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Analytical Pyrolysis of Thai Lignites

Naowarat Poolasap
Western Kentucky University

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ANALYTICAL PYROLYSIS OF THAI LIGNITES

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Naowarat Poolasap

July 1985

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ANALYTICAL PYROLYSIS OF THAI LIGNITES

Recommended 9 July 1985
(Date)

John W. Reasoner
Director of Thesis

John T. Riley

Gordon E. Schorp, Jr.

Approved July 18, 1985

Elmer Gray
Dean of the Graduate College

ACKNOWLEDGEMENTS

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ANALYTICAL PYROLYSIS OF THAI LIGNITES

Naowarat Poolasap   July 1985   78 Pages

Directed by: John W. Reasoner

Department of Chemistry   Western Kentucky University

Samples of four different Thai lignites were utilized
to study the effects of ceiling temperature and heating rate
on the overall yield and product distribution by the tech-
nique of analytical pyrolysis (pyrolysis-gas chromato-
graphy). Ceiling temperatures of 450°, 550°, 650°, 750°,
850°, and $950^{\circ}C$, a heating rate of $500^{\circ}C/sec$ and pyrolysis
intervals of 20 seconds were investigated. The results were
reported in terms of percentage high-volatile product and
low-volatile product fraction, weight-loss (% by weight),
and total yield (counts per milligram). One sample which
showed the highest sensitivity to changing ceiling tempera-
ture was selected to study the effect of heating rate on
overall yield and product distribution. Heating rates of
$500^{\circ}C/sec$ and $100^{\circ}C/sec$ (for an interval of 20 seconds) and
$500^{\circ}C/sec$ for one minute and $300^{\circ}C/min$ for two minutes were
employed in the study, at a ceiling temperature of $750^{\circ}C$.

The results of the above investigation may be summarized as follows:

1. All four samples are lignite A (rank) but give different pyrograms as a result of differences in maceral concentrations and chemical structure of each of the coals.

2. The total yield, high-volatile product, and weight-loss increase with increasing ceiling temperatures.

3. Heating rates in the range studied have no significant effect on the total yield and product distribution.

4. High-volatile product yield increases with increasing pyrolysis interval because of secondary cracking reactions but the overall product yield remains essentially constant.

INTRODUCTION

Over the past 50 years, the petroleum industry has made giant technological advances to meet the energy demands that have been imposed by transportation, household heating, power generation, and the wide range of petrochemicals. The present excessive demands placed on the availability of the limited resources of petroleum crude have accentuated the current energy problems. These problems will become increasingly severe as the petroleum reserves become depleted. The resolution of these problems requires the optimum utilization of other types of fuel.

Coal is a fossil fuel which could become a major source for energy and chemicals. Coal is also the most abundant fossil fuel in the world, comprising about 75% of the total world resources of fossil fuel.

One of the important methods used to study the amount of volatile yield and product distribution from coal as well as its structure is pyrolysis. The pyrolysis processes include the breaking down of the coal polymer and cracking molecules in the vapor phase to smaller molecular units and possibly some carbonaceous residue from the oil vapor.

Therefore, when coal is pyrolyzed, hydrogen-rich volatile matter is distilled and a carbon-rich solid residue (char or coke) is left behind. Furthermore, all coal conversion processes (liquefaction, gasification, and combustion) are initiated by pyrolysis.

The purpose of this project was to investigate the effect of ceiling temperature and heating rate on overall product yield and product distribution for Thai lignite samples using the technique of pyrolysis-gas chromatography (analytical pyrolysis). This technique also provides valuable information about the chemical structure of the coal.

Lignite, the lowest rank coal, is characterized by an abundance of terpenoid and alicyclic compounds with few aliphatic or aromatic species. It has higher moisture and oxygen content than high rank coal. In addition, the pyrolysis data may be useful in evaluating lignites for commercial coal projects.

HISTORICAL

Coal is a sedimentary rock accumulated as peat (partially decomposed vegetation) then buried and compacted in previous geologic ages. Coal may be classified according to rank (stage of metamorphoric development) -- lignite, subbituminous, bituminous, and anthracite.

Coal is composed principally of macerals and subordinately of minerals; it also contains water and gases in submicroscopic pores. Macerals are organic substances derived from plant tissues, cell contents, and exudates that were variably subjected to decay, incorporated into sedimentary strata, and then altered physically and chemically by natural (geoglogical) processes[1]. There are three major classes of macerals -- vitrinite, liptinite (or exinite), and inertinite -- which are recognizable in all ranks of coal except those of the highest rank. Coal is a heterogeneous substance due to its inheritance from the diversity of source materials that accumulated in peat swamps.

Organic Structure of Coal

The most widely held view of coal structure pictures coal as groups of fused aromatic and hydroaromatic ring

3

clusters, possibly linked by relatively weak aliphatic bridges. The ring clusters contain heteroatoms (oxygen, sulfur, and nitrogen) and have a variety of attached functional groups.

Several investigators have suggested coal structures which are based on constraints provided by available data. One such hypothetical coal molecule is presented in Figure 1[2]. Some of the details of the model are as follows:

1. The structure contains only one carbonyl group. The carbonyl concentration is based on the yield of CO_2 which is believed to be its thermal decomposition product. No other carbonyl groups are included as the carbonyl peaks from FTIR are very small (see Figures 2 and 3).

2. Other than hydroxyl oxygens, which are determined from FTIR, the remainder of the oxygen is shown in ether linkages, mainly oxygens linked to aromatic carbon on the basis of the position of the ether absorption in the infrared.

3. Infrared also shows the presence of strong hydrogen bonding which is indicated in Figure 1.

4. The nitrogen is shown only as part of an aromatic ring but sulfur is shown both in rings and as mercaptan side groups.

5. The structure contains ethylene bridges which break and stabilize in thermal decomposition.

5
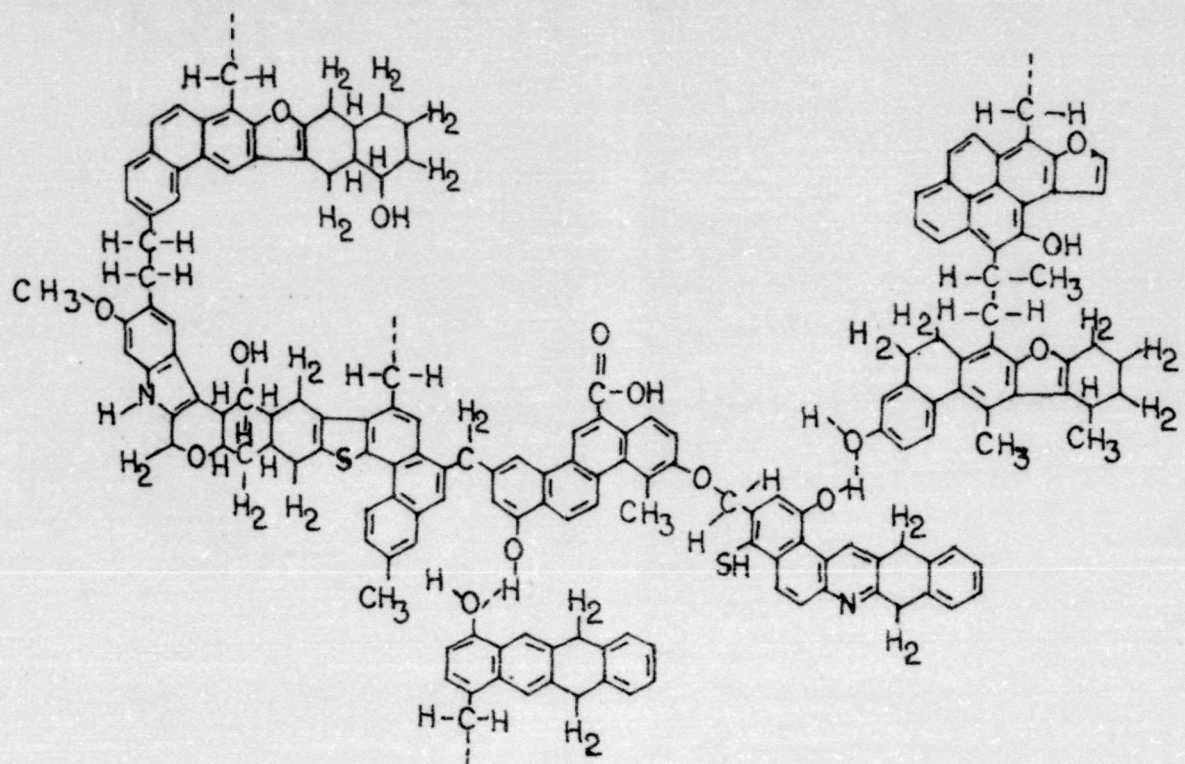
Figure 1 Summary of Coal Structure Information in a Hypothetical
Coal Molecule
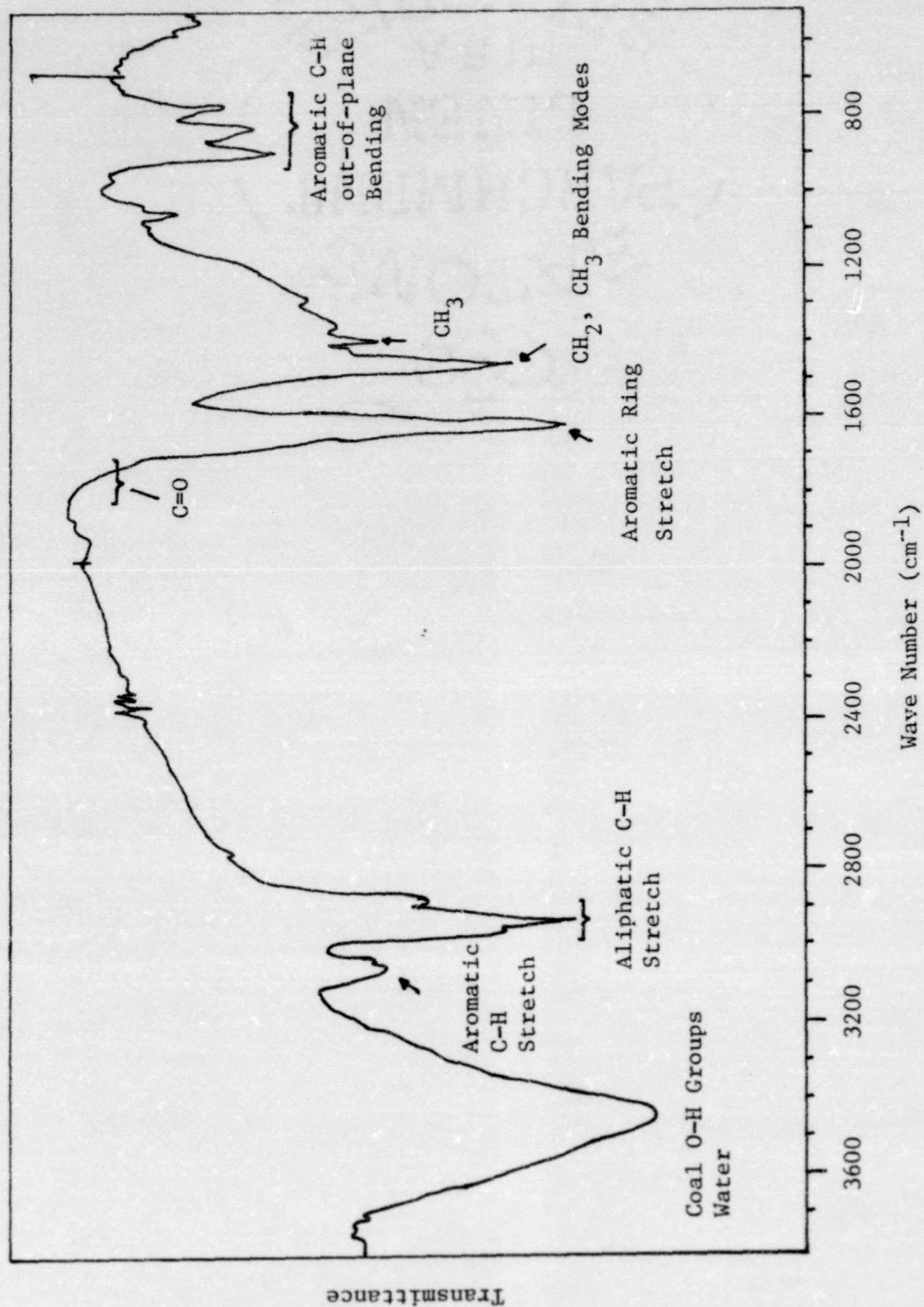
Figure 2   FTIR spectrum of high-volatile bituminous coal
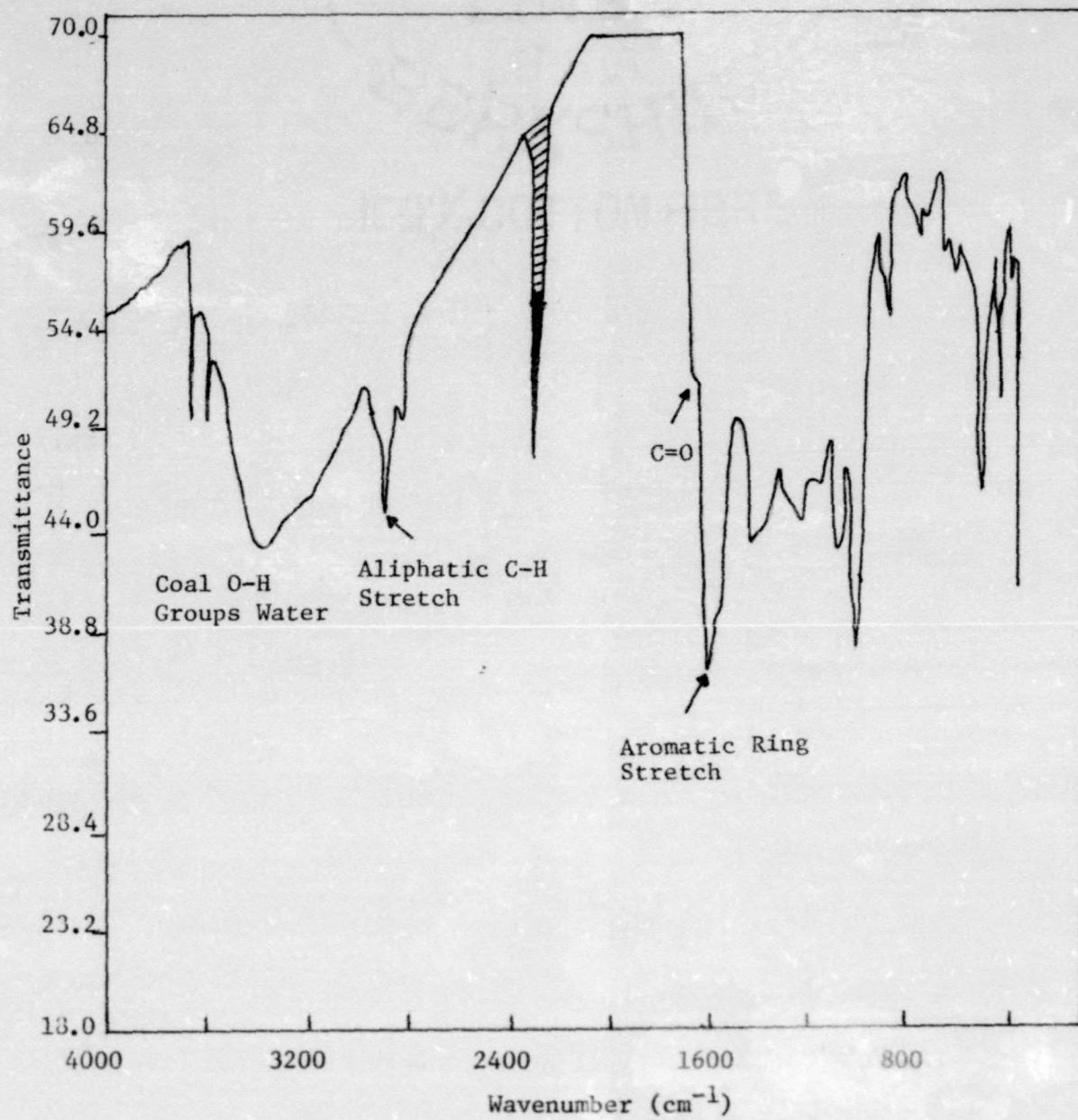
Figure 3   FTIR spectrum of the Texas lignite

As the rank of coal increases, the organic matter becomes higher in carbon content, lower in oxygen content, more aromatic (high degree of aromaticity) and contains more highly condensed ring structures.

Mechanism of Coal Pyrolysis

The mechanism of coal pyrolysis involves thermolysis of one or more covalent bonds holding the organic fragment to the coal matrix (polymer). Scission of C-C bonds produce free radicals which may then react in a number of different ways. The radicals may fragment into smaller radicals which are in turn stabilized by reaction with hydrogen. These smaller fragments would most likely be volatile and distill from the coal. Alternatively, the free radicals may couple to form char or coke.

