GC.
The values in parenthesis are CO yields from inert helium
pyrolysis runs under identical conditions. This could
introduce some error in the determination of the total
carbon conversion.

Table 5

Composition of Heavy Liquids from the
Flash Hydropyrolysis of New Mexico Coal

Peak No.	Component	% Peak Area
1	xylene	0.54
2	xylene	0.27
3	phenol	3.07
4	indene	6.45
5	naphthalene	60.80
6	quinoline	1.15
7	isoquinoline	0.29
8	C ₁ -naphthalene	1.25
9	C ₁ -naphthalene	0.32
10	biphenyl	0.03
11	acenaphthylene	14.98
12	acenaphthene	1.66
13	C ₁ -biphenyl/acenaphthene	1.79
14	fluorene	2.64
15	phenanthrene/anthracene	3.82

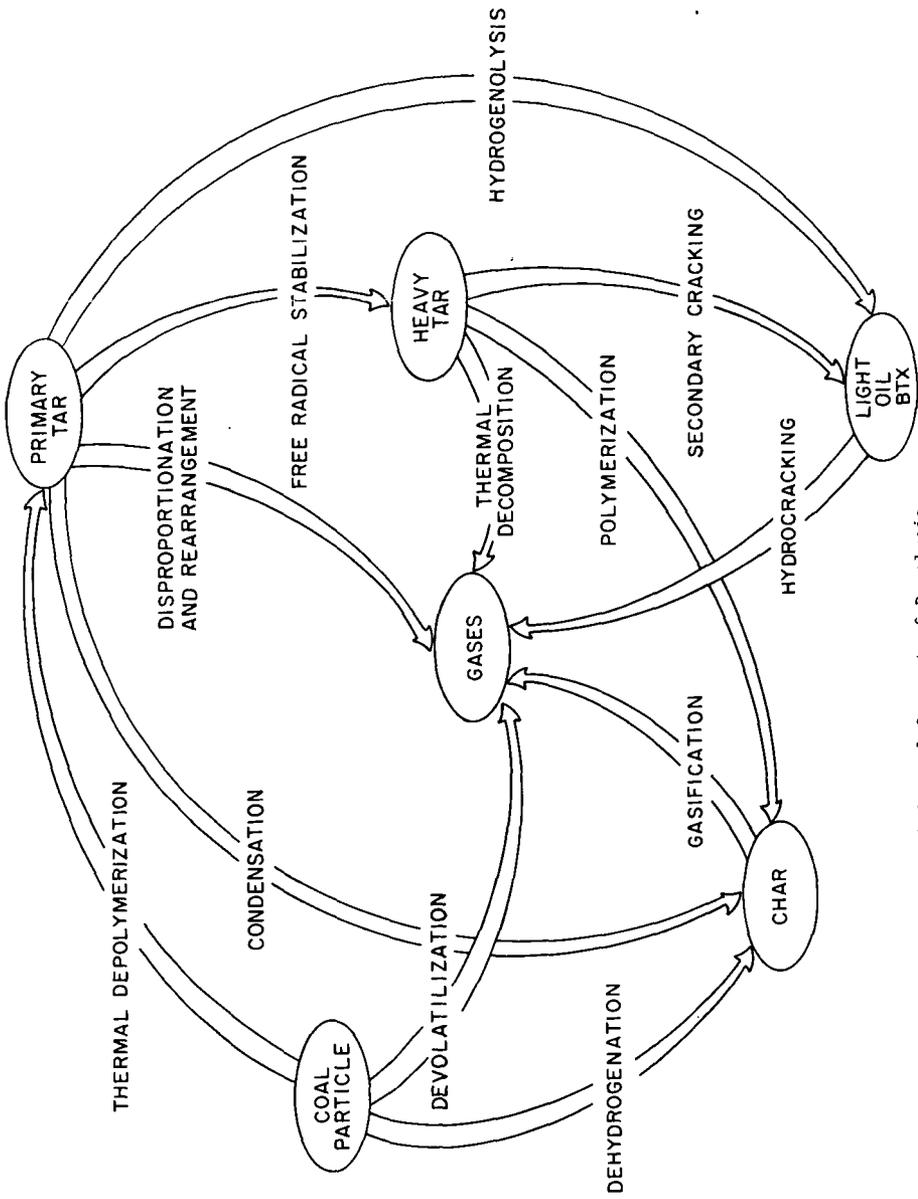


Figure 1. A General Concept of Pyrolysis

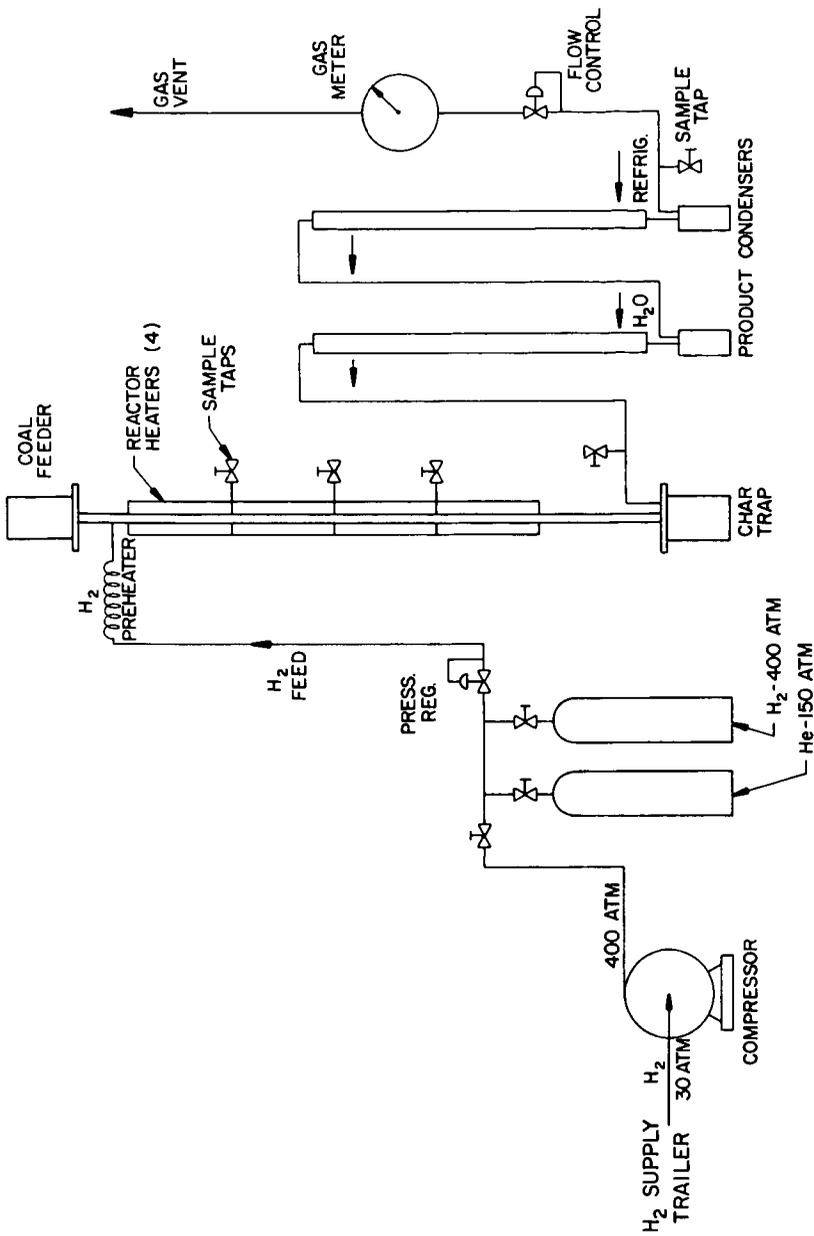


Figure 2. SCHEMATIC FLOWSHEET OF ENTRAINED TUBULAR REACTOR EXPERIMENT

COAL PARTICLE TEMPERATURE vs. TIME
PARTICLE SIZE - 100 μ
INITIAL TEMPERATURE - 20°C
GAS TEMPERATURE - 900°C

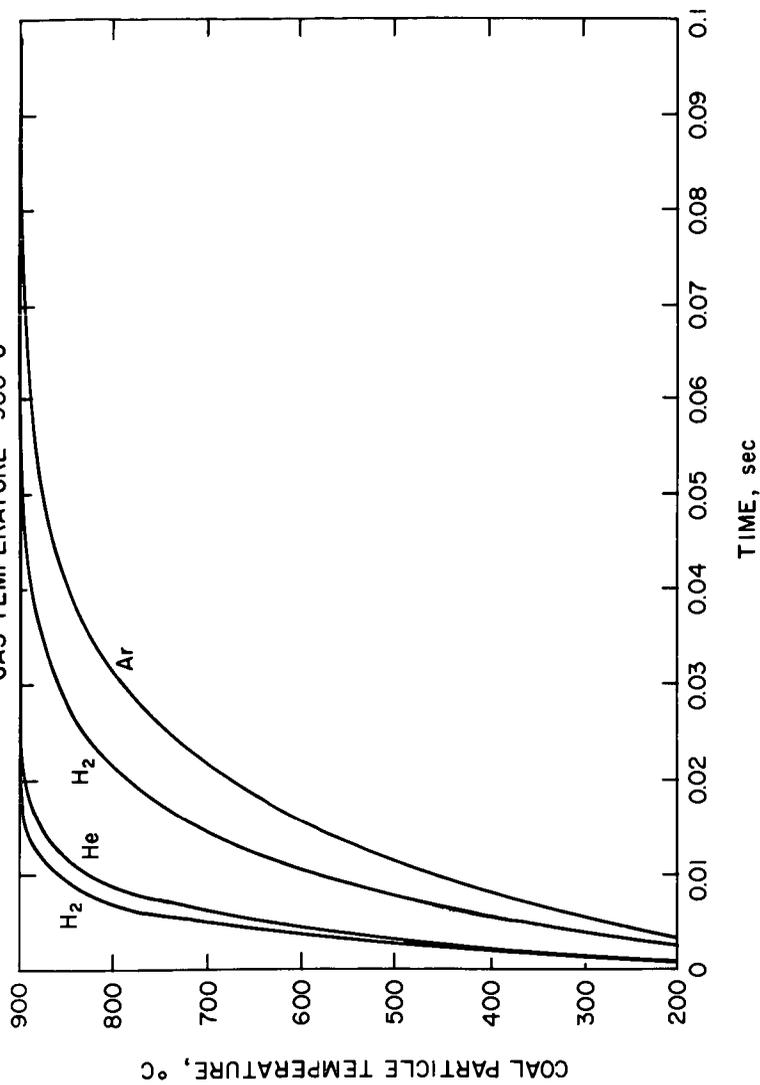


Figure 3. Coal Particle Temperature vs Time

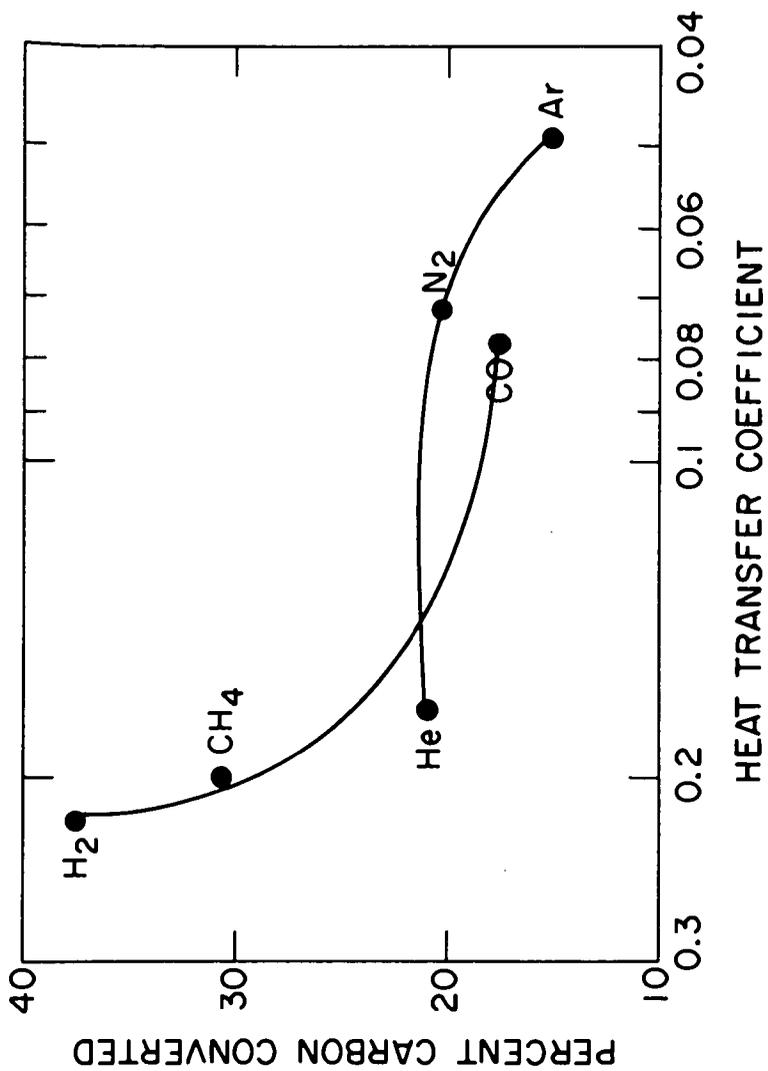


Figure 4. Percent Carbon Conversion at 900°C and 200 psi vs Heat Transfer Coefficient

