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MILLISECOND STEAM PYROLYSIS OF SHALE OIL
FOR PETROCHEMICAL INTERMEDIATES PRODUCTION

by

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

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ABSTRACT

Several different shale oils at various levels of hydrogenation from hydrogenated Paraho and Tosco II oil were pyrolyzed with steam at atmospheric pressure in a bench-scale unpacked tubular reactor. The reaction variables and their ranges studied were temperatures from 1602^oF to 1775^oF, residence times from a 0.05 sec., and the steam to oil mass ratio was kept constant at about 1.0.

The maximum yields of olefin products as a weight percent of feed were:

	Paraho			Tosco II		
	Hydrogenation Severity			Hydrogenation Severity		
	<u>High</u>	<u>Med.</u>	<u>Low</u>	<u>High</u>	<u>Med.</u>	<u>Low</u>
Ethylene	14.58	28.57	26.66	22.52	30.15	23.02
Propylene	4.45	13.39	9.65	8.06	12.60	9.60
Total Olefins	21.92	51.65	42.43	35.68	52.15	38.82

These experiments results indicate that the product yields for hydrogenated shale oils from Paraho and Tosco II showed expected trends with the exception of the severely hydrogenated Paraho and Tosco II oils which have a tendency to undergo steam reforming at the high temperature range studied due to the catalytic activity or surface reaction.

The results were correlated with a pyrolysis severity factor which combined the effect of reaction variables such

as temperature and residence time. Increased severity of operation resulted in decreased yields of ethylene, propylene, 1,3 butadiene, and total olefins. The total gas decreased, then increased above a severity factor of 1450, while the yield of hydrogen is increased.

Finally we concluded that hydrogenated shale oils should make excellent feedstocks for petrochemical intermediates production.

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DEDICATION

To my wife Nouria and my daughter Khulood.

INTRODUCTION

The petroleum shortage recently experienced by many nations throughout the world has created an intense interest in obtaining new and supplemental energy sources in the United States. While petroleum will continue to be the best source of supply, it must always be kept in mind that it is a limited resource that must be conserved. The industry must look forward to the use of coal, tar sands, and biomass for its long range needs (1). Since most of the important chemicals, plastics, and fibers are based on light olefins and aromatics which are derived today from limited petroleum and natural gas supplies, light distillates from shale oil can be an acceptable substitute feed for olefin product in a conventional pyrolysis unit. So we can say shale oil may be an important future olefins feedstock, and appears to be a promising replacement feed for olefin production units (1,2).

To date, the great majority of study and development work done on shale oil has been focused on its role as an alternate energy source. Ethylene is the most important product from the petrochemical refinery. The principal raw material for its production in the United States has been obtained from ethane and propane cracking obtained from natural gas and refinery fuels gas (3,4).

Petrochemical producers are expected to rely more on using naphtha and gas oil as a replacement feedstock (5,6).

Research and development of synthetic fuel from oil shale has been directed toward processing schemes involving retorting followed by a combination of coking, hydrostabilization, hydrodenitrogenation, reforming and cracking (7).

The chemical characterization of shale oil is very important in planning for the potential use of shale oil as an energy or as a chemical source. Shale oils produced in the United States and in other foreign countries were analyzed by a laboratory procedure which was a modification of the Bureau of Mines routine method. The results indicate that the oils differ greatly in such properties as nitrogen and sulfur content, pour point distillation range and hydrocarbon composition. Both source of shale and retorting conditions must be considered in predicting the composition of a crude shale oil (8). Crude shale oil has a high content of organic nitrogen up to 2.1 weight percent and 0.8 to 1.0 weight percent of sulfur content depending on the retorting conditions (9). Cady (10), reported that NTU shale oil consists of 39% hydrocarbons and 61% compounds of nitrogen, sulfur and oxygen, and the nonhydrocarbons are 36% nitrogen compounds, 6% sulfur compounds, and 19% oxygen compounds. Also, Poulson (11), characterized the

nitrogen type compounds in a shale oil light distillate (190-310°C). The light distillate comprises 15% on whole, and has as much as 20% nitrogen compounds, and over 90% of the nitrogen percent was basic. This basic nitrogen is a poison to most catalysts used in the refinery processes, and must be removed by hydrotreating the crude to reduce the heteroatoms to inorganic gases (8,12,13). Most of the processes in a refinery are catalytic, therefore, the basic nitrogen compounds present in crude shale oil would attack the acidic refinery catalysts if the shale oil is used as a refinery feedstock. Since most of the acidic catalysts are expensive, it is expensive to refine crude oil in a conventional petroleum refinery. Therefore, any alternative use of shale oil which does not need severe pre-refining of the feedstock can be both economical and practical (7,14). Since steam pyrolysis is not a catalytic process, it could be an alternative use of shale oil as a feedstock for production of petrochemical intermediates, such as ethylene, propylene, benzene, toluene, and xylene.