The Proposed Mechanism (highly simplified)

1. Thermolysis

$$R : R \xrightarrow{\text{heat}} R. + R. \text{ (Free radicals)}$$

bond within coal matrix

2. Add Hydrogen

$$R. + H. \longrightarrow R : H$$

from internal or external source
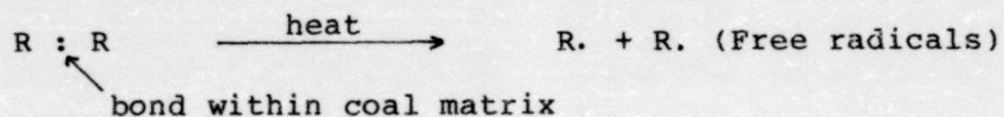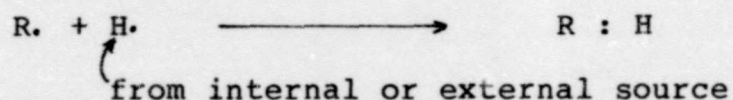
3. Fragmentation/Disproportionation

$$R. \longrightarrow R' : H + R''.$$

$$R''. \xrightarrow{H.} R'' : H$$

$$R. \longrightarrow R' : H + R''-CH=CH_2$$
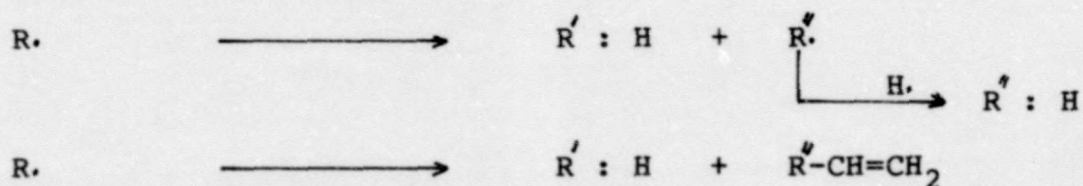
4. Couple to Form "Char"

$$R. + R. \longrightarrow R : R$$
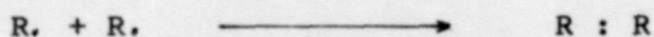
Yohimura et al.[3] reported that the activation energy estimated from the weight change was 11 kcal/mole in the temperature range 170-300°C. The activation energy for pyrolysis at 350°C was 22 kcal/mole, too small to break a C-C bond. Above 420°C, the C-C bonds were broken; the activation energy was 54 kcal/mole. Therefore, the very good candidates for low-temperature scission are

1. Benzylic ether (bond dissociation energy of 52 ± 5 kcal/mole).[4]

$$\text{C}_6\text{H}_5\text{-CH}_2\text{-O-C}_6\text{H}_5 \xrightarrow[\text{[H]}]{400\ C} \text{C}_6\text{H}_5\text{-CH}_3 + \text{C}_6\text{H}_5\text{-OH}$$
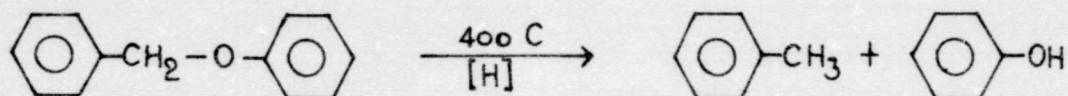
2. Aromatic units joined by ethylene bridges (bond dissociation energy of 56 ± 2 kcal/mole).[4]

3. Thioether $C_6H_5CH_2$-SCH_3 (bond dissociation energy of 51 kcal/mole).[5]

4. Hydrogen bond (bond dissociation energy of 2-10 kcal/mole).[6]

The breaking of labile bonds releases the ring clusters with their attached functional groups. These large molecules comprise a material called coal tar. Simultaneous with the evolution of tar molecules is the competitive cracking of the bridge fragments, attached functional groups, and ring clusters to form the light gas molecules as shown in Figure 4.[2]

Thermal decomposition data suggest the following relationship between the components of coal and the evolved
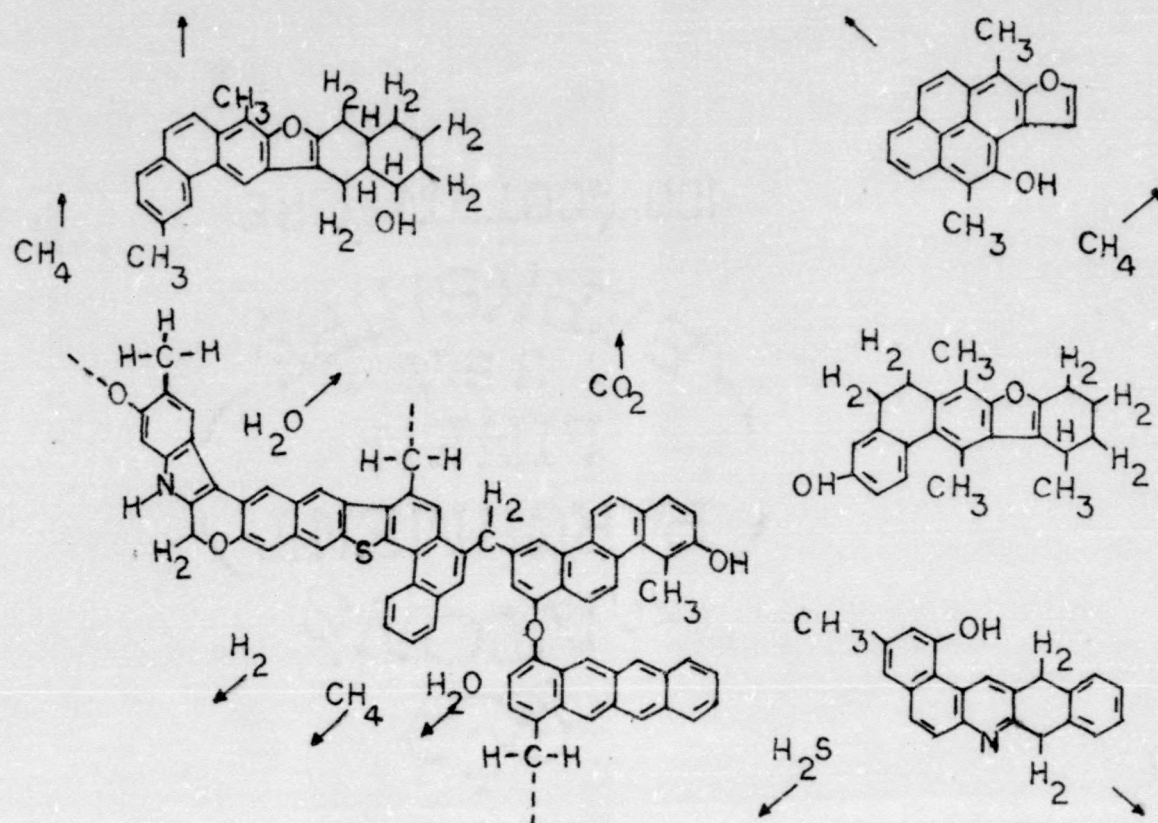
Figure 4   Cracking of Hypothetical Coal Molecule During
Thermal Decomposition

light species.[2] At low temperatures there is very little rearrangement of the aromatic ring structure. There is decomposition of the substituted groups and aliphatic (or hydroaromatic) structures resulting in CO_2 release from the carbonyl, H_2O from hydroxyl, hydrocarbon gases from aliphatics, H_2S from mercaptans, and some CO from weakly bound ether groups. At high temperature, there is breaking and rearrangement of the aromatic rings. In these processes, H_2 is released from the aromatic hydrogen, CS_2 from the thiophenes, HCN from ring nitrogen, and additional CO from tightly bound ether linkages. As this process continues the char becomes more highly condensed and more aromatic in nature (more graphitic).

From studying the product composition and kinetics of lignite pyrolysis, Suuberg and co-workers[7] concluded that the individual product yields vary with temperature in a series of steps indicative of the occurrence of five principal phases of devolatilization: moisture evolution at about $100^{\circ}C$; a large initial evolution of carbon dioxide beginning at about $450^{\circ}C$, probably from decarboxylations and a small amount of tar formation; evolution of chemically formed water and a small amount of carbon dioxide at $500-700^{\circ}C$; rapid evolution of carbon monoxide, carbon dioxide, tar, hydrogen, hydrocarbon gases, and only a little water at $700-900^{\circ}C$; and high temperature formation of carbon monoxide and carbon dioxide.

Thermal decomposition experiments yield information on the coal fragments (which are similar in composition to the parent coal) and on the concentration of chemical species and their relative bond strengths. The analytical techniques applied to the coals and thermal decomposition products include

1. gas chromatography and gas chromatography-mass spectrometry for identification of the decomposition products[8,9]

2. FTIR for the quantitative determination of hydroxyl, aliphatic (or hydroaromatic) and aromatic hydrogen, aliphatic and aromatic carbon, and qualitative determination of oxygen functional groups and the distribution of aromatic hydrogen[10]

3. carbon and proton NMR for determination of the fraction of aromatic carbon and hydrogen[11]

4. elemental analysis

5. gel permeation chromatography (GPC), vapor phase osmometry, and field ionization mass spectrometry for determining the molecular weight of coal fragments[12,13,14]

Pyrolysis

Pyrolysis is defined as the transformation of a substance into one or more substances by the application of heat alone or the decomposition of organic matter by heat in the absence of air. Pyrolysis is the oldest operation to be carried out on coal. Recent innovations in this area include vacuum pyrolysis in a mass spectrometer[15], laser

irradiation [16], "flash heating,"[17,18] and the use of arc plasma.[19]

Hanson et al.[16] reported their applications of laser pyrolysis gas chromatography (LPGC) to study the influence of coal composition on the distribution of gaseous products. LPGC provides a rapid method when used in conjunction with plasma stoichiometric analysis for determining the relative concentration of carbon, hydrogen, and oxygen in coals. Pyrograms and correlations between experimental results and elemental compositions were obtained.

Schulten[14] investigated pyrolysis-field desorption mass spectrometry which provides fast fingerprinting of organic and inorganic products. Two main groups of organic species were found:

(1) Fragments with mass numbers from 200 to 800 represent a complex mixture of aliphatic, olefinic, aromatic and heterocyclic guest molecules which are volatilized from coal at low temperatures.

(2) Fragments obtained at higher temperatures, with mass numbers from 800 to > 3,000 can be assigned to the host structure of the coal (coal matrix) and which give a regular, highly reproducible breakdown pattern.

Granger and Ladner [17] studied flash heating of pulverized coal by heating a thin layer of coal particles (size < 10 μm) for about one msec with a pulse of light derived from a Xe flash tube from which the UV component had been

removed. The quantities of tar and gas evolved were measured.

Graff et al.[18] also developed a laboratory reactor system to determine the products obtainable from the flash heating of raw coal in flowing hydrogen at < 100 atm pressure. The system provided for control of heating rate, solid-contact time, and vapor product residence time. A comparison of the results in which each of these time parameters was varied in turn illustrates their importance in determing the yields of alkane and single ring aromatics from the coal pyrolysis products.

Gray, Cogoli, and Essenhigh[20] studied coal pyrolysis and concluded the following:

(1) Rapid heating can raise coal samples to high temperatures without significant decomposition where they can then pyrolyze at a constant temperature with a yield of volatiles that is higher than can be obtained under any other experimental conditions.

(2) Pyrolysis at lower heating rates may cause part of the coal substance to cross-link during the period of temperature rise to the final, constant pyrolysis temperature. This cross-linking binds material that would otherwise be able to escape as volatiles, thus reducing the volatile yield.

Menster and co-workers[21] studied the devolatilization of coal by rapid heating which was attained with pulse-heating equipment. Subbituminous A to low volatile

bituminous coals were studied. All bituminous coals exhibited devolatilization curves which were characteristically similar (Figure 5), but the devolatilization curves of subbituminous A coal differed markedly (Figure 6). The weight losses are found to increase monotonically with temperature. The broadest peak is exhibited by the high volatile C bituminous (hvCb) coal which has the highest volatile matter content. For the higher rank bituminous coals, the peaks become progressively less intense with the increase in rank, and the peak position shifts to a higher temperature. In all instances the volatile yield corresponding to the peak in the weight-loss curves was greater than the volatile matter in the coal determined by the ASTM standard method of analysis. In fact, the yield of total volatiles may be increased as much as 36% by rapid heating. The products of devolatilization were gases, condensable material or tar, and residual char.

Suuberg et al.[7] studied the product compositions and formation kinetics on rapid pyrolysis of lignite and bituminous coals. Volatile yields were found to increase monotonically as the temperature increases, with the evolution of different products or groups of products occuring in sequential but overlapping temperature intervals. The lignite volatiles are dominated by CO, CO_2 and H_2O, while the main volatiles from the bituminous coals are tar and light hydrocarbons. Heating rate was reported to have a negligible effect on total yields or product distribution
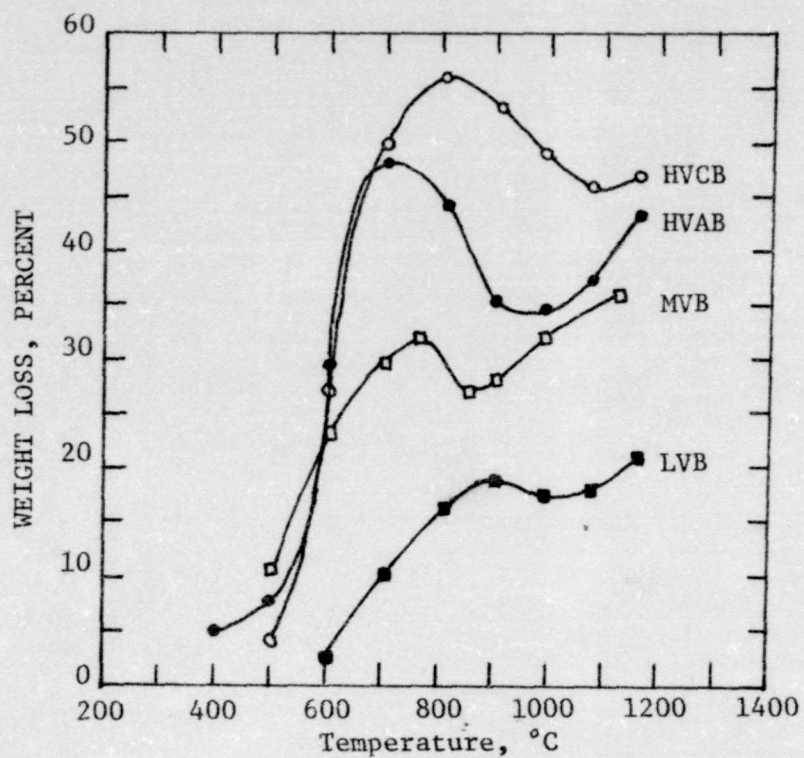
Figure 5 Devolatilization of Bituminous Coals by Rapid Heating
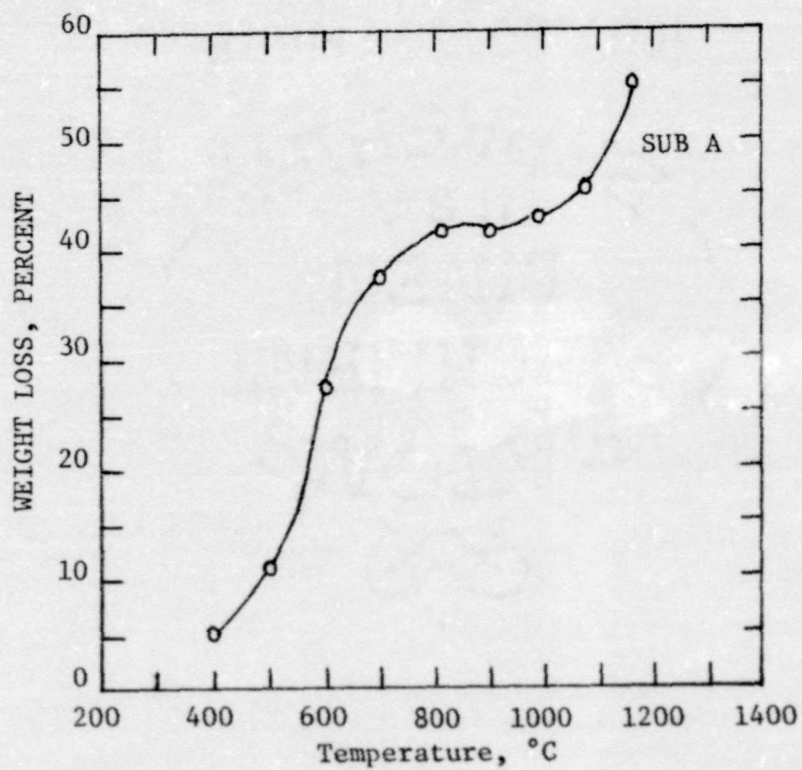
Figure 6 Devolatilization of Subbituminous Coal by Rapid Heating

from either coal. Pressure and particle size also have little effect on product yields from the lignite. In contrast, for bituminous coals, an increase in pressure or particle size results in less tar and more char and hydrocarbon gases, apparently reflecting mass transport limitation and the occurrence of secondary reactions within or on the coal particles. The kinetics of the evolution of different products from the lignite is successfully modeled by 1, 2, or 3 first-order decomposition reactions. For bituminous coal, a similar model which includes evaporation and diffusion of tar along with pyrolytic and secondary reactions was found to be consistent with the observed behavior.