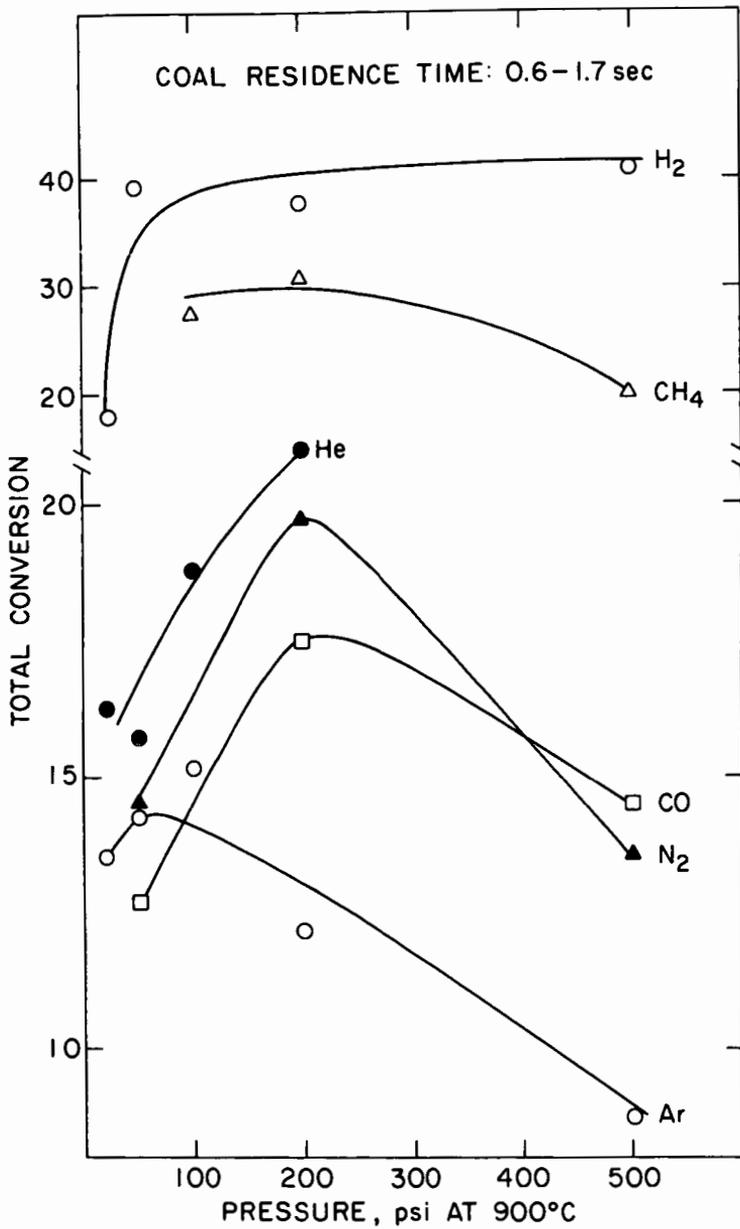


Figure 5. Total Conversion vs Pressure, at 900°C

FLASH PYROLYSIS OF NEW MEXICO SUBBITUMINOUS COAL WITH HELIUM
 PERCENT CARBON CONVERTED vs. TEMPERATURE
 PRESSURE - 20 psi
 RES. TIME - 0.5 to 0.6 sec.

