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AROMATIC FORMATION
AND DISTRIBUTION OF NITROGEN
AND SULFUR IN THE LIQUID
PRODUCTS OF STEAM
PYROLYSIS OF SHALE OIL

by

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

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ABSTRACT

Liquid products of steam pyrolysis of shale oil were analyzed for the amount of benzene, toluene, xylene (BTX), sulfur, nitrogen, carbon, and hydrogen.

Since it is believed that reaction time is the controlling factor in BTX formation, the selection of the runs for BTX analysis was based on the variation of residence time. It was found, however, that steam pyrolysis of shale oil under conditions used in this study does not produce an appreciable amount of BTX.

In order to study the effect of pyrolysis temperature, and reaction time on the distribution of sulfur, nitrogen, carbon, and hydrogen in the liquid products of steam pyrolysis of shale oil, a total of 14 runs were selected for elemental analysis. It was found that nitrogen and sulfur are concentrated in the liquid products; yet it appears that some nitrogen and sulfur atoms are cracked to gases. It was also found that the carbon to hydrogen ratio of the liquid products of steam pyrolysis of shale oil goes up as the temperature increases.

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DEDICATION

This Thesis is dedicated to my father, Hossain Kavianian.

INTRODUCTION

Oil shale is a potential source for a substantial amount of energy in the form of synthetic crude or shale oil. It is estimated (1) that 80 billion barrels of shale oil can be recovered from Green River formation deposits in Colorado, Utah, and Wyoming.

In spite of the vast amounts of energy that can be recovered from oil shale, its development is confronted with a number of technical, economic, environmental, and social problems.

One of the major problems associated with shale oil is its high nitrogen content (2% by wt.). As described by Poulson, et al, (2), over 85 percent of the nitrogen compounds in shale oil have basic properties. Dineen (3) reports that pyridines, dihydropyridines, indoles, and quinolines, all basic compounds, comprise over half the nitrogen compounds in shale gas oil.

The problems associated with basic nitrogen compounds of shale oil in petroleum refining have been described by Jensen (4) as:

"Nitrogen compounds not only impart undesirable properties to finished petroleum products, but their basic nature makes them effective poisons for the acidic catalysts used in petroleum refining."

Therefore, shale oil has to be pre-refined with major emphasis on nitrogen reduction before it can be used as a major part of refinery feed-stocks.

A study undertaken by D.P. Montgomery (5) showed that shale oil can be converted into petroleum products suitable for sale in present day markets. The basic processes are a series of coking, hydrostabilization, hydrodenitrification, reforming, and cracking. These processes, however, are normally complex in nature, relatively expensive, and would add to the over-all cost of products obtained from shale oil.

Also, by pre-refining shale oil, the hydrogenation capacity of a refinery would be cut down considerably. Therefore, any alternative use of shale oil which does not require pre-refining might be both practical and economical.

One of the alternative uses of shale oil would be as a feed-stock for steam pyrolysis to produce chemical intermediates, such as ethylene, propylene, benzene, toluene, and xylene. The petrochemical feed-stocks will be in high demand in the near future as Sherwin, et al (6) comments:

"Petrochemical feed-stock and energy demands equivalent to 42 percent of the projected U.S. crude and gas supply by the year 2000 is not viable. A number of significant changes will

have to occur if even our modest petrochemical growth rates projections are to be realized. These changes will take many forms, but without question, one of them will include the utilization of non-conventional hydrocarbon sources, coal and shale oil, as major petro-chemical feed-stocks."

An over-all research program has been developed at the Colorado School of Mines to study the utilization of shale oil obtained by different retorting processes as a feed-stock for steam pyrolysis. Experiments were conducted on a Tosco II, on an NTU simulated In-Situ whole oil, and on the vacuum distillates of these oils. The results of these experiments are presented by Fritzler (7) and Smith (8). These studies, however, were oriented toward maximization of ethylene and other light olefines. Steam pyrolysis of shale oil produces two kinds of products. One is the gaseous products and the other is the liquid hydrocarbons formed during pyrolysis. The major constituents of the gas are light olefins, butadiene, hydrogen, and light alkanes which makes the gas commercially valuable. However, the liquid products of steam pyrolysis of shale oil must be used commercially, if the over-all economics of the process is to be viable. As Ellis (9) comments:

"Aromatic hydrocarbons are obtained by pyrolysis of practically all other types of hydrocarbons at temperatures of 600-1100°C."

According to Kofman (10):

"Cracking at 700°C of low boiling (100°-150°C) hydrocarbons, from the pyrolysis of alcohol, yields 5.8 percent benzene, 19.5 percent toluene, and 18.5 percent xylenes."

The three chemicals benzene, toluene, and xylene (normally referred to as BTX) are widely used in industry as solvents, intermediates for resin manufacturing, synthetic fiber, and photographic chemicals. These chemicals also improve the knocking characteristics of gasoline and are a good blending stock for cracked gasoline.

The first purpose of this study was devoted to the investigation of BTX formation in steam pyrolysis of shale oil.

The second purpose of this study was to investigate the distribution of sulfur and nitrogen compounds in products of steam pyrolysis of shale oil. Practically all types of sulfur derivatives have been isolated from mineral oil distillates (9). Kazarnovskaya (11) states that elemental sulfur, hydrogen sulfide, mercaptans, thioethers, disulfides, and thiophenes are the predominant sulfur compounds in crude.

Presence of sulfur compounds in petroleum products creates many problems among which one can mention the following:

1. Corrosive action on metals.
2. Formation of sulfur dioxide and eventually sulfuric acid when the particular petroleum product is employed as a

fuel in an internal combustion engine.

3. Sulfur and sulfur derivatives cause stability and color problem in gasolines.

4. Sulfur compounds reduce the lead susceptibility of motor fuels, i.e., the greater the proportion of sulfur in fuel, the less increase in octane number will be realized upon addition of tetraethyl lead.

Therefore, because of the problems which sulfur creates in petroleum products, it might be of interest to see what happens to the sulfur present in the feed-stock of steam pyrolysis of shale oil.

Investigation of the distribution of nitrogen compounds in steam pyrolysis of shale oil comprises another part of this study.

To make steam pyrolysis of shale oil more economical, several alternatives may be chosen in the future to make use of the liquid products; for example, the liquid products might be used as a fuel oil, or they might be refined to more valuable products. In either case, the knowledge of the amount of nitrogen compounds in the liquid products is essential. If the liquid is to be used directly as fuel, one has to know the amount of nitrogen oxides which would be produced. If the liquid product is to be up-graded to motor fuel or home heating oil, the content of nitrogen compounds must be known in order to choose appropriate catalysts and conditions for

the nitrogen compound removal during refining. The health hazards involved in working with liquid products of steam pyrolysis of shale oil may be better defined by knowing the amount of nitrogen compounds which are present.

Also, if one is interested in the hydrocarbon part of the liquid products of steam pyrolysis of shale oil, quantitative determination of nitrogen compounds is essential, as these compounds contribute greatly to the non-hydrocarbon part of the liquids, as Cady (12) describes in a typical shale oil, out of 61 percent non-hydrocarbons, 60 percent are nitrogen compounds. After all, it is of interest to know what is the fate of nitrogen present in the feed-stocks of steam pyrolysis, and where it would end up.

The third purpose of this study was to determine the carbon and hydrogen content of the liquid products of steam pyrolysis of shale oil. The ratio of the weight of carbon to hydrogen is a good indication of suitability of a liquid hydrocarbon as a cracking feed-stock. Generally, for a liquid hydrocarbon, the lower this ratio, the better it is as a pyrolysis feed-stock. As will be discussed in a later section, the alkane series make the best feed-stock for pyrolysis units. Normally, in thermal cracking of hydrocarbons, one is interested in obtaining as much ethylene as possible.

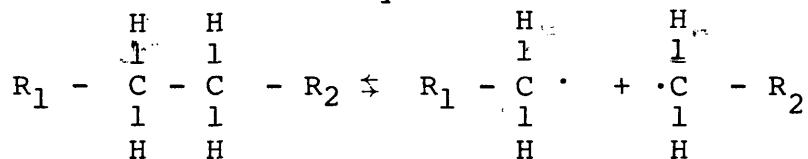
As will be discussed later, the reactions which lead to the formation of ethylene proceed via a free radical chain mechanism.

The rate controlling step in these series of reactions is the cleavage of a carbon-carbon (C-C) bond and formation of the free radical. The easier this step, the faster the reaction, and this leads to the formation of more ethylene. In un-saturated hydrocarbons (hydrogen deficient), carbon atoms are attached to each other by two chemical bonds, a σ -bond and a π -bond. Therefore, if a cracking feed-stock is composed entirely of un-saturated hydrocarbons, tremendous amounts of energy would be required to initiate the reactions. Consequently, as the hydrogen content of a pyrolysis feed-stock increases it is expected that more α -olefins will be obtained upon pyrolysis.

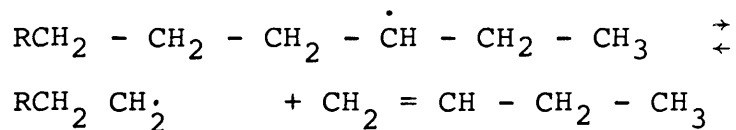
THEORY AND EXPERIMENTAL BASIS

It has been proposed, by several investigators, that thermal cracking of hydrocarbons occurs via a free radical chain reaction (13, 14, 15, 16).

The initiation reaction in the thermal cracking of a hydrocarbon is the homolysis of a carbon-carbon bond.



Free radicals are unstable species and undergo bond scission to transform themselves into more stable forms. The bond scission occurs at a carbon located β to the carbon bearing the free electron. The result is formation of an α -olefin and a newly formed free radical.



The repetition of β cracking yields considerable amounts of ethylene, relatively small amounts of methane, and α -olefins.

Previous work on steam pyrolysis of shale oil has been done by the Laramie Energy Research Center (LERC) of the Energy Research and Development Administration (ERDA) (17, 18), the Institute of Gas Technology (IGT) (19), and the Colorado School of Mines (7, 8, 20).

Considerable amount of ethylene was obtained in all of these studies with relatively low amount of methane, and α -olefins. One might say on a chemical ground, that these studies support the free radical mechanism of thermal cracking of hydrocarbons.

However, in all of the studies performed on steam pyrolysis of shale oil, attention has been focused only on the gaseous products.

As was mentioned previously, steam pyrolysis of shale oil produces gaseous and liquid products at the same time.

The compounds of major interest in the liquids are benzene, toluene, and xylene (BTX). If these chemicals are formed during steam pyrolysis of shale oil, they can greatly improve the overall economics of the process.

Generally, aromatics in the liquid products of steam pyrolysis of a hydrocarbon come from three different sources (18);

1. Aromatics native to the feed.

2. Aromatics formed from naphthenic compounds.
3. Aromatics formed from condensation of light olefins .

Aromatics Native to the Feed:

As far as aromatics native to the feed are concerned, one can say that the retort operating conditions have a large effect on the type and amount of aromatics formed in the product oil. It has been found that higher retort temperatures produce oils with higher degree of aromaticity (18, 21, 22). A study by the Bureau of Mines shows that at 1500°F the oil obtained is made up entirely of aromatic hydrocarbons (18).

Some of the more important reactions which occur during steam pyrolysis of a hydrocarbon are summarized below:

Alkanes	=	light olefins (23, 24)
Light olefins	=	aromatics + light olefins (16, 25)
Naphthenes	=	aromatic and/or light olefins (23)
Aromatics	=	unconverted (23, 24)

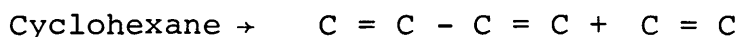
Since Aromatics remain unconverted in a steam pyrolysis unit, the aromatics which are native to the feed will end up in the liquid products of steam pyrolysis.

Aromatics Formed from Naphthenic Compounds

It has long been known that cyclohexane hydrocarbons can be catalytically dehydrogenated to corresponding aromatics. Some of the better catalysts for the reaction are platinum and

nickel. This process has been used to make benzene and alkyl benzenes from the petroleum fractions which are rich in naphthenic compounds (26). In the absence of a catalyst, however, it is quite doubtful if dehydrogenation of naphthenes is responsible for aromatic formation. The products of pure thermal cracking of naphthenes appear to be butadiene and ethylene rather than benzene. In the case of cyclohexane, Schmidt (27) has shown that ring rupture is the favored reaction over dehydrogenation. It seems likely, therefore, that any aromatic formed from naphthenic compounds is the result of secondary reactions between ethylene and butadiene initially formed.

Therefore, one can say that naphthenes in a steam pyrolysis unit can have two different fates, either form butadiene and ethylene, or be converted to aromatics. Therefore, part of the aromatic compounds in the liquid products of steam pyrolysis of shale oil are supplied by the naphthenic compounds native to the feed.



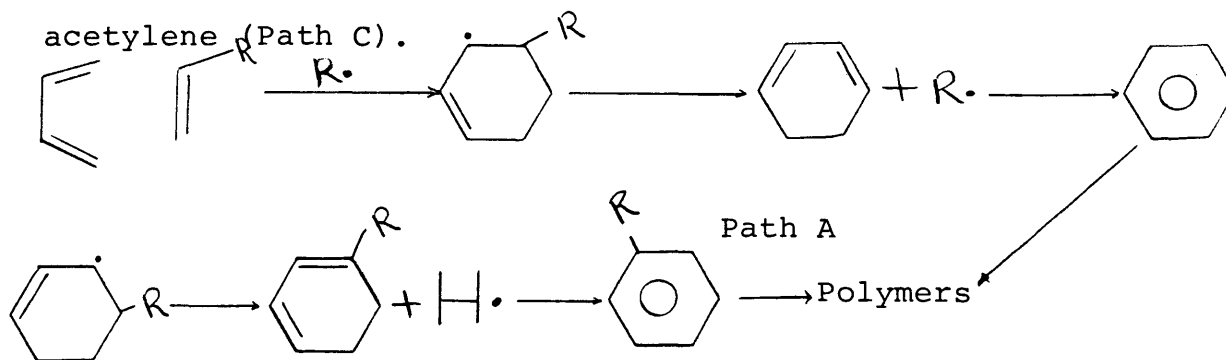
→ Aromatics

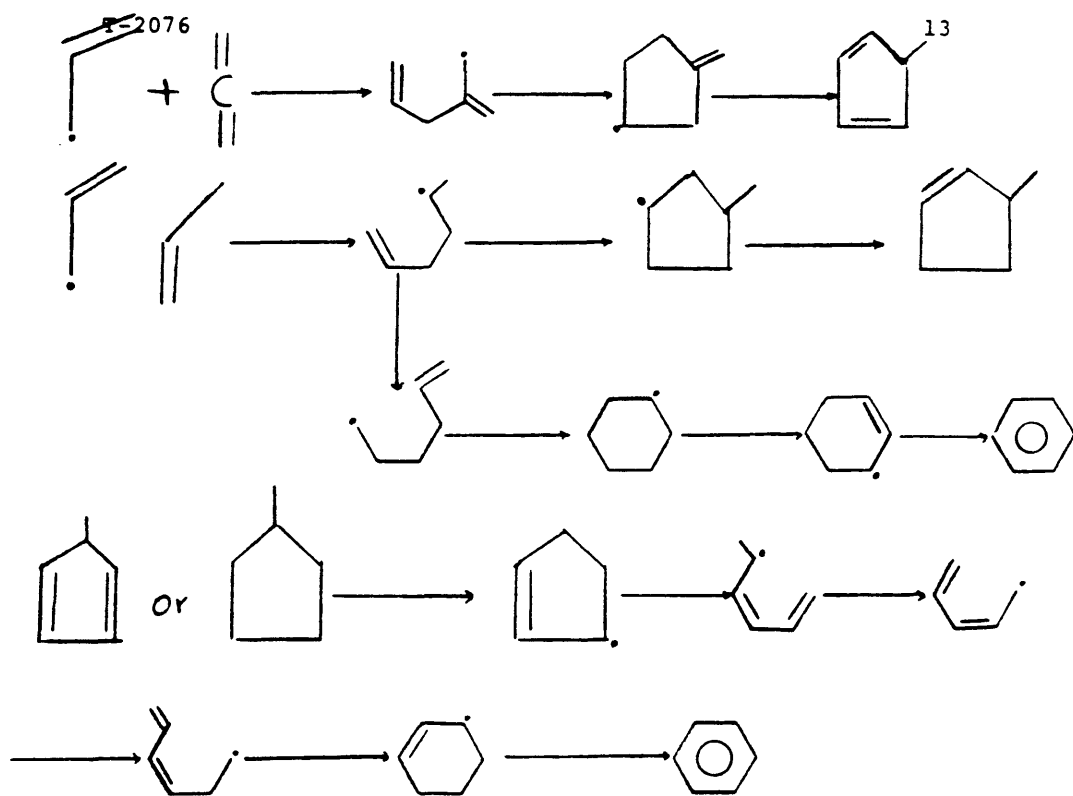
Based on the above discussion, one can say that feedstock composition is an important factor in the amount of

aromatics found in the liquid products of steam pyrolysis of shale oil. Feed-stocks having different paraffin-olefin-naphthene aromatic ratio (PONA) will undoubtedly produce gaseous as well as liquid products which differ widely in composition.