Dimitrova et al.[22] studied the product distribution from the flash pyrolysis of Bulgarian lignites. Maximum tar yields (15-18 weight% or 110-130% of the yields from Fischer pyrolysis) were produced from flash pyrolysis at $580^{o}-600^{o}C$ (contact times 0.5-1.5 sec). The liquid products contained up to 40% phenols, or twice the yield produced by slow coking of lignite. Gaseous products from flash pyrolysis (calorific value 18 MJ/kg) contained lower hydrogen and carbon dioxide contents but higher amounts of carbon monoxide and unsaturated hydrocarbons than that produced by slow coking.

Kothandaraman and co-workers[23] studied the mass loss dependence on ash content of lignite by flash pyrolysis. The organic mass removed from any coal as a result of

pyrolysis is often reported and compared on a dry, ash-free
(daf) basis, which implies that ash is chemically inert and
does not affect organic mass removal. Pyrolysis experiments
on lignite have shown that the mass losses decrease linearly
with increasing ash content. The mineral matter may act as
a catalyst for reactions in which the volatile compounds
decompose and are deposited on the interior surface of the
coal, thus decreasing the observed mass loss.

Neoh and Gannon[24] used rapid pyrolysis to study the
volatile yields from coals, varying in rank from lignite to
anthracite, by working under conditions of high heating rate
($100,000^\circ$ K/sec) and high temperature ($1600-2400^\circ$ K).
Positive correlations with coal reflectance and elemental
composition were obtained. The distribution of coal ele-
ments between the volatiles and residual char was also
investigated. The results show that hydrogen and oxygen
from the coal are preferentially distributed in the volatile
phase. Coal nitrogen evolution parallels the total vola-
tiles at high temperatures, whereas coal sulfur is prefer-
entially retained in the char and no relationship between
sulfur evolution and coal rank is evident.

Calkins et al.[25] concluded that when coal is flash
pyrolyzed above about 700°C, tar, char, and a range of low
molecular weight volatile products are produced in various
yields and proportions depending on the pyrolysis conditions
and the coal employed. It was found that ethylene, propyl-
ene and butadiene are formed in small but commercially

significant amounts. For a given set of pyrolysis conditions, the ethylene yield, for example, can vary from almost zero to 10-12 weight% depending on the coal type.

Pyrolysis-Gas Chromatography

Pyrolysis, or controlled thermal fragmentation, has been used to elucidate organic structure, while gas chromatography (GC) is an extremely powerful and sensitive analytical method for the separation and identification of volatile materials. Thus pyrolysis-gas chromatography originally evolved to extend the tremendous separation capability and resolution of GC to the characterization of non-volatile materials. Pyrolysis-gas chromatography gives a highly reproducible analytical system.

Studies utilizing pyrolysis-gas chromatography (PGC) have been done since 1954[26]. Currently, PGC is widely used in the characterization of insoluble materials and has also been applied to natural polymers (such as kerogen)[27], oil shale[28], recent sediments[29], coal[30,31], coal derived kerogen[32], maceral concen- trates[33,34], coal-tar pitches[35], batch autoclave hydrogenation products[36], and petroleum source rock[37]. Moreover, PGC has been used on organic polymers[38], micro-organisms[39], humic acids[40], and meteorites[41].

Suggate[42] was able to correlate differences in coal rank with the resultant pyrograms, even without any product identification. PGC has been used predictively in estimating the process yields from oil shale retorting[43] and in

determining the amount and type of products to be obtained
from in-situ coal gasification[44]. Van de Meent et al.[27]
demonstrated its usefulness in distinguishing between sedi-
mentary types (e.g. terrestrial versus marine). Variations
in the amount and distribution of aliphatic and aromatic
compounds released upon pyrolysis may indicate specific
structural differences in the insoluble materials being
examined[33,34].

Bricteun[45] identified coal components such as exinite
and vitrinite by a combination of pyrolysis with gas-chro-
matographic techniques. In this work coal (about 20 mg) is
quickly heated to a predetermined temperature of about
$1000^{o}C$ in a steady stream of nitrogen which feeds a
programmed chromatograph allowing the determination of
compounds containing up to 17 carbon atoms. This analytical
procedure demonstrates more clearly than infrared analysis
the chemical differences among the macerals. The exinite,
which is formed from the coalification of spores and the
cuticle of leaves, contains a greater amount of paraffinic
material than does vitrinite, which is derived from vegetal
tissue.

Romováček and Kubát[8] developed a technique for rapid
pyrolysis whereby the coal sample is dropped into a bath of
molten tin. The product gases are swept by an inert carrier
gas into a gas chromatograph, whereby the production of
selected low molecular weight hydrocarbons is monitored at
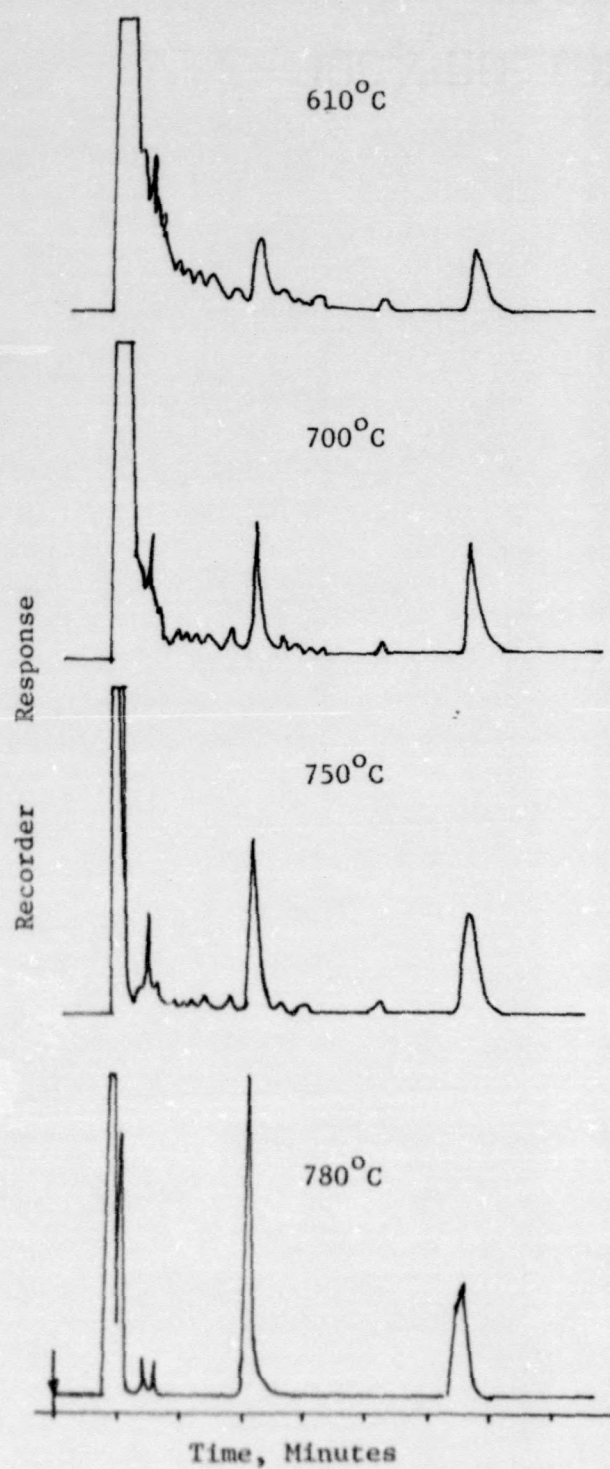several pyrolysis temperatures (Figure 7).

Figure 7   Chromatograms Obtained from a Bituminous Coal
            at Different Pyrolyzer Bath Temperatures (from
            Above 610, 700, 750, and 780°C)

From chromatographs shown in Figure 7 they determined
that at temperatures lower than $600^{\circ}C$ the decomposition of
coal is too slow to give satisfactory resolution of the
peaks. But above $750^{\circ}C$ the degradation is so intense that
the initial peaks corresponding to the non-aromatic hydro-
carbons almost completely disappear, and only the peaks at
the end of the chromatogram (mostly aromatic hydrocarbons)
remain.

Furthermore, they investigated the changing pyrograms
due to rank of coal substance as shown in Figure 8. The
height of peak 15 (methylcyclopentane) increases with de-
creasing rank and peak 24 (methylcyclohexane) attains its
maximum value with very good coking bituminous coals such as
E, as shown on Figure 8 (low volatile bituminous coal).

Pyrolysis-gas chromatography was used to characterize
quantitatively a series of high-to-low-volatile bituminous
Permain Australian coals[46]. The levels of n-alkanes,
n-alkenes and triterpenoids released by pyrolysis all de-
crease as a function of increasing rank; thus the coal
samples can be classified into three distinct groups (lower
rank bituminous, middle rank bituminous, and higher rank
coals). Carbon Preference Indices (CPI's) for alkanes and
alkene/alkane ratio also decrease as a function of rank.
CPI is calculated as follows:

$$\frac{1}{2}\left(\frac{\sum odd\ C_{11}-C_{29}\ hydrocarbons}{\sum even\ C_{10}-C_{28}\ hydrocarbons} + \frac{\sum odd\ C_{11}-C_{29}\ hydrocarbons}{\sum even\ C_{12}-C_{30}\ hydrocarbons} \right)$$
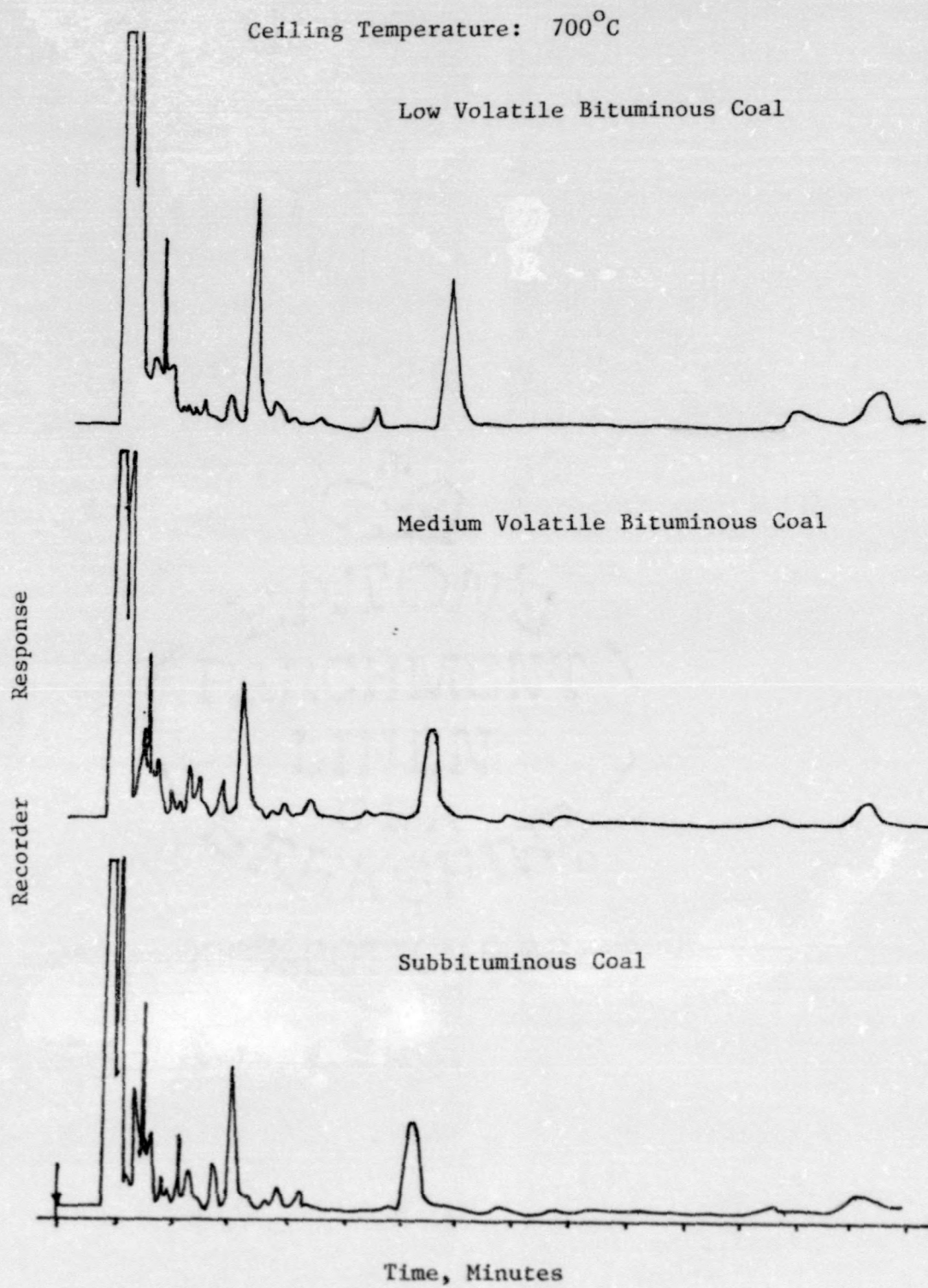
Figure 8 Chromatograms Obtained from Coals of Different Ranks

The triterpenoids have the hopane skeleton exclusively. The hopane isomeric distributions exemplify the geological maturity of bituminous coals relative to lignite. A significant correlation has been established between the level of n-alkanes and n-alkenes released under PGC conditions and the predicted oil yield by pyrolysis of these coals.

Saxby[47] has published the following equation which is able to predict the oil yield obtained from a coal by pyrolysis.

$$Oil(wt.\% - dry) = (1 - 0.01\ m)(66.7\ H/C - 57.0\ O/C - 33.3)$$

where m = weight % of ash, dry basis; H/C = atomic ratio of hydrogen to carbon; and O/C = atomic ratio of oxygen to carbon.

Lignite

Lignite suffers the least amount of metamorphic change during the coal forming process. As such, it retains greater fractions of moisture and volatile matter from the original peat material, and contains less fixed carbon than the high rank coals[48] -- bituminous and anthracite. The primary measure used to classify the lower rank coal is heating value. Therefore, lignite is defined as coal with a heating value less than 8,300 BTU/lb, on a moist, mineral-matter free basis[49].

Thai Lignite Resources

Thailand, like other countries, is being strongly affected by the energy crisis. The trouble is caused by

petroleum-derived energy consumption. Previous figures on
petroleum consumption show that this represents about 75% of
all energy consumed every year, and almost all petroleum
products have to be imported. Therefore, it is essential
that Thailand search for alternative energy sources within
the country as soon as possible. Coal is one such alterna-
tive source of energy. Coal in Thailand was first explored
in 1917 and has long been recognized as lignite.

Coal deposits have been found mostly in tertiary basins
throughout the country. About 80% of lignite seams are
stratified in small structural basins scattered throughout
the northern region. Thailand has 49 identified coal
deposits with probable reserves of at least 1,200 million
tons[50].

Most of the Thai lignites are used in electric power
plants. The remainder are used in tobacco curing plants and
cement factories.

Thai lignite samples employed in this study were
obtained from four different deposits known as Mae Moh and
Li from the north and Klong Wai Lek and Bang Pu Dam (Krabi
deposits) from the south as shown in Figure 9.