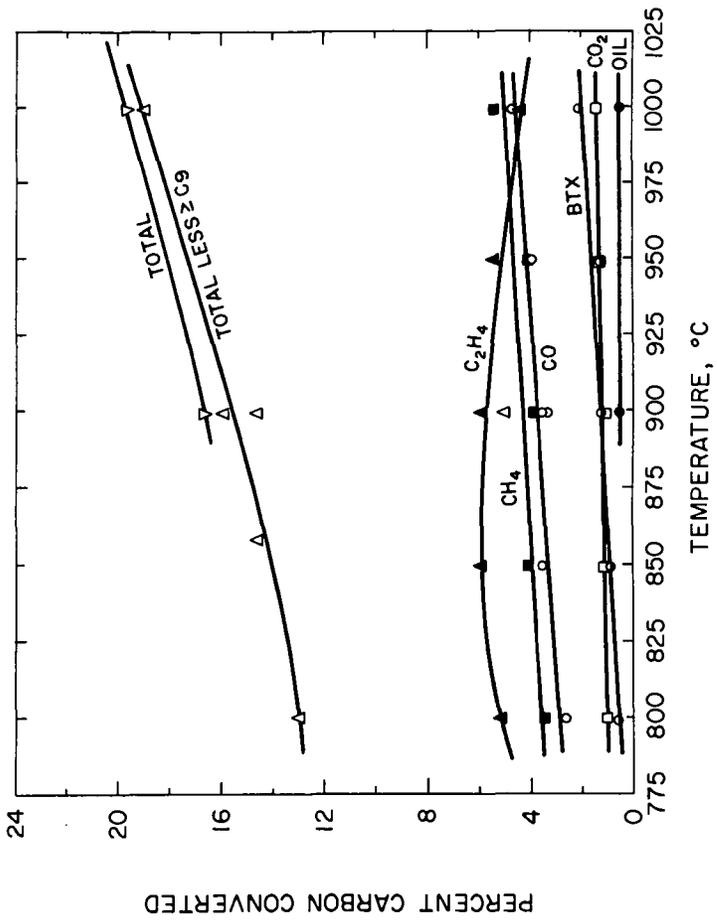


Figure 6. Product Yields vs Temperature at 20 psi He

ETHYLENE PRODUCTION BY FLASH PYROLYSIS OF
 NEW MEXICO SUBBITUMINOUS COAL
 TEMPERATURE - 800 - 1000°C

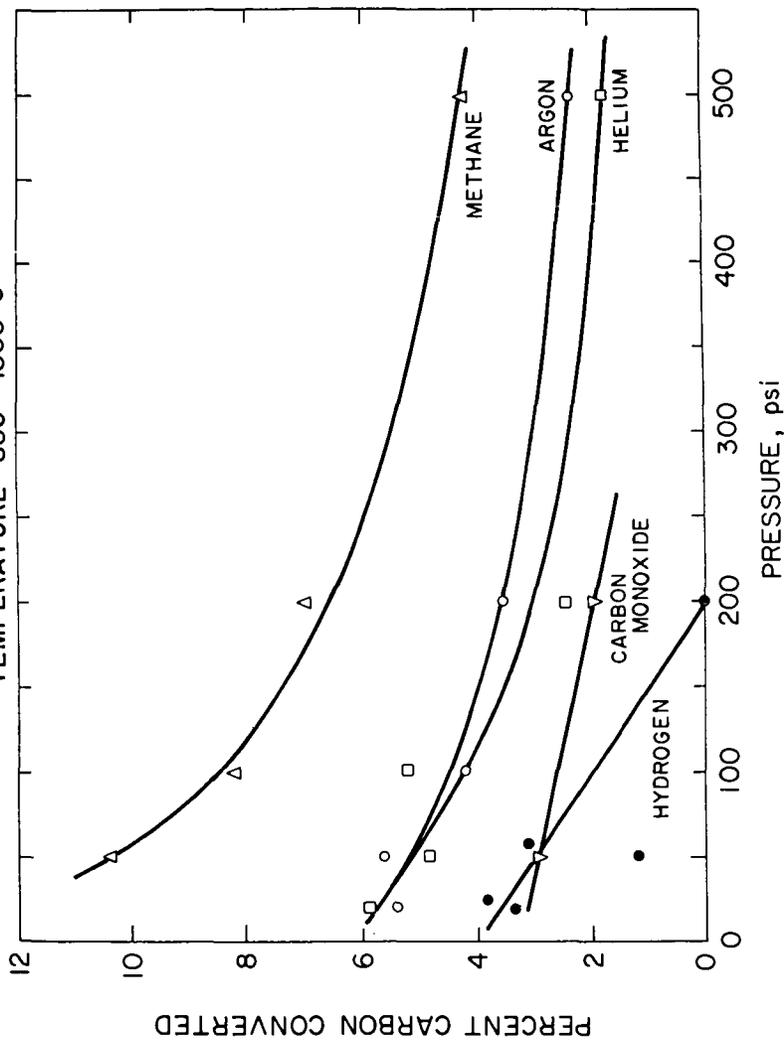


Figure 7. Ethylene Yield vs Pressure at 800° to 1000°C

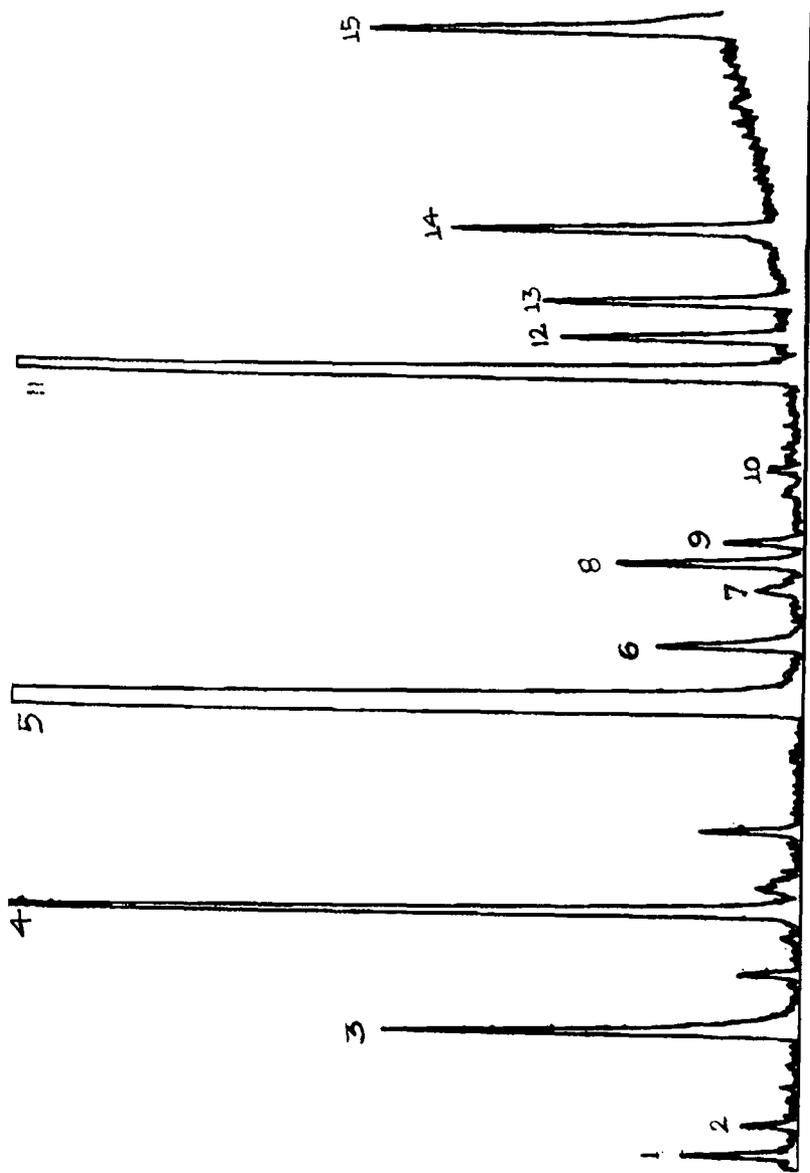


Figure 8. GC/MS Total Ion Chromatogram of a Pyrolysis Oil

CHARACTERIZATION OF COAL CHARs FROM A FLASH PYROLYSIS PROCESS BY
CROSS POLARIZATION / MAGIC ANGLE SPINNING ^{13}C NMR

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INTRODUCTION

In the last two decades, flash pyrolysis has been used to investigate the structure of coal and shale (1-4). Several coal conversion processes based on flash pyrolysis are under investigation in the United States (5-8), West Germany (9), and Australia (10,11,12). Studies of the molecular properties of the flash pyrolysis products have been confined to the liberated organic matter: volatile liquids and gases. Changes occurring in the organic structure of the chars are poorly understood.

The development of ^{13}C cross polarization (CP) (13) and Magic Angle Spinning (MAS) (14) Nuclear Magnetic Resonance (NMR) spectroscopy with high-power proton decoupling has allowed investigators to obtain spectra of the organic matter in solid coal (15-25). Sullivan and Maciel (26) and Dudley and Fyfe (27) have verified the quantitative reliability of this technique as applied to coal. ^{13}C NMR spectra of coal demonstrating the utility of both CP and MAS have been reported previously (15,16,18,21,22), however, there has been no reported investigation of ^{13}C CP/MAS NMR spectra of the chars produced by flash pyrolysis.

This paper reports the results of this technique applied to the study of chars produced by the flash pyrolysis of coal at progressively higher temperatures. The investigation has given valuable insight into the changes of organic composition of coal during carbonization as well as the optimum temperature for efficient conversion of coal into liquids and gases.