Extensive studies have been made on the effect of feedstock type on pyrolysis yields using both model compound and commercial feedstocks. It is believed that normal paraffins make the best feedstock for ethylene production, followed by branched paraffins, olefins,

naphthenes, and aromatics, i.e., paraffins react to form light olefins. The light olefins have a tendency to polymerize and condense into monoaromatics, naphthenes have a tendency to form higher aromatics, and aromatics are unconverted during pyrolysis (3,15,16,17,18). Zdonidik (3) reported that the sulfur and possibly nitrogen containing feedstocks require additional processing consideration adding to overall cost. The utilization of shale oil as a steam pyrolysis feedstock has long been considered in the United States by the Bureau of Mines, dating from the 1950's (19), the Institute of Gas Technology (20), and with extensive studies at the Colorado School of Mines in the 1970's.

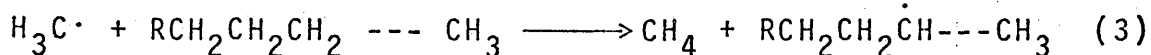
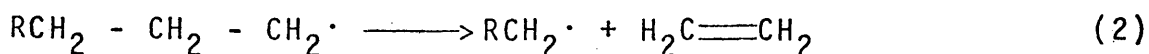
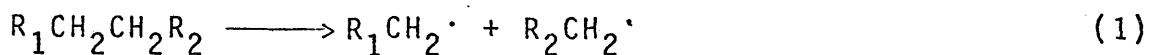
Finally, we conclude that shale oil can be a desirable substitute feed for olefin production in a conventional pyrolysis unit. While less desirable than today's better pyrolysis feed, shale oil may be an important future olefins feedstock.

Further study of the utilization of shale oil as a steam pyrolysis feedstock for production of petrochemical intermediates will continue at Colorado School of Mines. The main objectives of this thesis is to study, experimentally, the utilization of hydrogenated shale oil as a feedstock for steam pyrolysis at short residence time(0.05-0.1 seconds)

and high temperature (1600-1775 °F), and to investigate the effects of such variables on the yields of such valuable products as ethylene, propylene, butenes, and 1,3-butadiene. Further objectives of the study should be the maximization of ethylene production as well as the yields of light olefins, and the correlation of the experimental results with a pyrolysis severity factor which combined the effect of reaction variables.

EXPERIMENTAL STUDIESChemistry of pyrolysis:

Thermal rearrangements into isomers, thermal polymerizations, and thermal decompositions are all included in the term pyrolysis. It includes chemical change of a substance by means of heat alone (18). Many investigators proposed, that thermal cracking of hydrocarbon occurs via free-radical mechanisms (17,21,22,23). In the following reactions 1,2,3, the reaction is initiated by homolysis of carbon-carbon bonds in reaction 1. These free radicals are unstable species and they undergo bond scission to transform into more stable forms to give ethylene and a primary radical which has two fewer carbon atoms. The c-c bond scission occurs at the c-c- bond located β to the free radical carbon atom as stated by the empirical β -rule as in reaction 2. Then the newly formed primary free radical can undergo further β -scission to give ethylene and a small methyl radical, which can abstract a hydrogen radical from another paraffin molecule to produce a random secondary radical and methane as in reaction 3. This will in turn undergo β -scission and the process is repeated, leading to the formation of large amounts of ethylene, small amounts of methane and small amounts of α -olefins (24).