Pyrolysis-Gas Chromatography Applied to Lignite

Glam et al.[30] developed a technique for the rapid
characterization and screening of lignite samples by
pyrolysis-gas chromatography. The production of n-paraffins
and 1-olefins with 1-5 carbons was monitored. The peaks
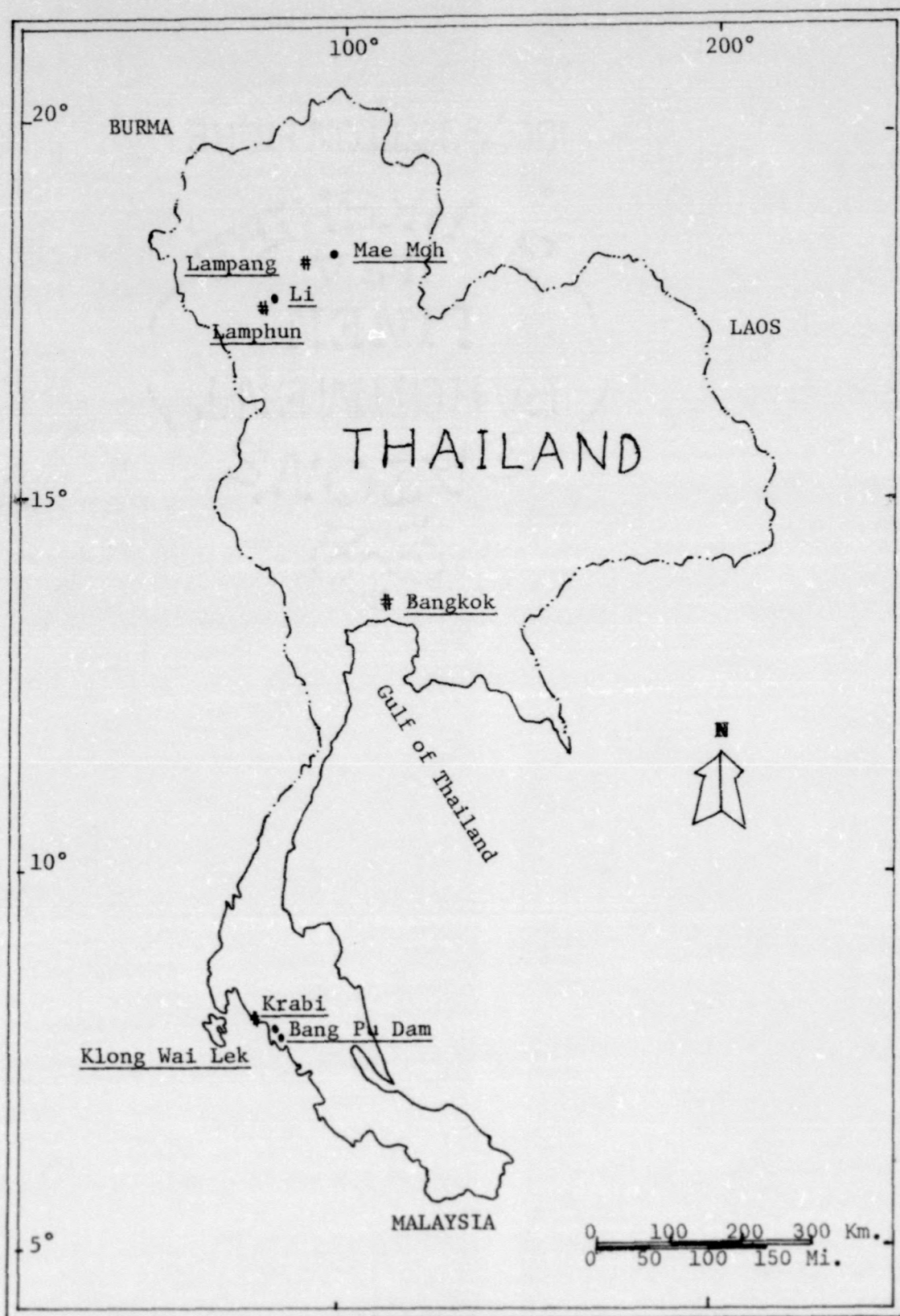(corresponding to C_1-C_5 n-paraffins and C_2-C_5 1-olefins) in

Figure 9 Location of Lignite Samples Deposits

the pyrograms and their elution time were compared with those obtained from the GC analysis of pure gases. Figure 10 portrays a typical pyrogram. Peak heights were found to be acceptable indicators of product yields. Significant differences in hydrocarbon ratios and yields can be discerned among the various lignite samples.

Chaffee et al.[46] used pyrolysis-gas chromatography in characterizing Victorian brown coal lithotypes. The pyrograms show marked changes in the predominance and distribution of specific molecular classes as a function of lithotype. Hydrogen-rich triterpenoid components are predominatly associated with the lighter lithotypes, whereas hydrogen-deficient phenolic components are more abundant in pyrolysates from the darker lithotypes. Carbon preference indices (CPI's) are >1 for the alkanes but <1 for the alkenes released by pyrolysis. Correlation of the components released with the maceral composition of the lithotypes have also been established.

Roberts and Sweeney[9] worked on low temperature $(400^{\circ}C)$ pyrolysis of Texas lignite which produced volatile products typical of coal tars, with tar evolution beginning at about $300^{\circ}C$. The most distinct feature of a typical gc-ms chromatogram of the volatile liquid and solid products from the pyrolysis is the series of peaks for n-alkane and 1-alkene pairs up to about C_{30}, which constitute about 3-5 % dry ,ash-free weight of the original. Other major products observed were toluene, C_2- and C_3- alkylbenzenes, phenol,
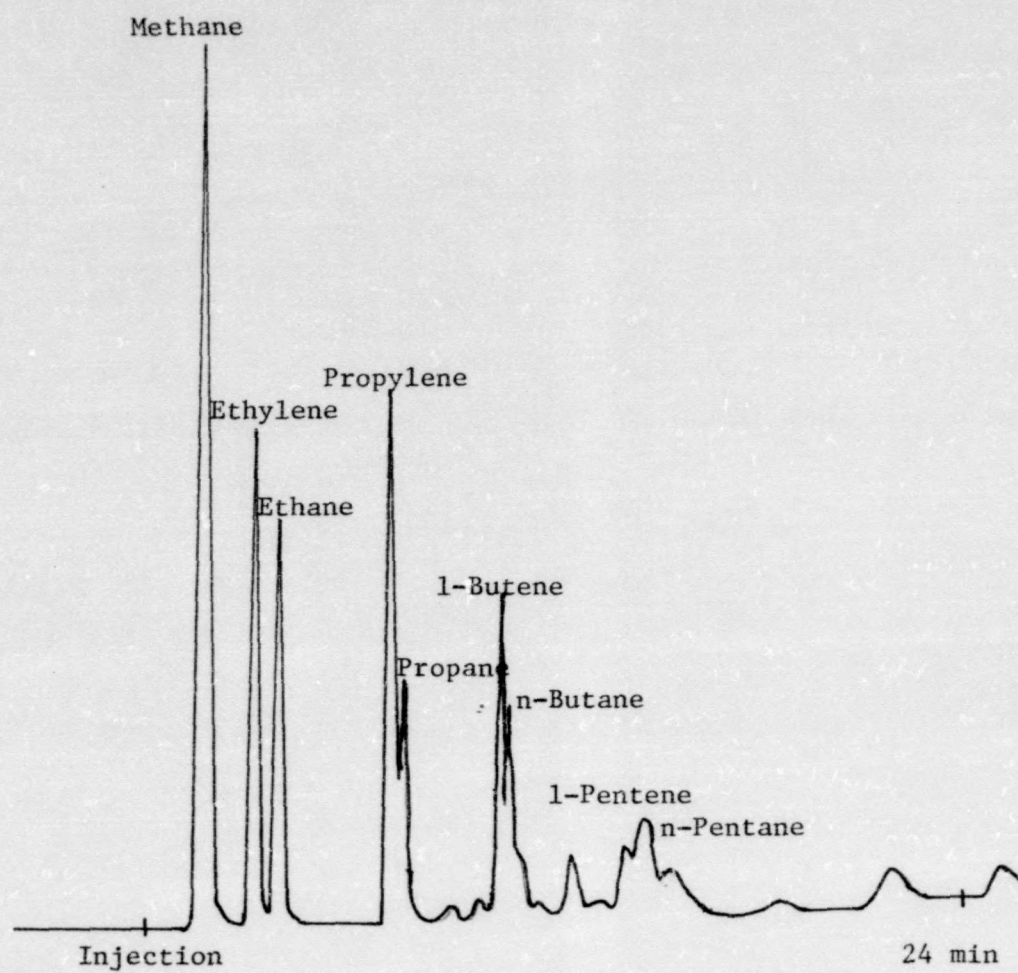
Figure 10.   Gas chromatogram from lignite pyrolysis

cresols, pristane, and phytane. Additionally, they con-
cluded that in the case of lower rank coals, in which more
phenolic and other oxygen substituted aromatics are present,
the alkyl radicals formed initially by cleavage at the
benzyl position would be capable of donating hydrogen atoms
to give terminal alkenes or accepting hydrogen atoms to give
n-alkanes. A broad range of alkanes and alkenes could be
produced by loss of ethylene from the alkyl radical to give
a new C-2 alkyl radical.

The research reported in this paper deals with the
effect of ceiling temperature and heating rate on overall
product yield and product distribution of four lignite
samples by rapid pyrolysis. Gas chromatography is used to
separate the pyrolysis products into gases and oils. Gases
in this context are those compounds which pass through the
GC column within 10 minutes at $60^{\circ}C$. Oils are those
materials which pass through the GC column during the
program from 60° to $250^{\circ}C$.

EXPERIMENTAL

The four lignite samples utilized in this study were
obtained from deposits located in the northern and southern
regions of Thailand. The purpose of this project was to
investigate the effect of ceiling temperature on the overall
product yield and product distribtion for these Thai
lignites. In addition, one of these samples which was the
most sensitive to temperature was selected to study the
effect of heating rate on the overall product yield and
product distribution.

Sample No. A was from Klong Wai Lek (Krabi deposits).
The stratigraphy of Klong Wai Lek consists of lignite,
ligneous clay, clay, siltstone, sandstone, and fossiliferous
limestone conglomerate. The thickness of the lignite seam
was about 15 to 20 meters (Figure 11).

Sample No. B was from Bang Pu Dam (Krabi deposits).
The sequence consists mainly of dark grey to greenish grey
claystone interbedded within the lignite seam (about 40
meters thick) and minor sandstone and shale beds (Figure
12).

Sample No. L was from Li deposit (Lamphun province).
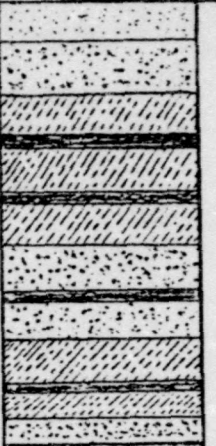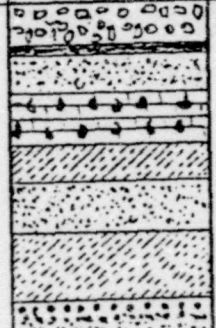The basin forms a flat-lying area of about 10 square km at
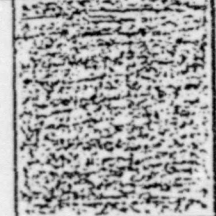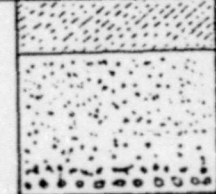
Thickness (meters)	Strati- graphic Column	Description	Age
40		Secuence of lignite, claystone and sandstone	TERTIARY
20		Soil cover	
30		Conglomerate, beach-sandstone, fossiliferous limestone, claystone, and coarsening upward sequence of sediment	
15-20		Main coal seam	
		Sandstone, siltstone, and claystone	

Figure 11   Stratigraphic Section of Klong Wei Lek Deposit
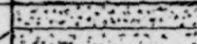
Thickness (meters)	Strati-graphic Column	Description	Age
2		Sand	
20		Alternative sand and massive clay stone	
30		Clay stone	TERTIARY
40		Lignite	
5		Basal clay stone	

Figure 12   Stratigraphic Section of Bang Pu Dam Deposit

470 meters above mean sea level, surrounded on three sides by mountains up to 700 meters high. The sequence of this basin, at least 90 meters thick, includes sandstone, shale, grey claystone, and coal (about 20-30 meters thick) (Figure 13).

Sample No. Q was from Mae Moh deposit (Lampang province). The basin was composed of Permo-Triassic Volcanic Group (basement of the basin) and Tertiary Group. The Tertiary Group consists mainly of freshwater mudstone with two lignite seams overlaid by a thick sequence of inter-bedded claystone, lignite, oil shale, and laminated mudstone (Figure 14). The samples were collected from the lower "Q" seam, generally 10-30 meters thick.

Preparation of Samples

The lignite samples were air-dried (because they were stored under water), crushed to 8 mesh and split. One-half of the 8 mesh coal was ground to 20 mesh and split again. One-half of the 20 mesh coal was ground to 60 mesh and stored under nitrogen in a freezer until used. Chemical and petro-graphic characteristics are given in Table 1.

Coal Characterization

Proximate analysis (moisture, ash, and volatile matter) data were obtained with a LECO MAC-400; carbon, hydrogen, and nitrogen data were obtained with the LECO CHN-600; and sulfur analysis data were obtained with the LECO SC-132. Heating value (BTU) data were obtained by the adiabatic bomb method (ASTM Method 2015), using a Parr model 1241
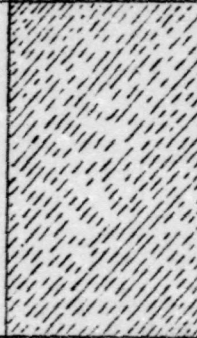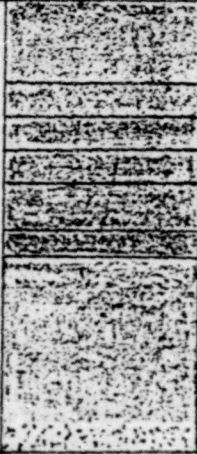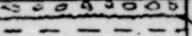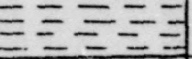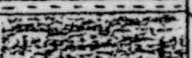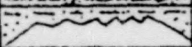
Thickness (meters)	Strati-graphic Column	Description	Age
3		Top soil	
1.5		Gravel beds	
6.8		Brown clay (shale)	
3.8		Shale & gravel	
2.3		Lignite & shale	
36		Lignite (locally interfinger-ing with sandy shale and sandstone)	TERTIARY
1.5		Brown clay (shale)	
0.7		Lignite	
1.5		Brown clay	
21.2		Lignite	
3		Brown clay	

Figure 13   Stratigraphic Section of Li Deposit
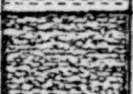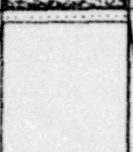
Thickness (meters)	Strati-graphic Column	Description	Age
75		Clay, sandy clay, clayey sand, brownish yellow to brownish red, stiff, high plasticity, slightly calcareous	
100		Shale, brownish gray, laminated to bedded, moderate-fissiled, highly calcareous, contains some thin conglomerate partings with insect parts and coal fragments	TERTIARY
40		Coal seam with some thin partings of ligneous shale and medium brown shale	
35		Claystone, pale to grayish brown, slightly to highly calcareous, with some insects and microfossils	
30		Coal seam, black, dull to shiny, with some thin partings of ligneous clay	
3.5		Fossiliferous claystone, brown to grayish brown, contains fossil of gastropod	
Total Depth of 263.65			

Figure 14   Stratigraphic Section of Mae Moh Deposit

TABLE 1

Coal Characterization Data

Proximate and Ultimate Analysis

Parameter	Sample No. A	Sample No. B	Sample No. L	Sample No. Q
% Moisture*	33.94	31.82	40.12	36.14
% Ash	11.23	10.76	2.10	9.18
% Volatile Matter	45.14	43.33	46.66	42.89
% Fixed Carbon	43.63	45.91	51.24	47.93
% Carbon	62.85	63.68	65.11	66.36
% Hydrogen	4.39	4.53	4.44	4.25
% Nitrogen	1.54	1.57	0.80	2.16
% Sulfur	3.45	3.96	2.66	2.68
% Oxygen (by diff.)	16.54	15.50	24.80	15.37

Forms of Sulfur, Heating Value and ASTM Rank

Forms of sulfur (dry basis)				
% Pyrite	1.39	2.01	0.58	1.00
% Sulfate	0.01	0.01	0.01	0.01
% Organic	2.05	1.94	2.07	1.67
Heating Value**	10,967	11,056	10,917	11,112
ASTM Rank	Lignite A	Lignite A	Lignite A	Lignite A

Maceral Compositions

Vitrinite	94.0	90.6	91.0	91.0
Liptinite	4.2	7.6	4.8	6.2
Inertinite	1.8	1.8	4.2	2.8

* Moisture as-determined, other values on a dry basis
** Heating value in BTU per pound

calorimeter. Analysis for forms of sulphur was conducted in accordance with ASTM Method 2492.

Maceral composition was identified by microscopic analysis with reflected light, 500 total counts for each analysis.

Pyrolysis Technique

This experiment employed a pulse-mode pyrolyzer which used resistively heated electrical filaments[51]. The pyrolysis temperature was controlled by the current passing through the platinum wire. Pyroprobe pyrolysis provided a very rapid rate of temperature increase to highly repro-ducible temperatures. The rapid flow of an inert gas over the sample minimizes the residence time of the released products in the "hot zone" and the formation of secondary pyrolysis was reduced. Both of these points represent major technical advantages over previous studies carried out in furnace and autoclave type apparatus.

Pyrolysis Instrument

Pyrolysis experiments were carried out with a Chemical Data System (CDS) model 100 Pyroprobe which was interfaced with a Varian model 3700 gas chromatograph (flame ionization detector). A Laboratory Data Control model 308 computing integrator was also employed in these studies.

The gas chromatograph was fitted with a 2 meter x 1/8 inch stainless steel column packed with 3% DEXIL 300 on chromosorb W-HP 80/100. The nitrogen (carrier gas) flow

rate was 15 mL per minute. The GC oven profile started at $60^{\circ}C$ for 10 minutes (the "isothermal region"), then ramped at $20^{\circ}C$ per minute to $250^{\circ}C$, then held for 20 minutes (the "programmed region").