EXPERIMENTAL

A high-volatile C bituminous (HVCB) Illinois Harrisburg (No. 5) coal was used. The analyses of the raw coal sample are given in Table 1. The coal was flash pyrolyzed in a quartz tube under a flow of helium. The tube was heated at a ramp-rate of $75^\circ\text{C}/\text{msec}$ to the desired final temperature with a 20 sec hold at the final temperature. Since only small quantities of coal were used for each run, a sample of sufficient size for NMR analysis and elemental analysis at each temperature was prepared by combining the products of replicate preparations.

Chars produced at 300° , 400° , 500° , 600° , 700° , and 800°C were studied. The ^{13}C CP/MAS NMR measurements of the chars were made on a JEOL FX60Q NMR spectrometer modified for CP and MAS. The spectra were recorded under standard conditions that have been described previously (26).

For the volatile analysis, the same sample of coal was heated in steps; first to 300°C , then successively to 400°C , 500°C , 600°C , 700°C , and to 800°C . The volatile matter was entrained in a helium flow of $35\text{ ml}/\text{min}$ and was analyzed by gas chromatography (GC) using a $2.5\text{ m} \times 3\text{ mm}$ stainless steel column packed with 3%

Table 1. Proximate and ultimate composition of the Illinois No. 5 (HVCB) coal sample. (moisture-free basis).

Proximate analysis	%	Ultimate analysis	%
Volatile matter	43.3	Hydrogen	4.72
Fixed carbon	44.3	Carbon	65.45
Ash	12.4	Nitrogen	1.13
		Oxygen (by diff.)	11.52
		Sulfur	3.91
		Low Temp. Ash	13.27

Dexsil 300 on 80/100 Chromosorb WHP connected to a flame ionization detector (FID). The column temperature was programmed from 50°C to 250°C at 8°C/min and held at the final temperature for 15 min.

RESULTS AND DISCUSSION

The GC traces of volatile products evolved at each charring temperature are shown in Figure 1. The evolution of decomposition products, gases and liquids, starts at 500°C, maximizes at 600°C, and completes at 700°C. At 800°C the main volatiles evolved are hydrogen and light hydrocarbon gases. The hydrogen to carbon atom ratios (H/C) of the coal and chars at each temperature are given in Table 2. There is little change in the H/C ratios at temperatures below 500°C. Above 500°C, the H/C ratios decrease as the temperature is increased. The data show a change in H/C value from 0.82 (highly benzenoid) at 500°C to 0.36 (highly graphitic) at 800°C. Based on similar results, polycondensation of the aromatic ring system occurring at the same time as dehydrogenation of the hydroaromatic and alicyclic systems has been suggested as a model for carbonization by early coal workers (28). However, ¹³C CP/MAS NMR results give an insight into the changes of the organic matter of chars.

Table 2. The atomic ratio of hydrogen to carbon (H/C) for coal and chars at each temperature step.

Temperature (°C)	Raw coal	300	400	500	600	700	800
H/C	0.87	0.87	0.85	0.82	0.57	0.54	0.36

¹³C CP/MAS NMR spectra of the raw coal and the six chars are illustrated in Figure 2. In general, the spectra exhibit two broad characteristic peaks. The chemical shifts are referenced to tetramethylsilane (TMS) with hexamethylbenzene (HMB) used as a secondary external standard. The chemical shift of the aromatic peak of HMB is taken to be 132.3 ppm relative to TMS. The peak at 129 ppm is assigned to sp² (mainly aromatic) carbon and the peak at 30 ppm is assigned to sp³ (saturated) carbon.

The ¹³C CP/MAS NMR spectra show (fig. 2) that the aliphatic carbon peak is progressively decreasing as the temperature is increased; while the aromatic carbon peak retains approximately the same height and shape. The peaks at 298 ppm and -37 ppm are spinning side bands (SSB). For a given temperature the NMR spectra provide a measure of the relative carbon distribution of the organic material remaining in the char. The relative percentages of aromatic (f_{ar}) and of aliphatic (f_{al}) carbons are calculated by dividing the integrated area of each individual carbon peak by the sum of the areas of the peaks. The f_{al} values of chars are shown in Figure 2. The f_{ar} of the raw coal is 67%. The initial stage

of heating (300°C) produces a char with 68% of f_{ar} , and successive heatings give chars with f_{ar} of 70% (400°C), 73% (500°C), 89% (600°C), 95% (700°C), and 96% (800°C). However, the actual amount of aromatic (w_{ar}) and aliphatic (w_{al}) carbon in char can be calculated by using the NMR measurements (f_{ar} ; f_{al}), the organic carbon content of the char ($\%C_{org}$), and the weight of the char (w_{char}).

$$w_{ar} = \%C_{org} \times f_{ar} \times w_{char}; w_{al} = \%C_{org} \times f_{al} \times w_{char}$$

Figure 3 shows the calculated values and the weight of char based on 100 g of raw coal used in relation to temperature: the amount of aromatic carbon in char (w_{ar}) remains relatively constant at each temperature, while the amount of aliphatic carbon in char (w_{al}) is reduced during higher temperature charring. At 600°C, both a large reduction of the aliphatic-carbon content and a maximum weight loss occur.

This study shows that the aliphatic part of the organic matter in coal is substantially lost during pyrolysis at temperature greater than 500°C. Although, the loss of aliphatic-bound carbon from coal may involve several mechanisms, it may have been volatilized directly or it may have been converted to an aromatic form from which it could volatilize or could become fixed as part of the char. The maximum temperature for efficient evolution of volatiles from coal by heat is at 600°C to 700°C. Also, the amount of carbonaceous residue at 800°C can be estimated from the aromatic-bound carbon of raw coal. The usefulness of the ^{13}C CP/MAS NMR technique as a tool for coal process research is clearly demonstrated.

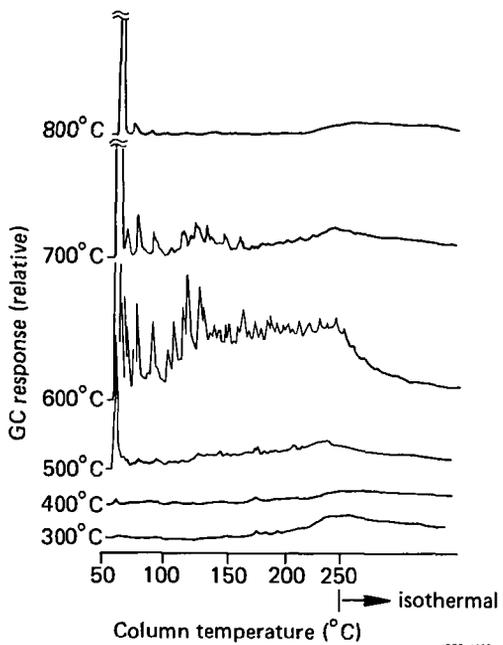
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REFERENCES