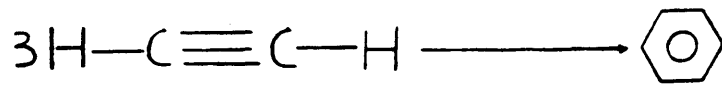
Aromatics Formed by Condensation of Light Olefins:

Most of the aromatics formed during thermal cracking of hydrocarbons come from the secondary reactions of light olefins, as has been found by McConaghy, et al (25) and comprehensively approved by Sakai (16). McConaghy (25) has suggested that aromatics in thermal cracking of hydrocarbons can be formed by three different mechanisms. The first proposed mechanism involves a path which is initially non-radical and proceeds through a Diels-Alder type reaction to form an adduct which is then successively dehydrogenated to benzene (Path A). The second suggested mechanism involves initial attack of a radical on an olefin through a variety of routes (Path B). Finally, the third suggested mechanism for formation of aromatics involves trimerization of acetylene (Path C).





PATH B



PATH C

Due to low concentrations at which acetylene is normally present, a significant contribution by a trimerization process seems highly unlikely.

Paths A and B are both possible, Path A involves the reaction between butadiene and an olefin and Path B involves the attack of an allene radical on an olefin. However, most of the cracking conditions are such that allene radical is present in low concentrations relative to that of butadiene so that on chemical grounds, one has to accept Path A as the predominant sequence of reactions which lead to the formation of aromatics. To demonstrate this, McConaghy (25) pyrolyzed ethylene and propylene at 800°C over a variety of contact times, only trace amounts of allene were detected in these reactions, indicating that it is highly unlikely that allene could compete effectively with ethylene and propylene in these reactions. The same study revealed that in pyrolysis of ethylene, concentration of butadiene when plotted as a function of contact time increases, passes through a maximum, and then starts to decrease; while concentration of aromatics increases steadily. These observations support the Diel-Alder type mechanism of formation of aromatics.

A study conducted independently by Sakai (16) et al leads to the same conclusion, as he summarizes:

"For pyrolysis of paraffinic hydrocarbons at 700-800°C, the yields of olefins such as ethylene, propylene, butanes, butadiene, and cycloolefins increase during the initial stage of the reaction, pass through their maxima, and later decrease; yields of aromatics, hydrogen, and methane however increase monotonically throughout the reaction course."

The work done by Griswold (20), Fritzler (7), and Smith (8) at Colorado School of Mines also support a Diels-Alder type reaction for formation of aromatics.

In these studies shale oil was pyrolysed over different contact times and temperatures, it was observed that concentration of total olefinic compounds and butadiene in the gas phase decreases as contact time increases, indicating that if butadiene and olefins are given enough time, they will react to form aromatics.

The key point about reactions of Path A (Diels-Alder Mechanism) is that when lower molecular weight aromatics are formed, the reactions will not stop there, but may continue by polymerization to mono-aromatics. Thus contact time becomes a very critical parameter in formation of aromatics, if one is interested in producing lower molecular weight aromatics, and his reaction conditions are such that the reaction time is too long, he will form polyaromatics instead of mono-aromatics, as will be discussed in a later section.

Nitrogen Distribution:

The importance of identification of nitrogen compounds in petroleum fractions has been described earlier and will not be further emphasized.

Although more than 30 different compounds bearing one or more atoms of nitrogen have been identified in petroleum fractions, all of these chemically different compounds can be categorized into two general classes; basic and non-basic nitrogen compounds.

Richter (27) defines basicity as the relative availability of electrons on the nitrogen atom.

Normally, nitrogen compounds having a $PK_a \geq 2$ are considered to be basic while those having a $PK_a \leq 2$ are classified as non-basic (27). Compounds having a nitrogen atom attached to one or more aromatic rings, such as pyridine and quinoline, show strong basicity due to rejection of nitrogen atom electrons by the aromatic ring, and thus availability of these electrons for reaction. Richter, et al (27) measured the basic and non-basic nitrogen content of 14 different crudes. The striking fact that they observed was that the ratio of basic nitrogen to total nitrogen was a constant irrespective of the source of the crude oil. If the same trend follows for shale oils, one can estimate the amount of basic

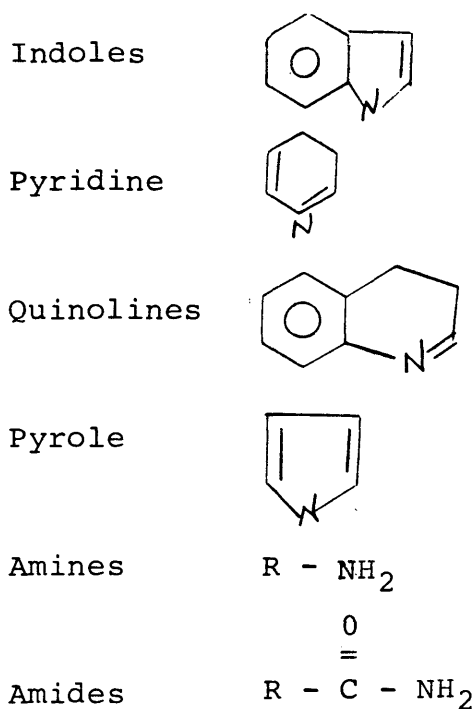
nitrogen in any shale oil having a knowledge of the total nitrogen in that oil, and the results of basic and total nitrogen for another shale oil. Knowledge of the amount of basic nitrogen compounds present is important as it is these compounds which attack the acidic refinery catalysts.

Due to relatively large molecular weight of nitrogen compounds, the amount of nitrogen increases with increase in boiling point of shale oil. Dinneen, et al (22) obtained 19 different U.S. and foreign shale oils. Four cuts were made from each sample. He called the cuts "Naphta," "light distillate," "heavy distillate," and "residuum." For all 19 samples, the concentration of nitrogen expressed as weight percent of the fraction increased with temperature of the cut.

Cook (28), conducted an experiment similar to that of Dinneen (22). He analyzed shale oils obtained at four different temperatures. It was found that the amount of nitrogen in the shale oil first increases with temperature, reaches a maximum for shale oil produced at 1400°F and then decreases with an increase in retort temperature. He also obtained four different cuts from a Colorado shale oil and analyzed them for nitrogen; it was also found that the percentage of nitrogen in a cut increases with the temperature of the cut.

Sohns, et al (17), in an independent study, also came to the conclusion that the amount of nitrogen in a shale oil cut increases with the temperature of the cut.

Among the many different kinds of nitrogen compounds which have been identified in petroleum and shale oil, one can mention the following compounds which exist in higher concentrations:



These nitrogen compounds and their derivatives exist together.

Normally the nitrogen compounds which are present in shale oil have relatively high molecular weight. Cook (28) has experimentally determined that 35 percent of nitrogen compounds in a shale gas oil are one ring compounds, 25 percent are two-ring compounds, and 40 percent are multi-ring compounds. Therefore, the average molecular weight of nitrogen compounds in shale oil is relatively high.

In nitrogen compounds present in shale oil, the nitrogen atom is attached to either one or more aromatic rings or a ring compound with at least one double bond. Aromatics are very stable compounds due to the resonance structure of the aromatic ring, and it requires a lot of energy to rupture an aromatic ring. Thermal cracking conditions normally do not supply the required amount of energy, and therefore, any nitrogen compound which has a nitrogen atom attached to one or more aromatic rings, such as carbazoles, quinoline, and indoles, will be expected to end-up in the liquid products. Compounds like pyroles, and pyridine are less stable than nitrogen compounds with aromatic rings. They require less severity of operation to crack and if they do so, the nitrogen atom might end-up in the form of less heavier compounds such as ammonia. Due to the nature of their bond, amines are easier to crack among nitrogen compounds. Consequently, most of the nitrogen compounds in shale oil will not be affected by pyrolysis, and will end-up in the liquid products, with the result that the concentration of nitrogen in the liquids is expected to be much higher than that of the feed-stock.

Based on the above discussion, one can hypothesize that concentration of nitrogen in the liquid products of steam pyrolysis of shale oil, should increase with temperature of pyrolysis, reach a maximum and then decrease at higher temperatures.

At relatively low temperatures, almost all of the nitrogen compounds present in the feed are expected to end-up in the liquid products, however, some of the heavier hydrocarbon molecules would also remain liquid so that the over-all concentration of nitrogen compounds in the liquid products will be relatively low. Data of Fritzler (7), and Smith (8), showed that as the temperature of pyrolysis decreases, more liquid products remain.

At moderate pyrolysis temperatures, more of the hydrocarbons present in the feed-stock will crack, while these moderate temperatures would not affect the nitrogen compounds, so that less liquid products would be obtained, but the liquid products will have a high concentration of nitrogen in them. Data obtained at Colorado School of Mines (7, 8) show that at very high pyrolysis temperatures, almost no liquid products are formed.

Effect of residence time on the concentration of nitrogen compounds in the liquid products of steam pyrolysis of shale oil can be predicted based on the foregoing discussion.

As has been mentioned before, in steam pyrolysis of hydrocarbons, low residence time is essential for maximization of olefinic compounds. As residence time of the hydrocarbon

in reactor increases, secondary reactions of olefins become predominant, and as mentioned earlier, the olefinic compounds will condense into aromatics. Therefore, one would expect that the concentration of hydrocarbon part of the liquid products to increase with residence time. Thus concentration of nitrogen compounds in the liquid products are expected to decrease with residence time.

The residence time in this study is based on the reactor void volume, the volumetric flow rate of steam at reaction temperature and atmospheric pressure, and the ideal gas volume of the oil.


The ideal condition which minimizes the efforts of data correlation in a steam pyrolysis unit, is an isothermal operation. However, it was found out during the experimental runs that maintaining an isothermal temperature profile is extremely difficult; hence, the residence time calculated by the above method, was corrected for non-isothermal behavior by Fritzler (7) using a correction factor as proposed by Davis and Farrell (30). Each increment of residence time is weighted by an exponential Arrhenius factor, $e^{(-E/RT_i)}$, where T_i is the average absolute temperature during the increment of residence time, E is 46 KCal and R is the universal gas constant. The corrected residence time is obtained by summing over all the increments as follows:

$$\Theta = \frac{\sum e^{(-E/RT_i)} i}{e^{(-E/RT_m)}}$$

where t_i is the incremental residence time sec.

T_m max temp or
corrected residence time sec.
 T_i temp. during increment i or

Distribution of Sulphur Compounds:

Typical sulfur compounds found in petroleum, coal oil, and shale oil are mercaptans (R-SH), sulfides (R-S-R'), disulfides (R-S-S-R'), and thiophene () (11)

Although shale oils typically contain a high content of nitrogen compounds, the amount of sulfur compounds present in shale oils is comparable with that of crude oil (0.6 percent by weight). (29, 31).

The problems associated with the presence of sulfur compounds in petroleum products have been described previously. Because of these problems it might be of interest to study the distribution of sulfur compounds in the products of steam pyrolysis of shale oil. Part of the sulfur present in the feed-stock becomes converted to hydrogen sulfide and ends up in the gaseous products as has been shown by Griswold (20), Fritzler (7), and Smith (8). The question to answer is how much of the sulfur present in the feed-stock ends up in the gas and what concentration of sulfur the liquid products are expected to have.

In a study performed by Universal Oil Products Company (29), crude oils from seven different sources were catalytically cracked, and the amount of sulfur in each gasoline

was measured. Different cuts of each gasoline was prepared and the amount of sulfur in each cut was quantitatively measured. Effect of conversion, catalyst, reactor temperature, and feed source on the distribution of sulfur compounds were studied.

The results of this study are summarized below:

1. Heavy ends of gasoline contain very high concentrations of sulfur.

2. Sulfur content of gasolines decreases as the conversion is increased.

3. Catalyst type has no effect on the distribution of sulfur compounds.

4. As the reactor temperature is increased, the gasolines produced contained greater amounts of sulfur for a variety of feed-stocks and over a wide range of sulfur contents.

In another study performed by Barron, et al. (31) crude oils from six different sources were thermally cracked, and the amount of sulfur in the gas and bottoms was measured. It was found that the sulfur becomes concentrated in the bottom fraction because, in every case, the sulfur content of the bottom was greater than in the charge stock; in other words, the major proportion of the sulfur originally present in the charge was contained in the bottom fraction. As will be seen later, this is not true for shale oil.

This study showed that conversion has little effect on sulfur distribution. Based on these studies, one would expect to observe the following phenomena concerning the distribution of sulfur compounds in steam pyrolysis of shale oil:

1) Concentration of sulfur compounds in the liquid products should increase with temperature, pass through a maximum, and decrease at higher temperatures (higher conversions).

2) Concentration of sulfur compounds in the liquids should be higher than that of the feed-stock.

3) Shale oils with higher sulfur content should give rise to liquids with higher sulfur concentration.

Effect of Residence Time:

As the reaction time increases, molecules of sulfur compounds spend more time in the reactor, and consequently the probability of a C-S bond rupture becomes higher. Whenever a bond between a carbon and sulfur atom is broken, the chances that the sulfur atom ends-up in the gas phase as H_2S becomes very high. It is therefore expected that concentration of sulfur in the liquids should decrease as residence time is increased.

EXPERIMENTAL EQUIPMENT

A schematic of the bench-scale unit used for pyrolysis of shale oils in this study has been shown in Figure 1. The design of the laboratory pyrolysis system has been previously described by Fritzler (7). The system can be divided into three sections.

- 1) feed system
- 2) reactor system
- 3) condensing and collection system.

Feed System:

Distilled water for generation of steam flows by gravity from two 250 ml. burrets to a Lapp, diaphragm metering pump. It then flows through a 24 inch section of schedule 40, 304 ss pipe which is packed with Coors ceramic balls. The pipe is inside a Lindberg single zone furnace which is connected to a Lindberg single zone controller. The temperature of the furnace can be controlled by the controller in the range of 200-1200°C. The temperature of steam generated inside the pipe is measured at three different locations by means of three type K, 0.04 inch O.D. 316 SS sheathed, grounded

thermocouples. Steam then flows through a one foot section of 1/4 inch 316 SS tubing wrapped with Briskheat heating tape. This section of tubing acts as a steam super-heater and maintains the steam temperature at about 700°F prior to mixing with oil at the reactor inlet. Shale oil is gravity fed to a liquid metronics pump from two 250 ml. burrets, the oil then flows through a section of 1/4 inch SS tubing; part of this section is wrapped with heating tapes which act as an oil preheat. The oil is normally preheated to about 350°F prior to mixing with steam at the reactor inlet. The heating tapes are controlled by 7 1/2-amp. rheostat.

Reactor System:

The reactor is a 14 inch length of 2 inch I.D., 316 SS tubing. The oil and steam mix together about 7 inches above the reactor. The mixture then flows through the reactor where pyrolysis reactions take place. The reactor is packed with 652, 3/8 inch Coors ceramic balls. The balls induce turbulence in the reactor and are also a media for heat transfer to the mixture of steam and oil. A schematic diagram of the reactor is shown in Fig. 2.

The reactor lies inside a Lindberg three zone furnace, which is controlled by means of a Lindberg three zone controller. The furnace temperature can be varied within the range of 200-1200°C.

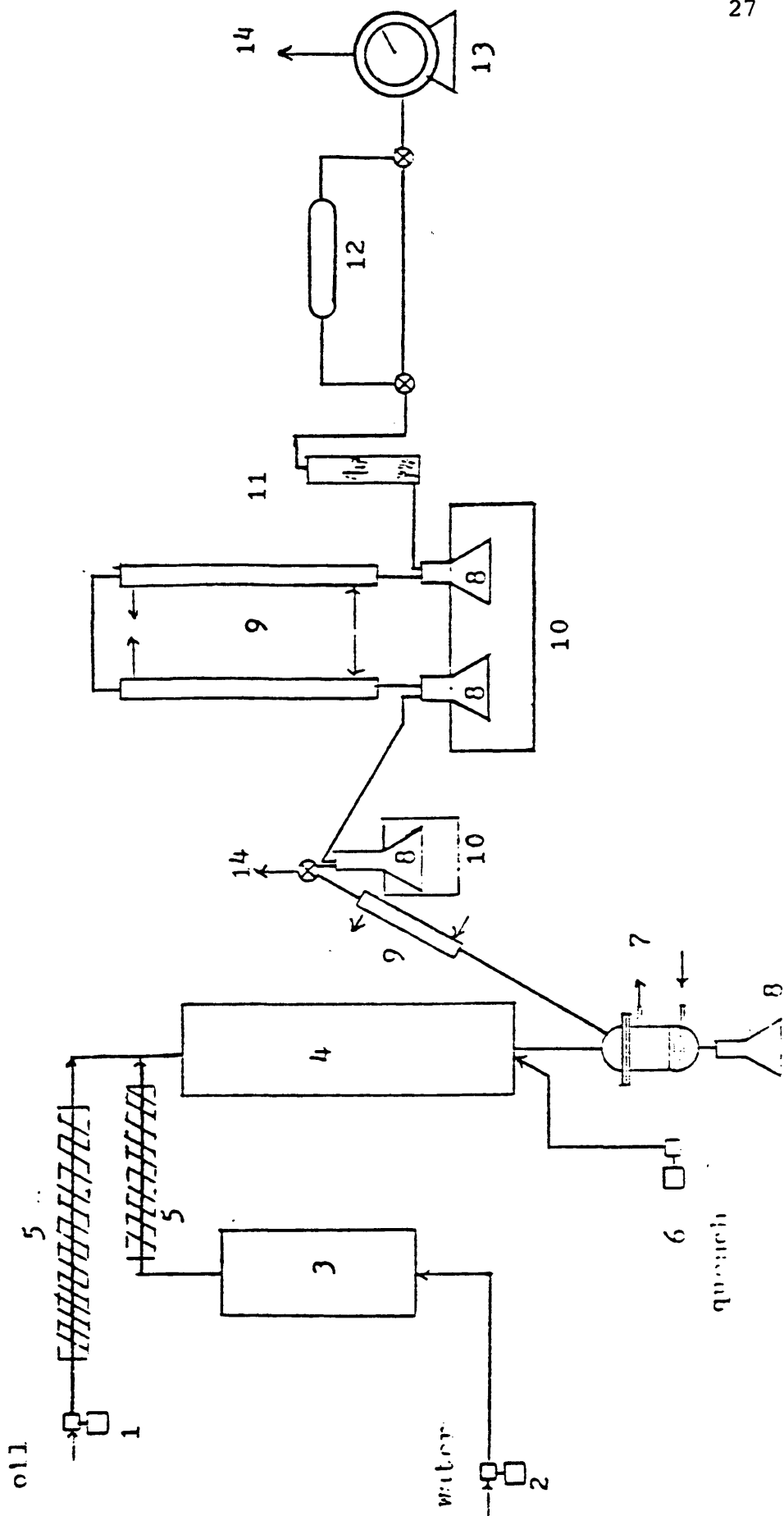


Figure 1. Pyrolysis reaction system

EQUIPMENT DIAGRAM LEGEND

1. Liquid Metronics Pump
2. Lapp pump
3. Single zone Lindberg furnace
4. Three zone Lindberg furnace
5. Heating tape
6. Centrifugal pump
7. Surge tank
8. Liquid collection flask
9. Chilled water condenser
10. Ice water bath
11. Glass wool filter
12. Sample bomb
13. Wet test meter
14. Vent