Previous Investigations:

The concept of utilization of shale oil in both fuel and petrochemicals has been examined in the past 30 years by several investigators. The previous pyrolysis experimental tests on crude shale oil were done by the Institute of Gas Technology in the 1950's (20), and at the Laramie Energy Technology Center of the Department of Energy (19, 28). In addition to these studies a group of studies were done at the Colorado School of Mines for the Steam Pyrolysis of Various Shale Oils(31,32,33,34,35,36,37,38). Also, several studies on the pyrolysis of crude shale oil and shale oil distillates have been done by DuPont (25,27), and by Stone and Webster (48).

Institute of Gas Technology (IGT):

The studies made by this institute involved high temperature, vapor phase cracking of hydrocarbons, and pyrolysis of a crude shale oil in a continuous flow vertical tube reactor (28). The shale oil studied was produced from the

Green River formation by the Bureau of Mines gas combustion and Union Oil Company processes. The experiments were run for reaction temperature over the 1400 to 1550 °F range, at reaction times of 1.0 to 4.5 a second and at partial pressures of the product gas from 0.64 to a 0.76 atm. Increased reaction time or temperature resulted in increased hydrogen and methane yields and results in decreased yields of ethane and proylene. Decreases in hydrocarbon partial pressure resulted in the expected increase in ethylene production. Yields of 21 weight percent of feed ethylene and 4 weight percent of feed propylene were obtained at the optimum conditions of the study. In addition this Institute developed a pyrolysis severity factor by combining the effects of temperature and residence time into a single variable which can be used to correlate yield data (20).

Laramie Energy Technology Center (LETC):

The earlier work at this center was conducted on high temperature retorting of oil shale in both a vertical tube externally heated (29), and an entrained solids retort (19). The high temperature is used by this center to investigate the effect of continuing the cracking process that is begun when the organic matter in the shale is converted to oil (19,29). In the first series, tests involving the retorting

of pulverized oil shale, entrained in steam or other gaseous media in a vertical tube high temperature retort. The produced oil did not contain the expected much larger amount of aromatics that those produced by conventional retorting. In another series of tests, shale oil from a conventional retort was thermally cracked for comparison with the higher temperature retorting results. The results show a significant conversion to the chemical intermediates of interest up to 20% ethylene by weight was obtained (19).

Colorado School of Mines:

In June 1976, an investigation to determine the suitability of shale oil as a feedstock for petrochemical intermediate production was initiated as a research program for studying the Utilization of Shale Oil as a Feedstock for Steam Pyrolysis. The investigators are Dr. Philip F. Dickson and Dr. Victor F. Yesavage, Department of Chemical and Petroleum-Refining Engineering, Colorado School of Mines (30).

First Griswold (31), pyrolyzed crude shale oil from the TOSCO II process in a bench scale pyrolysis unit with steam at atmospheric pressure in a tubular reactor filled with ceramic balls. The ranges of variables studied were: temperature 1300-1600 °F, residence time 0.4-1.2 seconds, and steam to hydrogen ratio 0.4 to 1.2. The results were

correlated with the modified pyrolysis severity factor. The maximum yields of ethylene, propylene, and total light olefin are given in Table 1.

Next Fritzler (32), pyrolyzed both TOSCO II and simulated in situ crude shale oils over reaction variables ranges of temperature 1305-1610 °F, residence 0.2-1.3 seconds, and steam to oil ratio 0.4-1.6. Also he modified the residence time for nonuniformity of the temperature along the reactor length, but he correlated his results with the same severity factor used by Griswold. The maximum yield of ethylene, propylene, and total olefin are given in Table 2.

For further investigations, Smith (33) pyrolyzed the vacuum distillates of a TOSCO II oil and simulated in situ oil. The conditions in this study are essentially the same as those used by Fritzler. Table 3 shows the results of the maximum yields of valuable products. The results of this table indicate that the distillate was greatly improved over the Tosco II whole oil, while the simulated in situ yields were comparable to those of the whole oil.