1. Retcofsky, H. L., Schweighardt, F. K. and Hough, M., *Anal. Chem.* 49, 585 (1977).
2. Bartle, K. D., *Rev. Pure Appl. Chem.* 22, 79 (1972).
3. Van Grass, G., de Leeuw, J. W., and Schenck, P. A., in Advances in Organic Geochemistry 1979, 3d. A. F. Douglas and J. R. Maxwell, Pergamon, Oxford, pp 485-494.
4. Romováček, Jirí and Jaroslav Kubát, *Anal. Chem.* 40, 1119-27 (1968).
5. Strom, A. H. and Eddinger, R. I., *Chem. Eng. Prog.* 67, 75 (1971).
6. Sass, A., *Chem. Eng. Prog.* 70, 72 (1974).
7. Sunberg, E. M., Peters, W. A., and Howard, J. B., *Fuel* 59, 405 (1980).
8. Che, S. C., Duraiswamy, K., Knell, E. W., and Lee, C. K., "Flash pyrolysis coal liquefaction process development," Occidental Research Corporation Final Report to the U.S. Department of Energy, Fe-2244-26, April 1979.
9. Peters, W., Gluckauf, 112, 8 (1976).
10. Collin, P. J., Tyler, R. J., and Wilson, M. A., *Fuel* 59, 479 (1980).

11. Tyler, R. J., Fuel 59, 219 (1980).
12. Collin, P. J., Tyler, R. J., and Wilson, M. A., Fuel 59, 819 (1980).
13. Pines, A., Gibby, M. G., and Waush, J. S., J. Chem. Phys. 59, 569 (1973).
14. Shaefer, J. and Stejskal, E. O., J. Am. Chem. Soc. 98, 1031 (1976).
15. Maciel, G. E., Bartuska, V. J., and Miknis, F. P., Fuel 58, 319 (1979).
16. Miknis, F. P., Sullivan, M., Bartuska, V. J., and Maciel, G. E., Organic Geochemistry, 3, 19 (1981).
17. Maciel, G. E., Sullivan, M. J., Szevereny, N. M., and Miknis, F. P., "Chemistry and physics of coal utilization-1980", Cooper, B. R., Petrakis, L., Eds., American Institute of Physics: New York, 66-81 (1981).
18. Zilm, K. W., Pugmire, R. J., Grant, D. M., Wood, R. E., and Wiser, W. H., Fuel 58, 11 (1979).
19. Maciel, G. E., Sullivan, M. J., Petrakis, L., and Grandy, D. W., Fuel 61, 411 (1982).
20. Zilm, K. W., Pugmire, R. J., Larter, S. R., Allan, J., and Grant, D. M., Fuel 60, 717 (1981).
21. VanderHart, D. L., and Retcofsky, H. L., Fuel 55, 202 (1976).
22. Retcofsky, H. L., and VanderHart, D. L., Fuel 57, 421 (1978).
23. Gerstein, B. C., Ryan, L. M., and Murphy, P. D., Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 24, 90 (1979).
24. Wemmer, D. E., Pines, A., and Whitehurst, D. D., Philos. Trans. R. Soc. London Ser. A 300, 15 (1981).
25. Barron, P. F., Stephens, J. F., and Wilson, M. A., Fuel 60, 547 (1981).
26. Sullivan, M. J. and Maciel, G. F., Anal. Chem. 54, 1615 (1982).
27. Dudley, R. L. and Fyfe, C. A., Fuel 61, 651 (1982).
28. Wang, Z. and Shou, J. K., Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 25, 171 (1980).



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Fig. 1. The GC traces of volatile products produced at each charring temperature.

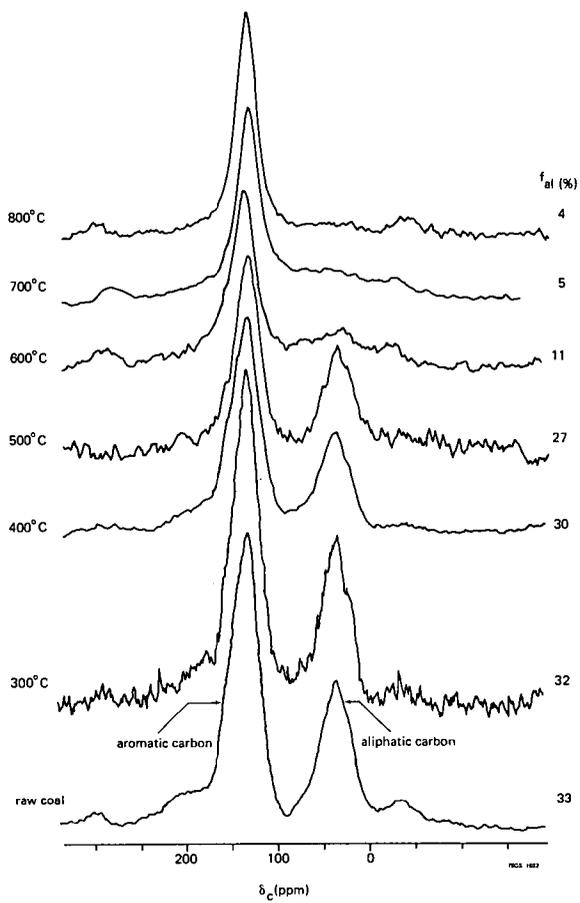


Fig. 2. ^{13}C CP/MAS NMR spectra of the raw coal and of the chars at the various charring temperatures.

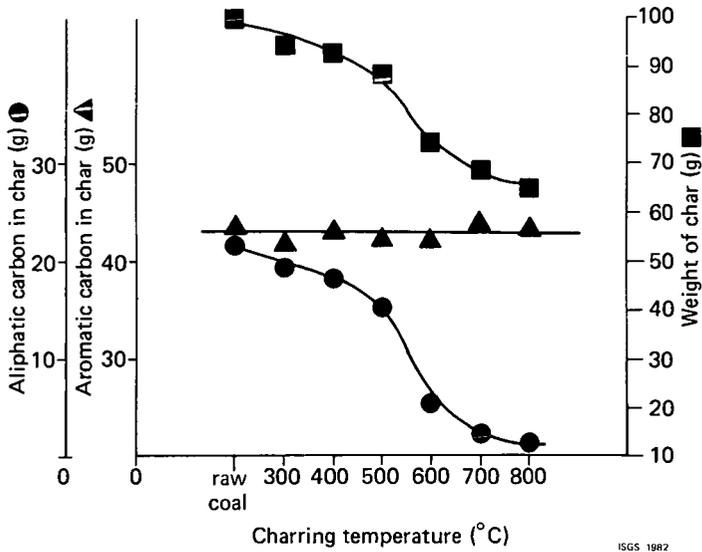


Fig. 3. The calculated amounts of aliphatic and aromatic carbon in char in relation to temperature and the weight of char based on 100 g of raw coal used.

