EVALUATION OF

REACTOR CATALYZED SECONDARY REACTIONS

IN THE

CAPTIVE SAMPLE PYROLYSIS REACTOR

by

KEVIN E. BENNET

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

MAY, 1976

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May 7, 1976

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Abstract

This work is concerned with the effect of the stainless steel
heating element in a captive sample reactor on the product distrib-
ution and weight loss measurements of coal pyrolysis.

Pyrolysis of Pittsburg bituminous coal and model compounds
(anthracene, camphor, durene, fluorene and napthalene) was accom-
plished under equivalent conditions of temperature, pressure, atmos-
phere, residence time and heating rate, but with changes in the
method of containment of the sample.

Evidence of cracking catalyzed by the stainless steel heating
element was not found to any appreciable extent.

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ACKNOWLEDGEMENT

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Much work has been accomplished and is continuing at the Fuels Research Laboratory of the Massachusetts Institute of Technology with batch reactors designed for experimental coal pyrolysis. These reactors normally utilize a three layer stainless steel screen to contain the coal sample to be pyrolyzed and to act as a resistance heating element. No work has been done to determine the effect of this stainless steel screen on product distribution. Anthony (1974), however, attempted to quantify the effect of cracking by the screen on weight loss measurements.

The work by Anthony, et al. (1974) on the devolatilization of coal relied on weight loss measurements to determine the kinetics of devolatilization. They utilized conditions of low pressure, small particle size and good particle dispersion on the screen to minimize the effects of hot screen secondary reactions (cracking) on their weight loss measurements.

Currently, Eric Suuberg is using a modification of the equipment built by Anthony et al. to determine the product distribution of pyrolyzed and hydrogasified coal. There is concern in that work that secondary reactions catalyzed by the stainless steel will effect the products of the gasification of coal. Stainless steel is known to catalyze cracking reactions of hydrocarbons at elevated temperatures. To assess current and previous work, the principal focus of this study is: Is it possible for the stainless steel heating element to extensively crack products of the pyrolysis process to increase the volatile weight yield of the coal samples and disturb the product distribution of the fixed volatile gases?

This problem has been addressed by comparisons of product
distributions from the pyrolysis of coal amd model compounds. The
pyrolyses were accomplished under equivalent conditions of temperature,
pressure, atmosphere composition, residence time, and heating rate,
but with changes in the method of containment of the coal sample.

Bituminous coal was chosen for this study instead of lignite
because the products of the pyrolysis of lignite are mostly light
gases with little tar formation.

In this study I utilized two changes in the containment of
the coal samples. The first was by reducing the number of layers
of stainless steel screen through which the volatiles from the
gasification process must pass to enter the general volume of the
batch reactor. The other change was in the coating of the stainless
steel screen with gold so that no volatiles could contact hot stain-
less steel.

The pyrolysis of the model compounds was undertaken to give
an indication of the stability of various large molecules under
the conditions of pyrolysis. Pyrolysis runs at atmospheric pressure
and vacuum with these compounds were made to determine if there
seemed to be any major differences in products attributable to
pressure.

LITERATURE

Cracking reactions of hydrocarbons catalyzed by various materials have been widely reported in the literature. The usual catalysts studied are coke, carbon and quartz, noted in decreasing order of (usual) activity, and stainless steel (see Figure 1).

Of the variables of temperature, pressure, residence time and atmosphere, temperature seems to be one of the most critical in determing extent of cracking, followed by residence time at the cracking temperature.

Davis and Place (1942) report that "at temperatures as low as 475°C., secondary decomposition of the tar (from coal pyrolysis) into permanent gases is appreciable." Gentry (1928) notes that if the volatile matter from the gasification of coal "is allowed to become superheated (above 450°C.) or to come in contact with incandescent surfaces, secondary reactions..." occur. Beyond this temperature (approximately 450°C.) they all note that cracking reactions increase rapidly with temperature, depending on residence time. If the pressure of the volatiles is reduced below 0.05 atm. the temperature of cracking increases to 800°C. (Gentry, 1928).

Gentry (1928) further notes that passing volatiles from the pyrolysis of coal over a glowing wire increased the hydrogen and unsaturated hydrocarbons by almost 300 percent. These reactions crack heavy saturated hydrocarbons with the formation of hydrogen and unsaturated compounds.

Hesp and Waters (1970) cracked volatile matter and tar from the pyrolysis of coal in static bed reactors with temperatures in the range of 500° to 1000°C. and residence times of 1 to 440 seconds.

Their reactor utilized coke as the catalytic material and they noted the general effect that as the temperature of cracking increased, the yield of gas and carbon increased with a corresponding decrease in residual tar. At temperatures of 500° to $700^\circ C.$, residual tar was the main product on a weight basis while at temperatures from 800° to $1000^\circ C.$, carbon was the main product by weight.

Their analysis of products obtained in the range of $500^\circ C.$ to $600^\circ C.$ suggested that the long side chains of relatively large aromatic or alicyclic molecules were removed to form light liquids and gaseous hydrocarbons.

The main gaseous component on a weight basis, found by Hesp and Waters (1970), was methane, which increased in relative amounts until a temperature of approximately $900^\circ C.$ Then the methane content decreased with a corresponding increase in carbon formation. At temperatures below $700^\circ C.$ the gaseous hydrocarbons of ethane, propane, ethylene, propylene and butylene were formed in significant amounts.

Crynes et al. (1969) reported on the pyrolysis of propane in a tubular 1/4 inch diameter stainless steel reactor 175 inches long at temperatures of 600° to $750^\circ C.$, with conversions from 2% to 70% respectively. Herroitt et al. (1972) also reported on propane pyrolysis in stainless steel reactors of the same construction at a temperature of $800^\circ C.$, pressure of 1 atm. and with a diluent of 50 mole percent of steam. They note that the results of pyrolysis with helium were identical to those using steam. Figure 2 gives a plot of conversion with respect to space time along with composition curves.

Griffiths and Mainhood (1967) determined that the yield of napthalene increases during the catalytic (carbon) cracking of tar

until approximately 650°C. and then decreases to trace levels at approximately 900°C. They also noted that propane reaches trace levels at 700°C., ethane at 780°C. and that methane decreases from a maximum at 750°C.

Davis and Farrell (1973) report on the thermal decomposition of paraffins in a packed silica reactor at temperatures from 807° to 923°C. with residence times of 0.1 second and approximately atmospheric pressure. They note that at 923°C. any paraffin larger than the butanes are completely decomposed (see Table 1).

On the formation of carbon from tar, Hesp and Waters (1970) note that residence time needed to be on the order of 2 minutes at temperatures of 900° to 1000°C. with coke catalyzing the reactions. Their highest gas yields, greater than 60% by weight, were obtained at 900° to 1000°C. at less than 20 seconds residenct times.

Anthony (1974) gives an experimentally measured correction for cracking and carbon deposition on stainless steel screens used in his research and as is used in this work. As seen in Figure 3, cracking corresponds to an approximate 10% weight gain by the coal sample in the pressure range of 0.001 to 1.0 atm. of helium.

There have been several suggestions for reducing the cracking reactions associated with stainless steel. Slotboom and Penninger (1974) observe that stainless steel reactors age over a period of hours (of operation) in hydrogenation reactions to produce a less active surface. Brooks (1966) suggests that hydrogen sulfide acts as an inhibitor by poisioning the stainless steel. Herroitt et al. (1972) treated their stainless steel reactor with hydrogen sulfide for 35 to 65 minutes at an unnoted temperature. They determined

that product composition and conversion were essentially identical to untreated reactors.

Slotboom and Penninger (1974) note that gold plated reactors give an initial reactivity near zero but the gold undergoes a slow process of activation (measured in hours) that affects only a part of the cracking products. Their explanation of this observation was the formation of coke on the reactor walls. The increased activity paralled the amount of coke deposited on the reactor walls.

EXPERIMENTAL APPARATUS

The basic design of the coal gasification reactor used in this work is as described by Anthony et al. (1974) in their work on high pressure coal-hydrogen kinetics. The specific reactor used for this study is a low pressure version of his apparatus with provisions for flushing the system with helium to collect the volatile fixed gases produced in the coal pyrolysis reactions.

As shown in Figure 4, the reactor consists of a glass vessel which encloses two electrodes which support an electrically heated screen and a thermocouple. The vessel can be evacuated and filled with a controlled atmosphere of helium and in special cases, oxygen.

Conax high pressure connectors are used for introducing electrical wires into the apparatus. The electrodes are machined from solid brass. The heating element and container of the coal for pyrolysis is constructed of 325 mesh stainless steel screen (4.5 by 5.0 cm.). The screen is folded into a 'sandwich' heating element by folding the screen into thirds with a finished dimension of 1.5 by 5.0 cm. The stainless steel screen has been used for several reasons (Anthony et al., 1974): i) the screens have less mass than a solid strip of stainless steel the same dimensions, ii) the screens have a large void space to permit easy escape of the volatiles during pyrolysis, iii) stainless steel has high electrical resistivity, making it suitable for a resistance heater, and iv) stainless steel has a high tolerance to temperature and corrosion.

The electrical system is constructed with dual heating circuits to control the heating rate (600 to 10,000°C./second) and final temperature (400 to 1200°C.). A simplified schematic of the elec-

trical system is shown in Figure 5. This system consists of two twelve volt batteries connected in series with the circuits by a power relay. The current in each branch of the system is controlled by variable resistors (one 1000 watt, 3 ohm, one 1000 watt, 1 ohm). At the beginning of a coal pyrolysis run, a preset timer is activated which closes the relay on the initial low resistance heating circuit, which controlls the heating rate. The timer then switches the relay to the higher resistance circuit which maintains the final temperature and run length.

To determine the time temperature history of the coal sample during pyrolysis, a 0.025 mm. chromel-alumel thermocouple is placed between the screen layers and connected, using $0^{o}C$. as a reference, to a Sanborn 380 recorder to record the time-temperature trace, as shown in Figure 6.

To analyze the fixed volatile gases from the gasification process, the reactor is flushed with helium through a lipophylic trap (Porapak Q) cooled to liquid nitrogen temperature. All gases except hydrogen and helium are retained by the trap. A schematic of the plumbing is illustrated in Figure 7. After collecting the products of pyrolysis, the trap is heated to $100^{o}C$. in boiling water to gasify all the condensed gases. Three valves are then opened to flush the gaseous compounds into a Perkin Elmer model 3920 gas chromatograph with Porapak Q columns. The injection of the gases occurs with the gas chromatograph columns cooled to $-70^{o}C$. with a temperature program of -70 to $240^{o}C$. at $32^{o}C$/minute. Dual detectors, thermal conductivity and flame ionization, are used with both detectors connected to a dual channel chart recorder and the thermal conductivity detector also connected to an electronic

integrator. A typical chromatogram is shown in Figure 8. Identification of components of the fixed volatile gases is determined by retention times and comparison of the output of the thermal conductivity detector and the flame ionization detector.