In another part of the study, the investigation was focused toward the liquid products of steam pyrolysis of shale oil. Kavarianian (34) studied the formation of aromatics and distribution of nitrogen and sulfur in liquid products of steam pyrolysis of whole shale oil and vacuum

TABLE 1. MAXIMUM LIGHT OLEFIN YIELDS (WT % OF FEED)
OF FEED WHOLE OIL (31)

	<u>TOSCO II</u> <u>Whole Oil</u>	<u>Simulated In Situ</u> <u>Whole Oil</u>
Ethylene	19.9	22.14
Propylene	8.5	11.4
Total olefin	28	38.7

TABLE 2. MAXIMUM LIGHT OLEFIN YIELDS (WT % OF FEED)
OF TOSCO II CRUDE SHALE OIL (32)

	<u>TOSCO II Crude</u> <u>Shale Oil</u>
Ethylene	24.2
Propylene	10.3
Total olefins	39.2

TABLE 3. MAXIMUM LIGHT OLEFIN (WT % OF FEED)
OF FEED DISTILLATE (33)

	<u>TOSCO II</u> <u>Vacuum Distillate</u>	<u>Simultate In Situ</u> <u>Vacuum Distillate</u>
Ethylene	22.62	28.80
Propylene	12.3	14.1
Total Olefin	40.5	47.2

distillates. The results show that the amount of nitrogen and sulfur in the liquid products is much higher than that of the feedstocks and carbon to hydrogen ratio of the liquid products is much higher than the feedstocks also. In a study related to the work done by Kavianian, Angelos (35) pyrolyzed several different shale oils at various levels of hydrogenation. He analyzed the liquid products for C_6-C_8 monoaromatics, benzene, toluene, and xylene (BTX). He reported BTX yields proved to be comparable to values reported in other studies, and the severity of feedstock hydrogenation seemed to have an effect in maximizing BTX formation.

For the effect of hydrogenation severity on pyrolysis yields, the vacuum distillates of TOSCO II and simulated in situ shale oil were hydrogenated at three levels of hydrogenation, mild, moderate, and severe, and each one was pyrolyzed at different values of the reaction variables. This study was done by three investigators, A. A. Ballut, H. R. Kavianian and C. F. Griswold. Ballut (36), pyrolyzed mildly hydrogenated vacuum distillates of TOSCO II and simulated in situ. The results show that the yields of valuable olefinic products were in general higher than those obtained using the whole shale oil or their vacuum distillates. In addition to this, the kinetics of crude shale

oil steam pyrolysis was studied using hydrogenated TOSCO II and simulated in situ shale oil. Kavarian (37), pyrolyzed moderately hydrogenated TOSCO II and simulated in situ shale oils; the experimental results indicate that these oils should make an excellent feedstock for steam pyrolysis. He developed a simulation model for steam pyrolysis of liquid hydrocarbons. Griswold (38), pyrolyzed the most severely hydrogenated TOSCO II and simulated in situ oil at conventional pyrolysis operating conditions. The results show that shale oil derived liquid should make excellent feedstocks for petrochemical production. Also, he investigated the gasification characteristics, by studying the role of steam reforming in laboratory reactors. The results show that the tendency of severely hydrogenated shale oil to undergo steam reforming to be a qualification to the potential advantages of using shale oil as a petrochemical feedstock. The maximum yields of olefin products found by the three investigators (36, 37, 38), at the reaction variables ranges 1300-1575 °F average temperature, 0.4-1.4 seconds residence time, and 0.24-1.15 steam to hydrogen ratio are presented in Table 4.

DuPont:

DuPont has initiated programs to evaluate new sources of feedstocks for petrochemical. Several steam cracking

TABLE 4. MAXIMUM LIGHT OLEFIN (WT % OF FEED) OF HYDROGENATED VACUUM DISTILLATES (36,37,38)

	<u>TOSCO II Hydrogenated Severity</u>			<u>LETC Simulated In Situ Hydrogenated Severity</u>		
	<u>Low</u>	<u>Med.</u>	<u>High</u>	<u>Low</u>	<u>Med.</u>	<u>High</u>
Ethylene	28.1	28.7	24.5	29.5	34.0	35.7
Propylene	12.9	12.7	14.7	31.1	14.7	15.4
Total Olefin	44.9	46.3	45.7	45.2	52.5	55.4

TABLE 5. SUMMARY OF STEAM PYROLYSIS YIELDS (WT % OF FEED) OF PARAHO SHALE OILS (1)