DEPOSIT FORMATION IN HEAT EXCHANGER FROM COAL DERIVED NAPHTHA

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INTRODUCTION

Coal derived naphthas have been observed to produce deposits in hydrotreaters, heat exchangers, heaters, and reactor inlets which operate at approximately 400°C. These deposits are black in appearance and cause plugging of the reactor components. This results in a shutting down of the system. Such downtime is expensive due to both production losses and repair costs. If causes for deposit formation can be identified and a probable mechanism found, it should be possible to decrease or eliminate this expensive reactor downtime.

There are two main objectives for this study. 1) Determine what classes of compounds are responsible for deposit formation. This involves concentrating various classes of compounds by both distillation and chromatographic means and developing a way to indicate their potential for deposit formation. 2) Indicate a possible mechanism for deposit formation. This includes an examination of the deposit and the identification of secondary products of deposit formation.

EXAMINATION OF DEPOSIT

A deposit was formed in a pilot plant heat exchanger from a coal derived naphtha. The heat exchanger was run at approximately 400°C in an atmosphere consisting of vaporized naphtha and hydrogen. The formation of the deposit had resulted in shutting down the pilot plant. It was estimated that 10g of deposit was formed from 50 gallons of full range (66-204°C) naphtha. Therefore, only 0.006% of the original material was involved in deposit formation.

The deposit was drilled out of the plugged heat exchanger. It was insoluble in pentane, dichloromethane, chloroform, methanol, dimethyl sulfoxide, and pyridine. The elemental analysis of the deposit is given in Table 1, along with that of a typical naphtha feed. These analyses were performed by Micro-Analysis of Wilmington, Delaware.

The N/C ratio in the deposit relative to the feed increased by a factor of 15.0 while that of S/C and O/C increased by 9.9 and 1.8, respectively. Therefore, the nitrogen and sulfur compounds were heavily involved in deposit formation. The S/N ratio of the deposit was 0.11.

This indicates that the deposit was not comprised predominantly of ammonium polysulfides. These polysulfides have been observed as deposit materials in hydrotreatment runs.

The fact that the O/C ratio only increased by a factor of 1.8 partially rules out an oxidative mechanism. The increase in oxygen could have been due to a small amount of oxidation which occurred after the deposit was collected. No precautions were taken at the time of collection to blanket it with nitrogen, and the deposit was several months old at the time of analysis.

CONCENTRATION OF DEPOSIT PRECURSORS

Coal liquid naphtha is a complex mixture. In order to identify the deposit precursors, they had to be concentrated. A combination of distillation and ion exchange chromatography was used to do this. The effect of these two concentration techniques was tested using TGA. From these experiments it was possible to identify the structural types responsible for much of the deposit formation.

The TGA experiment used to test concentrates for deposit formation consisted of heating the sample in a platinum boat from 25°C to 400°C, under nitrogen, at 20°/min. At 400°C the weight was recorded and the atmosphere switched to oxygen. The temperature was then increased to 700°C, and the material in the pan was burned off. This latter step allowed the tare of the balance to be checked.

It was determined that the residue remaining in the pan at 400°C was insoluble in common organic solvents. Herein, the insoluble residue is designated as "deposit."

It was shown in the pilot plant that the 177-204°C naphtha produced more deposit than the full range (66-204°C) naphtha. Therefore, various distillate cuts of the 177-204°C sample were prepared and tested for deposit formation. From these experiments it was found that the bottom 40% of the 177-204°C naphtha contained essentially all of the deposit precursors. The bottom 40% of the naphtha was used in the remainder of the experiments. It formed 1.73+ .04 Wt.% deposit on heating to 400°C.

Because of the large amount of nitrogen seen in the deposit, the nitrogen containing compounds were concentrated on an ion exchange resin. Basic nitrogen compounds such as quinolines, pyridines and amines have been reported to be removed by Amberlyst-15 ion exchange resin. (2,3) The resin was prepared as described elsewhere (3) and it was used to remove the basic nitrogen compounds. It was ultimately decided that a ratio of 2.3:1:resin:bottom 40% was needed to lower the basic nitrogen content from 1.4% to 88 ppm, as determined by nonaqueous titration. This was the lowest basic nitrogen level that could be achieved.

While it was not possible to get the basic nitrogen content below 88 ppm, the deposit formation from the sample of ion exchange treated effluent was reduced to 34.7% of its original level. The correlation between deposit formation as measured by TGA and basic nitrogen level is shown in Table 3.

The material retained by the Amberlyst-15 ion exchange resin was desorbed by a solution of ammonia saturated methanol. The methanol was stripped off at 50°C under a stream of nitrogen. The resultant material was called the basic nitrogen concentrate. Examination of this material by ^{13}C NMR showed it to contain nitrogen heterocycles, such as pyridines and quinolines, and phenols. When heated to 400°C, the basic nitrogen concentrate gave 4.95% deposit as compared with 0.60% deposit from the effluent from the ion exchange resin. The weighted sum of the amounts of deposit from the basic nitrogen concentrate and that of the base-free material was 1.74%, which compares well with 1.73% deposit in the unseparated material. This indicates that there is no interaction between the basic and base-free material. The basic nitrogen concentrate was used in the remainder of this work.

The elemental analysis of the basic nitrogen concentrate, base-free material and bottom 40% of the 177-204°C naphtha is shown in Table 2. While the Amberlyst-15 concentrated the basic nitrogen compounds, it also carried along a large amount of oxygen in the basic nitrogen concentrate. An examination of the material boiling above 200°C by both ^{13}C NMR and Mass Spectrometry showed no evidence for molecules containing both basic and phenolic functionalities on the same molecule. It was not possible to completely separate this residual oxygen by caustic extraction.

EFFECT OF HEATING ON STRUCTURE

In order to arrive at an understanding of the mechanism of deposit formation, the effect of heating on the structure of the basic nitrogen concentrate was observed using FT-IR. Due to small amounts of deposit (~1-5mg) formed in the TGA pan, the use of other analytical techniques was not possible.

Samples were prepared by heating the basic nitrogen concentrate in the TGA at 400°C for a desired length of time. The deposit was recovered from the pan by soaking the pan with its contents in methylene chloride and evaporating the methylene chloride under nitrogen. (4) The deposit was then made into KBr pellets as described previously. Spectra were run on a Digilab 15B FTS System. Two hundred co-added interferograms at 2 cm^{-1} resolution were taken for each sample.