EXPERIMENTAL PROCEDURE

EXPERIMENTAL PYROLYSIS RUN

In this experimental work on cracking, a typical run would be conducted as follows: A folded stainless steel screen would be 'prefired' or electrically heated in a helium atmosphere to remove any oils and impurities from its surface. A ground sample of Pittsburgh bituminous coal (53 to 88 um) of 10 to 20 milligrams was carefully spread in the center of a preweighed , prefired screen. The configuration of the screen would be of the prescribed form of three, two or one layers, depending on the experimental run in progress. The screen would then be reweighed and placed between the electrodes in the batch reactor. The thermocouple is positioned between the folds of the screen.

Next, the reaction vessel is evacuated to less than 0.1 mm. of mercury and flushed twice with helium to remove trace oxygen from the reactor. The vessel is then filled with the proper atmosphere to the pressure desired.

The timer and resistors are set to give the desired heating rate and final temperatures for the run. After firing, the pressure in the reactor is immediately increased to 9 to 12 pounds per square inch of helium. The reactor contents are flushed through the trap, the trap is sealed and placed in boiling water to gasify all traped products for gas chromatographic analysis.

The reactor is then opened and the screen and char removed and weighed immediately.

The heated products collected in the lipophylic trap are flushed into the gas chromatograph and then the temperature program

of the gas chromatograph is started (-70 to 240°C, at 32°C./minute).
The Porapak Q column separated the products collected and they are
detected by a tandem arrangement of thermal conductivity and flame
ionization detectors. A typical chromatogram is shown in Figure 8.

COATING OF SCREENS

I have coated screens with gold by evaporation to reduce their
activity with respect to cracking reactions during pyrolysis runs.
The screens are first cut as for a normal run and are boiled in
methylene chloride to remove residual oils and dirt. They are
dried and placed over desiccant to protect them from moisture.

A card board mask was made so that only the center two centi-
meters of the screen world be covered with gold, where the coal
sample would be contained. The screens were masked, placed in the
vacuum chamber of a commercial vacuum coating apparatus, and the
pressure reduced to less than 35 microns of mercury. No special
atmosphere other than reduced pressure was used.

Gold was evaporated at this pressure and allowed to condense
on the screen that was rotating on a turntable in the vacuum chamber.
The evaporation process progressed for 30 seconds to give a thick
even coating of gold. The vacuum was then slowly released, the
screen turned over and the process repeated for the other side.

This same process was used to check the feasibility of evap-
orating copper and was found to give a better coating than electro-
plating.

EXPERIMENTAL WORK AND OBSERVATIONS

CARBON DEPOSITS ON SCREENS

All authors, in the literature surveyed, that performed cracking of hydrocarbons at temperatures of approximately 1000°C, noted deposits of carbon on their catalyst. It was felt that in the batch gasification reactor, the stainless steel screen used should have carbon deposits in excess of the char that remains form the coal that has been pyrolyzed if cracking is indeed a problem.

To determine the extent of carbon deposition on the screens, it was first necessary to remove the char resulting from the coal sample from the screen. The screen was opened after determination of weight loss and the char was scraped out. The bituminous coal used for this study formed a continuous mass of char. Rather vigorous scraping was necessary to remove particles of coal traped in the holes of the screen. Because of the continuous nature of the char, it was never certain that complete removal could be achieved. It is possible that carbon deposited because of cracking was also removed by the scraping.

Another possible problem is the removal of tar that may have condensed on the screen during the cooling down period. The removal of this condensed tar by washing the screens in methylene chloride after scraping was attempted. No weight loss of the screens was detected to five decimal places (in grams) from washing the screens in this solvent.

Two screens that had been scraped, two screens that had been scraped and washed in methylene chloride, and one that had been just prefired were refired in an oxygen-helium atmosphere. From

each of these oxygen firings, the product gases were analyzed for carbon monoxide and carbon dioxide to give an indication of the mass of carbon that was left on the screen.

The screens were individually placed in the batch reactor and fired in an oxygen-helium atmosphere (5 psia oxygen and 10 psia helium). The product gases were analyzed by gas chromatography by the same techniques as product analysis..

After firing, the screens had a large weight gain due to oxidation of the stainless steel. The chromatograms all gave an enormous oxygen peak which completely masked any carbon monoxide and a carbon dioxide peak. It is unclear that the carbon contained on the screens would undergo complete oxidation. Without the carbon monoxide peak, the amount of carbon on the screen could not be determined. The scraping of char from the screens was unreproducable at best, as the bituminous char was extremely difficult to remove. The majority of the carbon dioxide detected probably arose from the char that was retained on the screen. This method for the determination of cracking was discontinued after these runs.

REMOVAL OF LAYERS OF SCREEN

To determine the effect of catalytic cracking caused by the stainless steel screen layers, coal was pyrolyzed under the same conditions of atmosphere (composition and pressure), heating rate, final temperature and residence time while removing layers of the stainless steel screen. The results of this procedure are tabulated in Table 2.

The results are presented in the milligram yield of volatiles divided by the original mass of the coal multiplied by 100 to give a percentage yield of the original mass of coal.

Originally, product analysis of pyrolysis products using this system have utilized a thermocouple with cellophane tape as a support. With further study, it was discovered that some cellophane was charred with each run, contributing large quantities of products to the spectrum of the coal pyrolysis products.

Runs conducted with the cellophane supported thermocouple would not reflect the true products of the pyrolysis. I continued work by initially determing final temperature using a thermocouple, but pyrolyzing coal at unchanged resistor settings without the benefit of temperature traces for each run. Toward the end of my experimental program a stainless sheathed thermocouple became available. This thermocouple was then used to monitor the temperature of the screens during pyrolysis. The runs presented in this section are within $\pm$ 10 percent of each other in final temperature. More accurate temperature correlations would give results with increased comparability.

During pumpdown of the vessel, some of the water contained in the coal samples is removed by evaporation. Table 3 shows variations in weight loss due to pumpdown on samples of coal. The results for the water analysis for these pyrolysis runs probably do not have good comparability.

SCREEN COATINGS

Slotboom and Penninger (1974) note that gold reactors initially have no activity for catalyzing cracking reactions of polyaromatic compounds. It was thought that by coating the screens used in the pyrolysis apparatus and comparing the fixed gas analysis of the coated screen and the uncoated screen, a comparison of the extent of cracking caused by the stainless steel could be determined.

Initially, electroplating was tried, but a complete even coating was difficult to obtain. I then evaporated gold (in vacuum) onto the screen. An even coat resulted from this method with good mechanical stability. I then discovered that screens that had been completely covered with gold were too conductive, that the electrical system could not heat the screens. I then coated the screens with a stripe of gold approximately two centimeters in length, where the coal sample would be placed. By adjusting the resistors of the electrical system, the same heating rate and final temperature could be obtained. Runs at atmospheric pressure and vacuum were accomplished (in helium) with gold coated three layer stainless steel screens.

Table 2 shows the average value of two runs each with the gold coated screen in vacuum (less than 0.05 mm of mercury, and at one atmosphere of helium. The results are the milligram yield of volatiles divided by the original mass of coal multiplied by 100 to give percentage yield of the original mass of coal.

CIRCULATION AND INITIAL RESIDENCE TIME OF VOLATILES

During the pyrolysis of materials at atmospheric pressure, definite circulation patterns were observed within the reactor. These patterns, as shown in Figure 9, bring fractions of the pyrolysis products in contact with the screen at an observed frequency of approximately once per second. During the five second runs of this study, the circulation patterns touched the screen four or five times.

During pyrolysis runs at vacuum, no circulation patterns were detected. The products appear to form a uniform aerosol in the reaction vessel.

Products leaving the bottom of the screen during pyrolysis at atmospheric pressure were observed to fall directly to the bottom of the reactor and a portion of the products were seen to condense on the cold floor.

During vacuum runs, the products would move away from the screen uniformly in all directions as an aersol and some products would condense on the cold surfaces of the reactor.

To secure some order of magnitude of the initial residence time of the volatiles near the stainless steel screen, I have used some major approximations. The effect of the screen on the volatiles is assumed to happen within a distance of one millimeter from the center of the screen (top and bottom, from where the coal sample is placed). I observed the time distance relationship for the volatiles to give an average velocity for determination of residence time. In vacuum, I took as a distance the distance from the screen to the reactor side wall. The time was the time for volatiles to condense noticably on the reactor wall (approximately 0.15 seconds) from the start of a run. This gives an average velocity of 20 cm. per second, for a residence time near the screen (1 mm. thick) of approximately 0.005 seconds.

For atmospheric work I took the distance to be from the screen to the floor of the reactor and the time as the time necessary for noticable condensation to occur on the floor of the reactor. This gives a residence time for atmospheric work as 0.006 seconds (time for condensation 0.2 seconds).

Granted, these measurements are inexact, but they give an order or magnitude of the residence time. Since these measurements are of the average velocity of the volatiles over the distance traveled,

assuming a plug of condensable material, the residence time for
the volatiles is conceivably much less than these calculations
indicate. Maximum residence time of volatiles in the vicinity
of the screen seem to be on the order of 0.01 second.

MODEL COMPOUNDS

Under the conditions of pyrolysis in this study, bituminous
coal decomposes to give 20 to 30% tar by weight. This tar is com-
posed of a large number of compounds, many of which have fused
aromatic ring structure. For example, napthalene accounts for
approximately 4% of this tar. Because of this composition, anthra-
cene, fluorene and mapthalene were chosen to study the stability
of these fused aromatic rings during pyrolysis. The two other
compounds, durene and camphor were chosen to study if saturated
substituents promote degradation of compounds during pyrolysis.
Penninger and Slotboom (1973) report on cracking of napthalene and
anthracene, while Otlay et al. (1973) studied the cracking of
fluorene.

The conditions under study were vacuum, one atmosphere of
helium, heating rate of $1200^{\circ}C$./second, a final temperature of
$1000^{\circ}C$., and a residence time of five seconds. Figure 10 shows
the structure of these compounds along with their molecular weight
and boiling point. Table 4 lists the results of the product analysis
of the pyrolysis of these compounds. In this set of runs, a filter
of glass wool was placed in the reactor to prevent any of the un-
pyrolyzed compound from entering the analysis system. This filter
also trapped water during exposure to the air giving rise to ghost
water peaks of varying size in the chromatogram of products. There-
fore, the water peak as percent of mass of model compound is not
presented since it is not relatable to the pyrolysis reactions.

The product spectrum of all the pyrolyzed compounds, except camphor, could be explained by small amounts of cracking, but is probably the result of reactions of the compounds with residual oxygen in the system as shown by the carbon oxide peaks.

The product spectrum of camphor shows a wide variation of products as are reported, but there were also large quantities of heavier products not tabulated.

FINDINGS

In the experimental work for determination of carbon deposits
on the reactor screens it was found that there were two major problems.
First is the reproducibility of this technique and second is that
complete quantification of carbon momoxide and carbon dioxide was
not possible, therefore reliable determination of carbon left on
the screen was not possible. On close examination of the screens,
no definite deposits of carbon from cracking reactions were found.
Discolorations of the stainless steel screen (similar discolorations
were found on the gold coated screens) were not quite like carbon
and could possibly be black iron oxide (FeO). Two reactions that
could possibly lead to FeO production are:

$$CO_2 + Fe \longrightarrow CO + FeO$$

and

$$H_2O + Fe \longrightarrow H_2 + FeO$$
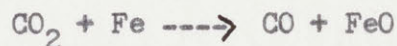
Thermodynamically, the equilibrium for these reactions lie to the
right. This could be responsible for the blackening of the screens.