	<u>Virgin</u>			<u>Hydrogeanted</u>	
	<u>LGO</u>	<u>HGO</u>	<u>Naphtha</u>	<u>LGO</u>	<u>HGO</u>
<u>Feedstock Reaction Conditions</u>					
T, F	1411	1371	1476	1411	1371
€ , sec.	0.32	0.32	0.36	0.34	0.32
Ratio	1.0	1.0	0.75	1.0	1.0
<u>Yields, Wt %</u>					
Ethylene	15.6	10.6	21.1	16.1	14.7
Propylene	11.6	7.5	11.2	11.3	10.6
Butadiene	3.3	1.5	3.9	2.9	2.3
Total Conversion to C ₄	49.8	36.4	57.8	46.9	46.0
Molar H/C of Liquid Products	-	-	11.1	1.23	-

experiments on shale oil have been performed by this company. Recently at DuPont, Glidden and King (1), pyrolysis was done on various cuts of a Paraho shale oil. A summary of pyrolysis yields of ethylene, propylene, and total olefins are shown in Table 5. The results show an increase in olefins yields from hydrotreating the light and heavy gas oils, and the molar H/C ration in the pyrolysis liquid show an acceptable reactor severity was obtained. In addition, Rudershausen and Thompson (27,49) studied the potential for converting Paraho shale oil to chemical feedstocks by such refinery processes as distillation, hydrocracking and reforming, pyrolyzed various fractions of the oil; whole, naphtha, LGO, MGO. The yield of ethylene ranged from 16.2 wt percent from whole oil to 12.6 wt percent from the naphtha. Yield of ethylene from pyrolyzing LGO increased from 11.4 wt percent to 18.5 wt %. A summary of their work is shown in Table 6.

Stone and Webster:

The experimental steam pyrolysis work undertaken on various shale oil feedstocks made by Korosi, et al (48), represent Stone and Webster's interest in the commercial utilization of alternative feedstocks for the manufacture of olefins. In their work raw atmospheric

TABLE 6. SUMMARY OF STEAM PYROLYSIS YIELDS (WT % OF FEED)
OF PARAHO SHALE OILS (27,49)

Feed	CONDITIONS			CONVERSIONS, WT %				
	$^{\circ}$ F	Sec.	Ratio	Methane	Ethylene	Propylene	Butadiene	Benzene
Naphtha (Straight Run)	1454	2.6	1.6	8.4	12.6	2.1	3.4	8.0
LGO (Straight Run)	1488	2.2	1.4	11.3	17.5	1.8	2.6	3.3
MGO (Straight Run)	1486	2.2	1.1	11.1	18.4	2.3	3.0	4.5
Crude (Whole)	1499	1.4	0.9	9.7	16.2	3.5	3.8	2.2
LGO (Straight Run)	1589	1.1	0.6	14.0	11.4	0.3	0.1	2.9
LGO (4x recycled)	1459	4.7	3.0	6.5	18.5	5.8	7.3	5.2
Cyclohexane	1502	2.4	1.5	4.9	16.2	0.7	3.5	4.4
Benzene	1445	2.5	1.2	8.8	11.2	2.5	1.6	3.3

and vacuum gas oil boiling range cuts of a Paraho shale oil were steam cracked to establish pyrolysis yields patterns and then compared with Arabian VGO yields. In addition, the effect of hydrotreatment and its influence on pyrolysis yields was studied on a pair of full-range raw and hydrogenated Occidental shale oil samples and then compared to a Mideast gas oil. Table 7 shows the summary results of their work. A maximum of 23.6 wt % of ethylene obtained from hydrogenated Paraho kerosine, which is higher than the ethylene yield obtained from petroleum pyrolysis, while the ethylene yields from Paraho raw AGO and VGO are less than those obtained from petroleum pyrolysis of Arabian VGO and Mideast AGO.

TABLE 7. SUMMARY OF STEAM PYROLYSIS YIELDS (wt.% of FEED)
OF PARAHO SHALE OIL AND PETROLEUM GAS OIL (48)

Feedstock	PARAHO		OCCIDENTAL		PETROLEUM		
	Hydrogenated Kerosine	Raw ATM.GO	Raw Vac.Go	Raw Full Range	Hydrogenated Full Range	Arabians VGO	Mideast AGO
Run Conditions							
T, °F	1535	1481	1427	1427	1481	1427	1481
θ, Sec.	-	0.2	0.3	-	-	-	-
R	0.7	0.7	1.0	1.0	1.0	1.0	0.7
Yields, wt %							
Ethylene	23.6	15.9	14.4	13.1	19.8	16.1	20.8
Propylene	12.1	10.3	10.5	11.0	13.9	12.0	14.9
Butadiene	4.6	3.6	3.6	3.5	5.0	4.2	4.8
Total Olefin	61.4	47.5	44.0	45.0	60.0	48.7	59.2

Effect of Pyrolysis Condition on Yields:

The most significant variables that influence the product distribution achieved in a steam pyrolysis process are, feed composition, reaction temperature, reaction time, and steam to mass ratio (39,40).