The injector temperature was maintained at $270^{\circ}C$ and the Pyroprobe/GC interface unit at $200^{\circ}C$. The integrator was set up to count the accumulated signal over one minute increments.

Procedure

Quartz tubes (2.4 mm od x 25 mm long) were fitted with quartz wool plugs and heated twice for 20 seconds at $950^{\circ}C$ to burn away any organic contaminants present. Subsequently, the tubes were manipulated with tweezers because it was quite easy to obtain pyrograms of "skin oils" if the tubes came in contact with the skin.

Small portions (3-5 mg) of the lignites were precisely weighed into a clean quartz tube using a Mettler model H-20T (sensitivity ± 0.01 mg). The loaded and weighed tubes were placed inside the coil of the CDS Pyroprobe heater unit and then placed inside the interface unit attached to the injection port of the gas chromatograph. The samples were heated to $200^{\circ}C$ (the equilibrium temperature of the Pyroprobe/GC interface unit) under nitrogen and allowed to equilibrate for 20 minutes, then pyrolyzed.

For studying the effect of ceiling temperature, the samples were pyrolyzed at various ceiling temperatures (450°, 550°, 650°, 750°, 850°, and $950^{\circ}C$) at a linear

heating rate of 500°C per second and a total pyrolysis interval of 20 seconds. Pyrolysis products were swept directly into the column. The pyrograms were recorded and electronically integrated over one minute increments.

For studying the effect of heating rate, sample No. B was pyrolyzed at 750°C ceiling temperature at various heating rates.

1. Heating rate   500°C/sec, interval 20 seconds
2. Heating rate   100°C/sec, interval 20 seconds
3. Heating rate   500°C/sec, interval 1 minute
4. Heating rate   300°C/min, interval 2 minutes

Between runs the column was heated to 300°C then held for 10 minutes to minimize build-up of organic material.

Identification of Pyrolysis Products

Pyrolysis-gas chromatography peaks were identified by measurements of retention time and by comparing with the retention time of various pure hydrocarbon standards, where available, to those derived from the sample being pyrolyzed.

RESULTS AND DISCUSSION

Three simultaneous reactions occuring during pyrolysis in an inert atmosphere are devolatilization, cracking, and decomposition. For convenience, the products of pyrolysis are classified as char, tar, and gas. Char is defined as the undistillable material that remains in the form of a solid. Tar is defined as the distillable liquid (low-volatile product) which has a molecular weight larger than C_6. Gas is defined as those components lighter than C_6 (high-volatile product). Both tar and gas (total yield product) occur in the form of vapor when coal is pyrolyzed. During pyrolysis, all of the chemical reactions are assumed to be first-order with respect to the concentration of the reactants. The temperature is the most important factor that effects the product distribution, weight-loss and total yield product.

Effect of Ceiling Temperature

The ceiling temperature was selected at 450°, 550°, 650°, 750°, 850°, and $950^{\circ}C$ for pyrolysis of the four lignite samples. The results of these experiments are shown in Tables 2-5. The data were processed to obtain the arithmetic mean of the high-volatile product, weight-loss

TABLE 2

Product Data from the Pyrolysis of Lignite A

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Ceiling Temperature 450°C				
A1	21.44	78.56	43.69	41,953
A2	20.07	79.93	44.33	38,114
A3	20.72	79.28	43.14	41,286
Average	20.74	79.26	43.72	40,451
Standard Deviation	0.68	0.68	0.60	4.97[a]
Ceiling Temperature 550°C				
A5	25.70	74.30	47.84	186,210
A6	25.42	74.58	45.66	179,674
A7	24.69	75.31	46.31	168,267
A8	24.19	75.81	46.52	170,951
Average	25.00	75.00	46.58	176,276
Standard Deviation	0.69	0.69	0.91	4.66[a]
Ceiling Temperature 650°C				
A9	33.16	66.84	56.64	324,295
A10	31.40	68.60	52.24	292,793
A11	32.46	67.54	52.91	306,200
Average	32.34	67.66	53.93	307,763
Standard Deviation	0.89	0.89	2.37	5.14[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 2 (continued)

Sample No.	% HV	% LV	% Wt. Loss	Yield *

Ceiling Temperature 750°C

A12	37.44	62.56	53.89	369,365
A13	37.66	62.34	57.25	379,526
A14	36.29	63.71	55.05	379,761
Average	37.13	62.87	55.40	376,217
Standard Deviation	0.74	0.74	1.70	1.58[a]

Ceiling Temperature 850°C

A15	41.65	58.35	56.44	422,042
A16	40.87	59.13	61.50	395,245
A17	39.99	60.01	59.01	399,818
A18	42.53	57.47	58.08	417,874
Average	41.26	58.74	58.76	408.745
Standard Deviation	1.08	1.08	2.11	3.23[a]

Ceiling Temperature 950°C

A19	44.48	55.52	58.68	433,638
A20	44.82	55.18	59.60	429,930
A21	44.17	55.83	58.65	427,988
Average	44.49	55.51	58.97	430,519
Standard Deviation	0.32	0.32	0.55	0.67[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 3

Product Data from the Pyrolysis of Lignite B

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Ceiling Temperature 450°C				
B1	16.11	83.89	35.18	55,125
B2	15.94	84.06	35.41	51,660
B3	16.84	83.16	36.52	56,608
Average	16.30	83.70	35.70	54,464
Standard Deviation	0.48	0.48	0.72	4.66[a]
Ceiling Temperature 550°C				
B4	21.17	78.83	40.90	210,003
B5	22.53	77.47	41.50	209,065
B6	22.59	77.41	43.72	211,199
Average	22.10	77.90	42.04	210,089
Standard Deviation	0.80	0.80	1.48	0.51[a]
Ceiling Temperature 650°C				
B7	28.45	71.55	44.81	336,541
B8	29.50	70.50	48.61	377,029
B9	26.40	73.60	46.90	361,183
Average	28.12	71.88	46.77	358,251
Standard Deviation	1.58	1.58	1.90	5.70[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 3 (Continued)

Sample No.	% HV	% LV	% Wt. Loss	Yield *

Ceiling Temperature 750°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
B10	33.00	67.00	47.12	421,526
B11	34.02	65.98	50.28	444,191
B12	34.69	65.31	52.51	463,862
Average	33.90	66.10	49.97	443,193
Standard Deviation	0.85	0.85	2.71	4.78[a]

Ceiling Temperature 850°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
B13	39.87	60.13	57.29	518,465
B14	38.12	61.88	55.97	531,209
B15	39.61	60.39	56.47	519,619
Average	39.20	60.80	56.58	523,098
Standard Deviation	0.94	0.94	0.67	1.35[a]

Ceiling Temperature 950°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
B16	41.07	58.93	60.40	537,418
B17	42.56	57.44	57.71	523,171
B18	43.96	56.04	58.04	550,176
Average	42.53	57.47	58.72	536,922
Standard Deviation	1.44	1.44	1.48	2.52[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 4

Product Data from the Pyrolysis of Lignite L

Sample No.	% HV	%LV	% Wt. Loss	Yield *
Ceiling Temperature 450°C				
L1	12.62	87.38	49.49	55,212
L2	14.35	85.65	45.52	56,296
L3	14.84	85.16	45.52	57,758
Average	13.94	86.06	46.84	56,422
Standard Deviation	1.17	1.17	2.29	2.26[a]
Ceiling Temperature 550°C				
L4	21.34	78.63	52.31	205,616
L5	19.15	80.85	52.68	201,129
L6	19.77	80.23	52.68	193,352
Average	20.10	79.90	52.56	200,032
Standard Deviation	1.14	1.14	0.21	3.10[a]
Ceiling Temperature 650°C				
L7	25.85	74.15	56.17	272,773
L8	24.47	75.53	55.39	270,295
L9	25.59	74.41	57.14	265,859
Average	25.30	74.70	56.23	269,642
Standard Deviation	0.73	0.73	0.88	1.30[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 4 (Continued)

Sample No.	% HV	% LV	% Wt. Loss	Yield *

Ceiling Temperature 750°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
L10	29.81	70.19	57.32	313,414
L11	29.29	70.71	59.10	349,471
L12	29.02	70.98	58.94	340,324
L13	29.84	70.16	58.54	330,522
Average	29.49	70.51	58.48	333,433
Standard Deviation	0.40	0.40	0.81	4.63[a]

Ceiling Temperature 850°C

L14	33.30	66.70	---	385,077
L15	32.70	67.30	60.20	389,659
L16	33.24	66.76	61.58	355,404
L17	32.02	67.98	60.94	374,180
Average	32.82	67.18	60.91	376,080
Standard Deviation	0.59	0.59	0.69	4.05[a]

Ceiling Temperature 950°C

L18	35.93	64.07	64.33	402,115
L19	36.27	63.73	64.90	389.386
L20	36.43	63.57	59.60	377,595
Average	36.21	63.79	62.94	389,699
Standard Deviation	0.26	0.26	2.91	3.15[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 5

Product Data from the Pyrolysis of Lignite Q

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Ceiling Temperature 450°C				
Q1	12.06	87.94	38.37	31,906
Q2	17.24	82.76	38.04	28,703
Q3	10.48	89.52	39.05	25,923
Average	12.33	87.67	38.49	28,844
Standard Deviation	3.44	3.44	0.52	10.38[a]
Ceiling Temperature 550°C				
Q4	24.13	75.87	46.50	142,430
Q5	25.44	74.56	40.29	154,840
Q6	25.70	74.30	47.22	160,344
Average	24.88	75.12	44.67	152,538
Standard Deviation	0.81	0.81	3.80	6.02[a]
Ceiling Temperature 650°C				
Q7	34.38	65.62	48.99	276,491
Q8	34.46	65.54	50.37	290,371
Q9	33.74	66.26	51.76	284,439
Average	34.19	65.81	50.37	283,767
Standard Deviation	0.39	0.39	1.38	2.45[a]

* Yield in counts per milligram of coal
a = % standard deviation

Table 5 (continued)

Sample No.	% HV	% LV	% Wt. Loss	Yield *

Ceiling Temperature 750°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Q10	38.78	61.22	55.19	303,590
Q11	38.47	61.53	---	330,008
Q12	39.94	60.06	54.48	316,286
Q13	38.71	61.29	52.48	310,743
Average	38.98	61.02	54.05	315,157
Standard Deviation	0.66	0.66	1.41	3.55[a]

Ceiling Temperature 850°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Q14	41.66	58.34	57.32	344,806
Q15	44.82	55.18	53.37	356,557
Q16	43.39	56.61	53.75	347,474
Average	43.29	56.71	56.21	349,612
Standard Deviation	1.58	1.58	3.31	1.76[a]

Ceiling Temperature 950°C

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Q17	51.17	48.83	57.04	372,698
Q18	51.61	48.39	56.50	377,028
Q19	48.98	51.02	56.75	374,945
Average	50.59	49.41	56.76	374,890
Standard Deviation	1.41	1.41	0.27	0.58[a]

* Yield in counts per milligram of coal
a = % standard deviation

and total yield (counts per milligram) and the percent standard diviation for each of the four lignite samples. These results are summarized in Table 6. All four lignite samples show the high-volatile product, weight-loss, and total yield to increase as the temperature increases (Figures 15, 16, and 17).

Figure 15 presents the high-volatile product curves for the four different lignite samples over a ceiling temperature range from 450° to 950°C. All of the high-volatile product curves have a characteristic shape in common, although they differ in detail. Sample Q gives the highest high-volatile product yield in the ceiling temperature range of 650° to 950°C. The high-volatile products are hydrocarbon gases and light aromatics which are the result of thermolysis of bridge fragments, attached functional groups, and ring clusters. It would appear, therefore, that lignite Q contains organic structures or bridges which are more readily fragmented into lower molecular weight products than are the others.

Figure 16 presents the weight-loss curves of four lignite samples at different ceiling temperatures (450° to 950°C). Sample L exhibits the broadest peak and has the highest volatile matter content (see Table 1). These results are in good agreement with those of Mentser et al[21].

Kothandaraman et al.[23] reported that the mass loss decreases linearly with the increase in ash content. From this experiment, the observation of three of the four
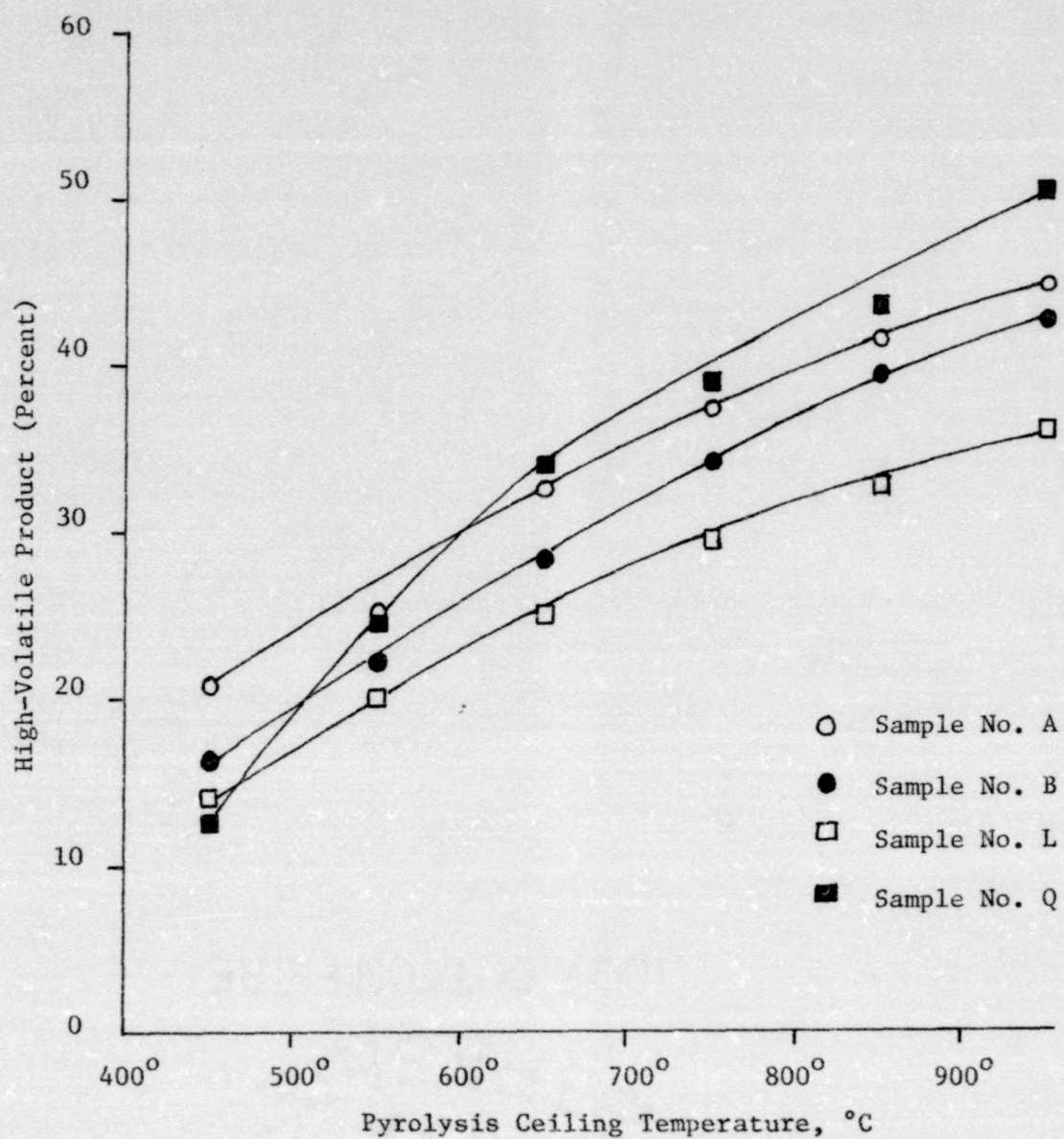
Figure 15.   Effect of Temperature on High-Volatile Product
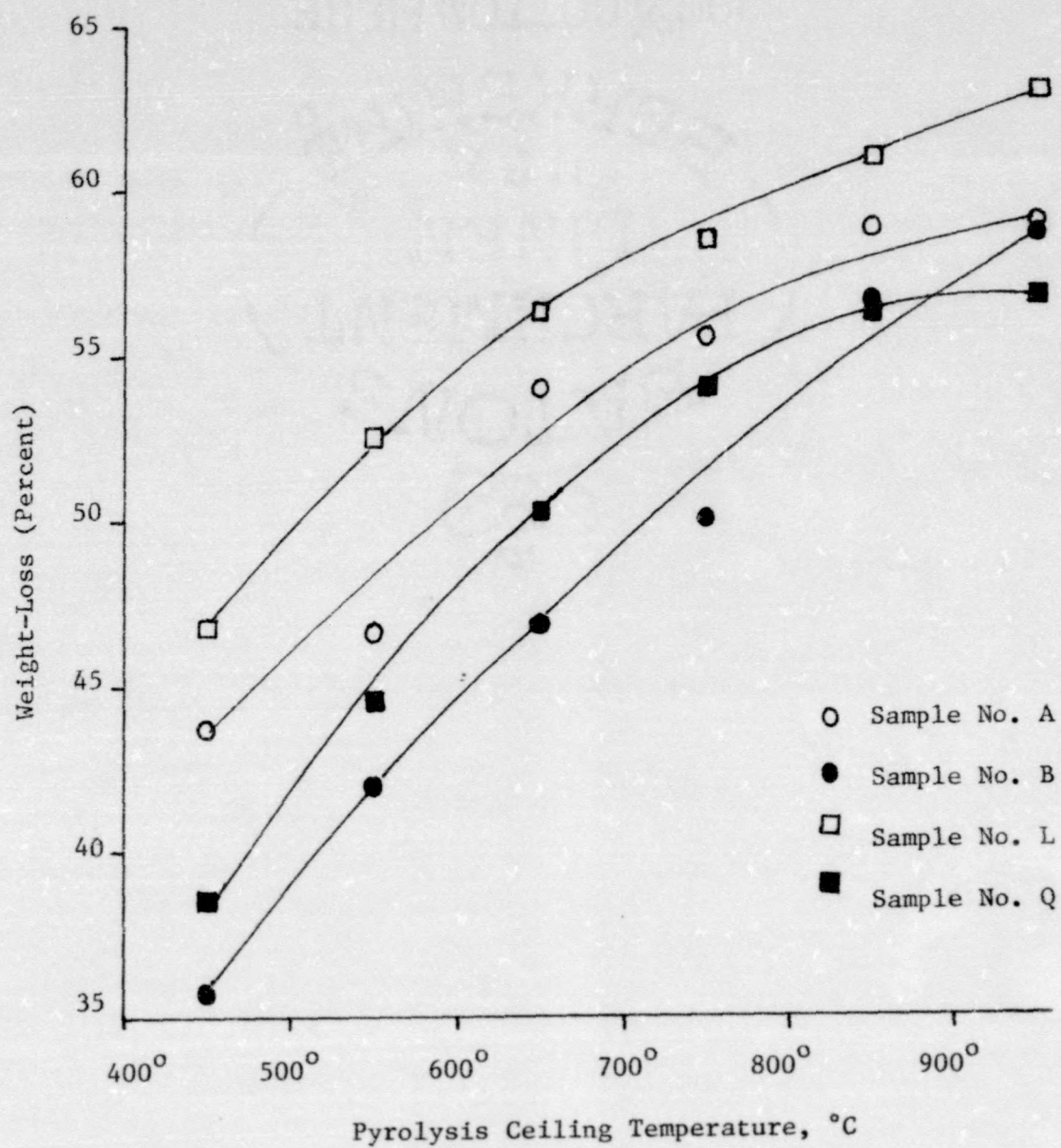from Four Lignite Samples.