After scraping off the char after a run, no tar was found that
could be removed by methylene chloride. Close observation of the
screen after scraping showed incomplete removal of the char. I
was unable to reproduce the weight gain of the screens mentioned
by Anthony in 1974 and noted in Figure 11.

This methodology was not sensitive enough to indicate the
existance of cracking or give any insight into the nature of changes
in product distribution.

Table 2 lists the change in product composition with screen
configuration. Unfortunately, the analysis of hydrogen, a major

cracking product, was not possible with the gas chromatography system now in use.

Figures 12, 13, and 14 demonstrate trends in the products evolved by the pyrolysis reactions. Values are arranged in decreasing order of severity in cracking. The three layer screen should have the greatest tendency to crack products and the gold coated screen should have the least.

Carbon monoxide, Figure 12, shows a large difference in percentage yield in the change from three layers to two layers, while the removal of one more layer does not reduce the percentage evolved by a large degree. The inclusion of the gold coated screen, the lowest activity of this set, gives the impression of relatively constant percentage evolution of carbon monoxide.

Carbon dioxide production seems to be relatively stable with a maximum variation of 0.31 percentage points. This does not seem to be significant with comparisons of the three layer to the gold coated screen.

Table 13, gives the trends in the evolution of methane, ethane, and ethane. All three compounds seem to have stable percentage yields. Propane, Figure 14, is quite stable in yield. Possibly its yield is decreasing, but without any great variations. Propylene has greater variations in maximum and minimum values, approximately 0.4 percentage points, but there seems to be no definite trend.

Water has a great variation of percentage yields in all runs. This is probably due to water loss during pumpdown. Table 3 shows the weight loss on pumpdown. I feel that on this basis, the water variations in these pyrolysis runs do not present any useful information for this study in cracking.

In general, all percentage yields of each product under dif-
fering containment configurations are close together. There seem
to be no major trends of product yields. For the small differences
in product analysis to be meaningful, closer temperature control
should be observed. Also shown in Table 2 is the analysis of the
gases produced from the pyrolysis of coal contained in a three layer
stainless steel screen and a three layer gold coated screen at
vacuum conditions. The stainless steel screen released less volatiles
than the coated screen. The stainless steel screen run is not an
average value and was heated to a lower final temperature than the
other groups. It is presented as general information as a run with
final temperature of $800^{o}C$. rather than information concerning
volatile evolution with respect to method of containment.

From Davis and Farrell (1973) (Table 1), all the small hydro-
carbons, butanes and below, should be decomposed in 0.1 second or
less. If the stainless steel screen produced a major effect of
cracking, there should be a noticable effect in reducing the area
of the screen by two thirds. There seems to be no noticable trend
produced by changing screen configurations.

The effect of circulation within the reactor effectively
lengthens the residence time of the volatiles in the vicinity of
the stainless steel screen. With a period of circulation of once
per second, an approximation of the increase in residence time
during an atmospheric five second run might be on the order of 0.1
second for a fraction of the volatiles.

At an initial residence time of 0.01 second, very little cracking
should occur. Extrapolating from Figure 2 on propane pyrolysis,
conversion should be on the order of one or two percent at most.

Calculated residence time of this work is extremely short when compared to other studies of cracking. During some pyrolysis runs (heating rate 10,000°C./sec.), devolatilization is essentially complete in approximately 0.1 second, as seen in Figure 11. At a heating rate of 1000°C/second, one second is required to reach the same temperature, but the period of maximum volatile evolution is much more brief.

The pyrolysis of model compounds, anthracene, durene, fluorene, and camphor was conducted to observe the stability of these compounds under conditions of pyrolysis (Table 4).

Of these compounds, only camphor contained oxygen. Analysis of the pyrolysis products of anthracene, durene and fluorene give indications of carbon oxides. These oxides are products from impurities in the pyrolyzed compounds or result from residual oxygen in the reactor. The reported analysis of the pyrolysis products contains only essentially trace amounts of these reported compounds.

Anthracene, durene, fluorene, and napthalene are stable compounds under these conditions of pyrolysis.

Camphor gave extensive products under the vacuum and atmospheric conditions of pyrolysis. It is unclear that these products represent cracking products that were catalyzed by the stainless steel screen. A comparison of these products with the products from a gold coated screen would be interesting.

Camphor, by its structure (Figure 10) is a strained molecule. It is much less stable than the other, aromatic molecules which contain, with the exception of fluorene, unstrained six carbon rings.

The screens from the pyrolysis of all compounds, except camphor, were extremely clean on removal from the reactor. The screens from both atmospheric and vacuum runs of camphor were discolored with an extremely slight tinge of brown, possibly finely divided carbon or other compounds, resulting from cracking reactions.

None of the literature surveyed give experimental kinetic parameters for their observed cracking reactions of these model compounds. If these parameters of pre-exponential factors and activation energies were available, an estimate of the extent of expected cracking for this experimental reactor could be determined.

CONCLUSION

From this set of experiments, I have not been able to detect cracking catalyzed by stainless steel to any appreciable estent. This work covers atmospheric (helium) and vacuum pyrolysis conditions at a final temperature of 1000°C. and a residence time of five seconds.

If cracking was a problem with this batch reactor and stainless steel screen, I would expect that the yield of light unsaturated hydrocarbons would be much greater that it is. The cracking of the coal tar, yield 20 to 30% by weight, potentially represents a large quantity of these unsaturated hydrocarbons. It would also be expected, in more extreme cases of cracking, that much carbon would be deposited on the screen.

The gold coated stainless steel screens seem to be of the same activity in this study as the uncoated stainless steel, but should continue to be used in comparison work.

This work should be extended to determine if cracking is a problem with the high pressure vessel with hydrogen and helium at atmospheres.

CALCULATIONS

To determine the quantities of compounds detected by the thermal conductivity detector and integrated by the electronic integrator, all that is needed is a calibration standard, to give the response of the detector to a known amount of material and a response factor to relate the areas recorded by the integrator of other compounds to a common basis due to the differing sensitivities of the detector to various compounds.

Carbon dioxide was used as a calibration standard for this work because the response of the thermal conductivity detector is quite linear to carbon dioxide over a wide range of concentrations.

After each run, a minimum of three samples (0.5 ml., measured at ambient temperature and pressure) of carbon dioxide was injected into the $240^{\circ}C$. Porapak Q column with the thermal conductivity detector maintained at $100^{\circ}C$. The peak areas as determined by the integrator were averaged and were used in the following relationships.

Equation (1) is simply a ratio of areas, knowing the volume equivalancy of one area, the volume/area relationship of the same compound is easily determined.

$$\frac{A_1}{A_2} V_{cal} = V_{run}$$

where:

A_1 = Area of carbon dioxide peak from product analysis.

A_2 = Average area of peak from calibration samples.

V_{cal} = Volume of calibration sample in milliliters.

V_{run} = Volume of carbon dioxide in product analysis in milliliters.

Equation (2) is a simple relationship involving relating the molecular weight in grams and molar volume to a known volume to determine the mass of the detected volume of compound.

$$\frac{V_{run}(T_o)}{V^o(T_D)} MW_{co_2} = M_{co_2}$$

where:

V^o = Molar volume, 22.4 milliters/millimole

T_o = Standard temperature, 273^oK.

T_D = Temperature of room, 300^oK.

MW_{co_2} = Molecular weight of carbon dioxide, 44 mg/m. mole

M_{co_2} = Mass of carbon dioxide in product analysis, in mg.

To determine the mass of the other components in the product mixture, I used the relationship discribed in Basic Gas Chromatography, published by Varian Aerograph Corporation.

$$\frac{A_1 (RF_1)}{A_{co_2} (RF_{co_2})} M_{co_2} = M_i$$

where:

A_1 = Integrated area of the ith component in product analysis.

M_i = Mass of ith component in products, in milligrams.

RF_1 = Response factor for ith component.

RF_{co_2} = Response factor for carbon monoxide, 0.915.

The response factor is an experimental factor which relates the sensitivity of the thermal conductivity detector to various compounds. These tabulated retention factors are accurate for the temperature of the thermal conductivity detector in the range of 85 to 125^oC., consult Table 5.

TEMPERATURE MEASUREMENT

Temperatures of the screen during a run were recorded as a millivolt signal from a chromel-alumel thermocouple using the triple point of water as a reference temperature. The voltage signal was recorded by a Sanborn 380 chart recorder. A typical time temperature record is reproduced in Figure 6.

From the time temperature trace, the heating rate, residence time, and final temperature can be determined. The heating rate is defined in this work as the slope, in degrees C. per second, of the first three quarters of the rising temperature trace. This is the time in which the initial heating circuit is controlling the heating of the screen. The residence time is the length of the plateau in millimeters divided by 20 millimeters/ second. The final temperature is the temperature equivalent of the millivolt input to the chart recorder. The conversion charts, millivolts to degrees centigrade, are from The Omega Temperature Measurement Handbook.

IDENTIFICATION OF PEAKS

The peaks of the product analysis chromatogram were identified by comparison of retention times (Table 6) of the pure compounds and a comparison of the response of the thermal conductivity and flame ionization detectors. Notice that there is no response in the flame ionization detector for nitrogen, oxygen, carbon monoxide, carbon dioxide or water, while hydrocarbons give a large response.

SUGGESTIONS FOR FURTHER WORK

In further studies in the determination of the extent of
cracking in these experimental apparatuses, I have several suggestions.
One major product of cracking reactions at high temperatures is hydrogen.
In this work I have not been able to determine the hydrogen content
of the product gas due to the type of column in the gas chromatography
equipment used in this work. It would be very informative to observe
the change in hydrogen evolution with changes in pyrolysis conditions.

In work with the high pressure equipment the problem of cracking
may be more severe. With longer residence times (of hydrogasification)
and higher pressures, the convective circulation patterns should be
more intense, resulting in a higher fraction of the volatiles con-
tacting the hot stainless steel screen after their initial escape
from the screen. Product analysis of the products of straight stain-
less steel screens and gold coated screens should be compared.

It is possible that the size of the coal sample might be impor-
tant in controlling repeatability of the experimental gasification
process. Many researchers (Davis and Place, 1924, Greensfelder et
al., 1949, Griffiths and Mainhood, 1967, Hesp and Waters, 1970, and
Romovacek et al., 1972) have reported extensive cracking catalyzed
by coke and carbon. Information concerning product distribution
as a function of coal sample size may be of interest in determining
the extent of cracking catalyzed by residual coke.

In the study of model compounds, a higher heating rate may be
desirable to give higher screen temperatures during volatilization
of the sample. The compounds examined boil or sublime around 200°C.
This temperature is reached in this work approximately 0.2 seconds
into the heating cycle with approximately 0.8 seconds left to reach

the temperature under study, 1000°Centigrade. If the heating rate was increased to $10,000^{\circ}$C./second, which is feasible with current equipment, 200°C. is reached in 0.02 seconds and the temperature of interest (1000°C.) is reached in 0.1 second.