Feed Composition:

Several studies have been made to investigate the effect of feedstocks type on pyrolysis yields using both pure compounds and commercial feedstocks, Vanderkooi (39) and Zdonik, et al. (3), have studied the conversion of wide range of feedstocks to ethylene, and have summarized that, for ethylene production, the feedstocks in order of decreasing convertability are: normal paraffins, naphthenes, olefins, and aromatics (39,3). Paraffins generally react to form light olefins (3,39,15). The lighter olefins (ethylene, propylene, butylene, butadiene) have a tendency to polymerize and condense into mono-aromatics such as benzene and toluene (16,41,17). Naphthenes and higher olefins present in the feed have a tendency to form higher aromatics (3, 39,41). The aromatics may rearrange but are essentially unconverted during pyrolysis (3,39).

Adams (28), reported ethane can yield about 75% ethylene. From this we can say the yield of light olefins is

a strong function of the average molecular weight of the feedstock. Thus as a general rule, the heavier the feedstock the lower will be the yield of petrochemical. The kind and the properties of the feedstocks used in this study will be discussed later.

Reaction Temperature:

The cracking temperature is important in pyrolysis of a hydrocarbon. The rate of cracking of feedstocks to hydrocarbon will increase with high temperature. Vanderkooi (39) reports that as the cracking temperature is increased, hydrogen, methane, and ethylene yields increase, propane, butanes, and pentanes increase and then decrease, and hexanes and non-aromatics decrease. Also, Chambers and Potter (42) report that cracking reactions at highest temperature gave maximum ethylene yields.

Few studies on the effect of high temperature on the distribution of products have been found in the literature. The Institute of Gas Technology (20) made some tests on the pyrolysis of shale oil between 1400 and 1550 °F. Typical highest temperatures conducted at Colorado School of Mines are 1300-1630 °F (31, 32) and 1400-1670 °F (33). In the present study, the highest temperatures range covered are 1600 - 1775 °F more details about the effect of this high temperature will be discussed later.

Reaction Time:

The contact time is a significant variable, that influences the product distribution in steam pyrolysis. Chambers and Potter (42,43) reported that low hydrogen residence time is essential for maximum yields of ethylene or total olefins. Other investigators with petroleum derived feedstocks at constant severity, report that high yields of more valuable olefins are generally obtained at shorter residence time and higher temperature than vice-versa (40). Also, Kamptner (44) explained the importance of residence time; the occurrence of disturbing secondary reaction, are generally noticeable in a reduction in the yield of valuable primary cracked products. Thus the shorter the residence time, the smaller the effect of secondary reactions.

The previous studies have been made with residence time ranges of 1.0-4.5 seconds (20), 0.5-1.5 seconds (39), 0.27-1.34 seconds (32), 0.4-1.2 seconds (32), 0.39-1.13 seconds (33), 0.04-0.1 seconds (36), and 0.01-0.1 seconds (40). The important restriction on short residence time operation has been in the past, the metallurgical requirements necessitated by higher temperature operation. Thus over the past decade, design contact times have been reduced in several stages from 2.0 seconds

to 0.25 second while providing an increase in ethylene yield and decrease in relative tail gas production. In this study we propose to investigate steam pyrolysis under short residence times ranging from 0.05 to 0.105 seconds.

Steam to Oil Mass Ratio:

It has been reported (45) that the function of dilution steam in steam pyrolysis of hydrocarbon for production of light olefins are: lowering of hydrocarbon partial pressure resulting in better selectivity for olefins, reducing coke formation, and an oxidizing effect on the tube metal to diminish significantly the catalytic effect of iron and nickel which would promote carbon forming reactions. Also, the presence of steam in pyrolysis acts as an oil preheat source and as a carrier medium. The mass ratio is heavily dependent on feedstocks, increasing with increasing high boiling fractions.