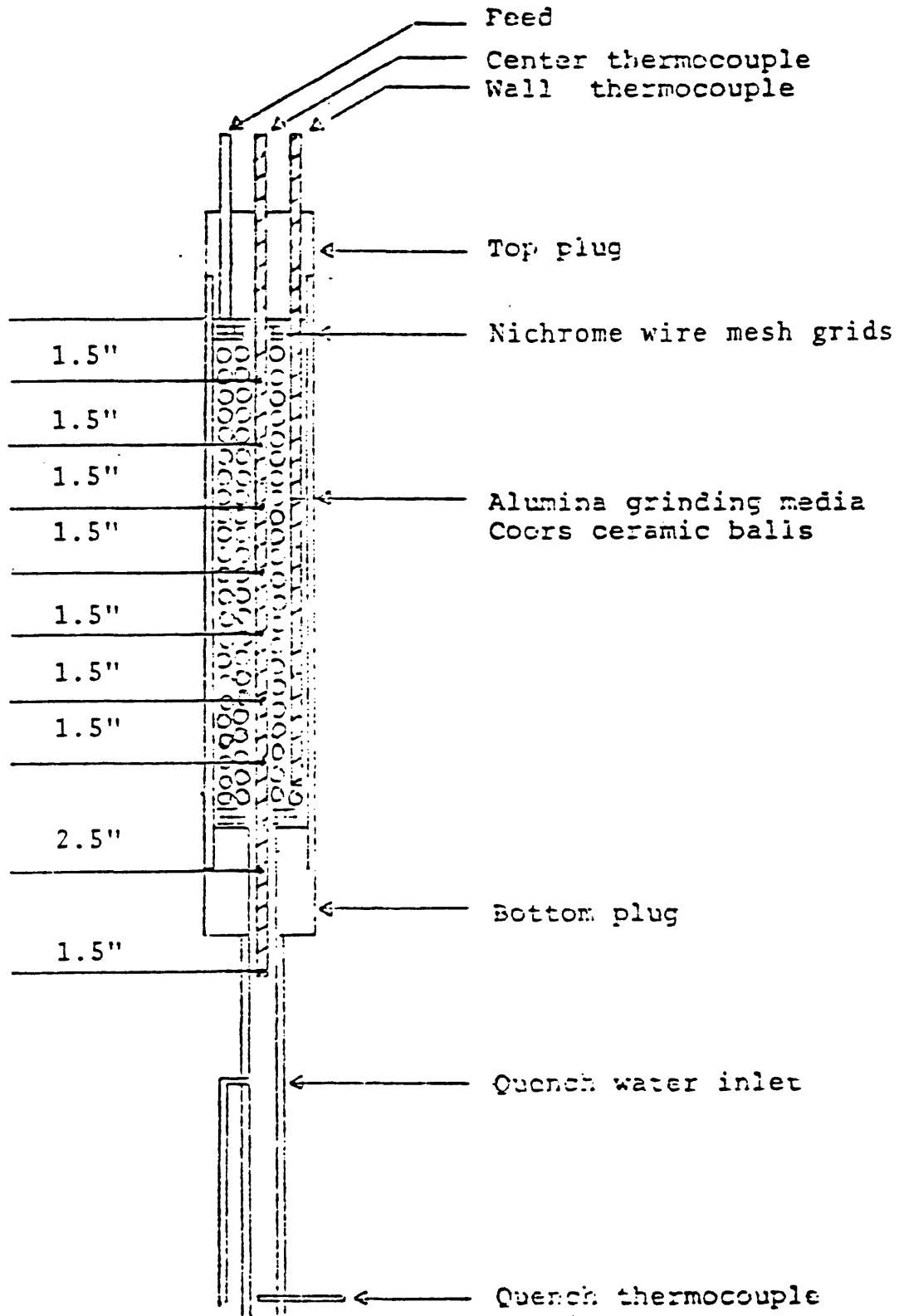


Figure 2. Cutaway view of reactor

Temperatures inside the reactor are measured by means of nine type K, 0.04 inch O.D., 316 SS sheathed, grounded thermocouples. These thermocouples are connected to an Omega automatic scanner and an Omega digital indicator.

The products flow out of the reactor through a piece of 1 inch I.D. 316 SS tubing where they meet the quench water which cools them down and consequently some of the heavier compounds condense at this stage. The products then flow to a surge tank, where the first gas-liquid separation takes place.

The quench water is gravity fed from a 250 ml. buret to a centrifugal pump. The quench water enters the 1 inch tube 3 inches below the bottom of reactor. The quench water flow rate is controlled by means of a Brooks rotameter.

Condensing and Collection System:

As mentioned before, the first gas-liquid separation takes place inside the surge tank. The liquid products condensed in the surge tank are collected in an Erlenmeyer flask located below the surge tank. The gases then pass through a double pipe heat exchanger where they are further cooled down. The liquid products obtained in the heat exchanger flow back to the surge tank. The heat exchanger has 1/2 inch diameter galvanized steel pipe shells with 1/4 inch, 316 SS tubing inside, through which the gases pass. The gases then pass through a series of Erlenmeyers located in ice baths. These

flasks act as both a condensing and collection system. After passing through a double pipe heat exchanger and a filter to remove any traces of entrained liquids, the gases are metered by a Precision Scientific Wet Test meter. At this point gas samples are collected in 316 SS flow-through bombs. One 300 ml. bomb and one 1000 ml. bomb are collected during each run.

The liquid products obtained in collection system are prepared for analysis by a procedure which will be explained in a different section. The liquid products are distilled by a Precision Scientific Distillation Unit. After a series of Distillation and Centrifugation, the liquids are analyzed for benzene, toluene, and xylene content.

The gaseous products are analyzed by a Carle-Model III Analytical Gas Chromatograph equipped with a series-bypass switching option. The chromatograph and its operational procedure has been described by Smith (8).

EXPERIMENTAL PROCEDURE

This section can be divided into four parts:

- a) Experimental procedure for preparation and operation of the pyrolysis unit.
- b) Operation of the gas chromatograph.
- c) Preparation of liquid products for BTX analysis.
- d) Preparation of liquid products for elemental analysis.

a) The experimental procedure for preparation and operation of the pyrolysis unit has been previously described by Fritzler (7) and Smith (8). It will be mentioned here very briefly.

Prior to each run, the reactor shell, nichrome grids, surge tank, and ceramic balls are weighed. The reactor is then put in the three zone furnace, and the desired temperature of operation is set on the three zone controller. After the system reaches the desired temperature, the single zone furnace is turned on and the flow of water is started; steam super-heater is also turned on at this point. After the steam reaches a temperature of about 700°F, the system is ready for the experimental run. The amount of water and oil

in the burrets are recorded and the flow of oil is then started. After about 20 to 30 minutes, when the system reaches steady state, a gas sample is taken for analysis. The system can be shut down shortly after the gas sample has been taken.

The amount of shale oil and steam flow into the system during the run are recorded at this point, and the system is allowed to cool down. The reactor shell, ceramic balls, and nichrome grids are weighed after each run to determine the amount of coke laydown. The amount of gaseous products produced during the run is also recorded after each run.

b) The procedure for operation of the gas chromatograph has been discussed by Smith and will not be mentioned here.

c) Preparation of liquid products for BTX analysis: Liquids from steam pyrolysis of shale oil are relatively heavy and viscous with a pour point, normally above room temperature. Since a direct water-quench is used at the exit of the reactor to stop the pyrolysis reactions, the liquid products contain relatively large amounts of water which has to be separated before further analysis can be carried out. Some of this water forms a two-phase mixture with the liquid hydrocarbons and can easily be separated. The rest of the water, however, forms an emulsion with the liquid

hydrocarbons. Distillation was used to separate as much water as possible. Since we are interested in obtaining data which would relate the original feed and BTX found in the liquids quantitatively, extensive weighing was required in every step of the analysis.

The outline of the procedure that was used follows:

(1) All of the liquids obtained in the condensing system were weighed and poured into a single flask. After approximately one hour, a water phase appears on the top which can be separated. This water has been saved for further analysis (denoted as "water from surge tank").

(2) The remaining liquid from step (1) was completely mixed and about 100 ml. was poured into a 150 ml. distilling flask which had previously been weighed. The weight of the sample was obtained by difference. Boiling chips were added for smooth boiling. The sample was distilled using an ASTM distillation apparatus. A 600°F cut was obtained and weighed. We refer to this step as "Primary Distillation" and the distillate was called "Initial Product." At the end of the "Primary Distillation," the distilling flask was reweighed to obtain the amount of residue.

(3) The distillate from step (2) contains relatively large amounts of water. Centrifugation was used, at this point, to separate the water and hydrocarbons into different phases.

After about 45 minutes, a two, and for some runs three, phase mixture is obtained. Since the water phase is either in the lower or middle phase, a syringe is used to pull the water out. This water has been called "distillate water" and it has been weighed and retained for all runs.

(4) A recentrifugation similar to step (3) is carried out at this point.

(5) Since the primary distillation ended at 600°F, there are some heavy ends present in the liquid. These would interfere with the xylene peak in a liquid chromatograph. The liquid at this point is redistilled and a 400°F naphta cut is obtained. This step is called "redistillation" and the distillate called "Final Product" which is ready for BTX analysis.

The BTX analysis has been performed by the TOSCO Corporation by liquid chromatography methods.

d) The liquid products of steam pyrolysis of five simulated in-situ vacuum distillates and four Tosco vacuum distillates were prepared for carbon, hydrogen, nitrogen, and sulfur analysis. The method of preparation of these samples was as follows:

The liquids collected in different parts of the condensing system are poured into a single flask. Rigorous shaking is applied to ensure proper mixing and uniformity of sample.

After about one hour a two phase mixture will be observed; the top phase is entirely water and can easily be separated. The bottom phase is a mixture of hydrocarbons and water in the form of emulsion. This sample then was sent to Colorado School of Mines Research Institute for elemental analysis.

In order to examine the distribution of sulfur and nitrogen in the liquid products of the whole oils, a sample of the liquid products from steam pyrolysis of a Tosco II whole oil and a simulated in-situ whole oil were prepared by the above procedure. Also two cuts of the simulated in-situ whole oil were prepared by distillation.

RESULTS AND DISCUSSION

This section is divided into two parts:

a) Presentation and discussion of results of BTX Analysis of liquid products of steam pyrolysis of shale oil.

b) Presentation and discussion of results of elemental analysis on the liquid products of steam pyrolysis of shale oil.

a) Results of BTX Analysis:

A total of eight liquid samples were selected for BTX Analysis. As mentioned before, residence time is believed to be the controlling factor in aromatic formation during pyrolysis of hydrocarbons. Due to this reason, the selection of the samples was based on variation of residence time. The BTX analysis was performed by Tosco Corporation. Appendix Tables A1 and A2 show the results of mass balances for the whole oils and vacuum distillates, respectively. Appendix Table A3 shows the results of mass balances obtained during the preparation of liquid samples for BTX analysis.

In order to minimize the amount of losses, the decision was made to stop the distillation at the primary stage, and obtain a cut in the range of 350 to 400°F. The procedure for this step has previously been described. Using Table 1 in conjunction with the data presented in Appendix Tables A1 through A3. The amount of BTX per unit weight of shale oil fed into the system can be calculated. These results are summarized in Table 2. A sample calculation can be found in the appendix. Figures 3 and 4 show the yield of different gaseous products obtained from steam pyrolysis of shale oil as a function of contact time. These figures have been reproduced from the data of Fritzler (7) and Smith (8), respectively. The purpose of showing these figures here is a qualitative support of formation of aromatics by a Diel-Alder type reaction (already discussed in the theory and experimental basis section). This mechanism states that aromatics are formed by reaction between an olefin and butadiene. However, the reaction involves several elementary steps and requires a certain amount of time for completion. On the other hand, if the reaction is given too much time, the mono-aromatics formed will polymerize into polyaromatics.

As can be seen from Figure 3 and 4, yield of butadiene and total olefins decrease as the reaction time increases, indicating that butadiene and olefins indeed may react

Table 1

BTX Analytical Results

Run No.	Temp. °F	Residence Time Sec.	Water Separated MI	Naphtha MI	Benzene Wt. % of Naphtha	Toluene Wt. % of Naphtha	Xylene Wt. % of Naphtha	Type of Oil
8	1592	0.271	0.3	0.6	0	0	1.1	TOSCO whole
16	1525	0.400	1.8	3.3	0	2.8	7.1	NTU whole
17	1525	1.222	0.7	3.6	0.4	1.4	5.4	NTU whole
18	1515	0.683	4.7	4.5	0	2.2	10.9	NTU whole
4-D	1522	1.124	2.3	0.9	0	0	0.4	NTU Vac. Dis.
8-D	1518	0.174	21.0	13.0	3.2	7.8	7.2	NTU vac. Dis.
15-D	1530	0.937	32.0	3.0	0	0	3.8	TOSCO Vac. Dis.
19-D	1501	0.186	75.0	8.0	1.1	5.7	11.7	TOSCO Vac. Dis.

TABLE 2. BTX YIELDS

Run No.	G R A M S				Reaction Time Sec.	Temp °F
	Benzene Per 100 gm of Shale Oil	Toluene Per 100 gm of Shale Oil	Xylene Per 100 gm of Shale Oil	Tot. BTX Per 100 gm of Shale Oil		
8	0	0	0.0106	0.0106	0.271	1592
16	0	0.11	0.29	0.4	0.400	1525
17	1.96×10^{-2}	6.88×10^{-2}	0.265	0.354	1.222	1525
18	0	0.13	0.64	0.77	0.683	1515
4-D	0	0	0.01	0.01	1.124	1522
8-D	0.45	1.10	1.02	2.57	0.174	1518
15-D	0	0	0.29	0.29	0.937	1530
19-D	0.119	0.616	1.26	2.0	0.186	1501