Dr. W. A. Peters has suggested that model compounds could be injected into the stainless steel screen while it is at the temperature under study. The injection can take place at vacuum or at somewhat above atmospheric pressure, through a gas chromatography septum. Compounds that could be studied by this injection method would include gases or liquids, behavior of which, under reactor conditions is of interest in the analysis of fixed gases from coal pyrolysis.

As a comparative study, cracking by stainless steel screens can be compared with cracking by passivated stainless steel screens. Brooks (1966) suggests ways for passivation of stainless steel. He mentions pretreatment of stainless with hydrogen sulfide or with water. Interestingly, water has been used to 'activate' stainless steel for use in catalyzing cracking reactions. Brooks (1966) also cites a report of the use of copper to prevent surface cracking of hydrocarbons. Of these passivation methods mentioned, I would suggest the pretreatment of stainless steel screens in hydrogen sulfide and the coating of stainless steel with copper.
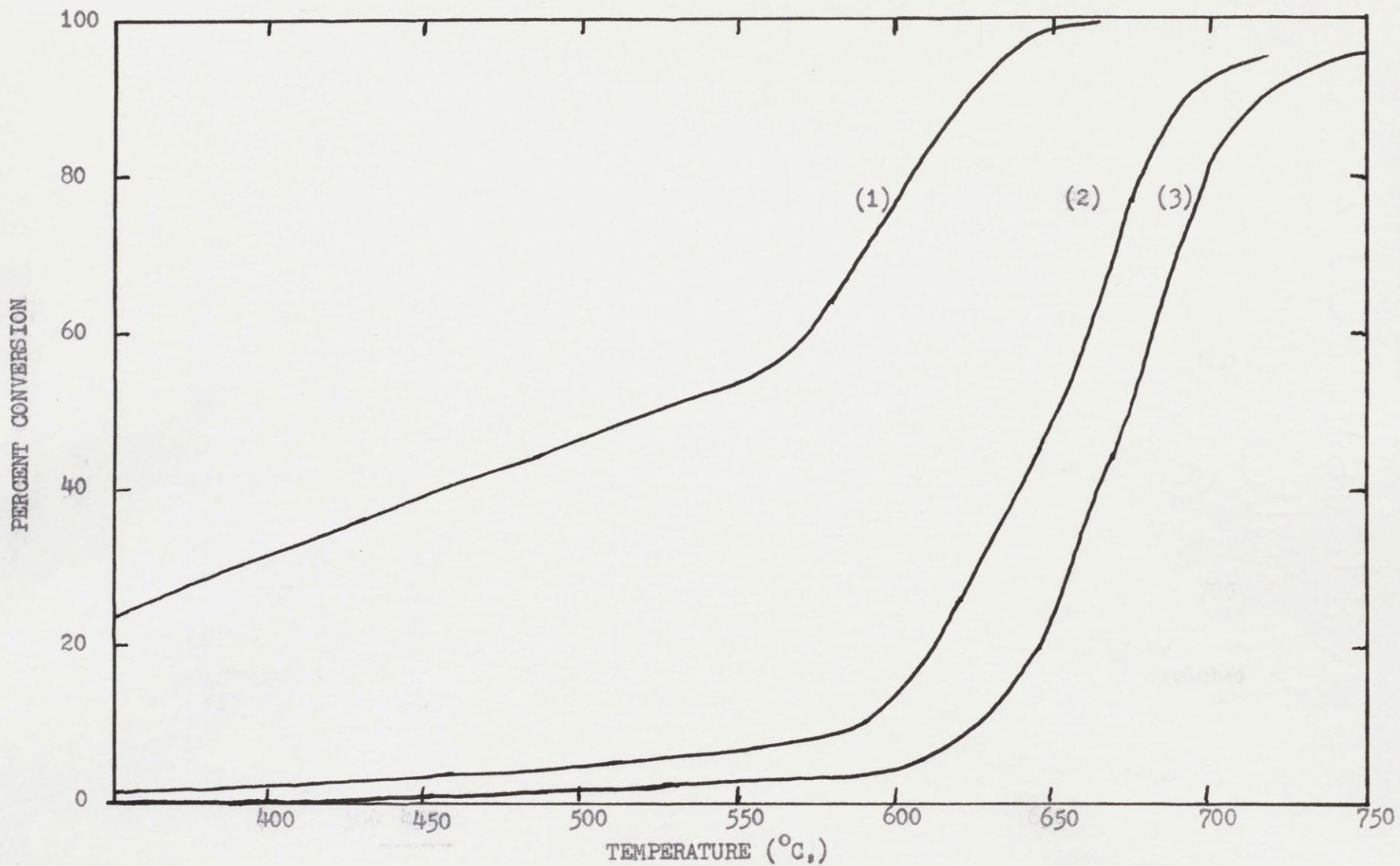
FIGURES

Figure 1: ACTIVITY OF COKE, CARBON, AND QUARTZ determined by the decomposition of cyclohexane. (1) coke, (2) spectral carbon, (3) quartz. Romovacek et al. (1972).
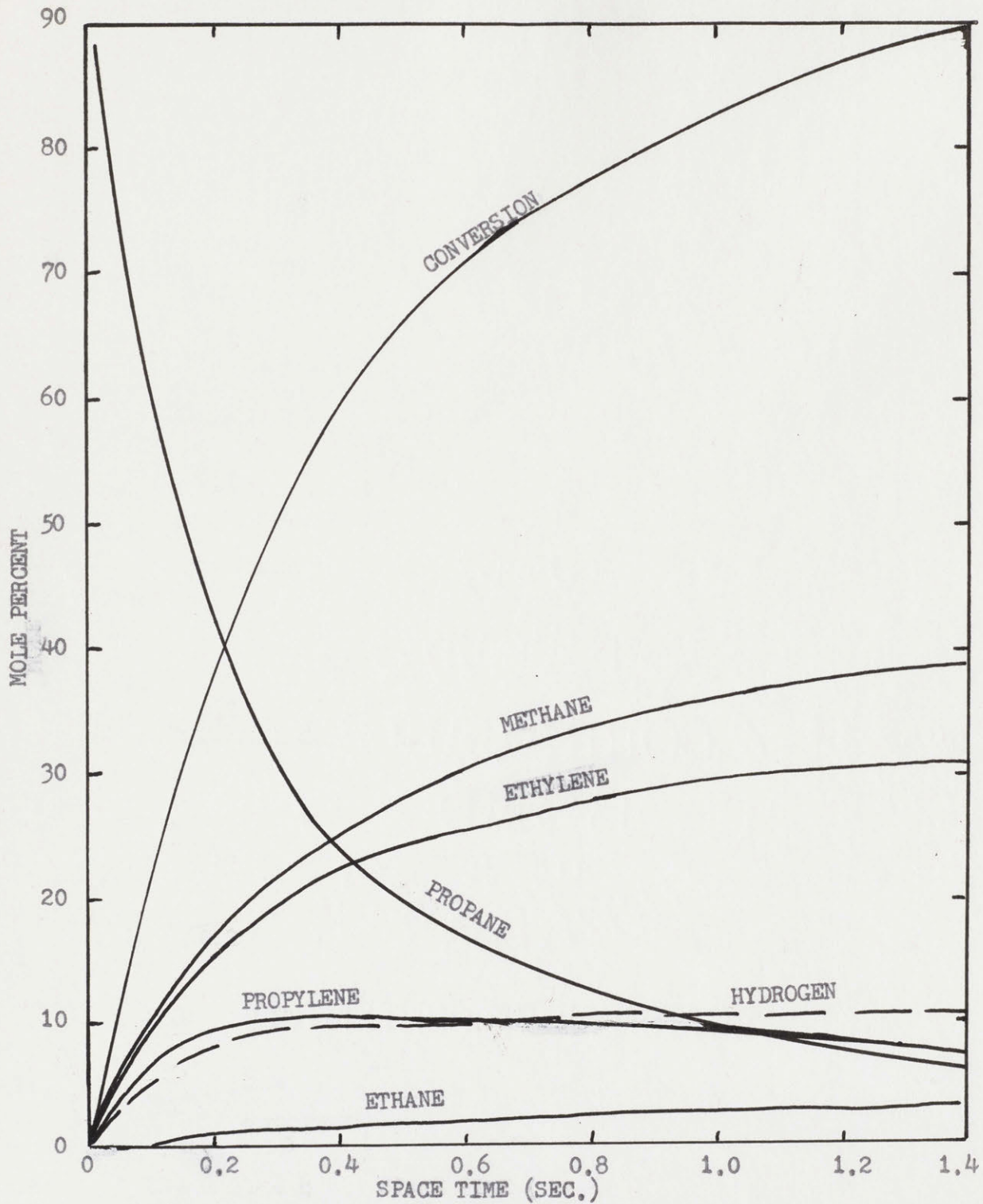
Figure 2: CONVERSION OF PROPANE in a stainless steel reactor at 800°C.,
           pressure of one atmosphere and 50 mole percent steam as a
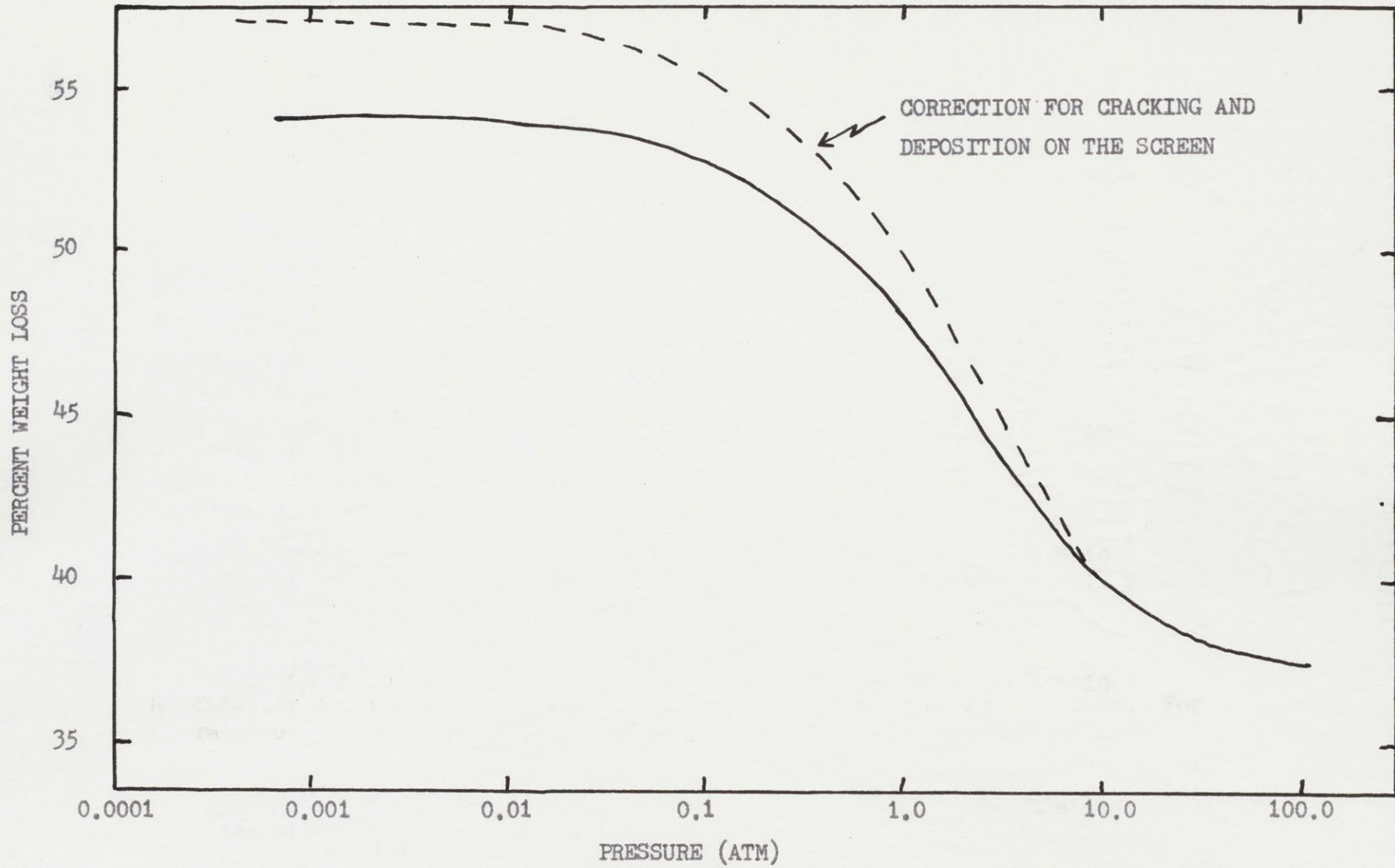   dilutant. Herriott et al. (1972).