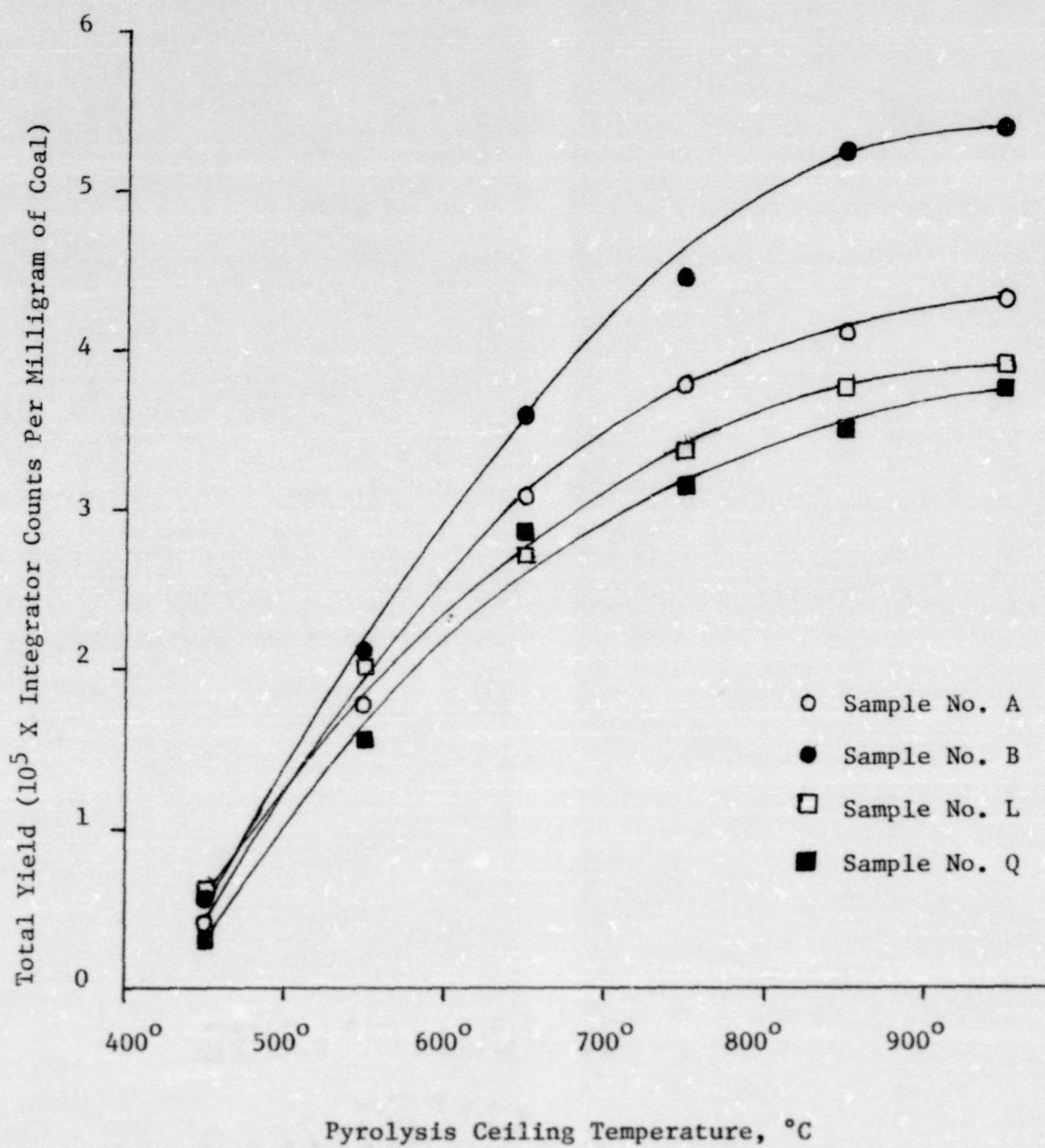Figure 16   Effect of Temperature on Weight-Loss from
Four Lignite Samples.

Figure 17   Effect of Temperature on Total Yield from
Four Lignite Samples.

TABLE 6

Comparison of Product Yield and Distribution
as a Function of Ceiling Temperature

Sample No.	Ceiling Temp. °C	High-Volatile Product (%)	Weight-Loss (%)	Total Yield Counts/ mg	% SD
A	450	20.74 ± 0.68	43.72 ± 0.60	40,451	4.97
B		16.30 ± 0.48	35.70 ± 0.72	54,464	4.66
L		13.94 ± 1.17	46.84 ± 2.29	56,422	2/26
Q		12.33 ± 3.44	38.49 ± 0.52	28,844	10.38
A	550	25.00 ± 0.69	46.58 ± 0.91	176,276	4.66
B		22.10 ± 0.80	42.04 ± 1.48	210,089	0.51
L		20.10 ± 1.14	52.56 ± 0.21	200,032	3.10
Q		24.88 ± 0.81	44.67 ± 3.80	153,538	6.02
A	650	32.34 ± 0.89	53.93 ± 2.37	307,763	5.14
B		28.12 ± 1.58	46.77 ± 1.90	358,251	5.70
L		25.30 ± 0.73	56.23 ± 0.88	269,642	1.30
Q		34.19 ± 0.39	50.37 ± 1.38	283,767	2.45
A	750	37.13 ± 0.74	55.40 ± 1.70	376,217	1.58
B		33.90 ± 0.85	49.97 ± 2.71	433,193	4.78
L		29.49 ± 0.40	58.48 ± 0.81	333,433	4.63
Q		38.98 ± 0.66	54.05 ± 1.41	315,157	3.55
A	850	41.26 ± 1.08	58.76 ± 2.11	408,745	3.23
B		39.20 ± 0.94	56.58 ± 0.67	523,098	1.35
L		32.82 ± 0.59	60.91 ± 0.69	376,080	4.05
Q		43.29 ± 1.58	56.21 ± 3.31	349,612	1.76
A	950	44.49 ± 0.32	58.97 ± 0.55	430,519	0.67
B		42.53 ± 1.44	58.72 ± 1.48	536,922	2.52
L		36.21 ± 0.26	62.94 ± 2.91	389,699	3.15
Q		50.59 ± 1.41	56.76 ± 0.27	374,890	0.58

lignite samples agrees with their conclusions as shown in Table 7.

Figure 17 presents the total yield curves for each of the four lignite samples over the temperature range from 450° to 950°C. Sample B shows the greatest sensitivity to changing ceiling temperature in terms of total product yield, suggesting that lignite B contains an organic structure and/or bitumen which readily undergoes thermolysis to yield organic fragments of such a size as to be in the gas and oil range. Sample Q behaves quite differently. The total product yield at ceiling temperatures above 650°C is lowest for lignite Q. This lignite, however, yields the greatest high volatile (gas) product over the same temperature range, suggesting that the organic material in sample Q is undergoing more extensive fragmentation to yield light hydrocarbon gases or low molecular weight compounds.

Theoretical oil yield can be calculated by means of Saxby's equation[47]. The results are listed in Table 8.

$$\text{Oil (wt. \% dmmf)} = 66.7 \text{ H/C} - 57.0 \text{ O/C} - 33.3$$

Comparison of Pyrograms

Pyrolysis-gas chromatograms (pyrograms) are characterized by the maceral concentrations and chemical structure of the coal samples. Therefore, the compositions and relative amounts of products formed depend upon the ceiling temperature, heating rate, and of course, the organic

TABLE 7

Weight-Loss and Ash Content

Sample No.	% Ash (dry basis)	% Weight-Loss (daf basis)
A	11.23	74.56
B	10.76	62.17
L	9.18	66.36
Q	2.10	79.90

TABLE 8

Percentage of Oil Yield

Sample No.	H/C	O/C	% Oil
A	0.84	0.16	13.61
B	0.85	0.15	14.80
L	0.82	0.27	6.00
Q	0.77	0.15	9.51

structure of the coal itself. Analysis of these products

nould provide valuable information about the coal structure.

Pyrograms for the four lignite samples are presented in

Figures 18, 19, 20, and 21. One may conclude that there are

three distinct pyrograms. Lignite samples A and B give

similar fragment (compound) patterns, although they are

slightly different in fine structure. Samples L and Q give

pyrograms distinctly different from the previous two samples

and also different from each other.

Pyrograms of samples A and B indicate that these

samples contain similar molecular units. One may also con-

clude that lignite A and lignite B were deposited in a simi-

lar environment. The low-volatile envelope of the sample B

pyrogram is larger than that of sample A, an indication that

sample B gives higher oil yield than does sample A. This

conclusion is in agreement with the ultimate and petro-

graphic analysis and with Saxby's equation (see Table 8).

The pyrogram of sample L shows a predominant peak at

retention time 14.14 minutes which is close to that of

naphthalene (see Table 9). It is expected, therefore, that

sample L has the greatest degree of aromaticity. This is in

agreement with the petrographic analysis; sample L has the

highest percentage of the inertinite group (see Table 1) and

shows the highest ratio of oxygen to carbon (see Table 10).

In estimating the f_a, one uses this equation[52]:

$$f_a = \frac{F.C.}{1.032} \times \frac{1}{C}$$

Sample No. A

Attenuator: 32

Ceiling Temperature: 450°C
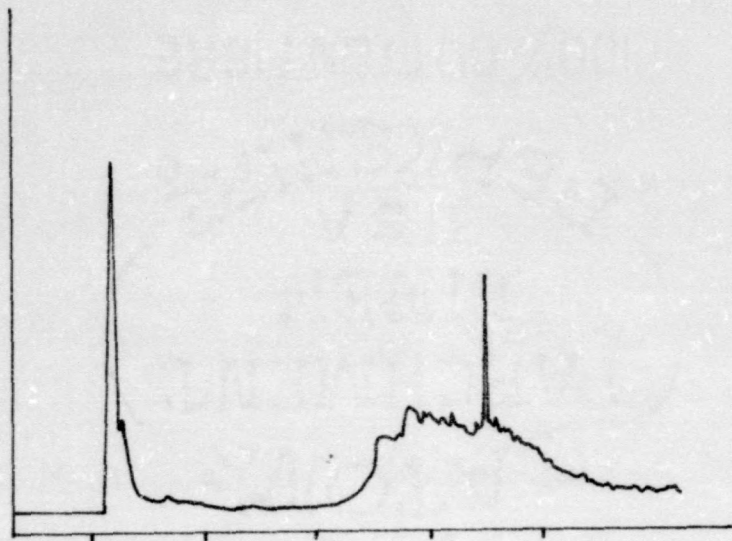
Ceiling Temperature: 550°C

Figure 18 Pyrograms Obtained from Lignite A at Different
Ceiling Temperatures

Sample No. A

Attenuator: 64

Ceiling Temperatures:

650°C

750°C

850°C

950°C

Figure 18 (continued)

Pyrograms Obtained from Lignite A at Different
Ceiling Temperatures

Sample No. B

Attenuator: 32

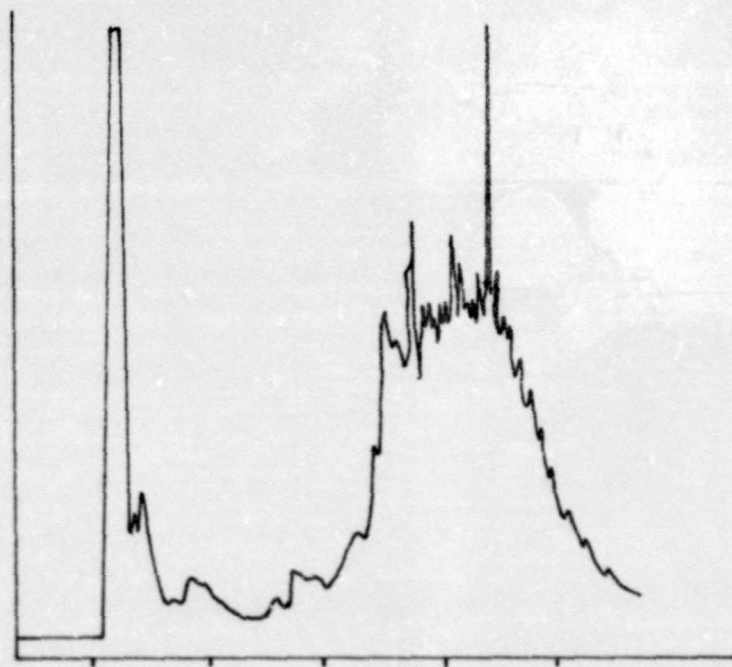Ceiling Temperature: 450°C

Ceiling Temperature: 550°C

Figure 19   Pyrograms Obtained from Lignite B at Different
Ceiling Temperatures

Sample No. B

Attenuator: 64

Ceiling Temperatures:

Figure 19 (continued)