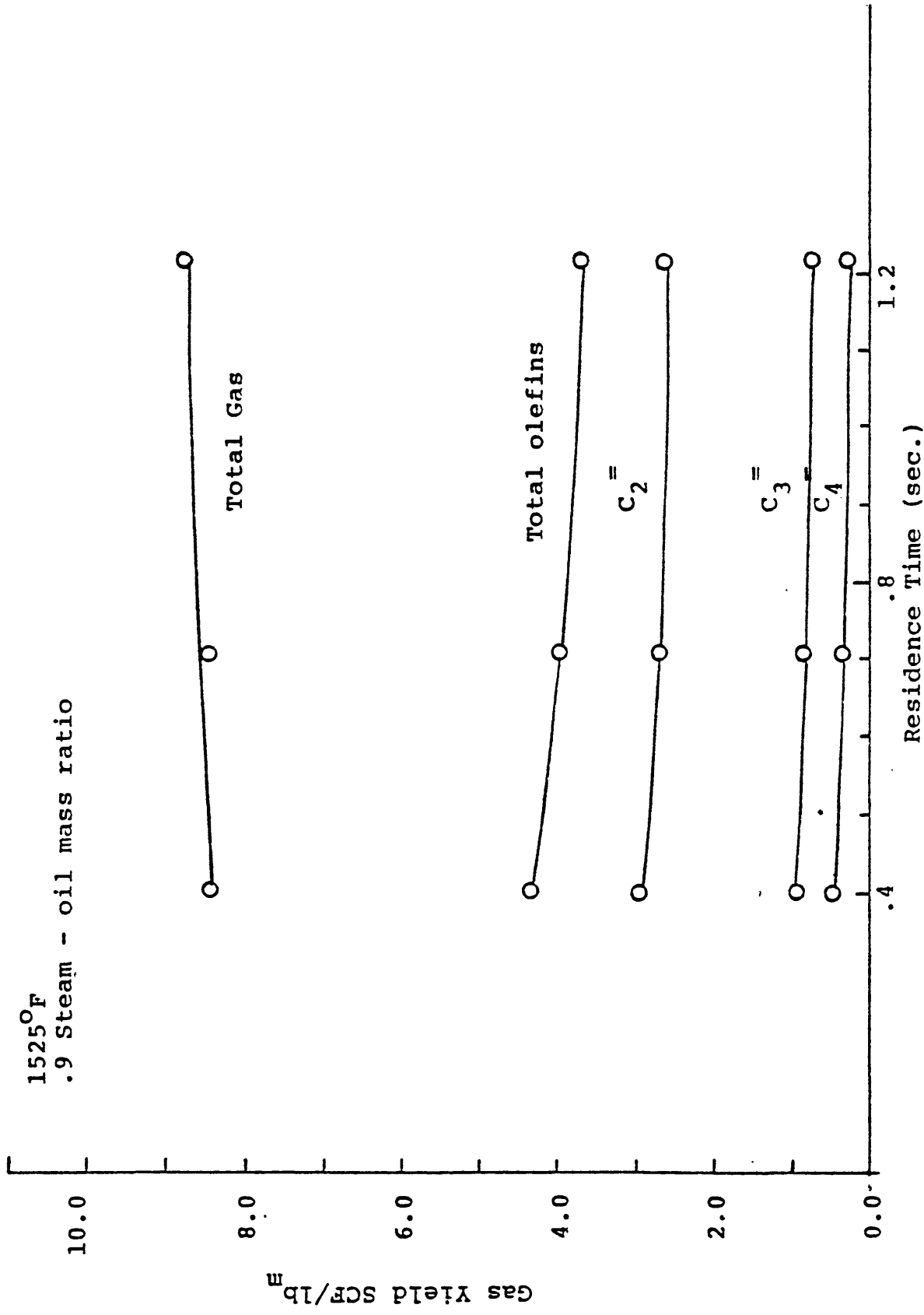


Figure 3. Effect of residence time on volumetric gas yields for NTU oil

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○ = Ethylene

△ = Propylene

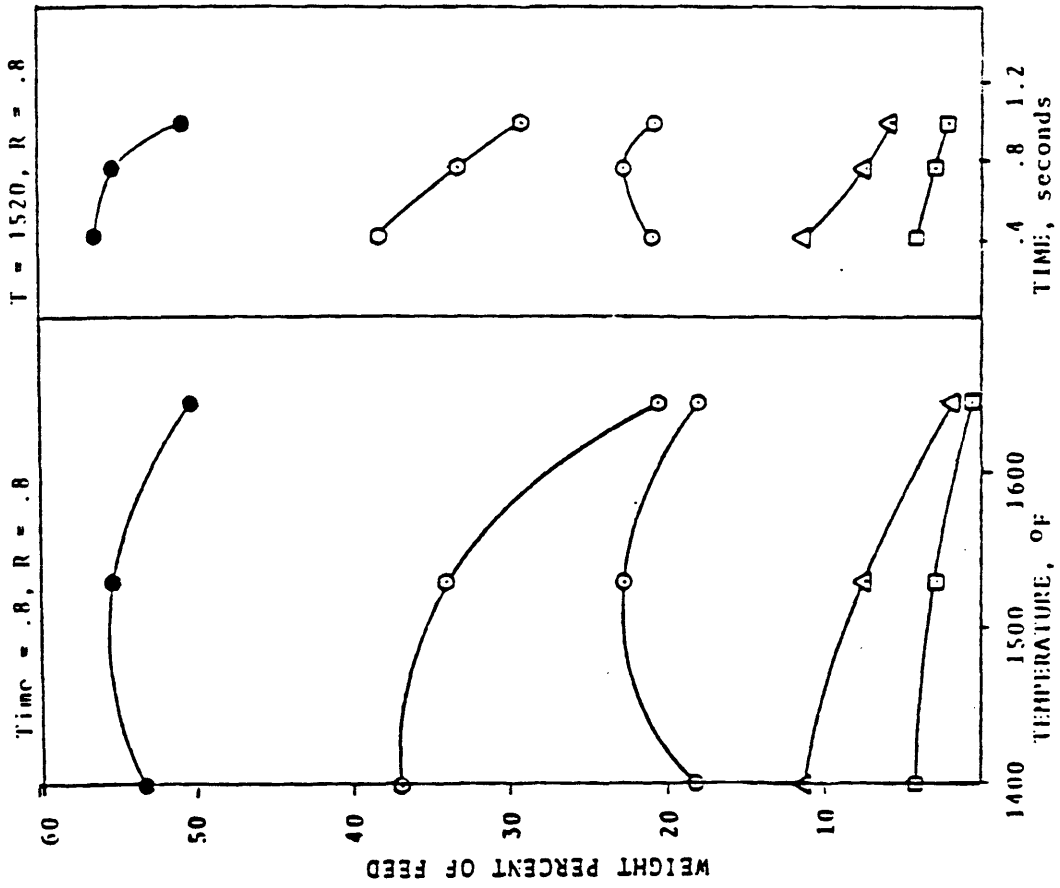
◻ = 1,3 Butadiene

○ = Total Olefins

● = Total Gas

Figure 4. TOSCO II

DISTILLATE: Effects
of Operating Variables



with each other to form aromatics. So, on chemical grounds it is expected that the yield of BTX should increase as the contact time increases. However, a study of Table 2 and comparison of runs 16, 17, and 18 reveals the fact that the yields of toluene, xylene, and total BTX go through a maximum for the range of reaction times investigated. The data has been plotted in Fig. 5.

This also supports the theory of formation of aromatics by a Diels-Alder type reaction during pyrolysis of shale oil. A possible reason for the drop in yield of BTX at higher reaction times may be that the monoaromatics formed initially undergo polymerization as they are given more and more time.

Further inspection of Table 2 reveals the following facts:

1. Negligible amounts of benzene were obtained for the whole oil samples tested, both BTU and TOSCO.

A comparison of runs number 8 and 19-D indicates that vacuum distillation increases BTX formation. These two runs are for Tosco II crude oil and Tosco II vacuum distillate, respectively, and both have been performed at a relatively short reaction time. Comparison of runs 16 and 8-D reveals the same fact for NTU oil. Runs 4-D and 8-D are NTU vacuum distillate performed at long and short reaction times, respectively. Based on the discussion above, it is expected that BTX concentration would reach a maximum at moderate reaction times and then would drop to a low value due to further

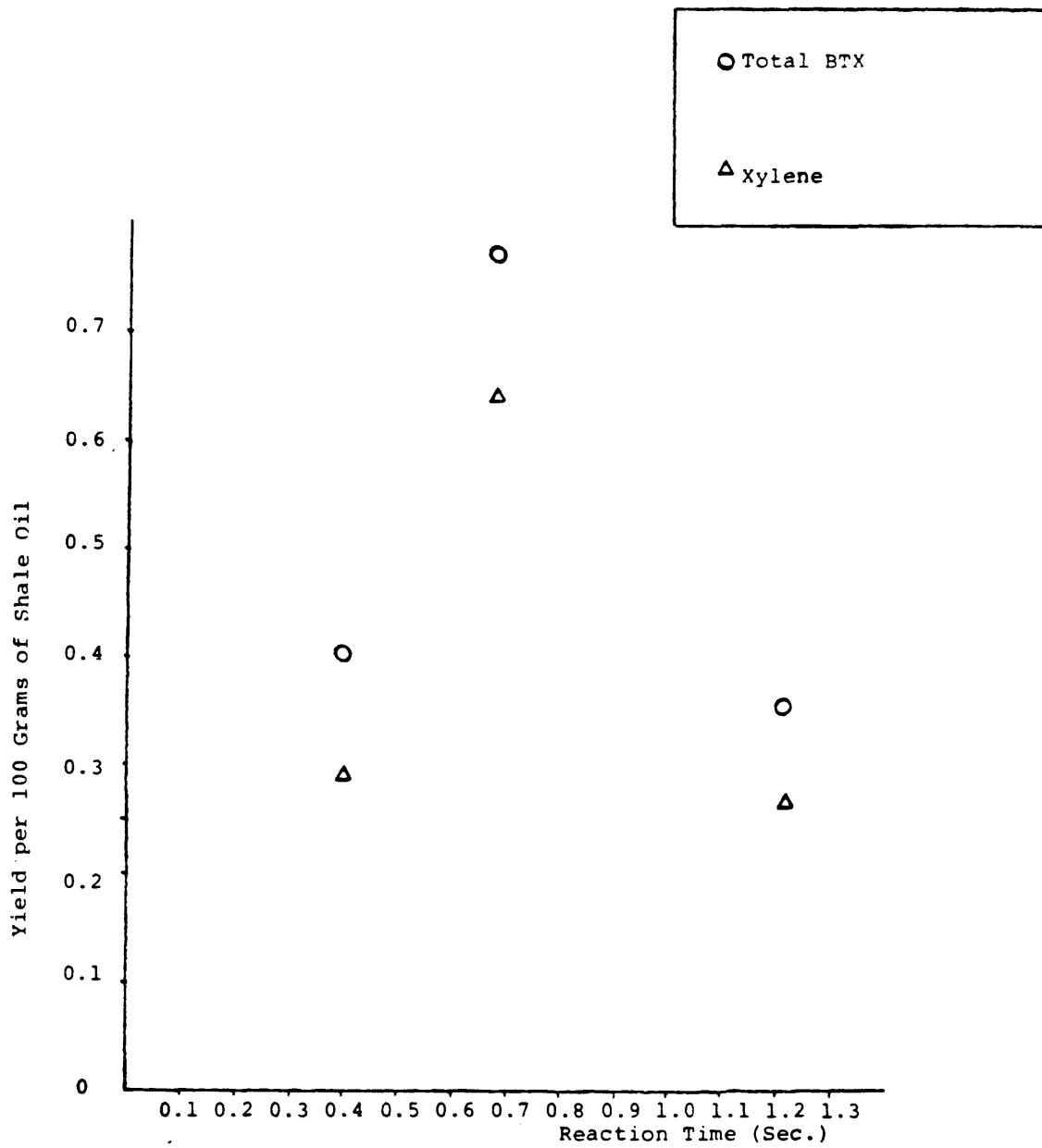


Figure 5. Effect of Reaction Time on Xylene and Total BTX Yield.

reactions which convert light aromatics to heavy poly-aromatics.

3. As can be seen from the data presented in Table 2 steam pyrolysis of shale oil under the conditions used in this study does not produce an appreciable amount of BTX. For most of the runs, the amount of BTX obtained is almost negligible. The maximum amount of BTX obtained is 2.57 grams per 100 grams of shale oil. There is a possibility that a significant quantity of naphthalene and heavier aromatics are formed.

b) Results of Elemental Analysis:

This section is divided into three sub-sections:

- 1) Discussion of results obtained on sulfur analysis.
- 2) Discussion of results obtained on nitrogen analysis.
- 3) Discussion of results obtained on carbon and hydrogen analysis.

1) Results of Sulfur Analysis

Physical properties, distillation data, and the results of elemental analysis on the shale oils used in this study are shown in Table 3. Table 4 presents a summary of the runs for which the liquid products were selected for analysis. Table 5 shows the results of sulfur analysis on the liquid products. The analysis has been performed by the Colorado School of Mines Research Institute.

TABLE 3.

CHARACTERIZATION OF
SHALE OIL FEEDSTOCKS

PROPERTY	TOSCO II		Simulated in situ	
	Crude Oil	Vac. Dist.	Crude Oil	Vac. Dist.
Specific gravity @ 60°F	0.9335	0.8883	0.9054	0.8789
API gravity	20.0°	27.7°	24.7°	29.5°
Volume % Distilled				
Boiling Point (°F)				
IBP	168°F	164°F	256°F	240°F
100	-----	-----	-----	-----
200	1	2	0.1	-----
300	6	12	1	3
400	15	26	9	15
500	26	44	23	35
600	38	62	38	56
700	50	75	55	72
800	61	86	71	85
900	73	93	85	93
1000	82	95	92	95
% Residuum	18	5	8	5
TOTAL	100	100	100	100
Elemental Analysis (weight %)				
C	84.69	84.74	83.94	84.35
H	10.72	11.76	11.59	12.15
O	1.45	0.83	1.22	1.24
N	1.85	1.57	1.49	1.59
S	0.85	0.63	0.63	0.78
C/H	7.9	7.2	7.24	6.94
Basic N	0.18	0.36	0.21	0.27

Table 4

Runs Selected for Elemental Analysis

<u>Run</u>	<u>Residence (sec) Time</u>	<u>Temperature °F</u>	<u>Corrected Residence Time</u>	<u>Type of Oil</u>
2-D	0.7498	1598	0.536	NTU-Distillate
4-D	1.1435	1522	1.002	NTU-Distillate
8-D	0.3725	1518	0.174	NTU-Distillate
1-D	0.7288	1499	0.370	NTU-Distillate
12-D	0.7531	1397	0.563	Tosco-Distillate
9-D	0.7518	1544	0.401	NTU-Distillate
14-D	0.8375	1644	0.697	Tosco-Distillate
13-D	0.7532	1528	0.612	Tosco-Distillate
19-D	0.4068	1501	0.186	Tosco-Distillate
12-W	0.7180	1528	0.447	Tosco-Whole
18-W	0.6830	1515	0.1947	NTU-Whole (head)
18-W	0.6830	1515	0.1947	NTU-Whole 200 ⁻ °C
18-W	0.6830	1515	0.1947	NTU-Whole 200 ⁺ °C
15-D	0.9370	1530	0.9373	Tosco-Distillate

Table 5

Results of Sulfur Analysis on the Liquid Products

<u>Run</u>	<u>Wt. % Sulfur</u>	<u>Type of Oil</u>
2-D	0.70	NTU-Distillate
4-D	0.59	NTU-Distillate
8-D	0.89	NTU-Distillate
1-D	0.96	NTU-Distillate
12-D	1.10	Tosco-Distillate
9-D	0.82	NTU-Distillate
14-D	0.78	Tosco-Distillate
13-D	0.74	Tosco-Distillate
19-D	0.79	Tosco-Distillate
12-W	0.79	Tosco-Whole
18-W	0.93	NTU-Whole (head)
18-W	0.84	NTU-Whole (+200°C)
18-W	1.03	NTU-Whole (-200°C)
15-D	0.85	Tosco-Distillate

Sulfur analysis has been done by Colorado School of Mines Research Institute by Calorimeter Bomb Wash method.

Using Tables 3 through 5 together with the data of Appendix Tables A1 and A2 (results of mass balances for the whole oils and vacuum distillates), Table 6 can be constructed.

This table shows the amount of sulfur present in the feed and also in the liquid products; the difference is assumed to have been converted to H_2S or to be present in the coke. A sample calculation can be found in the Appendix.

Study of Table 6 reveals the following facts:

1. Effect of temperature on the concentration of sulfur in the liquid products can be seen by comparing runs 2-D, 1-D, and 9-D for the NTU oil, and runs 12-D, 13-D, and 14-D for the Tosco oil. The sulfur concentration for these runs has been plotted vs. temperature in Fig. 6. As can be seen, for both oil, the concentration of sulfur in the liquid product decreases with pyrolysis temperature. As the reactor temperature increases, the probability of a C-S bond rupture becomes higher, and every time the bond between a sulfur and a carbon atom is broken, the chances that the sulfur atom reacts with hydrogen and forms hydrogen sulfide becomes relatively high. Therefore, on theoretical grounds, one would expect that the concentration of sulfur in liquids should decrease with temperature at a constant reaction time.

2. Comparison of runs 4-D, 8-D, and 9-D for the NTU oil, and runs 13-D, and 19-D for the toscos oil indicates that at

Table 6
Results of Sulfur Analysis on the Liquid Products of Steam
Pyrolysis of Shale Oil

RUN	Residence time (sec.)	Temp. °F	Wt. % Sulfur		Amount of sulfur		Ratio of sulfur in liquid to sulfur in feed	Type of Oil
			in feed	in liquid	in feed	in liquid		
			gms	gms	gms	gms		
2-D	0.7498	1598	0.78	0.70	1.22	0.46	0.38	NTU-Distillate
4-D	1.1435	1522	0.78	0.59	0.83	0.24	0.29	NTU-Distillate
8-D	0.3725	1518	0.78	0.89	2.78	1.11	0.40	NTU-Distillate
1-D	0.7288	1499	0.78	0.96	2.38	1.32	0.56	NTU-Distillate
9-D	0.7518	1544	0.78	0.82	2.27	0.99	0.44	NTU-Distillate
12-D	0.7531	1397	0.63	1.10	1.51	1.15	0.76	Tosco-Distillate
13-D	0.7532	1528	0.63	0.74	1.13	0.50	0.44	Tosco-Distillate
14-D	0.8375	1644	0.63	0.78	1.01	0.47	0.47	Tosco-Distillate
15-D	0.9370	1530	0.63	0.85	0.70	0.36	0.52	Tosco-Distillate
19-D	0.4068	1501	0.63	0.79	2.32	1.11	0.48	Tosco-Distillate
12-W	0.7180	1528	0.85	0.79	1.46	0.66	0.45	Tosco-Whole
18-W	0.6830	1515	0.83	0.93	3.43	1.66	0.48	NTU-Whole (head)
18-W	0.6830	1515	0.83	0.84				NTU-Whole (+200°C)
18-W	0.6830	1515	0.83	1.03				NTU-Whole (-200°C)

Sulfur Analysis has been done by Colorado School of Mines Research Institute using
"Calorimeter Bomb Wash" method.