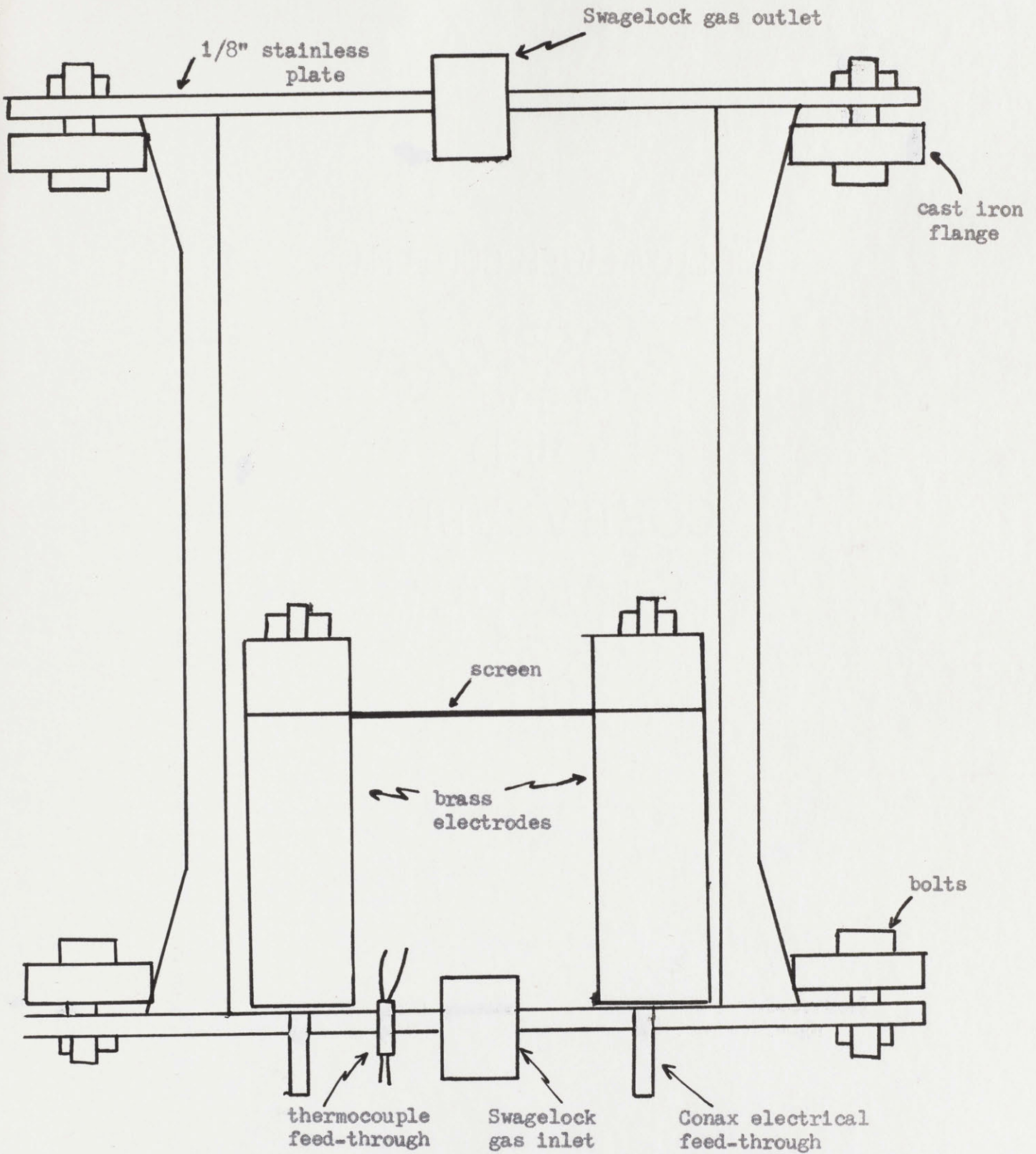Figure 3: CORRECTION FOR CRACKING of the products of bituminous coal gasification. For heating rates of 650° to 10,000°C./second. Anthony (1974).

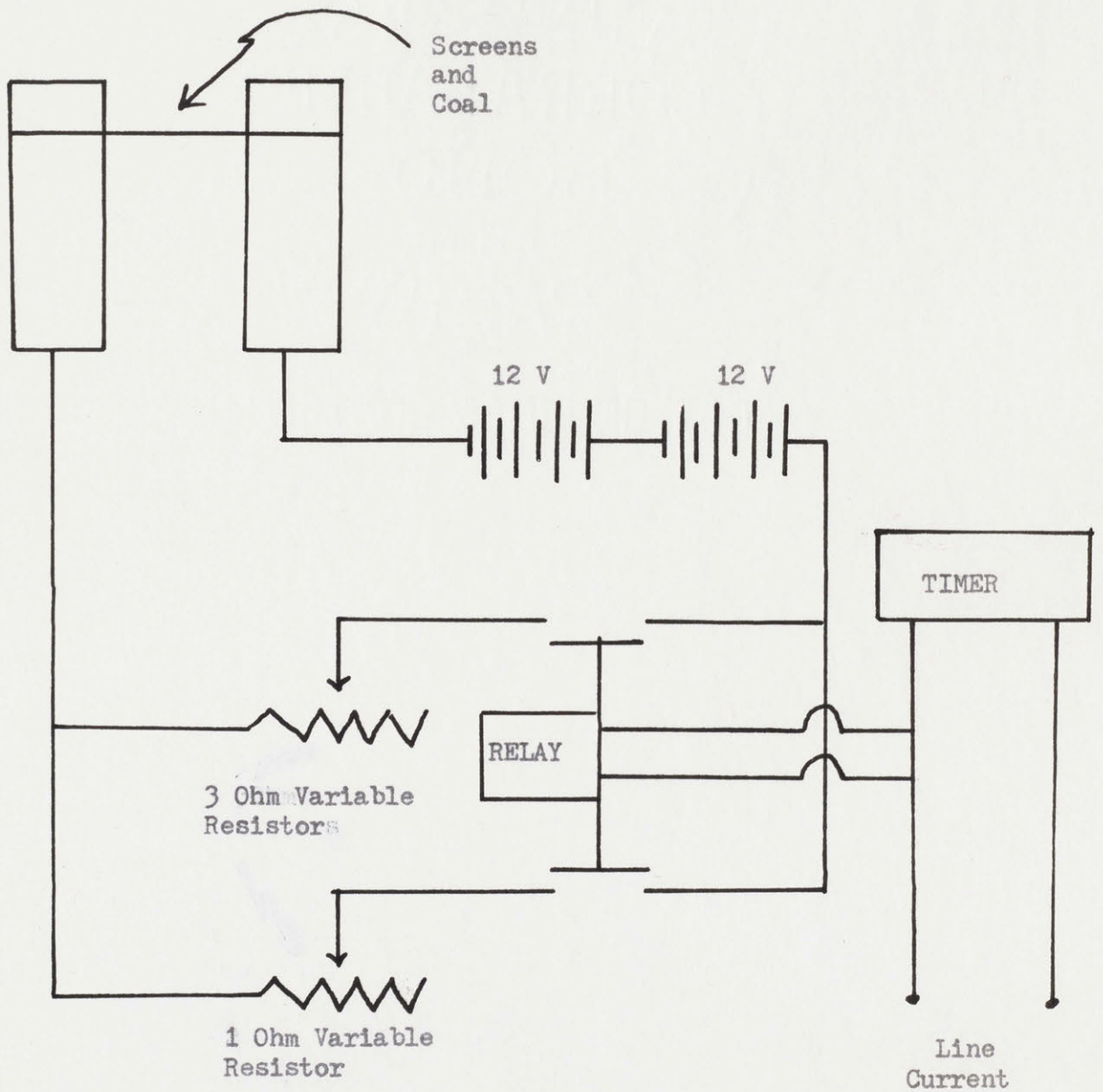Figure 4: LOW PRESSURE BATCH REACTOR as used in this experimental work.
Suuberg (1975).