Pyrograms Obtained from Lignite B at Different
Ceiling Temperatures

Sample No. L

Attenuator: 32

Ceiling Temperature: 450°C

Ceiling Temperature: 550°C

Figure 20   Pyrograms Obtained from Lignite L at Different
Ceiling Temperatures

Sample No. L

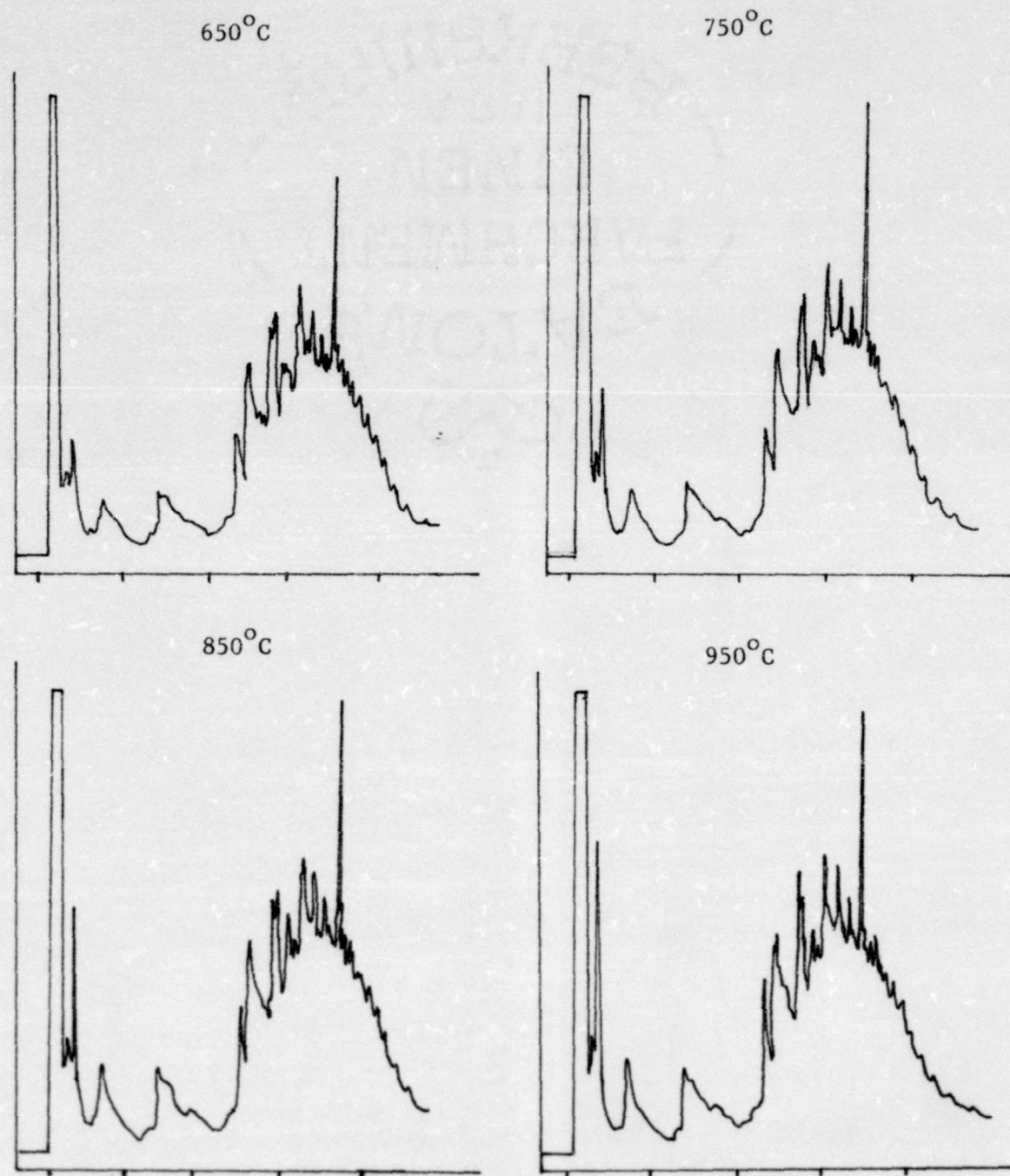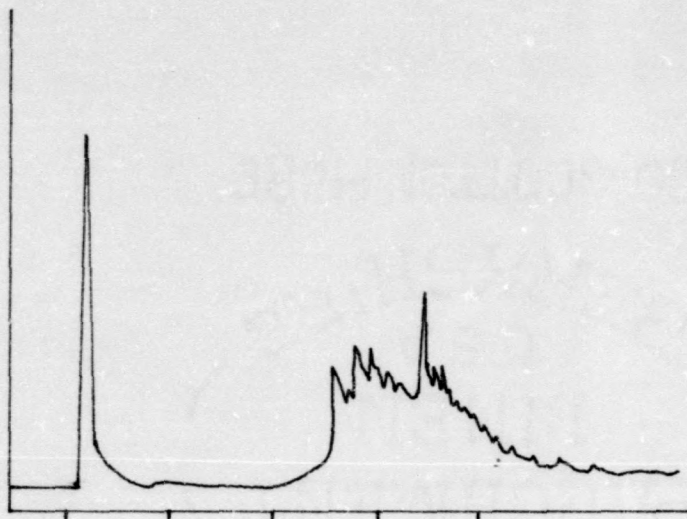Attenuator: 64

Ceiling Temperatures:

650°C

750°C

850°C

950°C

Figure 20 (continued)

Pyrograms Obtained from Lignite L at Different
Ceiling Temperatures

Sample No. Q

Attenuator: 32

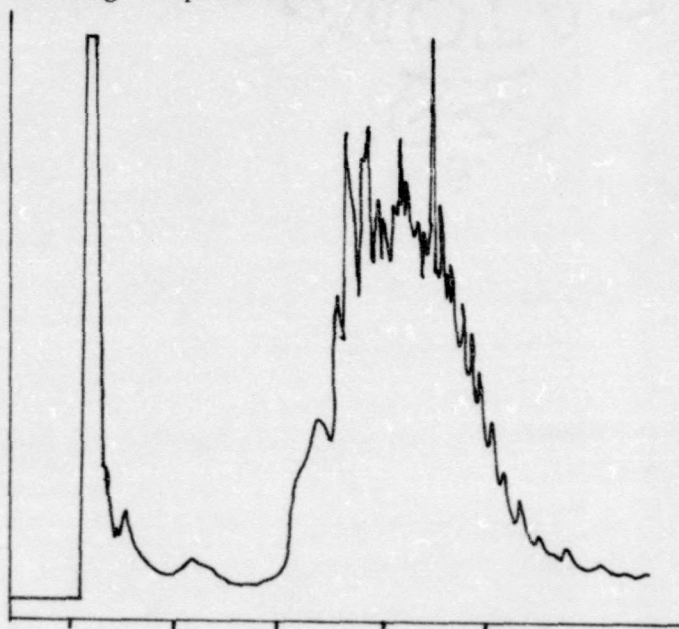Ceiling Temperature: $450^{\circ}C$

Ceiling Temperature: $550^{\circ}C$
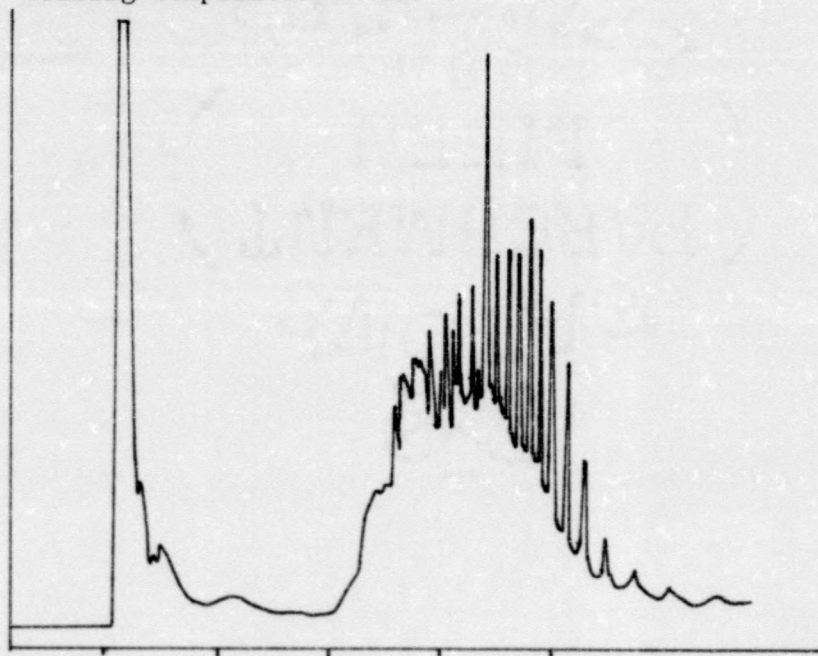
Figure 21   Pyrograms Obtained from Lignite Q at Different
Ceiling Temperatures

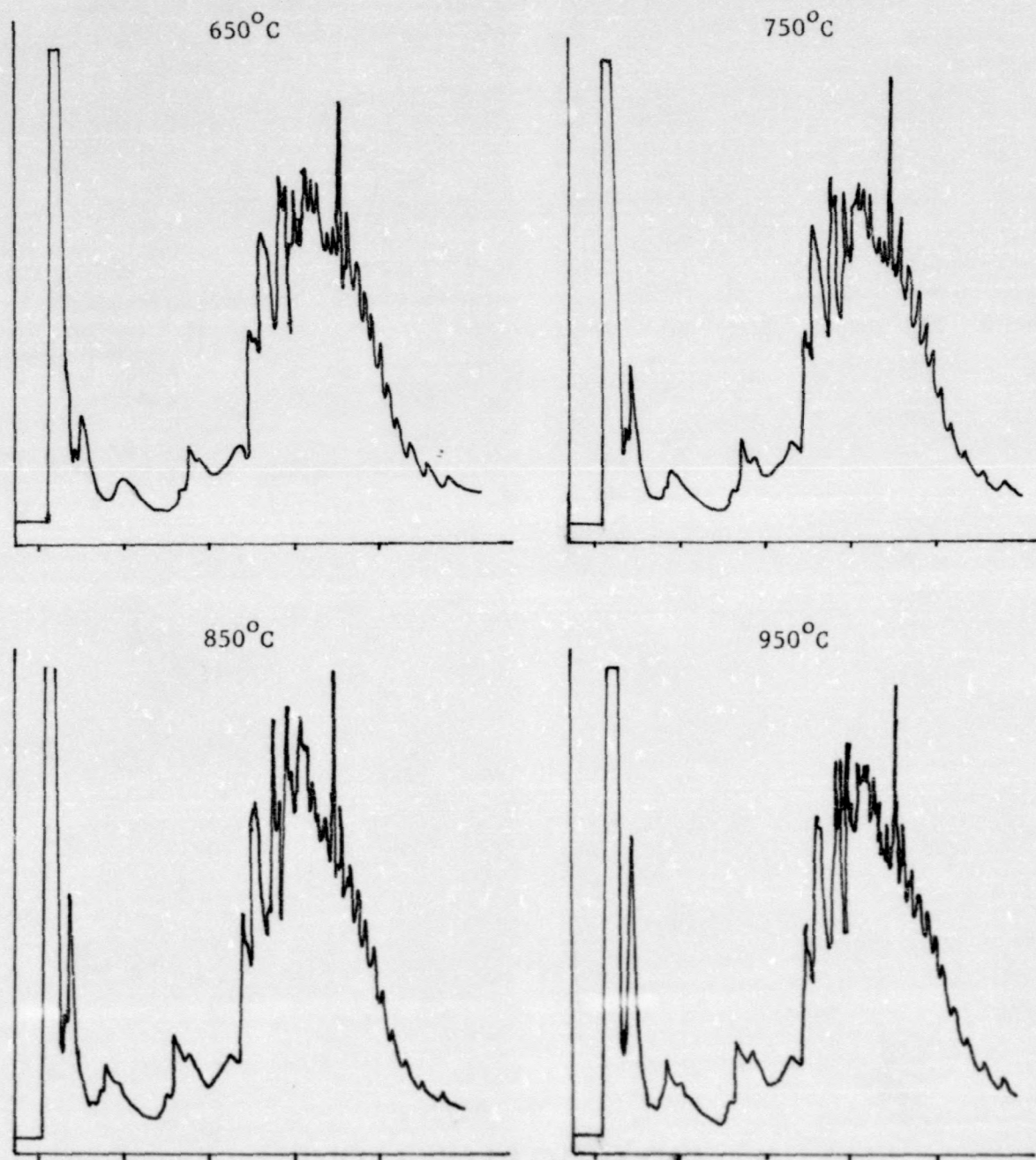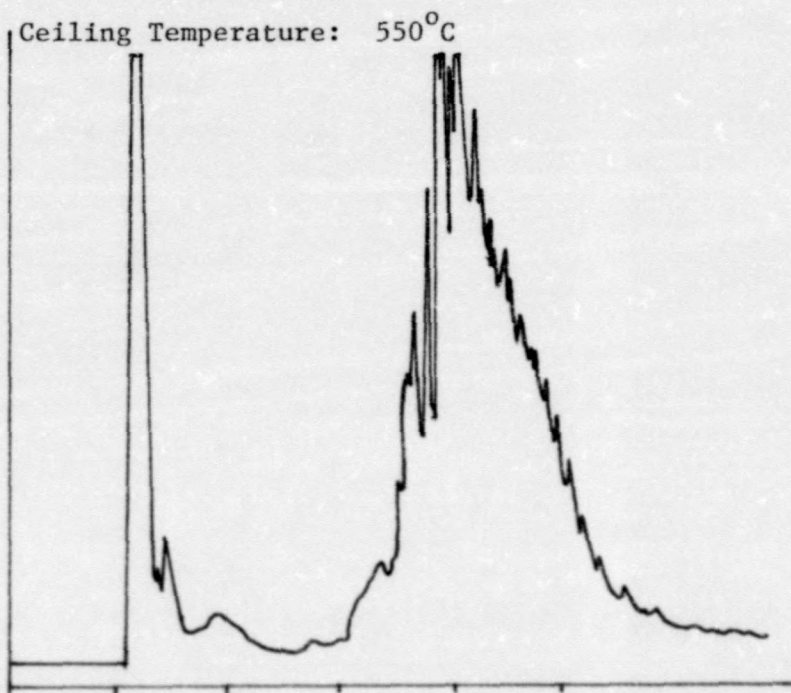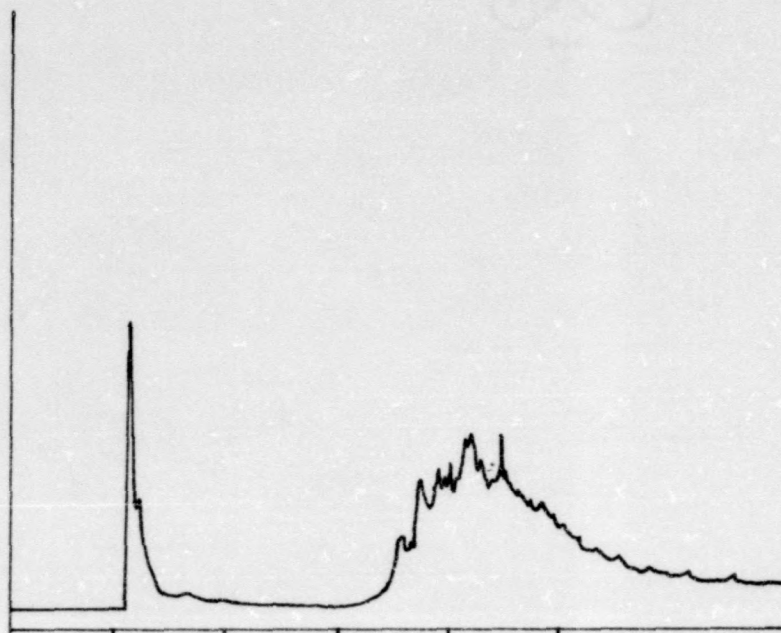Sample No. Q

Attenuator: 64

Ceiling Temperatures:

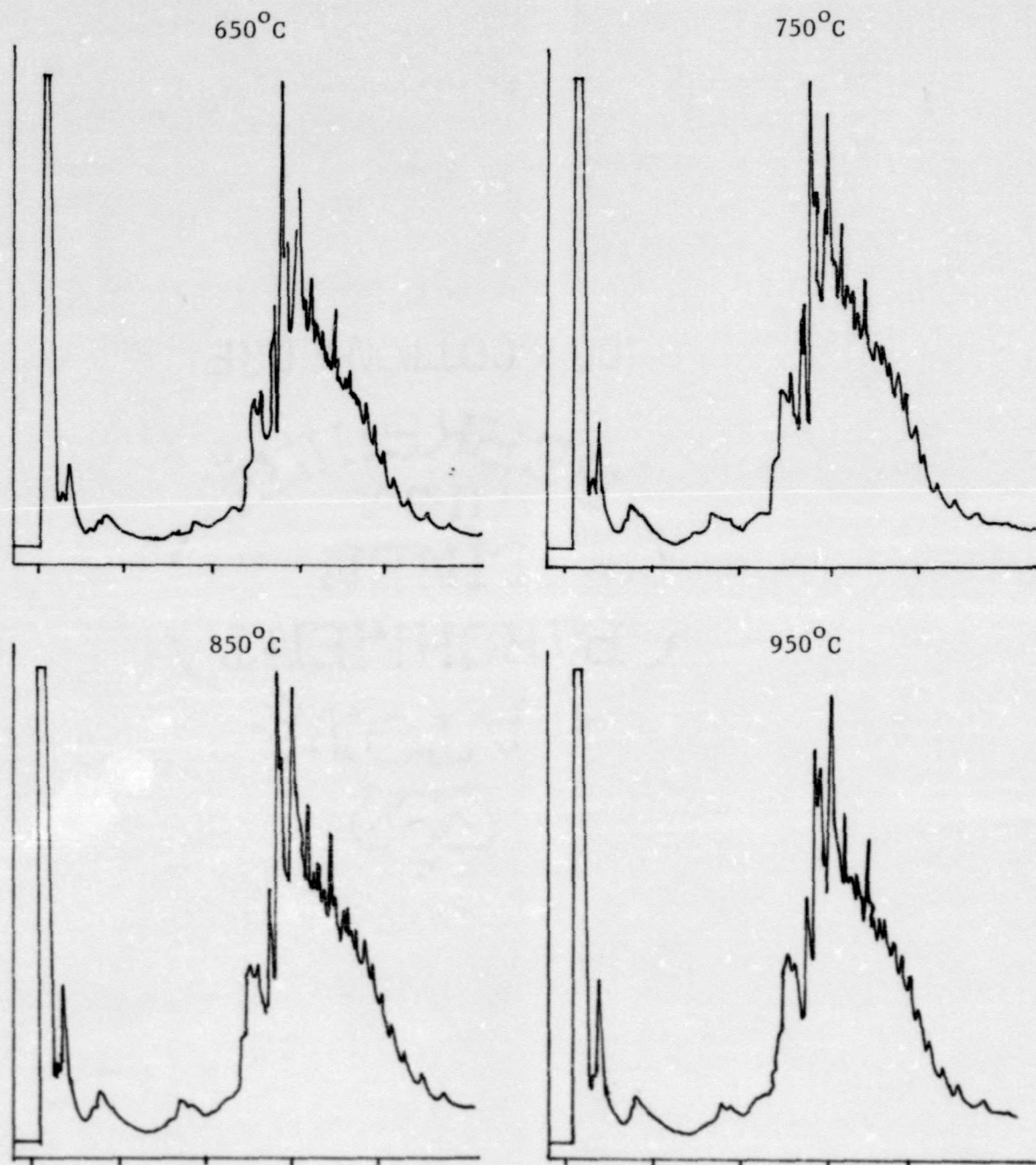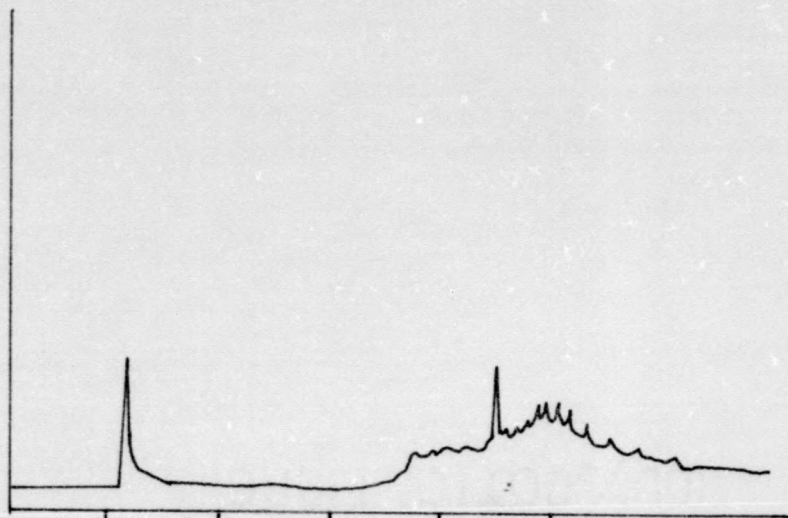650°C   750°C

850°C   950°C
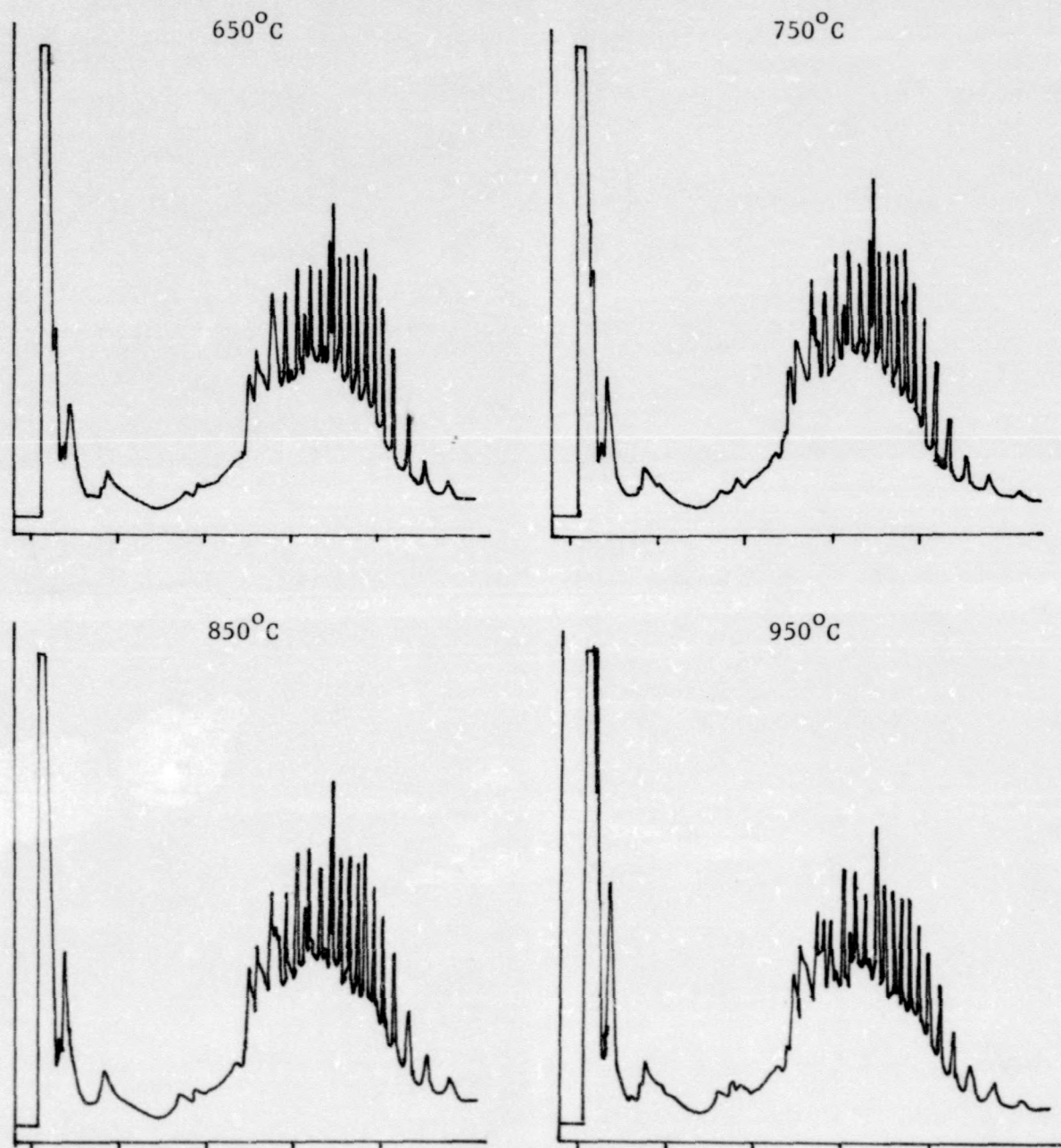
Figure 21 (continued)

Pyrograms Obtained from Lignite Q at Different
Ceiling Temperatures

TABLE 9

Characterization of Selected Peaks

Standard Hydrocarbons Aliphatic Compounds	Retention Time (min)	Characteristic of peaks (RT, min) Sample A	Sample B	Sample L	Sample Q	Standard Organic Compounds Aromatic Compounds Retention Time (min)	Aromatic Compounds
n-Hexane	0.88	0.82	0.68	0.62	0.74		
n-Heptane	1.25	1.06	--	--	1.39	1.22	Benzene
n-Octane	2.03	2.00	2.18	2.07	2.24	2.00	Toluene
n-Nonane	3.50	3.82	--	--	4.36	3.32	Ethylbenzene
n-Decane	7.21	7.19	8.75	--	--		
n-Undecane	13.29	12.29	12.86	13.21	12.95		
n-Dodecane	13.75	13.71	13.76	13.81	13.82		
n-Tridecane	14.70	14.71	14.60	14.14*	14.62	14.35	Naphthalene
n-Tetradecane	15.48	15.35	15.39	15.24	15.35		
n-Pentadecane	16.05	16.11	16.00	16.00	16.00	16.06	Diphenylmetane
n-Hexadecane	16.86	16.72	16.80	16.60	16.62		
n-Heptadecane	17.27	17.35*	17.29*	17.41	17.35*		
n-Octadecane	17.80	17.76	17.76	17.61	17.80		
n-Nonadecane	18.28	18.14	18.26	18.32	18.32		

* predominant peak

TABLE 10

Calculated Aromaticity

Sample No.	% F.C. (daf)	% C (daf)	f_a
A	49.19	70.80	0.67
B	51.44	71.36	0.70
L	52.33	66.51	0.76
Q	52.77	73.06	0.70

The results in Table 10 also suggest that sample L should have the highest aromatic content.

The pyrogram of sample Q (see Figure 21) shows a unique fragment or compound pattern which is characterized by what appears to be nearly equal amounts of a series of n-alkanes. The elution times for a series of pure hydrocarbons and organic compounds are shown in Table 9. The predominant peak at retention time 17.35 minutes corresponds to n-heptadecane. Indeed, the retention times from the pyrogram of lignite Q closely match those of a series of n-alkanes (see Table 9). These results indicate that lignite Q has a different organic structure and depositional environment than lignites A, B, and L.

Effect of Heating Rates

Heating rate is classified into four groups:

1. Slow heating   heating rate $< 1^{\circ}C/sec$

2. Intermediate heating heating rate 5 to $100^{\circ}C/sec$

3. Rapid heating   heating rate 500 to $100,000^{\circ}C/sec$

4. Flash heating   heating rate $> 10^{6}\,^{\circ}C/sec$

The data shown in Figure 17 indicate that sample B is the most sensitive to changing ceiling temperature. Therefore, sample B was selected to study the effect of heating rate on overall product yield and product distribution. The experimental data are shown in Tables 11 and 12.

Overall product yield and weight-loss at various heating rates show no significant difference. The high-volatile product from pyrolysis at heating rate $500^{\circ}C/sec$

TABLE 11

Product Distribution as a Function of Heating Rate

Sample No.	% HV	% LV	% Wt. Loss	Yield *
Heating Rate 500°C/sec, Interval 20 sec				
B10	33.00	67.00	47.12	421,526
B11	34.02	65.98	50.28	444,191
B12	34.69	65.31	52.51	463,862
Average	33.90	66.10	49.97	443,193
Standard Deviation	0.85	0.85	2.71	4.78[a]
Heating Rate 100°C/sec, Interval 20 sec				
B19	34.70	65.30	51.38	425,328
B20	35.00	65.00	50.00	423,493
B21	32.68	67.32	50.50	431,663
Average	34.13	65.87	50.63	426,828
Standard Deviation	1.26	1.26	0.70	1.00[a]
Heating Rate 300°C/min, Interval 2 min				
B22	36.64	63.36	52.00	445,214
B23	36.65	63.35	53.62	446,836
B24	35.26	64.74	51.39	436,618
Average	36.18	63.82	52.34	442,889
Standard Deviation	0.80	0.80	1.15	1.24[a]
Heating Rate 500°C/sec, Interval 1 min				
B25	38.33	61.67	51.12	457,928
B26	37.00	63.00	54.84	466,770
B27	36.86	63.14	52.51	454,716
Average	37.40	62.60	52.82	459,805
Standard Deviation	0.81	0.81	1.88	1.36[a]

* Yield in counts per milligram of coal
a = % standard deviation

TABLE 12

Product Distribution from Sample B
as a Function of Heating Rate

Heating Rate	Interval	High-Volatile Product (%)	Weight-Loss (%)	Total Counts/ mg	Yield % SD
500°C/sec	20 sec	33.90 ± 0.85	49.97 ± 2.71	443,193	4.78
100°C/sec	20 sec	34.13 ± 1.26	50.63 ± 0.70	426,828	1.00
500°C/sec	1 min	37.40 ± 0.81	52.82 ± 1.88	459,805	1.36
300°C/min	2 min	36.18 ± 0.80	52.34 ± 1.15	442,889	1.24

for one minute and at 300°C/min for two minutes are higher than that at 500°C/sec and at 100°C/sec for 20 seconds because of secondary cracking reactions. Thus, within the limitations of this experiment, the heating rate has no significant effect on total yield and product distribution as in agreement with Su1berg's report[7].

Mentser et al.[21] reported that the weight-loss obtained from rapid pyrolysis was up to 50% higher than proximate volatile matter yield (ASTM standard method of analysis). This conclusion is supported by Kimber and Gray[52]. Our results do generally support this view, as shown in Table 13.

Changing of the Pyrograms Due to Changing Heating Rate

Pyrograms obtained at 750°C, heating rate 500°C/sec and 100°C/sec, intervals of 20 seconds, were similar in fragment pattern but were a little different in relative amounts of fragment compounds (see Figure 22). When the heating rate was 500°C/sec for one minute, the height of peaks Nos. 1, 2, and 3 was higher than when using intervals of 20 seconds -- the result of secondary cracking reactions. The shape of the envelope clearly shifts toward the lower retention time (lower molecular weight) products upon prolonged heating.

TABLE 13

Increased Volatiles from Rapid Pyrolysis

| Sample No. | Volatile Matter Content, % | | Increase Factor |
	Dry Basis	From Weight-Loss	
A	45.14	58.97	1.31
B	43.33	58.72	1.36
L	46.66	62.94	1.35
Q	42.89	56.76	1.32

Sample No. B

Heating Rate: $500^{\circ}C/sec$ $100^{\circ}C/sec$

Pyrolysis Interval: 20 seconds   20 seconds

Heating Rate: $500^{\circ}C/sec$ $300^{\circ}C/min$

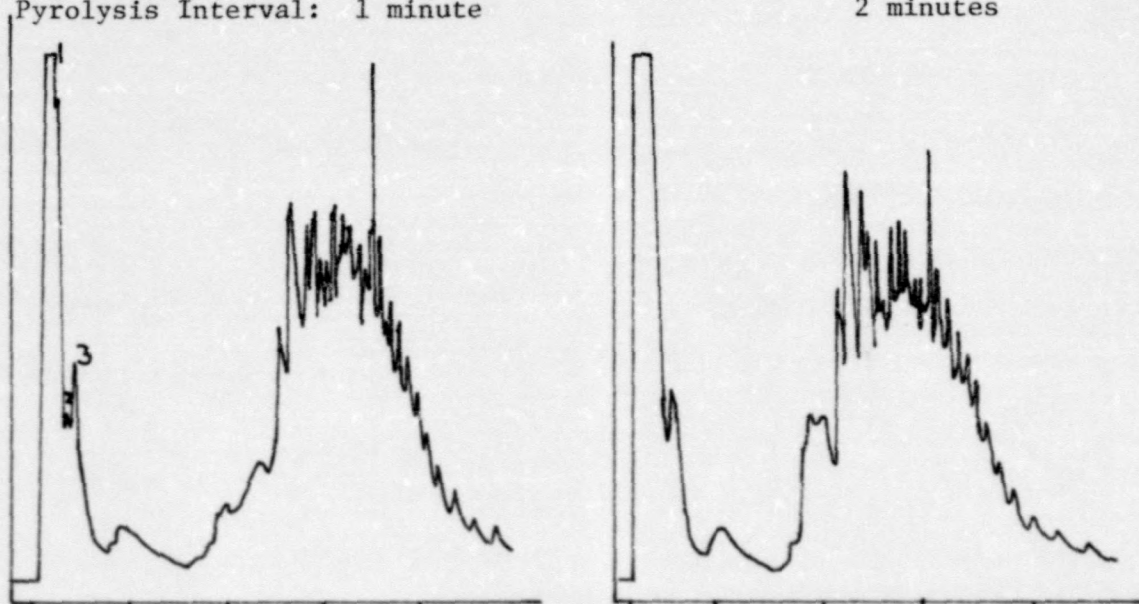Pyrolysis Interval: 1 minute   2 minutes

Figure 22   Pyrograms Obtained from Lignite B at Ceiling Temperature of $750^{\circ}C$ with Various Heating Rates

SUMMARY

The technique of analytical pyrolysis has been employed to study effects of ceiling temperature and heating rate on overall yield and product distribution of four Thai lignite samples.

Total yield, high-volatile product yield, and weight-loss all increase with increasing ceiling temperature. Pyrograms indicate that sample A and sample B have similar chemical structure while sample L and sample Q show quite different and unique fragmentation patterns. Sample L also appears to have a higher degree of aromaticity than other samples. This conclusion can be supported by petrographic analysis (highest concentration of the inertinite group). The pyrogram of sample Q is characterized by nearly equal amounts of a series of n-alkanes which suggest a high liptinite content. Sample B, however, has the highest liptinite concentration and gives the highest oil yield (by calculation). One may conclude that sample B and sample Q have different aliphatic and alicyclic interstitial and bridging groups because sample B and sample Q have the same degree of aromaticity (calculated). Therefore, sample B may

contain smaller molecule units or more easily fragmented units.

Heating rate (within the limits tested) has no significant effect on the overall yield and product distribution but the pyrograms show differences in the relative peak heights in the low-volatile fraction, most likely due to secondary cracking reactions.

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