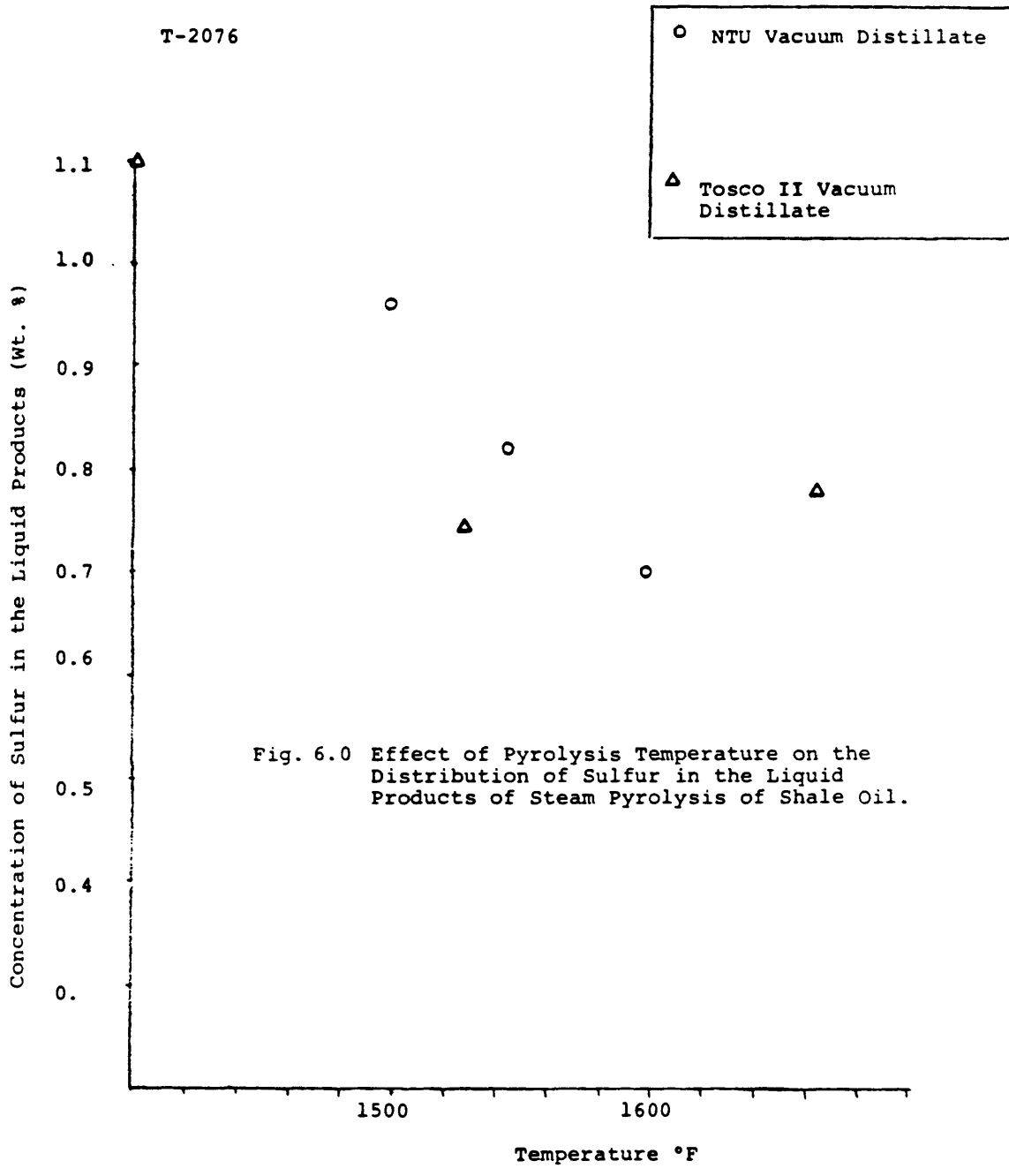


Fig. 6.0 Effect of Pyrolysis Temperature on the Distribution of Sulfur in the Liquid Products of Steam Pyrolysis of Shale Oil.

a constant temperature, the concentration of sulfur in the liquid products passes through a maximum as the reaction time increases. The data has been plotted in Fig. 7.

3. Study of runs 18-W in Table 6 shows that the concentration of sulfur in the heavier cut (+200°C) is less than the lighter cut (-200°C). This indicates that most of the compounds present in the NTU-oil boil at a temperature lower than 200°C.

4. The last column of Table 6 shows the ratio of weight of sulfur present in the liquid to the weight of sulfur present in the feed. For most of the runs, this ratio is in the neighborhood of 0.5 indicating that almost half of the sulfur present in the feed ends-up in the liquid products, and the other half becomes converted to H₂S or ends up in the coke.

5. It can be seen from Table 6 that the concentration of sulfur in the liquids is generally higher than the feed. In other words, sulfur becomes concentrated in the liquid products.

2. Results of Nitrogen Analysis:

Results of nitrogen analysis have been shown in Table 7. The analysis has been done by Colorado School of Mines Research Institute using "Kjeldahl-Gunning" method. Using Table 7 in conjunction with the data of Appendix Tables A1 and A2 (results of mass balances for the whole oils and vacuum distillates), Table 8 can be constructed. A sample calculation can be found in the appendix.

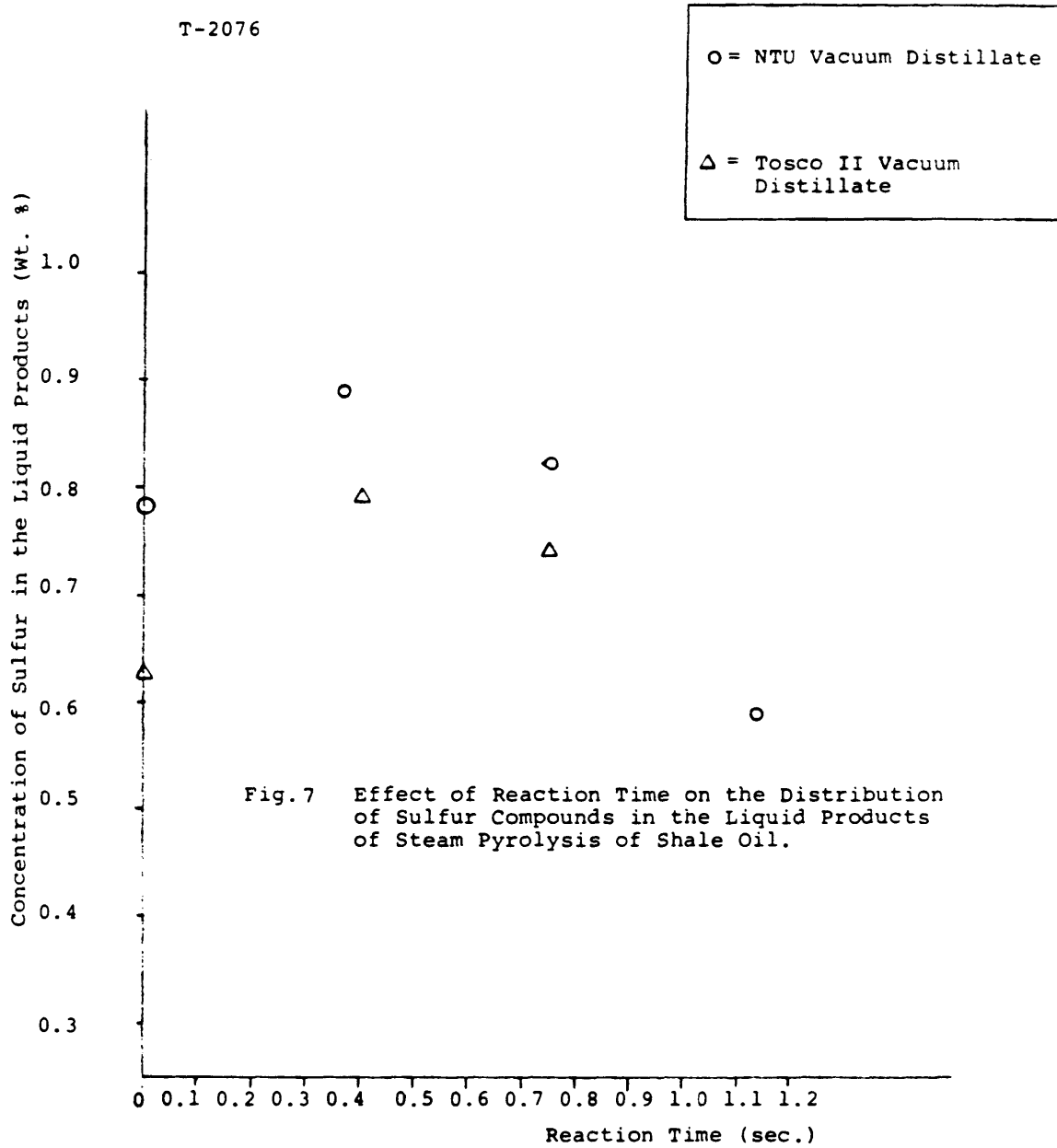


Table 7

Results of Nitrogen Analysis on the Liquid Products

<u>Run</u>	<u>Wt. % N₂</u>	<u>Type of Oil</u>
2-D	2.39	NTU-Distillate
4-D	1.49	NTU-Distillate
8-D	1.81	NTU-Distillate
1-D	2.44	NTU-Distillate
12-D	1.86	Tosco-Distillate
9-D	2.38	NTU-Distillate
14-D	2.03	Tosco-Distillate
13-D	1.95	Tosco-Distillate
19-D	0.98	Tosco-Distillate
12-W	2.00	Tosco-Whole
18-W	4.16	NTU-Whole (head)
18-W	2.51	NTU-Whole (+200°C)
18-W	1.38	NTU-Whole (-200°C)
15-D	2.29	Tosco-Distillate

Nitrogen Analysis has been done by Colorado School of Mines Research Institute by "Kjeldahl-Gunning Method."

Table 6
Distribution of Nitrogen in the Liquid Products of Steam Pyrolysis of
Shale Oil

Run	Residence time (sec.)	Temp. °F	Wt. % Nitrogen in feed	Wt. % Nitrogen in liquid	Amount of N ₂ in feed (gm.)	Amount of N ₂ in liquid (gm.)	(N ₂) Feed (N ₂) Liquid	Type of Oil
2-D	0.7498	1598	1.59	2.39	2.49	1.57	0.63	NTU-Distillate
4-D	1.1435	1522	1.59	1.49	1.70	0.61	0.36	NTU-Distillate
8-D	0.3725	1518	1.59	1.81	5.66	2.26	0.40	NTU-Distillate
1-D	0.7288	1499	1.59	2.44	4.86	3.34	0.69	NTU-Distillate
9-D	0.7518	1544	1.59	2.38	4.63	2.89	0.68	NTU-Distillate
12-D	0.7531	1397	1.57	1.86	3.75	1.95	0.52	Tosco-Distillate
14-D	0.8375	1644	1.57	2.03	2.51	1.23	0.49	Tosco-Distillate
13-D	0.7532	1528	1.57	1.95	2.82	1.31	0.47	Tosco-Distillate
19-D	0.4068	1501	1.57	0.98	5.79	1.38	0.24	Tosco-Distillate
15-D	0.9370	1530	1.57	2.29	1.74	0.97	0.56	Tosco-Distillate
12-W	0.7180	1528	1.85	2.00	3.18	1.68	0.53	Tosco-Whole
18-W	0.6830	1515	1.49	4.16	6.17	--	--	NTU-Whole (head)
18-W	0.6830	1515	1.49	2.51	--	--	--	NTU-Whole (+200°C) ⁵
18-W	0.6830	1515	1.49	1.38	--	--	--	NTU-Whole (-200°C)

The following conclusions can be drawn by studying Table 8:

1. Comparison of runs 2-D, 1-D, and 9-D for the NTU oil, and runs 12-D, 13-D, and 14-D, for the Tosco oil, indicates that temperature has little effect on the concentration of nitrogen in the liquid products. Nitrogen concentration in the liquids, slightly decreases for the NTU oil, and slightly increases for the Tosco oil. The results have been plotted in Fig. 8. This difference in behavior between the liquid products obtained from NTU oil and from Tosco II oil, could be attributed to the difference in the nature of nitrogen compounds in the two oils. The average temperature in a simulated in-situ process is lower than the average temperature of a Tosco retorting unit. Therefore on physical grounds, one would expect that a Tosco II oil should carry more heavier ends than the oil obtained by a simulated in-situ process. For example, if the nitrogen compounds of a simulated in-situ oil are of the amine or amide types, and that of a Tosco II oil are of the quinoline or indole types, the behavior that each oil shows with temperature is the one which is expected.

2. By comparing runs 4-D, 8-D, and 9-D in Table 8, it can be seen that at a nearly constant temperature, the concentration of nitrogen in the liquid products increases with reaction time, passes through a maximum, and then decreases

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○ = NTU Vacuum Distillate

△ = Tosco II Vacuum Distillate

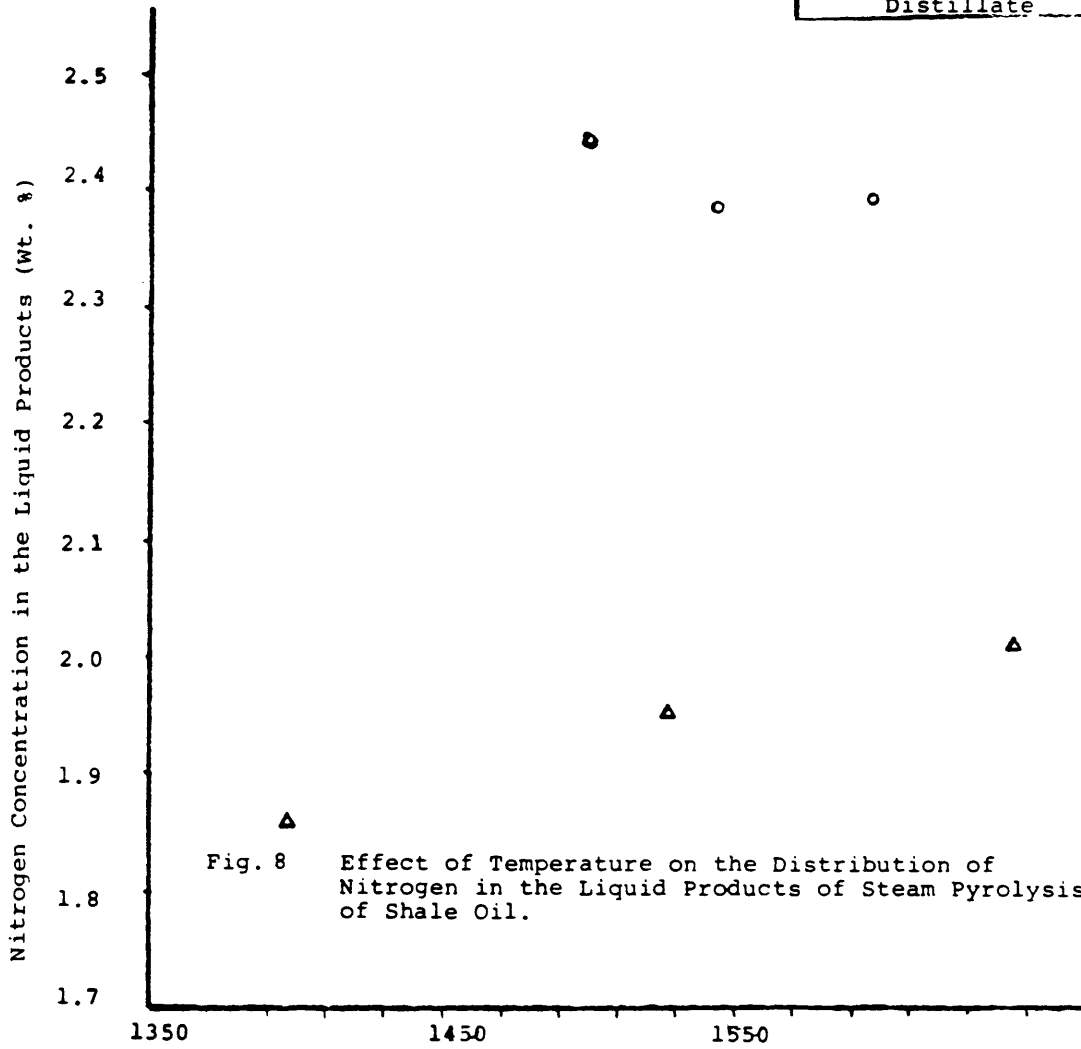


Fig. 8 Effect of Temperature on the Distribution of Nitrogen in the Liquid Products of Steam Pyrolysis of Shale Oil.

at higher reaction times. These runs have been obtained by pyrolysis of a simulated in-situ shale oil. Comparison of runs 13-D, and 15-D, in Table 8 which have been obtained by pyrolysis of a Tosco II shale oil, indicates that at a constant temperature, the concentration of nitrogen increases with the reaction time for the range studied. The results have been shown in Fig. 9. It is expected that for Tosco II oil at longer reaction times, the concentration of nitrogen in the liquid products would decrease; as longer residence times would cause secondary reactions to occur, and this in turn contributes to an increase in the hydrocarbon part of the liquid products and consequently a decrease in the overall concentration of nitrogen in the liquids.

3. It can also be seen from Table 8 that nitrogen becomes concentrated in the liquid products. For almost all runs, the concentration of nitrogen in the liquids is higher than that of the feed. Run 4-D has been made at a relatively long reaction time, and consequently secondary reactions cause the concentration of the hydrocarbon part of the liquids to go up; this in turn decreases the over-all concentration of nitrogen in the liquids.

4. By studying runs 18-W in Table 8, it can be seen that most nitrogen compounds present boil at a temperature higher than 200°C. This indicates that nitrogen compounds present in liquids have relatively high molecular weight.