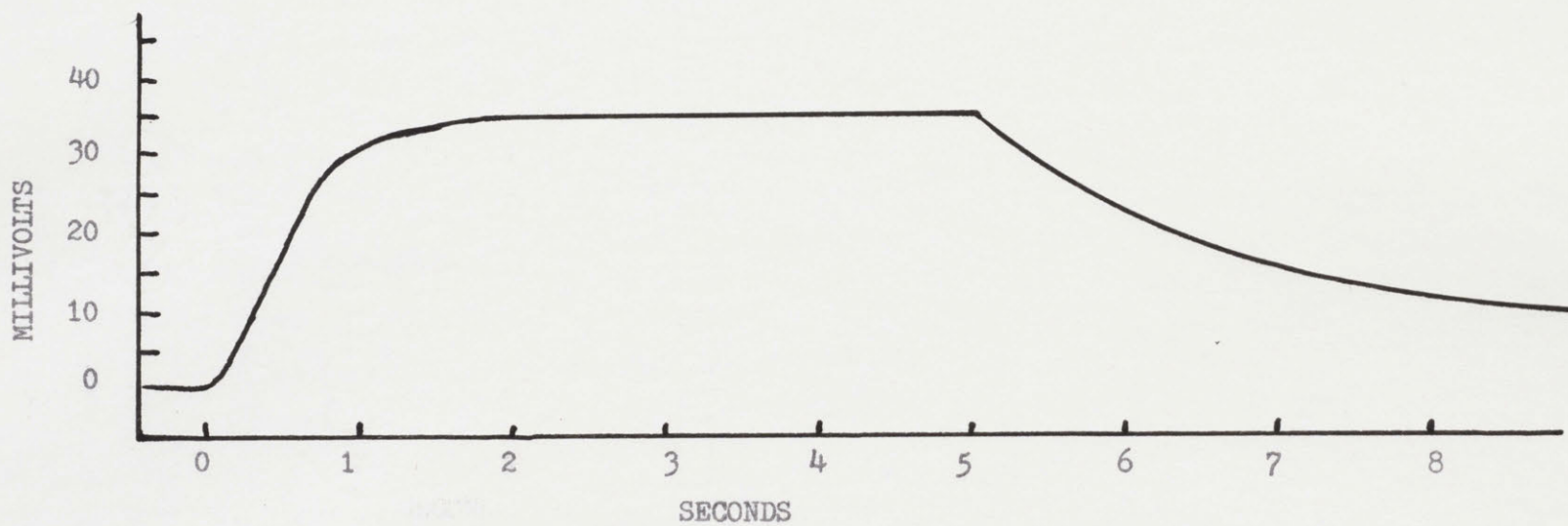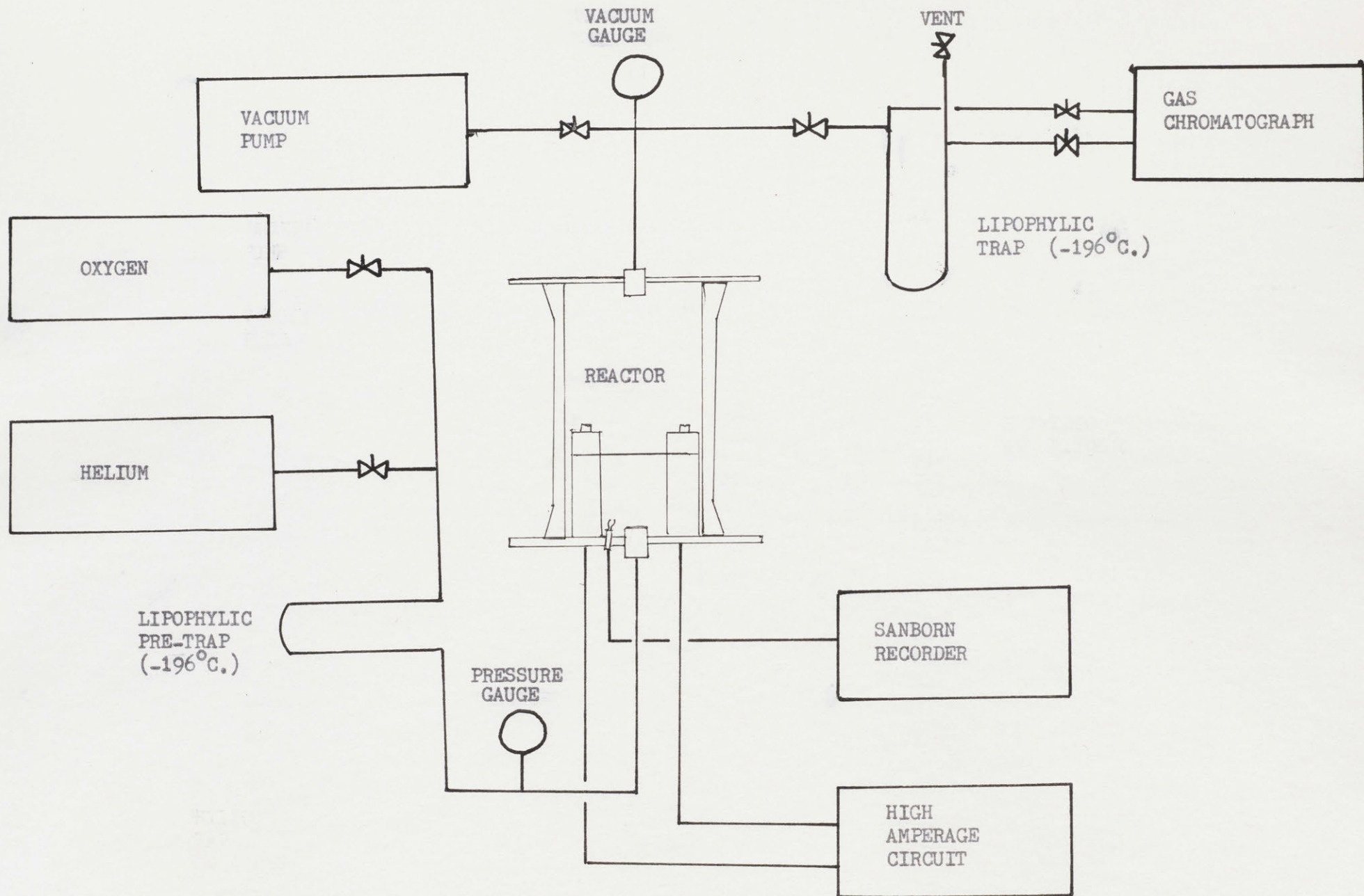Figure 5: REACTOR ELECTRICAL SYSTEM. Anthony et al. (1974).

Figure 6: TIME-TEMPERATURE TRACE of a typical atmospheric pressure
            pyrolysis run.

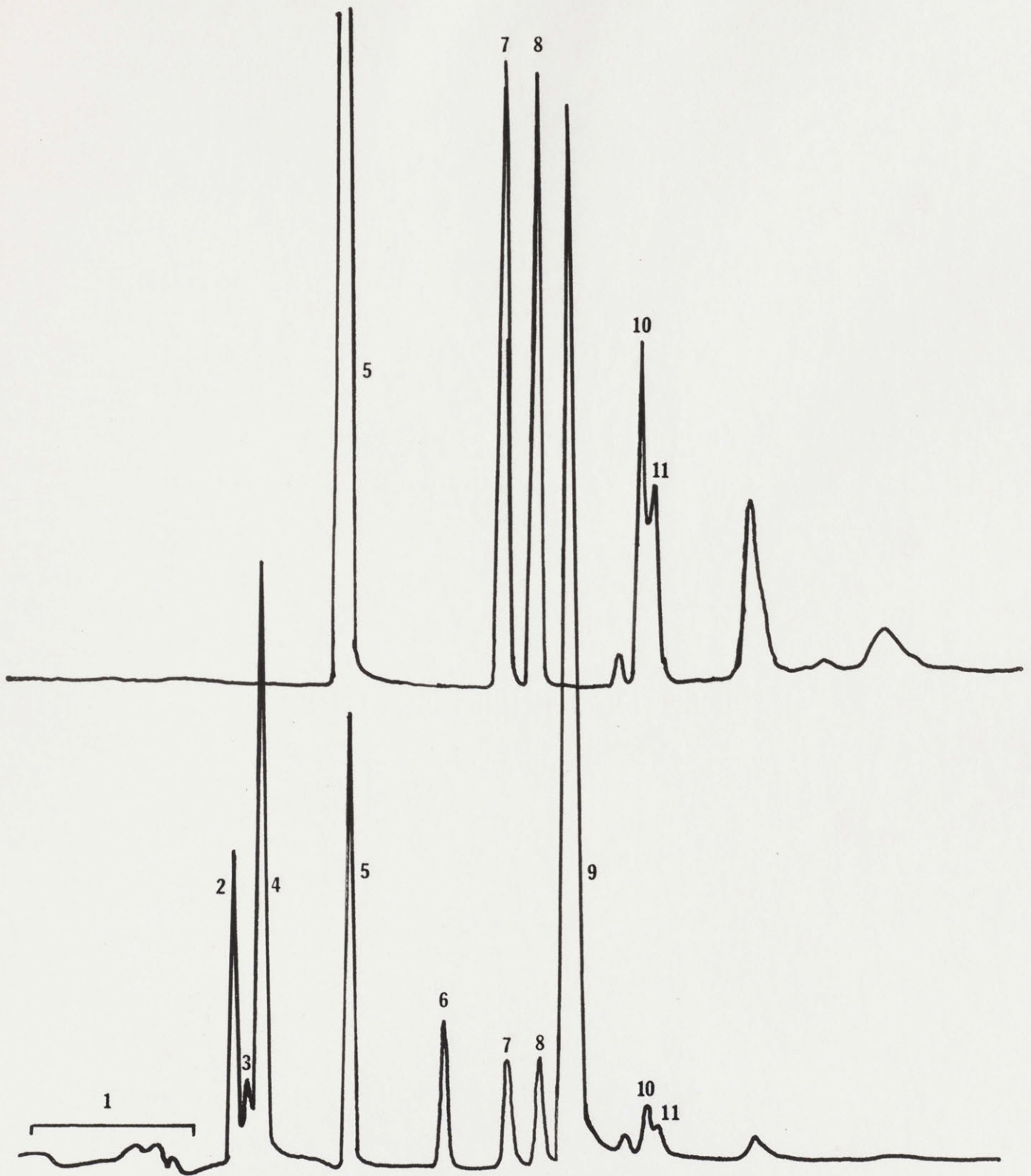Figure 7: BATCH REACTION SYSTEM PLUMBING for collection and analysis of fixed volatile gases.

Figure 8: TYPICAL GAS CHROMATOGRAM of the fixed volatile gases
from the pyrolysis of bituminous coal.

1.) pressure variations   7.) ethylene
2.) nitrogen   8.) ethane
3.) oxygen   9.) water
4.) carbon monoxide   10.) propylene
5.) methane   11.) propane
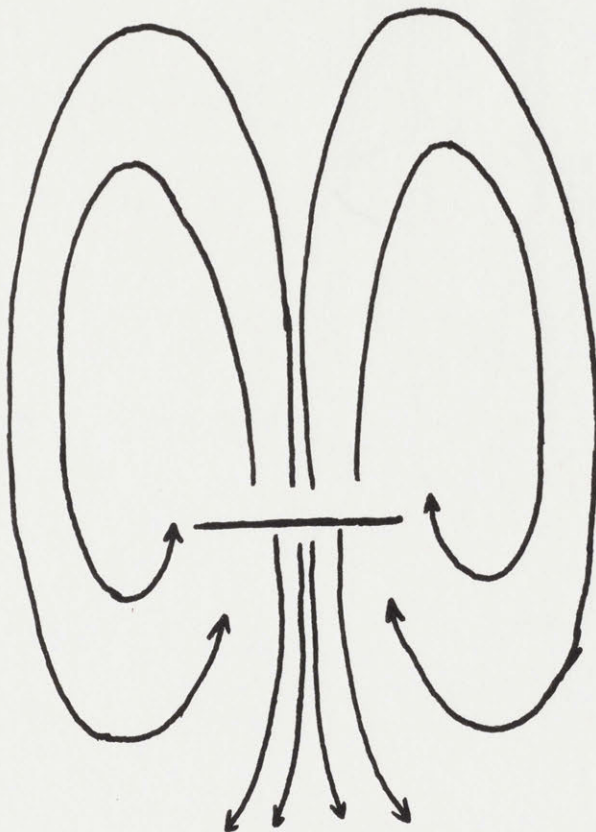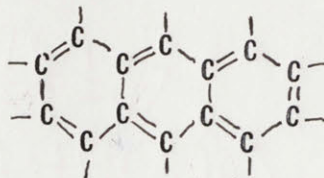6.) carbon dioxide

Figure 9: CIRCULATION PATTERNS in the low pressure batch reactor
at atmospheric pressure, period of approximately one
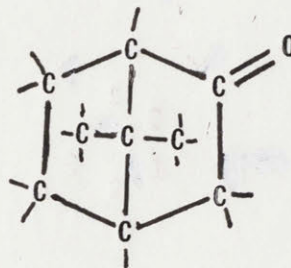second.