Visual observation of the spectra showed changes in aromatic C-H, aliphatic C-H and hydroxyl bands at 3000-3100 cm^{-1} , 2820-3000 cm^{-1} , and 3100-3600 cm^{-1} , respectively. These three bands were curve resolved and integrated using the methods of Painter, et al. (4) The integrated intensities for the three regions were plotted against heating time at 400°C and are shown in Figure 1. Substantial decreases were seen in all three of these regions with increased sample heating time.

MECHANISTIC CONSIDERATIONS

The decreases in aromatic C-H, aliphatic C-H, and hydroxyl bands described above have substantial implications for deposit formation. The loss of aliphatic C-H indicates a pyrolysis type of reaction. An analysis by gas chromatography of the TGA gaseous effluent shows the presence of light alkanes and alkenes as would be expected from a pyrolysis reaction.

The loss of aromatic C-H indicates a cross-linking of free radicals formed during pyrolysis with the subsequent formation of higher molecular weight molecules. The addition of octahydrophenanthrene to the basic nitrogen concentrate lowered the amount of deposit formed by 52%. Presumably, this is due to the capping of free radicals formed during pyrolysis.

The loss of O-H indicates either a loss of adsorbed water or a condensation reaction with a subsequent loss of water. The amount of water formed during heating was measured by gas chromatography. The adsorbed water in the feed was also measured. The amount of water produced during heating was substantially larger than the amount of adsorbed water on a molar basis. This indicates that some deposit formation occurs through condensation (phenol coupling) reactions. Reactions like these have been shown to occur upon heating naphthol to 400°C.⁽⁵⁾ Silylation of the phenols with BSTFA resulted in a 24% decrease in the amount of deposit formed.

CONCLUSIONS

The heat exchanger deposit precursors are concentrated in the basic nitrogen concentrate obtained from the naphtha bottoms. This concentrate contains both heterocyclic nitrogen compounds and phenols. The primary reactions responsible for deposit formation were: 1) condensation of phenols, and 2) pyrolysis of alkylated nitrogen heterocycles.

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REFERENCES

1. Kara, S., Kobylnski, T. P., Beuther, H. Preprints Div. Petrol. Chem., 1982, 27, 849.
2. Jewell, D. M., Weber, J. H., Bunger, J. W., Plancher, H., Latham, D. R. Anal. Chem., 1972, 44, 1391.
3. Jewell, D. M., Albaugh, E. W., Davis, E. W., Ruberto, R. G. Ind. Eng. Chem. Fundam., 1974, 13, 1974.
4. Painter, P. C., Snyder, R. W., Starsinic, M., Coleman, M. M., Kuehn, D. W., Davis, A. Applied Spectroscopy, 1981, 35, 475.
5. Poutsma, M. L., Dyer, C. W., J. Org. Chem 1982, 47, 3367.

TABLE 1
ELEMENTAL ANALYSIS OF FEED AND DEPOSIT

<u>ELEMENTAL</u>	<u>FEED</u>	<u>DEPOSIT</u>
%C	83.92	73.63
%H	10.86	5.74
%O	5.14	8.22
%N	0.52	6.86
%S	0.23	1.83
%Ash	0.00	3.73
H/C	1.55	0.94

TABLE 2
ELEMENTAL ANALYSES OF BASIC NITROGEN CONCENTRATE,
 BASE FREE MATERIAL, AND BOTTOM 40% FRACTIONS

	<u>Bottom 40%</u>	<u>Basic Nitrogen Concentrate</u>	<u>Base Free Material</u>
% Carbon	79.67	78.25	80.30
% Hydrogen	8.44	7.95	8.94
% Nitrogen	1.54	3.54	0.14
% Oxygen	9.59	10.04	10.03
% Sulfur	0.65	0.22	0.58
H/C	1.27	1.22	1.34

TABLE 3
EFFECT OF BASIC NITROGEN ON DEPOSIT FORMATION

<u>Basic N Content</u>	<u>Wt.% Deposit</u>
88 ppm	.60%
173 ppm	.83%
280 ppm	1.40%
1.39%	1.73%

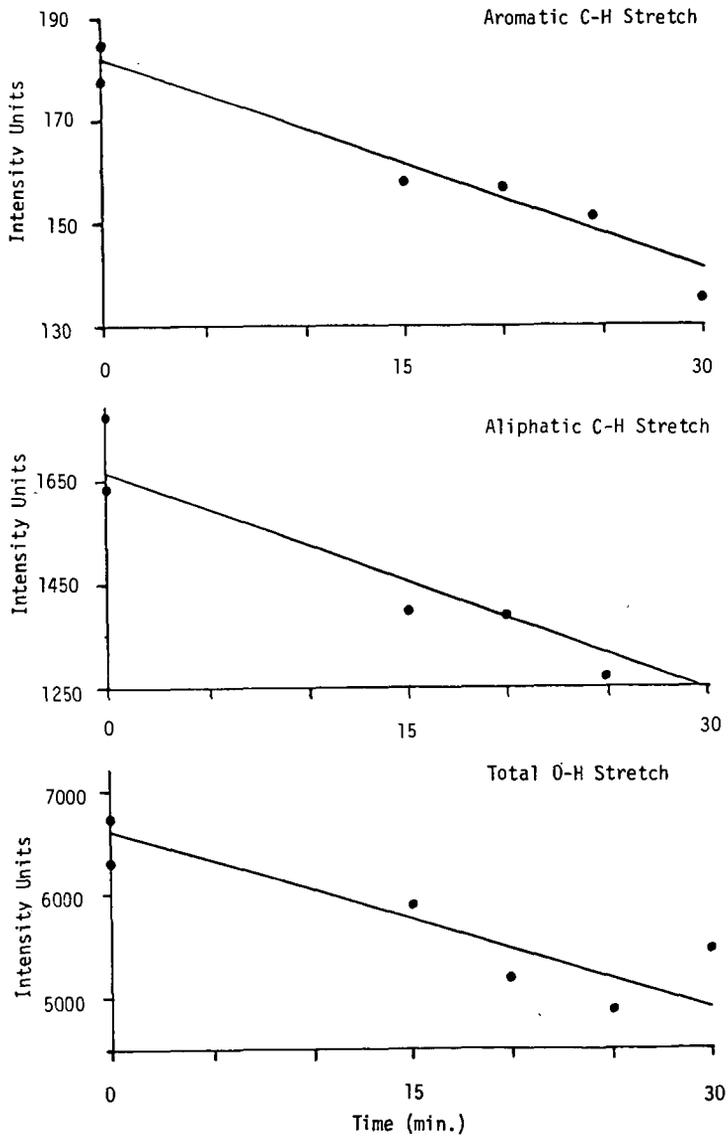


Figure 1. Integrated Intensities vs. Time at 400°C