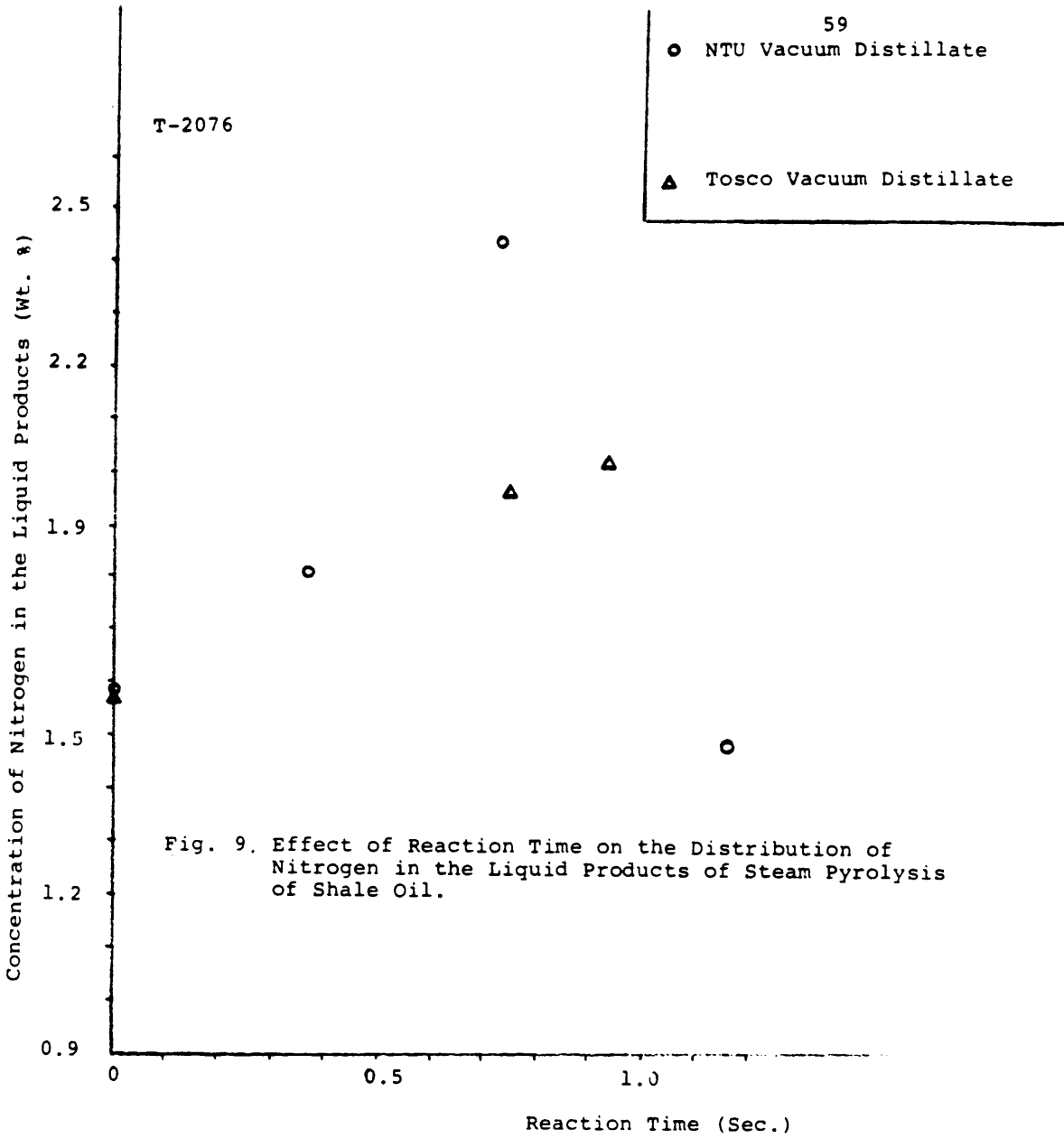


Fig. 9. Effect of Reaction Time on the Distribution of Nitrogen in the Liquid Products of Steam Pyrolysis of Shale Oil.

5. Last column of Table 8 shows the ratio of the amount of nitrogen in the liquid to that of the feed. As can be seen, considerable amounts of nitrogen, originally present in the feed, ends-up in the gas phase or coke. It is possible that some of the feed nitrogen becomes converted to ammonia.

3) Results of Carbon and Hydrogen Analysis:

Results of carbon and hydrogen analysis on the liquid products of steam pyrolysis of shale oil are shown in Table 9. The analysis has been done by "Colorado School of Mines Research Institute" using "Combustion Furnace" method. Using this table in conjunction with Appendix tables reproduced from the data of Fritzler (7) and Smith (8), Table 10 can be constructed. From Table 10, one can observe the following:

1. Comparison of runs 2-D, 1-D, and 9-D indicates that the carbon to hydrogen ratio of the liquid products, obtained by pyrolysis of a simulated in-situ shale oil, increases with temperature at a constant reaction time. Comparison of runs 12-D, 13-D, and 14-D reveals the same fact for liquid products obtained by pyrolysis of a Tosco II vacuum distillate. An increase in the carbon to hydrogen ratio for the liquid is accompanied by a decrease in the carbon to hydrogen ratio of the gas. The results have been shown in Fig. 10.

By comparing runs 8-D, 1-D, and 9-D, it can be seen that the carbon to hydrogen ratio of the liquids obtained by pyrolysis of a simulated in-situ vacuum distillate, increases

Table 9

Results of Carbon and Hydrogen Analysis on the Liquid Products

<u>Run</u>	<u>Wt. % C</u>	<u>Wt. % H</u>	<u>Type of Oil</u>
2-D	84.9	5.47	NTU-Distillate
* 4-D	56.2	6.76	NTU-Distillate
8-D	84.7	6.75	NTU-Distillate
1-D	85.9	6.33	NTU-Distillate
12-D	86.2	7.04	Tosco-Distillate
9-D	88.0	6.29	NTU-Distillate
14-D	82.0	4.93	Tosco-Distillate
13-D	88.0	5.72	Tosco-Distillate
19-D	79.6	6.71	Tosco-Distillate
12-W	77.1	6.47	Tosco-Whole
18-W	86.6	5.97	NTU-Whole (head)
18-W	86.0	5.78	NTU-Whole (+200°C)
18-W	85.2	7.06	NTU-Whole (-200°C)
15-D	89.3	5.31	Tosco-Distillate

Carbon and hydrogen analysis has been done by the Colorado School of Mines Research Institute using "Combustion Furnace" method.

* Most probably incorrect.

Table 10

Distribution of Carbon and Hydrogen in the Liquid and Gaseous Products of
Steam Pyrolysis of Shale Oil

Run	Residence Time (Sec.)	Temp. °F	Carbon to Hydrogen Ratio of Gas	Carbon to Hydrogen Ratio of Liquid	Carbon to Hydrogen Ratio of Feed	Type of Oil
2-D	0.7498	1598	4.32	15.52	6.94	NTU-Distillate
4-D	1.1435	1522	4.52	8.31	6.94	NTU-Distillate
8-D	0.3725	1518	4.88	12.55	6.94	NTU-Distillate
1-D	0.7288	1499	4.79	13.57	6.94	NTU-Distillate
9-D	0.7518	1544	4.73	13.99	6.94	NTU-Distillate
12-D	0.7531	1397	5.04	12.24	7.21	Tosco-Distillate
13-D	0.7532	1528	4.59	15.38	7.21	Tosco-Distillate
14-D	0.8375	1644	3.69	16.63	7.21	Tosco-Distillate
15-D	0.9370	1530	4.53	16.82	7.21	Tosco-Distillate
19-D	0.4068	1501	4.74	11.86	7.21	Tosco-Distillate
12-W	0.7180	1528	4.52	11.92	7.90	Tosco-Whole
18-W	0.6830	1515	4.76	14.51	7.24	NTU-Whole (head)
18-W	0.6830	1515		14.88	7.24	NTU-Whole (+200°C)
18-W	0.6830	1515		12.07	7.24	NTU-Whole (-200°C)

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○ NTU Vacuum Distillate

△ Tosco Vacuum Distillate

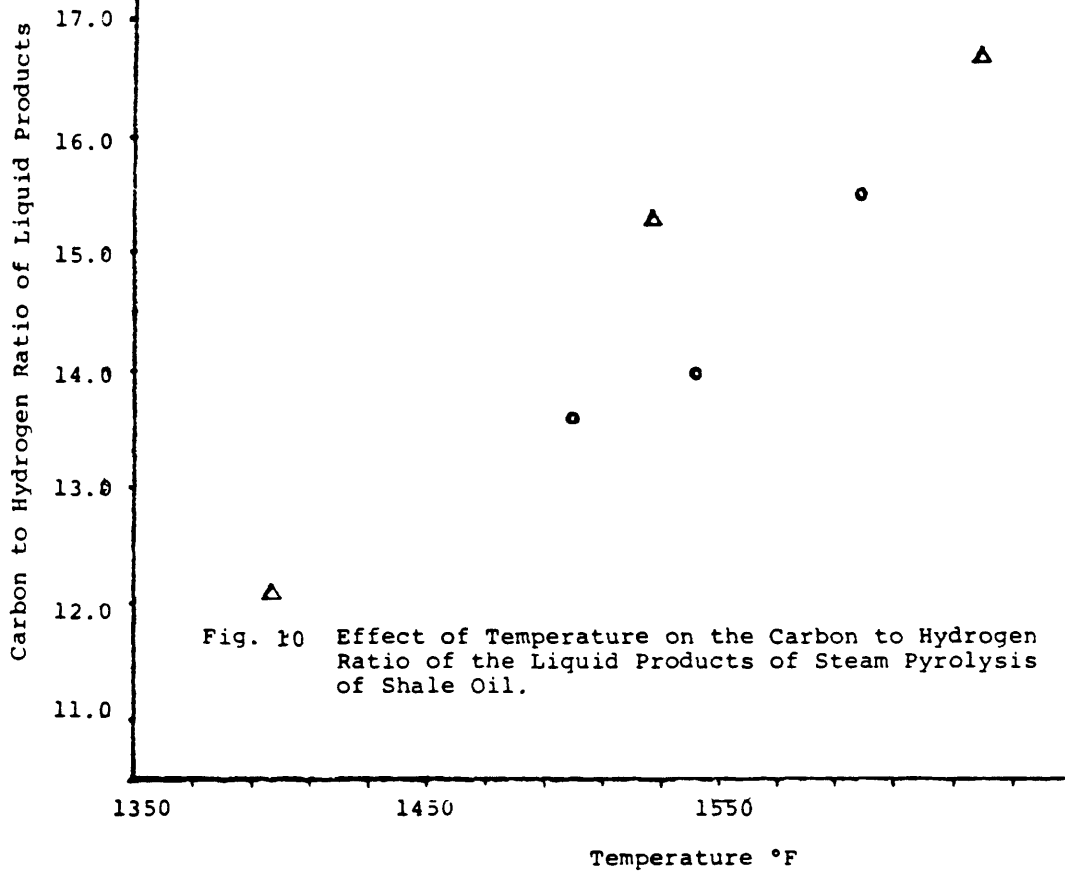


Fig. 10 Effect of Temperature on the Carbon to Hydrogen Ratio of the Liquid Products of Steam Pyrolysis of Shale Oil.

with residence time. Comparison of runs 13-D, 15-D, and 19-D, shows the same trend for liquids obtained from the Tosco oil. The results have been plotted in Fig. 11.

3. Study of runs 18-W indicates that as the temperature of the cut goes up, the carbon to hydrogen ratio increases.

4. Table 10, also indicates that the liquid products of steam pyrolysis of shale oil have a relatively high carbon to hydrogen ratio. As the carbon to hydrogen ratio increases the liquids lose their suitability as a cracking feed-stock. Therefore, it can be said that the liquid products are not a good feed-stock for thermal cracking.

Assuming that the coke is made up of entirely carbon, and using the following relationships, an over-all mass balance can be made on the carbon and hydrogen. The results have been shown, for carbon and hydrogen, in Tables 11 and 12, respectively. A sample calculation can be found in the Appendix.

$$\begin{aligned} (\text{Carbon in the feed}) &= (\text{carbon in liquid}) + (\text{carbon in the gas}) + \\ &\quad (\text{carbon in the coke}) \end{aligned}$$

$$\begin{aligned} (\text{Hydrogen in the feed}) &= (\text{hydrogen in the liquid}) + \\ &\quad (\text{hydrogen in the gas}) \end{aligned}$$

As can be seen from these tables, both the carbon and hydrogen mass balances generally close to within 5 percent which is a good indication of the accuracy of the analysis.

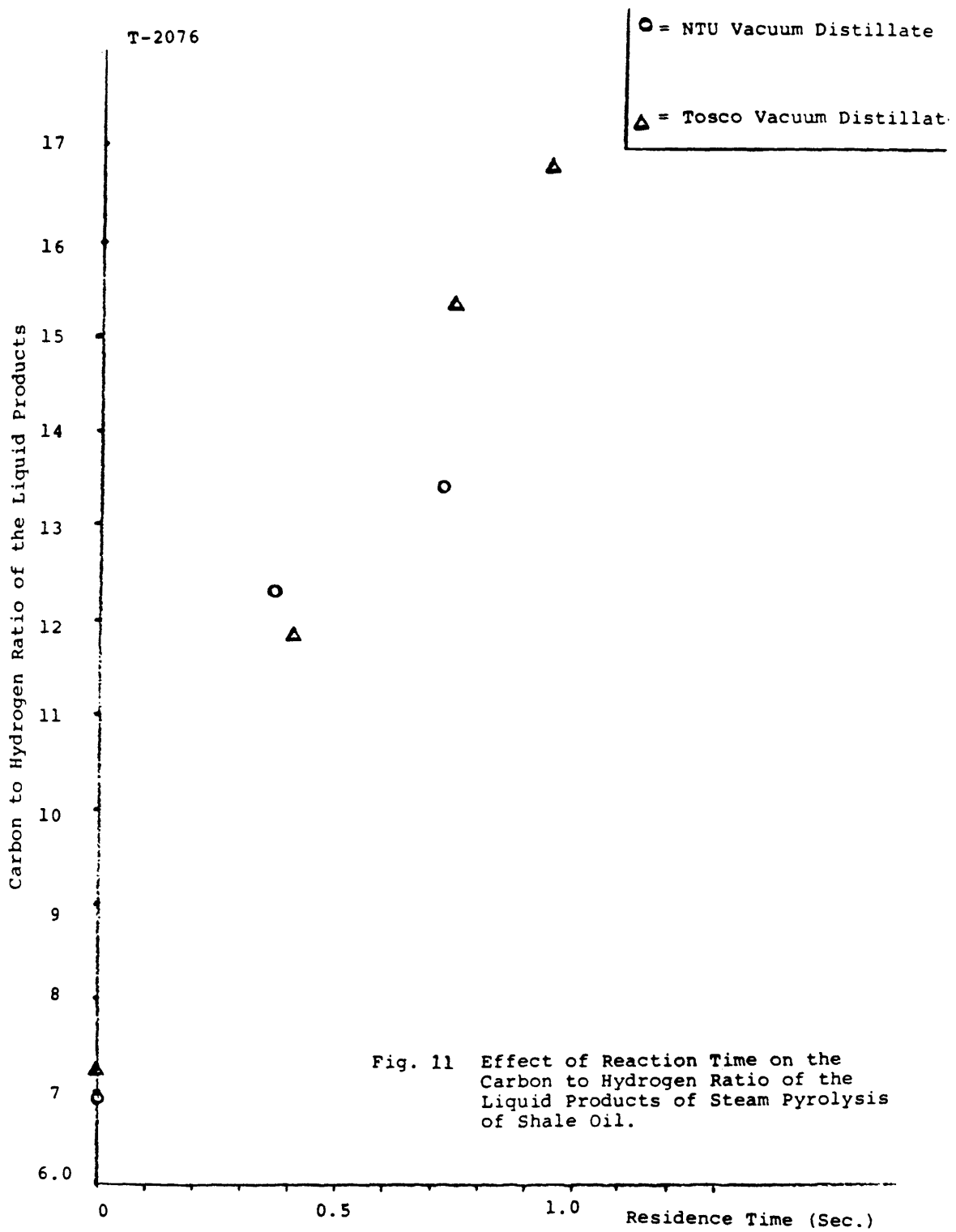


Table 11

Results of Over-all Carbon Balances

Run	Carbon in the Feed	Carbon in the Liquid	Carbon in the Gas	Carbon in the Coke	Total	Difference	Percent Difference	Type of Oil
2-D	131.96	59.82	62.48	5.60	127.90	4.06	3.08	NTU-Distillate
* 4-D	90.07	24.64	43.58	7.35	75.57	14.50	16.10	NTU-Distillate
8-D	300.25	116.31	176.32	0.78	293.41	6.84	2.28	NTU-Distillate
1-D	257.62	125.54	127.58	1.40	254.52	3.10	1.20	NTU-Distillate
9-D	245.39	114.87	127.50	1.34	243.71		0.68	NTU-Distillate
15-D	94.09	40.94	43.47	8.71	93.12	0.97	1.03	Tosco-Distillate
14-D	135.49	53.37	57.97	14.60	125.94	9.55	7.05	Tosco-Distillate
13-D	152.05	64.22	78.19	7.39	149.80	2.55	1.68	Tosco-Distillate
12-D	202.49	95.56	103.02	0.10	199.08	3.41	1.68	Tosco-Distillate
19-D	312.39	121.66	166.75	8.44	296.85	15.54	4.97	Tosco-Distillate

* Most probably incorrect.