ANTHRACENE

      Molecular Weight   178.24

      Boiling Point   340°C.

CAMPHOR

      Molecular Weight   152.24

      Sublimination Point 204°C.

DURENE

      Molecular Weight   134.22

      Boiling Point   196.8°C.
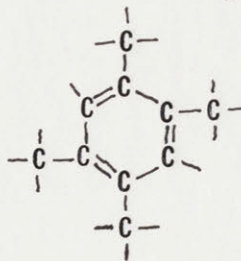
FLUORENE

      Molecular Weight   166.23

      Boiling Point   293°C.
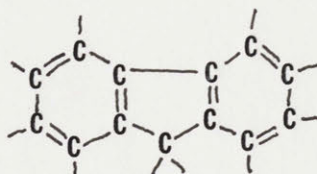
NAPTHALENE

      Molecular Weight   128.19

      Boiling Point   340°C.
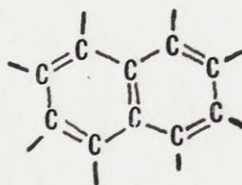
Figure 10: STRUCTURE OF MODEL COMPOUNDS with molecular weights
and boiling points at atmospheric pressure.
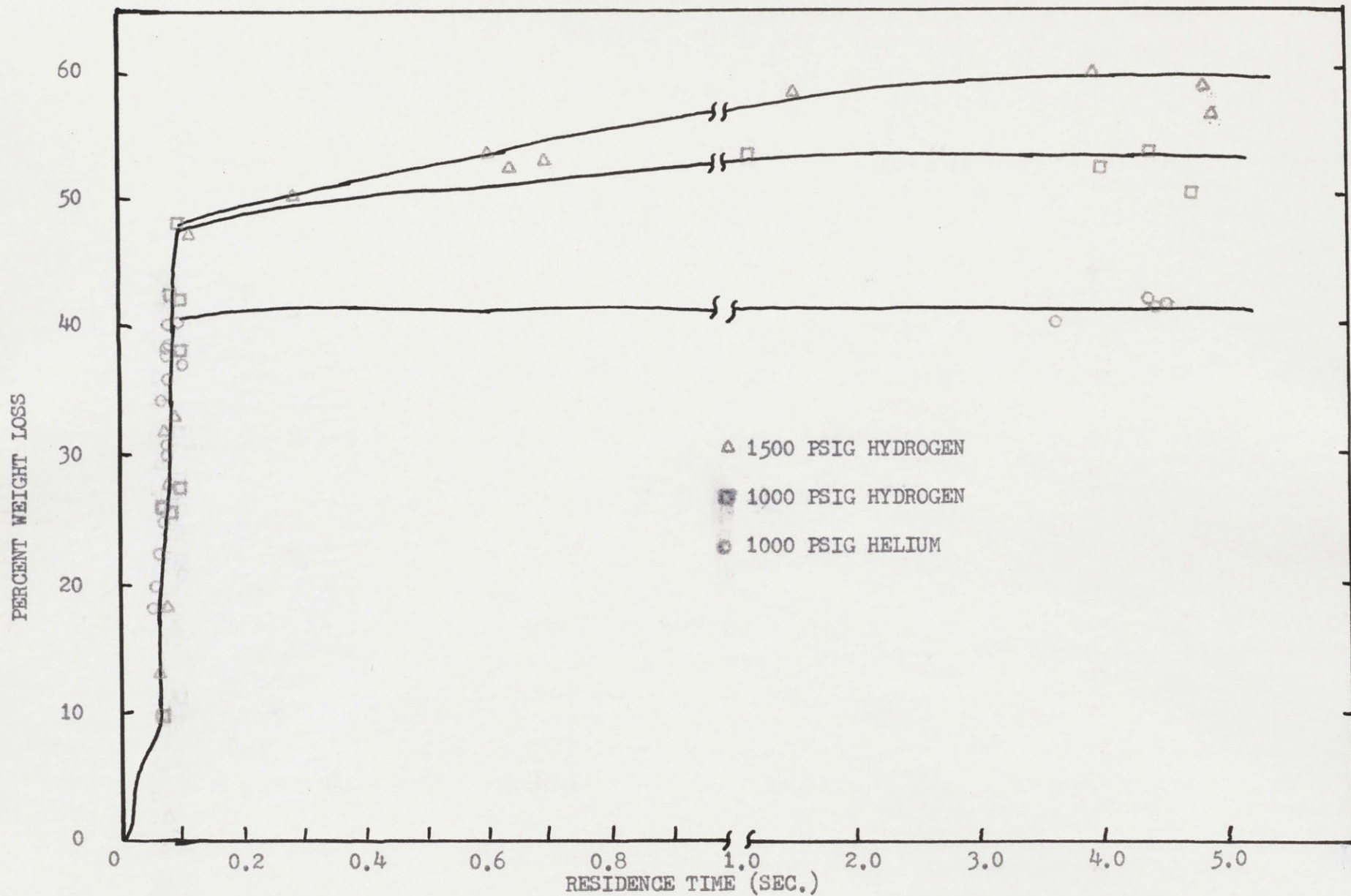
Figure 11: WEIGHT LOSS WITH TIME for lignite in hydrogen and in helium. Heating rate: 10,000°C./sec. Final temperature: 1000°. From Anthony (1974).
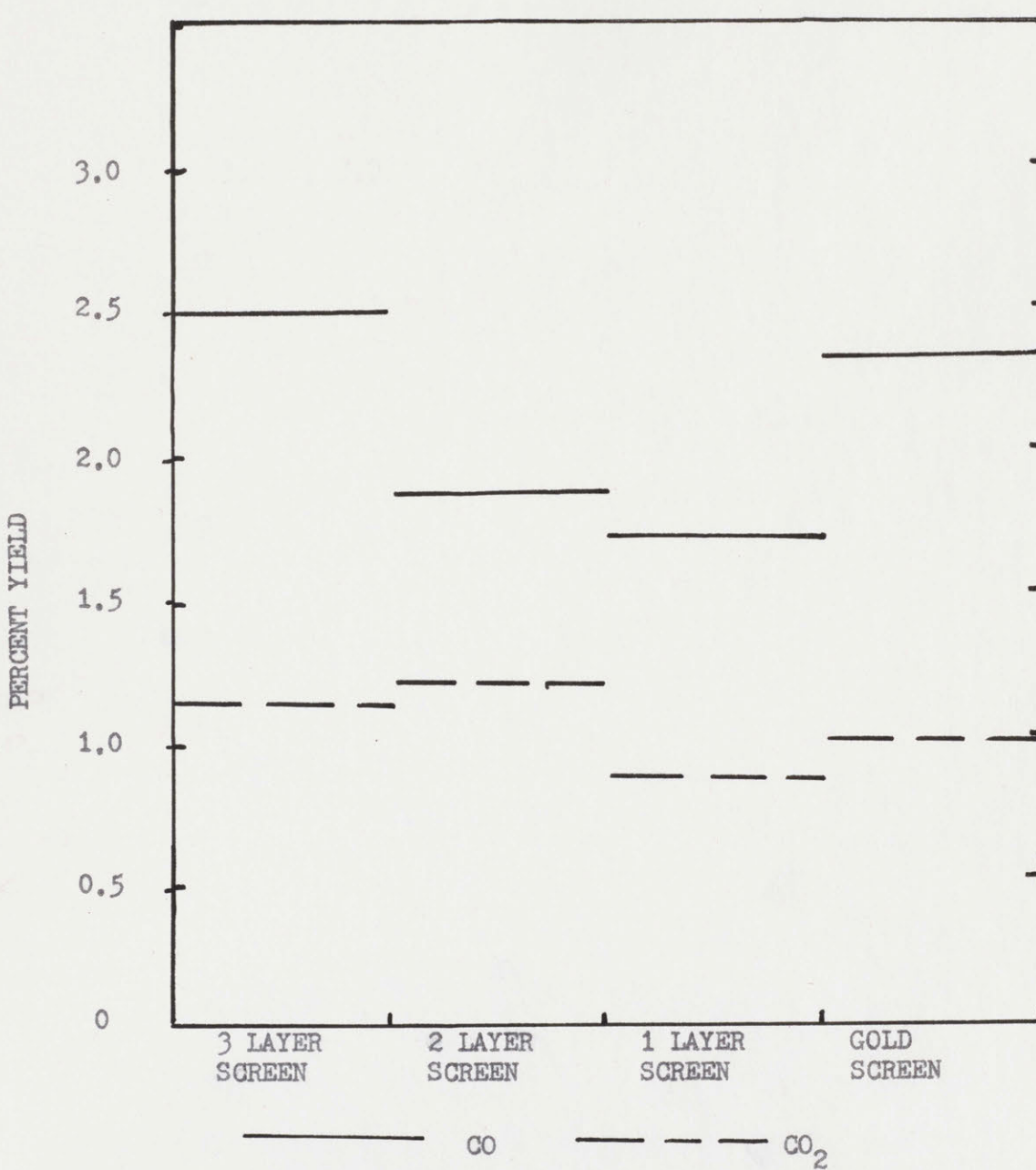
Figure 12: CARBON MONOXIDE AND CARBON DIOXIDE yield from pyrolysis of bituminous coal.
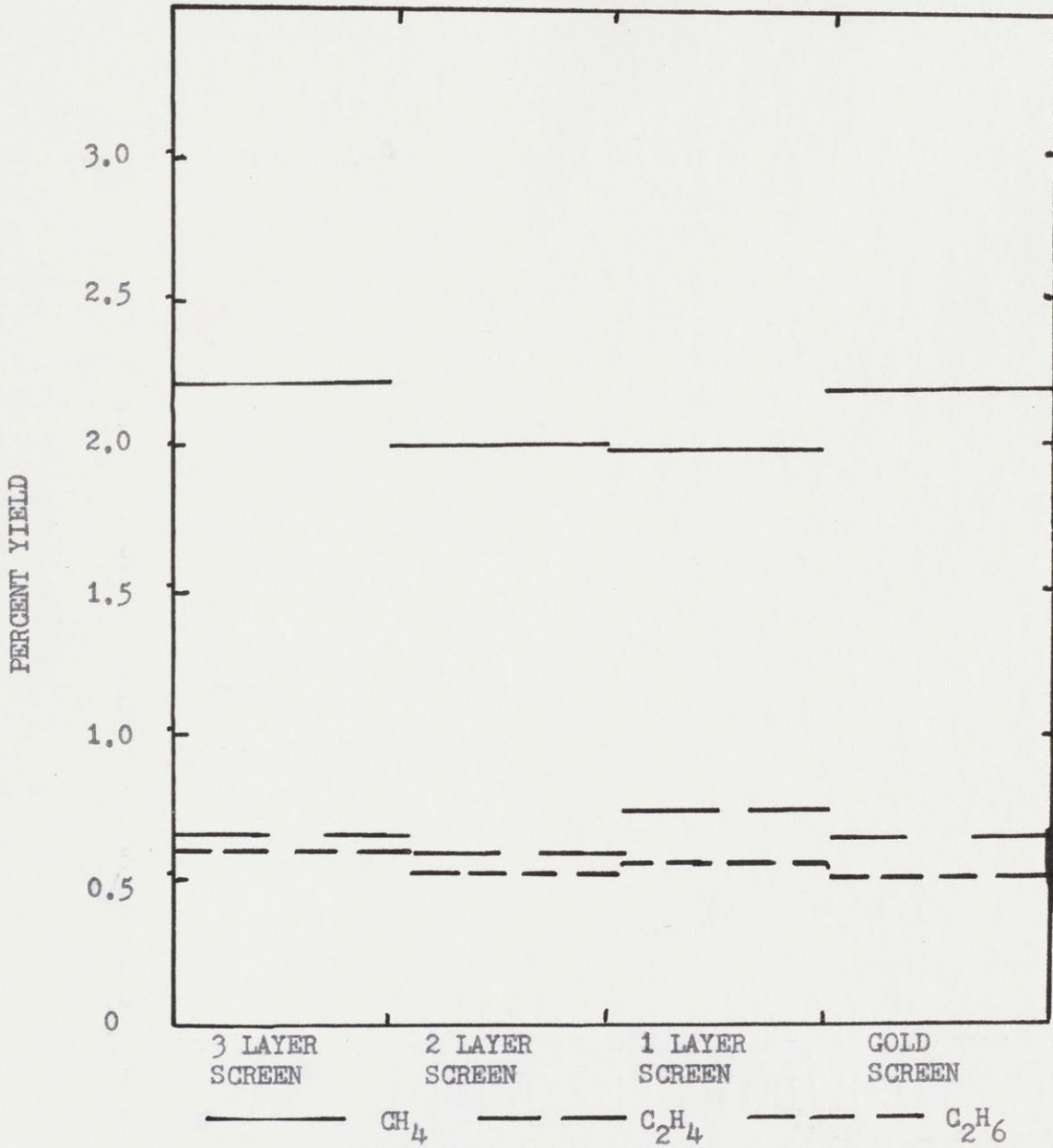
Figure 13: METHANE, ETHYLENE AND ETHANE yield from pyrolysis
of bituminous coal.
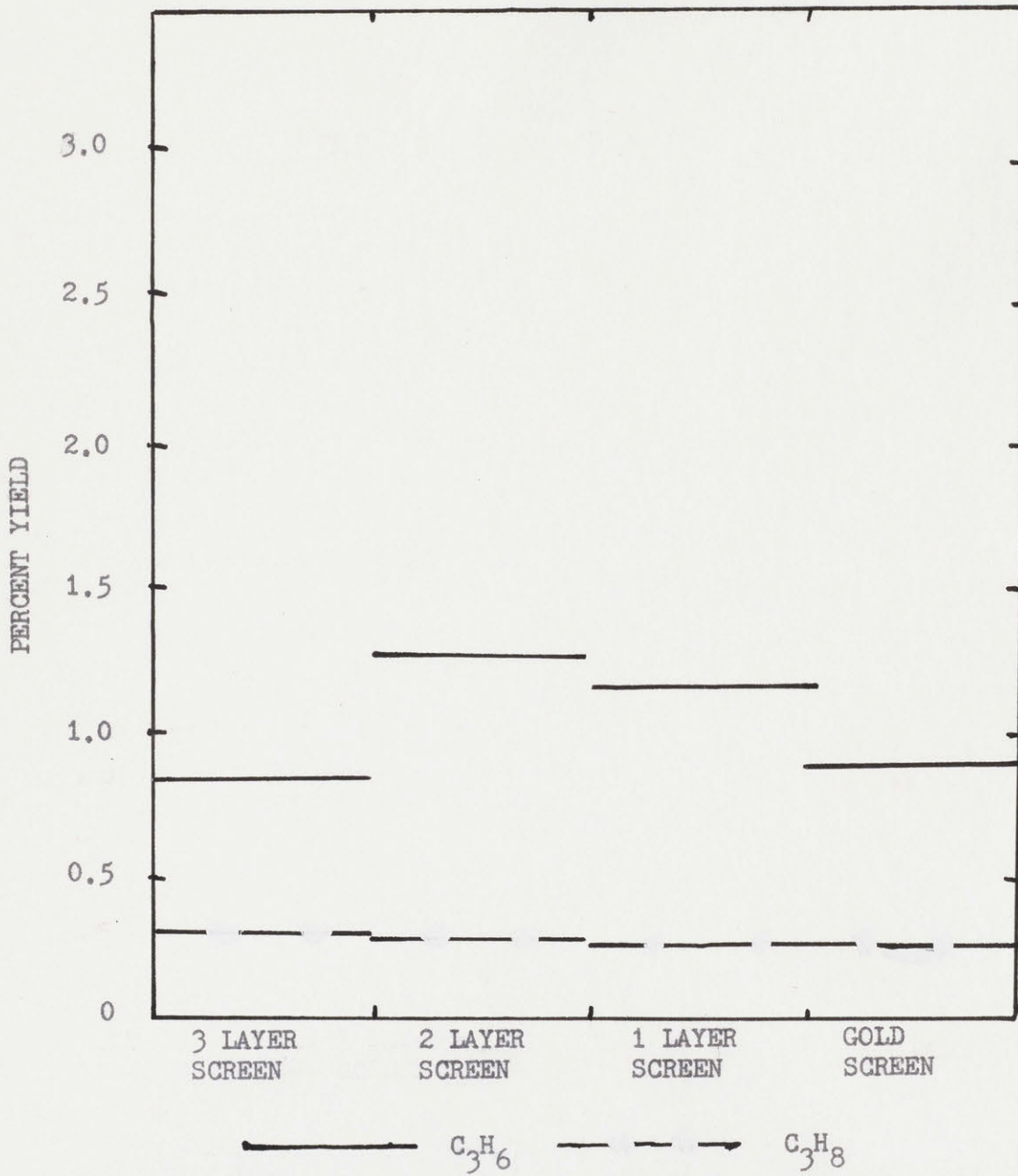
Figure 14: PROPYLENE AND PROPANE yield from pyrolysis of bituminous
            coal.