Table 12
Results of Over-All Hydrogen Balances

<u>Run</u>	<u>Hydrogen in feed</u>	<u>Hydrogen in liquids</u>	<u>Hydrogen in gas</u>	<u>Total Difference</u>	<u>Percent Difference</u>	<u>Type of Oil</u>	
2-D	19.01	3.85	14.47	18.32	0.69	3.63	NTU-Distillate
4-D	12.97	2.96	9.65	12.61	0.36	2.78	NTU-Distillate
9-D	43.25	9.27	36.23	45.50	-2.25	-5.20	NTU-Distillate
1-D	37.11	9.25	26.62	35.87	1.24	3.34	NTU-Distillate
9-D	35.35	8.21	26.98	35.19	0.16	0.45	NTU-Distillate
15-D	13.06	2.43	9.60	12.03	1.03	7.89	Tosco-Distillate
14-D	18.80	3.21	15.70	18.91	-0.11	-0.59	Tosco-Distillate
13-D	21.10	4.17	17.04	21.21	-0.11	-0.52	Tosco-Distillate
12-D	28.10	7.89	20.43	28.32	-0.22	-0.78	Tosco-Distillate
19-D	43.35	10.26	35.20	45.46	-2.11	-4.87	Tosco-Distillate

CONCLUSIONS

a) BTX Formation

1) Negligible amounts of benzene were obtained for the whole oil samples tested, both NTU and TOSCO.

2) Yields of toluene, xylene, and total BTX go through a maximum for the range of reaction times investigated.

3) Steam pyrolysis of shale oil under the conditions used in this study does not produce an appreciable amount of BTX. The maximum amount of BTX obtained is 2.57 grams per 100 grams of shale oil.

4) Data obtained at Colorado School of Mines on steam pyrolysis of shale oil supports a Diels-Alder type mechanism for formation of aromatic compounds.

5) Vacuum distillation of shale oil increases BTX formation during steam pyrolysis.

6) There is a possibility that a significant quantity of naphthalene and heavier aromatics are formed.

b) Sulfur Distribution:

1) At a constant reaction time, concentration of sulfur in the liquid products decreases with an increase in the reactor temperature.

2) At a constant temperature, concentration of sulfur compounds in the liquid products passes through a maximum as reaction time increases.

3) For most of the runs used in this study, about half of the sulfur, originally present in the feed, ends-up in the liquid products.

4) Concentration of sulfur in the liquids, for almost all of the runs, is higher than the feed, indicating that sulfur becomes concentrated in the liquids.

c) Nitrogen Distribution:

1) At a constant reaction time concentration of nitrogen in the liquid products obtained from an NTU-oil slightly decreases with temperature, while concentration of nitrogen in the liquid products obtained from a Tosco oil slightly increases with temperature. However, over-all effect of temperature on the concentration of nitrogen in the liquids is very small.

2) At a constant temperature, concentration of nitrogen in the liquid products increases with reaction time.

3) Nitrogen becomes concentrated in the liquid products of steam pyrolysis of shale oil.

4) As the temperature of a cut increases, the concentration of nitrogen in the cut goes up.

d) Carbon and Hydrogen Distribution:

1) At a constant reaction time, the carbon to hydrogen ratio of the liquid products of steam pyrolysis of shale oil increases with temperature.

2) An increase in the carbon to hydrogen ratio of the liquids is normally accompanied by a decrease in the carbon to hydrogen ratio of the gas.

3) At a constant temperature, the carbon to hydrogen ratio of the liquid products increases as the reaction time goes up.

4) The carbon to hydrogen ratio of a cut increases with the temperature of the cut.

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APPENDICES

APPENDIX A

Table A1 MASS BALANCES FOR WHOLE OILS

Run #	Steam (gm)	Quench (gm)	Oil (ml)	Total (gm)	Liquid (gm)	Solid (gm)	Gas (gm)	Total (gm)
TOSCO II								
3	167.0	398.5	215.8	767.6	788.6	9.25	92.43	890.28
5	117.0	773.5	154.0	1034.72	934.85	14.20	72.58	1021.63
6	164.0	800.0	231.0	1180.33	1051.95	5.90	81.73	1139.48
7	136.0	436.0	191.5	751.34	45.20	10.90	81.34	737.44
8	382.0	609.0	370.5	1337.97	1292.68	14.50	154.45	1461.63
9	128.0	365.0	140.5	624.58	474.95	4.40	56.41	1535.76
10	84.0	248.0	197.0	516.49	541.50	13.80	80.45	635.75
11	196.0	556.0	128.0	871.87	1154.85	4.50	52.09	1211.44
12	132.0	739.0	184.0	1073.32	824.40	8.80	79.17	912.37
NTU								
13	214.0	843.0	270.0	1301.46	765.10	3.00	126.80	894.90
14	215.0	291.0	233.5	717.41	636.90	1.20	98.97	737.07
15	187.0	499.0	260.0	921.40	811.10	5.40	119.85	936.35
16	306.0	1009.0	334.0	1617.40	154.70	4.10	166.29	1685.09
17	181.0	445.5	167.0	777.70	655.60	4.20	78.23	738.03
18	176.0	340.0	457.0	939.77	751.80	6.15	207.86	965.80
19	351.0	705.0	440.0	1454.38	1248.10	5.40	202.76	1456.26
20	159.0	405.0	235.0	776.77	671.50	2.70	112.07	786.26
21	386.0	1017.0	472.1	1830.44	1112.10	2.90	213.77	1328.77

Table A2 MASS BALANCES FOR VACUUM DISTILLATES

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Run No.	IN			OUT			Total Grams out	Difference	
	Oil (ml)	H ₂ O (ml)	Quench (ml)	Total Grams in	Gas (gm)	Solids (gm)			Total liq. Prod. (gm)
1	347.5	216.5	710	1231.9	167	1.4	1087.9	1256.3	24.4
2	178	143	969	1268.4	85	5.6	1216.05	1306.65	38.25
3	252.5	178	562	961.9	112.2	8.05	855.25	975.5	13.6
4	121.5	120	121	347.8	58.8	7.35	276.3	342.45	-5.35
7	441.5	292.5	256	936.5	257.8	.85	728.1	986.75	50.25
8	405	265	300	921.0	230.5	.8	709.95	941.25	20.25
9	331	128	234	652.9	168.3	1.35	482.3	651.95	-.95
10	356	261	453	1026.9	210.4	5.8	909.25	1125.45	98.55
11	221	127.5	235	556.7	115.5	1.95	389.2	506.65	50.05
22	--	--	--	--	--	--	--	--	--
12	269	131	146	516.0	134.1	0.1	377.5	511.7	-4.3
13	202	138	162	479.4	104.7	7.4	365.2	477.3	-2.1
14	180	113	176	448.9	84.8	14.6	335.9	435.3	-13.6
15	125	115	119	345.0	59.8	8.7	283.1	351.6	6.6
16	414.5	96	1065	1529.2	219.2	3.4	1440	1662.6	133.4
18	457.5	260	648	1314.4	239.9	2.05	1129.5	1371.45	57.05
19	415	235	223	826.6	219.3	8.45	628.3	656.05	29.45
21	250	177	248	647.1	129.4	5.3	530.9	605.6	18.5

Table A3. LIQUID ANALYSIS-MASS BALANCES

Run Number	8	10	11	12	13	15	16	17	18	19	20	21	1-D	3-D	4-D
Surge Tank H ₂ O Empty Bottle ²						517.2	873.8	519.3	519.3	518.5	516.0	520.8	520.0	519.4	355.0
Surge Tank H ₂ O Full Bottle ²						999.1	1881	1035.5	741.5	1096.5	981.7	910.0	1248.2	1034.5	529.8
Wt of H ₂ O															
Extra H ₂ O Before Taking Sample						103.9	220	0.0	1.8	199.5	28.6	32.0	0.75		0.0
Empty Distilling Flask	75.5	123.4	97.8	90	147.3	86.0	71.3	95.7	93.2	90.5	85.8	79.0	86.5	78.8	83.6
Full Distilling Flask	213.9	227.7	221.4	187.5	253.0	174.3	287	183.7	114.5	184.2	208.4	221.5	213.9	198.5	155.0
Wt of Feed						123.6	97.5	106.3							
Distilling Flask After Dist.	96.0	147.5	104.5	104.3	170.1	101.3	85.3	107.8	113.8	107.3	119.7	101.3	107.3	87.6	97.4
Initial Product Empty Bottle	104.2	104.7	104.4	104.2	104.7	104.7	105.3	104.7	104.7	183.5	180.8	182.5	181.0	180.2	106.4
Initial Product Full Bottle	219.0	183.5	203.7	182.8	186.0	175.5	205.5	181.0	194.0	254.2	268.2	301.7	285.6	285.4	160.8
Net Wt. Recovered Initially		78.8	99.3	78.6	81.3										
Amt. of Initial Loss															
Empty Distillate H ₂ O Bottle	104.0	104.0	355.0	354.5	103.8	103.8	103.8	103.8	103.8	103.8	103.8	103.8	103.2	103.3	102.9
Full Distillate H ₂ O Bottle	169.3	188.5	410.0	421.5	141.3	182.6	182.6	153.7	169.7	160.1	163.5	191.1	143.2	136.6	
Net wt. of H ₂ O Recovered ²		65.3	84.5												
Re-distilling Flask Empty	89.2	105.5	95.8	84.7	126.6	126.0	126.0	125.2	126.5	124.7	124.4	125.9	125.1	124.9	124.1

Table A3 -(Cont.)

Run Number	8	10	11	12	13	15	16	17	18	19	20	21	1-D	3-D	4-D
Re-distilling Flask Full	99.0	114.7	113.0	96.3	145.6	139.8	139.5	140.5	133.4	135.1	134.6	140.2	167.7	129.4	
Wt. wt. of Feed	9.8	9.2													
Final Product Empty Bottle	104.7	104.7	105.3	104.6	103.4	103.3	103.6	103.4	103.5	103.0	102.6	102.7	102.8	103.1	
Final Product Full Bottle	111.7	107.5	111.0	109.8	110.1	110.2	110.0	113.1	109.6	111.7	109.4	113.0	138.0	108.0	
Amount of Naphtha	7.0	2.8													
Redistilling Flask After Redistill.	91.0	111.7	104.3	89.5	138.3	133.6	133.1	130.8	126.3	126.6	128.0	130.0	132.0	124.3	
Initial Prod. Bottle After Cent.					109.4	106.8	108.3	106.2	186.3	185.2	184.4	182.7	187.4	107.8	

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Table A3 (Cont.)

Run Number	5-D	7-D	8-D	9-D	10-D	11-D	12-D	13-D	14-D	15-D	16-D	17-D	18-D	19-D	20-D
Re-distilling Flask Full	136.8		168.1												
Net Wt. of Feed															
Final Product Empty Bottle	102.6		102.8	102.6	102.9	102.7	103.2								
Final Product Full Bottle	114.0		136.6	105.8		105.2	124.5								
Amount of Naphtha															
Re-distilling Flask After Re-distill.	125.1		133.1												
Initial Prod. Bottle After Cent.	109.0		111.2												

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APPENDIX B

Sample calculation for run #17:

$$\text{wt. of oil flowed} = (\text{volume}) (\text{density})$$

$$\text{wt. of oil flowed} = (167) (0.8082)$$

oil fed \longrightarrow gas + hydrocarbon in liquid + coke

$$\begin{aligned} \text{Amount of hydrocarbon in liquids} &= \text{wt. of oil fed} - \text{wt. of gas} - \text{wt. of coke} \\ &= (167) (0.8082) - 78.23 - 4.20 \\ &= 52.54 \text{ grams} \end{aligned}$$

$$\begin{aligned} \text{Amount of hydrocarbon used in distillation feed} &= \text{Amount of naphtha recovered} + \text{Bottom products of distillation} \\ &= 2.88 + (12.1 + 7.9) = 22.8 \text{ grams} \end{aligned}$$

$$\frac{\text{Amount of benzene}}{100 \text{ gm of shale oil}} = \frac{\text{Amount of benzene in Naphtha}}{100 \text{ grams of naphtha}}$$

X Amount of hydrocarbon in liquids

Amount of hydrocarbon in distillation feed

$$X \frac{100 \text{ gms}}{\text{wt. of oil}}$$

$$= \frac{0.4 \times 3.6 \times 0.8 \times 52.54 \times 100}{100 \times 22.8 \times 167 \times 0.8082} = 1.96 \times 10^{-2} \text{ grams}$$

Similar relations exist for toluene and xylene

$$\begin{aligned} \frac{\text{Xylene}}{100 \text{ gm shale oil}} &= \frac{1.4 \times 3.6 \times 0.8 \times 52.54 \times 100}{100 \times 22.8 \times 167 \times 0.8082} \\ &= 6.88 \times 10^{-2} \text{ grams} \end{aligned}$$

$$\begin{aligned} \frac{\text{xylene}}{100 \text{ gm shale oil}} &= \frac{5.4 \times 3.6 \times 0.8 \times 52.54 \times 100}{100 \times 22.8 \times 167 \times 0.8082} \\ &= 0.265 \text{ grams} \end{aligned}$$

$$\frac{\text{gms total BTX}}{100 \text{ gm of oil}} = 0.354$$

APPENDIX C

Sample calculation for distribution of sulfur: run #2-D

Wt. of oil flowed = (volume) (Density)

Wt. of oil flowed = (178) (0.8789) = 156.44

Wt. of sulfur in the feed = $\frac{(\text{wt. of oil flowed})(\text{wt. \% sulfur})}{100}$

Wt. of sulfur in the feed = $\frac{(156.44)(0.78)}{100} = 1.22$

Oil → gas + hydrocarbon in liquid + coke

Amount of liquid = (oil fed) - (gas) - (coke)

Amount of liquid = (156.44) - (85) - (5.6) = 65.84

Wt. of sulfur in liquid) = $\frac{(\text{Wt. of liquid})(\text{Wt. \% sulfur})}{100}$

Wt. of sulfur in liquid) = $\frac{(65.84)(0.70)}{100} = 0.46$

APPENDIX D

Sample calculation for N₂ distribution: run # 2-D.

$$\begin{array}{l} \text{(Wt. of} \\ \text{oil} \\ \text{flowed)} \end{array} = (\text{volume})(\text{density})$$

$$\begin{array}{l} \text{(Wt. of} \\ \text{oil} \\ \text{flowed)} \end{array} = (178)(0.8789) = 156.44$$

$$\begin{array}{l} \text{(Wt. of N}_2 \\ \text{in the feed)} \end{array} = \frac{(\text{Wt. of oil})(\text{Wt. \% N}_2)}{100}$$

$$\begin{array}{l} \text{(Wt. of N}_2 \\ \text{in the feed)} \end{array} = \frac{(156.44)(1.59)}{100} = 2.49$$

$$\begin{array}{l} \text{(Amount of} \\ \text{liquid)} \end{array} = (\text{oil fed}) - (\text{gas}) - (\text{coke})$$

$$\begin{array}{l} \text{(Amount of} \\ \text{liquid)} \end{array} = (156.44) - (85) - (5.6) = 65.84$$

$$\begin{array}{l} \text{(Wt. of N}_2 \\ \text{in liquid)} \end{array} = \frac{(\text{Wt. of liquid})(\text{Wt. \% N}_2)}{100}$$

$$\begin{array}{l} \text{(Wt. of N}_2 \\ \text{in liquid)} \end{array} = \frac{(65.84)(2.39)}{100} = 1.57$$

APPENDIX E

Sample calculation for C and H₂ distribution: run #2-D

$$(\text{Wt. of feed}) = (\text{volume of oil})(\text{density})$$

$$(\text{Wt. of Feed}) = (178)(0.8789) = 156.44$$

$$\begin{aligned} (\text{Wt. of carbon} &= \frac{(156.44)(84.35)}{100} = 131.96 \\ \text{in the feed}) & \end{aligned}$$

$$\begin{aligned} (\text{Wt. of H}_2 &= \frac{(\text{Wt. of feed})(\text{Wt. \% Hydrogen})}{100} \\ \text{in the feed}) & \end{aligned}$$

$$\begin{aligned} (\text{Wt. of H}_2 &= \frac{(156.44)(12.15)}{100} = 19.01 \\ \text{in the feed}) & \end{aligned}$$

$$(\text{Carbon/H}_2) \text{ feed} = \frac{131.96}{19.01} = 6.94$$

$$(\text{Wt. of gas}) = \frac{(\text{wt. of feed})(\text{wt. \%})}{100}$$

$$(\text{Wt. of gas}) = \frac{(156.44)(51.38)}{100} = 80.38$$

The actual amount of each component in the gas and its actual amount of carbon and hydrogen can be calculated as follows; a sample calculation is given for CH₄ and the result of calculations for this run has been summarized in the following table. For each run one has to construct a similar table.