TABLES

COMPOUND	TEMPERATURE (°C.)					
	807	830	854	877	900	923
Ethane	22.3	33.0	46.1	60.8	75.0	87.2
Propane	44.1	60.1	75.9	88.4	95.9	99.1
Butanes	59.7	76.3	89.2	96.6	99.3	99.94
Pentanes	71.0	85.9	95.2	99.0	99.89	100.00
Hexanes	79.1	91.6	97.8	99.7	99.98	100.00
Heptanes	85.0	95.0	99.0	99.91	100.00	100.00
Octanes	89.2	97.0	99.6	99.97	100.00	100.00

Table 1: PARAFFIN CONVERSION for various temperatures, residence time of 0.1 second in a silica bed. Davis and Farell (1973).

COMPOUND	3_{atm}	2_{atm}	1_{atm}	$GOLD_{atm}$	3_{vac}	$GOLD_{vac}$
CO	2.52	1.85	1.74	2.34	2.30	2.74
CH_4	2.23	2.07	2.03	2.20	1.15	1.77
CO_2	1.12	1.18	.87	1.03	.77	.99
C_2H_4	.67	.60	.78	.68	.38	.63
C_2H_6	.60	.55	.58	.54	.38	.59
H_2O	4.45	5.51	6.40	5.69	1.76	7.36
C_3H_6	.88	1.28	1.16	.88	.31	.73
C_3H_8	.34	.33	.29	.29	.15	.27

Table 2: YIELD OF PRODUCTS from pyrolyzing bituminous coal contained in stainless steel and gold coated screens. Five second residence time at 1000°C.

The results are presented in the milligram yield of volatiles divided by the original mass of the coal multiplied by 100 to give a percentage yield of the original mass of coal. Headings of 3, 2, and 1 refer to the number of layers of stainless steel, gold refers to gold coated stainless steel.

Mass of Sample	Mass Lost	Percent Mass Lost
12.17	.05	0.40
21.38	.21	1.00
10.38	.15	1.45
15.43	.19	1.22
15.48	.17	1.10
18.19	.24	1.32
17.08	.29	1.70
16.00	.21	1.31

mass is measured in milligrams

Table 3: WATER LOSS DURING PUMPDOWN of bituminous coal samples.

The results are presented in the milligram yield of
volatiles divided by the original mass of the coal
multiplied by 100 to give the percentage yield of
the original mass of coal.

PRODUCT   COMPOUND

	DURENE		FLUORENE		NAPTHALENE		ANTHRACENE		CAMPHOR	
	atm	vac	atm	vac	atm	vac	atm	vac	atm	vac
CO	.09	.30	0	.15	0	0	0	.25	1.04	1.80
CH_4	.09	0	0	.01	0	0	0	0	.46	.14
CO_2	.01	.03	0	.04	0	0	0	.03	.01	.02
C_2H_4	.02	.01	0	0	0	0	0	0	.51	.49
C_2H_6	0	.01	0	0	0	0	0	0	.07	.18
H_2O	-	-	-	-	-	-	-	-	-	-
C_3H_6	0	0	0	0	0	0	0	0	.37	.83
C_3H_8	0	0	0	0	0	0	0	0	.08	.12

Table 4: YIELD OF PRODUCTS from the pyrolysis of model compounds in atmospheric
pressure (helium) and vacuum. Compounds were contained in stainless
steel at $1000^{\circ}C$, with a five second residence time.

COMPOUND		RESPONSE FACTOR
Nitrogen	N_2	.67
Oxygen	O_2	.80
Carbon Monoxide	CO	.67
Methane	CH_4	.45
Carbon Dioxide	CO_2	.915
Ethylene	C_2H_4	.59
Ethane	C_2H_6	.59
Water	H_2O	.55
Propylene	C_3H_6	.68
Propane	C_3H_8	.68
Other Hydrocarbons	C_xH_y	.70

Table 5: RESPONSE FACTORS for compounds under study.
Factors are accurate for a thermal conductivity
detector with temperature between $85°$ and $125°C$.
(Varian Aerograph Corporation)

57

COMPOUND		RETENTION TIMES (TRIAL)		
		(1)	(2)	(3)
Nitrogen	N_2	338	322	366
Oxygen	O_2	364	345	390
Carbon Monoxide	CO		360	405
Methane	CH_4	544	529	581
Carbon Dioxide	CO_2		677	727
Ethylene	C_2H_4		797	850
Ethane	C_2H_6		847	899
Water	H_2O	970	950	1000
Propylene	C_3H_6	1040	1040	1080
Propane	C_3H_8		1070	1094

Table 6: RETENTION TIMES in seconds for compounds of
interest in this study of fixed volatile products.

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