Appendix E continued

$$\begin{array}{l} \text{(Amount of} \\ \text{CH}_4 \text{ in} \\ \text{the gas)} \end{array} = \frac{(\text{Wt. of feed})(\text{Wt. \% CH}_4)}{100}$$

$$\begin{array}{l} \text{(Amount of} \\ \text{CH}_4 \text{ in} \\ \text{the gas)} \end{array} = \frac{(156.44)(14.91)}{100} = 23.33$$

$$\begin{array}{l} \text{(Amount of} \\ \text{CH}_4 \text{ in} \\ \text{the gas)} \end{array} = \frac{(\text{Molecular Wt. of carbon}) (\text{amount of CH}_4) (\text{number of carbon atoms})}{(\text{Molecular weight of CH}_4)}$$

$$\begin{array}{l} \text{(Amount of} \\ \text{carbon due} \\ \text{to CH}_4) \end{array} = \frac{(12)(23.33)(1)}{16} = 17.49$$

$$\begin{array}{l} \text{(Amount of} \\ \text{hydrogen due} \\ \text{to CH}_4) \end{array} = \frac{(\text{molecular wt of hydrogen}) (\text{amount of methane}) (\text{number of H}_2)}{(\text{molecular weight of CH}_4)}$$

$$\begin{array}{l} \text{(Amount of} \\ \text{hydrogen due} \\ \text{to CH}_4) \end{array} = \frac{(2)(23.33)(2)}{16} = 5.83$$

Appendix E continued

<u>Component</u>	<u>Actual grams</u>	<u>Actual grams of Carbon</u>	<u>Actual grams of Hydrogen</u>
H ₂	1.39	0	1.39
CO	4.74	2.03	0
CH ₄	23.33	17.49	5.83
C ₃ H ₈	0.1095	0.09	0.02
C ₃ H ₆	7.95	6.81	1.14
n-butane	0.28	0.23	0.05
H ₂ S	0.22	0	0.01
1-butene	0.38	0.32	0.06
trans-butene	0.55	0.47	0.08
C _i S-butene	0.05	0.04	0.01
C ₄ H ₆	2.75	2.45	0.30
CO ₂	0.74	0.20	0
C ₂ H ₄	35.36	30.30	5.06
C ₂ H ₆	2.57	2.05	0.52
	Total	62.48	14.47

$$(C/H)_{\text{gas}} = 4.32$$

Appendix E continued

$$(\text{Wt. of liquid}) = (\text{Wt. \% of feed})(\text{Wt. of feed})/100$$

$$(\text{Wt. of liquid}) = (45.04)(156.44)/100 = 70.46$$

$$(\text{Wt. of carbon in liquid}) = (\text{Wt. \% C})(\text{Wt. of liquid})/100$$

$$(\text{Wt. of carbon in liquid}) = (84.9)(70.46)/100 = 59.82$$

$$(\text{Wt. of H}_2 \text{ in liquid}) = (5.47)(70.46)/100 = 3.85$$

$$(\text{C/H})_{\text{liq}} = \frac{59.82}{3.85} = 15.52$$

APPENDIX F

The data in this appendix has been reproduced from the data of Fritzler (7), and Smith (8), and has been used in calculations for the amount of carbon and hydrogen in the gaseous products.

RUN NUMBER 22677201R

REACTION TEMPERATURE 1315.0 DEG F
REACTION TIME 0.603 SEC
STEAM-OIL RATIO 0.455
PYROLYSIS SEVERITY FACTOR 1315.9

GASEOUS PRODUCTS

WT % OF FEED 98.24
SCF/LB OF FEED 7.00

COMPONENT	HOL MGAS	WT % GAS	WT % FEED	SCF/LB FEED
HYDROGEN	11.63	0.97	0.49	0.91
CARBON MONOXIDE	2.89	3.33	1.67	0.23
MEthane	32.16	21.25	10.67	2.53
PROPANE	0.33	0.60	0.30	0.23
PROPYLENE	11.16	19.34	9.72	0.80
N-BUTANE	0.21	0.51	0.26	0.22
HYDROGEN SULFIDE	0.19	0.27	0.14	0.22
1-BUTENE	1.11	2.50	1.29	0.09
ISOBUTYLENE	0.09	0.60	0.00	0.00
TRANS-2-BUTENE	0.45	1.03	0.52	0.04
CIS-2-BUTENE	0.12	0.20	0.14	0.01
1-3 BUTADIENE	3.23	7.70	3.62	0.25
CARBON DIOXIDE	0.17	0.33	0.16	0.01
ETHYLENE	32.45	37.50	18.84	2.55
ETHANE	3.00	4.00	2.41	0.30
ISOBUTANE	0.01	0.01	0.01	0.00

LIQUID PRODUCTS

WT % OF FEED 40.28

SOLID PRODUCTS

WT% OF FEED 1.43

RUN NUMBER T622770019

REACTION TEMPERATURE 1501.0 DEG F
 REACTION TIME 0.106 SEC
 STEAM-OIL RATIO 0.637
 PYROLYSIS SEVERITY FACTOR 1326.6

CASEOUS PRODUCTS

WT % OF FEED 56.25
 SCF/LB OF FEED 9.00

COMPONENT	NOL X OAB	WT % GAS	WT % FEED	SCF/W FEED
HYDROGEN	13.84	1.18	0.66	1.25
CARBON MONOXIDE	3.40	4.11	2.31	0.31
METHANE	31.37	21.21	11.93	2.82
PROPANE	0.32	0.59	0.33	0.03
PROPYLENE	10.66	18.91	10.64	0.96
N-BUTANE	0.22	0.53	0.30	0.02
HYDROGEN SULFIDE	0.03	0.05	0.03	0.00
1-BUTENE	1.16	2.75	1.55	0.10
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.46	1.09	0.62	0.04
CIS-2-BUTENE	0.12	0.28	0.16	0.01
1-3 BUTADIENE	3.27	7.46	4.20	0.29
CARBON DIOXIDE	0.18	0.36	0.20	0.02
ETHYLENE	31.49	37.23	20.94	2.83
ETHANE	3.37	4.27	2.40	0.30
ISOBUTANE	0.00	0.00	0.00	0.00

Liquid products
 WT % OF FEED 41.46

Solid products
 WT % OF FEED 2.29

RUN NUMBER 160271015

REACTION TEMPERATURE 1330.0 DEG F
 REACTION TIME 0.937 SEC
 STEAM-OIL RATIO 1.036
 PYROLYSIS SEVERITY FACTOR 1526.7

GASEOUS PRODUCTS

WT % OF FEED 90.00
 SCF/LB OF FEED 0.99

COMPONENT	MOL X GAS	WT % GAS	WT % FEED	SCF/LB FEED
HYDROGEN	14.95	1.40	0.71	1.34
CARBON MONOXIDE	6.50	0.47	4.31	0.90
METHANE	35.94	26.02	13.05	3.23
PROPANE	6.11	0.22	0.11	0.01
PROPYLENE	5.73	11.21	5.70	0.91
N-BUTANE	0.14	0.39	0.20	0.01
HYDROGEN SULFIDE	0.04	0.06	0.03	0.00
1-BUTENE	0.27	0.71	0.36	0.02
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.30	0.70	0.10	0.03
CIS-2-BUTENE	0.03	0.00	0.04	0.00
1-3-BUTADIENE	1.69	4.24	2.16	0.10
CARBON DIOXIDE	0.75	1.60	0.00	0.07
ETHYLENE	31.33	40.90	20.61	0.07
ETHANE	0.23	3.12	1.39	0.120
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 41.29

SOLID PRODUCTS

WT % OF FEED 7.64

RUN NUMBER F1931770014

REACTION TEMPERATURE 1644.0 DEG F
 REACTION TIME 0.697 SEC
 STEAM-OIL RATIO 0.707
 PYROLYSIS SEVERITY FACTOR 1001.1

GASEOUS PRODUCTS

WT X OF FEED 50.17
 SCF/LB OF FEED 11.56

COMPONENT	MOL X GAS	WT X GAS	WT X FEED	SCF/# FEED
HYDROGEN	27.54	3.37	1.69	3.16
CARBON MONOXIDE	6.80	11.55	5.80	0.79
METHANE	40.92	39.44	19.79	4.60
PROPANE	0.01	0.02	0.01	0.00
PROPYLENE	1.34	3.41	1.71	0.15
N-BUTANE	0.03	0.12	0.06	0.00
HYDROGEN SULFIDE	0.05	0.09	0.05	0.01
1-BUTENE	0.01	0.03	0.02	0.00
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.06	0.21	0.11	0.01
CIS-2-BUTENE	0.00	0.01	0.01	0.00
1-3 BUTADIENE	0.36	1.17	0.59	0.04
CARBON DIOXIDE	0.71	1.90	0.99	0.08
ETHYLENE	21.26	36.19	18.16	2.44
ETHANE	1.32	2.40	1.20	0.15
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT X OF FEED 40.70

SOLID PRODUCTS

WT X OF FEED 9.13

RUN NUMBER #1526770013

REACTION TEMPERATURE 1526.0 DEG F
 REACTION TIME 0.612 SEC
 STEAM-OIL RATIO 0.769
 PYROLYSIS SEVERITY FACTOR 1464.3

GASEOUS PRODUCTS

WT % OF FEED 59.21
 SCF/LB OF FEED 9.26

COMPONENT	HOL X GAS	WT X GAS	WT X FEED	SCF/A FEED
HYDROGEN	10.46	0.93	0.52	0.97
CARBON MONOXIDE	4.45	5.52	3.05	0.41
METHANE	30.06	27.60	15.24	3.61
PROPANE	0.15	0.29	0.16	0.01
PROPYLENE	6.91	12.80	7.11	0.64
N-BUTANE	0.17	0.44	0.24	0.02
HYDROGEN SULFIDE	0.05	0.07	0.04	0.00
1-BUTENE	0.30	0.95	0.53	0.04
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.30	0.06	0.47	0.03
CIS-2-BUTENE	0.04	0.11	0.06	0.00
1-3 BUTADIENE	2.00	4.00	2.65	0.19
CARBON DIOXIDE	0.45	0.93	0.51	0.04
ETHYLENE	32.98	40.97	22.02	3.06
ETHANE	2.75	3.66	2.02	0.26
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 40.67

SOLID PRODUCTS

WT % OF FEED 4.12

RUN NUMBER #1924770012

REACTION TEMPERATURE 1397.0 DEG F
 REACTION TIME 0.563 SEC
 STEAM-OIL RATIO 0.592
 PYROLYSIS SEVERITY FACTOR 1310.2

GASEOUS PRODUCTS

WT % OF FEED 53.08
 SCF/LB OF FEED 7.48

COMPONENT	HOL X GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN	4.83	0.36	0.19	0.36
CARBON MONOXIDE	3.94	4.09	2.17	0.29
HEPTANE	32.49	19.34	10.27	2.43
PROPANE	0.46	0.76	0.40	0.03
PROPYLENE	13.64	21.30	11.31	1.02
N-BUTANE	0.22	0.47	0.25	0.02
HYDROGEN SULFIDE	0.05	0.06	0.03	0.00
1-BUTENE	2.20	4.76	2.92	0.17
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.51	1.07	0.57	0.04
CIS-2-BUTENE	0.21	0.43	0.23	0.00
1-3 BUTADIENE	3.91	7.86	4.17	0.29
CARBON DIOXIDE	0.23	0.39	0.21	0.02
ETHYLENE	32.77	34.13	18.12	2.45
ETHANE	4.46	4.97	2.64	0.33
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 46.86

SOLID PRODUCTS

WTX OF FEED 0.04

RUN NUMBER #N506770009

REACTION TEMPERATURE 1544.0 DEG F
 REACTION TIME 0.401 SEC
 STEAM-OIL RATIO 0.440
 PYROLYSIS SEVERITY FACTOR 1402.0

GASEOUS PRODUCTS

WT % OF FEED 54.67
 SCF/LB. OF FEED 0.79

COMPONENT	HOL X GAS	WT X GAS	WT X FEED	SCF/W FEED
HYDROGEN	9.07	0.84	0.46	0.87
CARBON MONOXIDE	3.07	4.59	2.51	0.34
METHANE	35.20	23.95	13.09	3.10
PROPANE	0.21	0.40	0.22	0.02
PROPYLENE	0.90	19.99	0.74	0.79
N-BUTANE	0.10	0.43	0.24	0.02
HYDROGEN SULFIDE	0.02	0.03	0.02	0.00
1-BUTENE	0.64	1.52	0.83	0.06
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.37	0.89	0.40	0.03
CIS-2-BUTENE	0.06	0.13	0.07	0.00
1-3 BUTADIENE	2.48	5.67	3.10	0.22
CARBON DIOXIDE	0.14	0.28	0.15	0.01
ETHYLENE	34.57	41.04	22.44	3.04
ETHANE	3.33	4.23	2.31	0.29
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 44.87

SOLID PRODUCTS

WT % OF FEED 0.46

RUN NUMBER #N50277M000

REACTION TEMPERATURE 1510.0 DEG F
 REACTION TIME 0.174 SEC
 STEAM-OIL RATIO 0.744
 PYROLYSIS SEVERITY FACTOR 1346.6

GASEOUS PRODUCTS

WT X OF FEED 61.19
 SCF/LB OF FEED 9.20

COMPONENT	MOL X GAS	WT X GAS	WT X FEED	SCF/# FEED
HYDROGEN	9.55	0.76	0.47	0.08
CARBON MONOXIDE	3.21	3.56	2.18	0.30
METHANE	30.64	19.45	11.90	2.82
PROPANE	0.31	0.55	0.33	0.03
PROPYLENE	11.92	19.19	11.74	1.06
N-BUTANE	0.28	0.65	0.40	0.03
HYDROGEN SULFIDE	0.07	0.09	0.05	0.01
1-BUTENE	1.55	3.43	2.10	0.14
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.48	1.05	0.65	0.04
CIS-2-BUTENE	0.10	0.21	0.13	0.01
1,3-BUTADIENE	3.61	7.72	4.73	0.33
CARBON DIOXIDE	0.16	0.29	0.10	0.01
ETHYLENE	35.33	39.23	24.00	3.25
ETHANE	3.19	3.79	2.32	0.29
ISOBUTANE	0.00	0.00	0.00	0.00

LIIQUID PRODUCTS
 WT X OF FEED 38.58

SOLID PRODUCTS
 WT X OF FEED 0.22

RUN NUMBER #N414770004

REACTION TEMPERATURE 1922.0 DEG F
 REACTION TIME 1.002 SEC
 STEAM-OIL RATIO 1.124
 PYROLYSIS SEVERITY FACTOR 1931.1

GASEOUS PRODUCTS

WT % OF FEED 92.05
 SCF/LB OF FEED 9.02

COMPONENT	MOL XGAS	HT % GAS	HT % FEED	SCF/LB FEED
HYDROGEN	14.81	1.36	0.71	1.34
CARBON MONOXIDE	4.24	5.41	2.82	0.38
METHANE	35.11	25.69	13.37	3.17
PROPANE	0.17	0.34	0.10	0.02
PROPYLENE	7.00	13.43	6.99	0.63
N-BUTANE	0.15	0.38	0.20	0.01
HYDROGEN SULFIDE	0.12	0.18	0.09	0.01
1-BUTENE	0.40	1.04	0.54	0.04
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.31	0.79	0.41	0.03
CIS-2-BUTENE	0.04	0.11	0.06	0.00
1,3-BUTADIENE	1.87	4.62	2.41	0.17
CARBON DIOXIDE	0.66	1.38	0.72	0.06
ETHYLENE	32.01	40.90	21.33	2.89
ETHANE	3.12	4.27	2.22	0.28
ISOBUTANE	6.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 41.06

SOLID PRODUCTS

WT % OF FEED 6.88

RUN NUMBER #11496770012

REACTION TEMPERATURE 1598.0 DEG F
 REACTION TIME 0.936 SEC
 STEAM-OIL RATIO 0.914
 PYROLYSIS SEVERITY FACTOR 1532.5

CASEOUS PRODUCTS

WT % OF FEED 51.38
 SCF/LB OF FEED 9.57

COMPONENT	MOL XCAS	WT % GAS	WT % FEED	SCF/A FEED
HYDROGEN	17.46	1.73	0.89	1.67
CARBON MONOXIDE	4.29	5.09	3.03	0.41
METHANE	36.07	29.02	14.91	3.53
PROPANE	0.07	0.15	0.07	0.01
PROPYLENE	4.79	9.00	5.00	0.46
N-BUTANE	0.12	0.34	0.18	0.01
HYDROGEN SULFIDE	0.16	0.27	0.14	0.02
1-BUTENE	0.17	0.47	0.24	0.02
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.24	0.67	0.35	0.02
CIS-2-BUTENE	0.02	0.06	0.03	0.00
1-3 BUTADIENE	1.29	3.42	1.76	0.12
CARBON DIOXIDE	0.41	0.92	0.47	0.04
ETHYLENE	31.95	43.98	22.60	3.06
ETHANE	2.16	3.19	1.64	0.21
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 45.04

SOLID PRODUCTS

WT % OF FEED 3.56

RUN NUMBER = 11336770401

REACTION TEMPERATURE 1499.0 DEG F
 REACTION TIME 0.370 SEC
 STEAM-OIL RATIO 0.709
 PYROLYSIS SEVERITY FACTOR 1380.2

GASEOUS PRODUCTS

WT % OF FEED 51.69
 SCF/LB OF FEED 7.97

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/M FEED
HYDROGEN	0.90	0.74	0.30	0.72
CARBON MONOXIDE	2.90	3.38	1.79	0.24
METHANE	34.00	22.14	11.45	2.71
PROPANE	0.32	0.57	0.30	0.03
PROPYLENE	10.94	18.69	9.66	0.87
N-BUTANE	0.20	0.47	0.24	0.02
HYDROGEN SULFIDE	0.13	0.18	0.09	0.01
1-BUTENE	1.05	2.39	1.24	0.08
ISOBUTYLENE	0.00	0.00	0.00	0.00
TRANS-2-BUTENE	0.42	0.96	0.50	0.03
CIS-2-BUTENE	0.12	0.28	0.15	0.01
1,3-BUTADIENE	3.01	6.60	3.41	0.24
CARBON DIOXIDE	0.19	0.36	0.19	0.02
ETHYLENE	33.66	38.34	19.82	2.68
ETHANE	4.01	4.89	2.53	0.32
ISOBUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS

WT % OF FEED 47.85

SOLID PRODUCTS

WT % OF FEED 0.46