Chambers and Potter (42,46) reported that ethylene and the unsaturated component yield are enhanced as the partial pressure is reduced, or in other words as the mass ratio is increased. Studies have been made with steam-hydrocarbon mass ratio of 0.5-1.0 (43), and 0.2-0.8 (39)

for feedstocks in the range of light naphtha to heavy gas oil. For oil shale the work done has been in the range of 0.4-1.2 (3), and 0.4-1.6 (32). It has been found (31,39) that the steam to hydrocarbon mass ratio had less effect on product yields than either the residence time or reaction temperature.

FEEDSTOCK CHARACTERISTICS

As previously discussed, the feedstock composition is an important factor in product composition and yield in steam pyrolysis. Hydrogenated shale oil feedstocks were used in the present study. Two different types of hydrogenated shale oil feedstocks were chosen:

- I. Paraho hydrogenated feedstocks (sample number, P-6281, P-6280, and P-3536).
- II. TOSCO II hydrogenated feedstocks (sample number, T-6199, T-6209, and T-6206).

These hydrogenated samples were prepared by Chevron Oil Company from vacuum distillates as part of a contract under the Department of Energy. The vacuum distillates were prepared at the laboratories of Lion Oil Company from crude shale oil.

In the hydrogenation process, the high pressure, temperature, and hydrogen atmosphere shifts the composition of feedstocks toward a highly paraffinic composition by a combination of ring saturation and bond breaking. Also, hydrogenation eliminates the undesirable elements such as, sulfur, nitrogen, oxygen, and metals. Therefore, hydrogenation improves the quality of feedstock for pyrolysis, and it also provides a cleaner feedstock (38).

In order to study the effect of prefining of feedstocks, on the yield of valuable products, three levels of hydrogenation were selected for pyrolysis runs, indicated by nitrogen content. The hydrogenated samples used range in nitrogen content from 0.048 to 0.44 wt% for the Paraho shale oils, and from 0.04 to 0.85 wt% for TOSCO II shale oils. The characteristics of each sample are presented in Tables 8 and 9.

TABLE 8. CHARACTERIZATION OF TOSCO II FEEDSTOCKS

<u>Oil No.</u>	<u>6209</u>	<u>6199</u>	<u>6206</u>
Product Inspections			
Gravity, °API	39.5	36.7	33.8
Anline Point, °F	161.5	151.1	136.7
Sulfur, wt%	0.02 ¹	0.05 ¹	0.02 ¹
Nitrogen, wt%	0.035	0.30	0.82 ³
Carbon, Wt%	86.29 ¹	86.11 ¹	86.11 ¹
Hydrogen, Wt%	13.67 ¹	13.34 ¹	13.06 ¹ (12.89) ²
Chromatographic Simulated TBP, °F			
St/5	215/301	192/300	228/323 ³
10/30	331/421	333/428	350/444
50	496	515	542
70/90	590/734	619/775	647/793
95/99	798/910	835/945	844/969
Estimated H ₂ Conc., SCF/BBL	-	1190	840
Estimated Liquid Yields LV% of feed	-	103.8	102.5
C/H Ratio	6.31	6.46	6.59
Molar H/C Ratio	1.90	1.86	1.82

1 Huffman Laboratories

2 Griswold (38)

3 Kavianian

TABLE 9. CHARACTERIZATION OF PARAHO FEEDSTOCKS

<u>Oil Number</u>	<u>6280</u>	<u>6281</u>	<u>3536</u>
Product Inspection:			
Gravity, ° API	37.0	-	34.2
Sep. Gravity	0.84	-	0.854
Anline Point, °F	171.7	-	-
Sulfur, Wt. %	0.02 ¹	0.03 ¹	0.09 ¹
Nitrogen, Wt. %	0.05	0.27	0.4 ³
Carbon, Wt. %	86.36 ¹ (86.0) ²	86.43 ¹ (87.09) ⁴	86.58 ¹ (85.9) ²
Hydrogen, Wt. %	13.44 ¹ (14.0) ²	13.22 ¹ (13.96) ⁴	13.27 ¹ (13.7) ²
Chromatographic Simulated TBP, °F			
St/5	71/257	-	-
10/30	316/452	-	-
50	563	-	-
70/90	677/824	-	-
95/99	881/	-	-
Estimated H ₂ Conc., SCF/BBL			
		-	
Estimated Liquid Yield LV% of Feed			
	-	-	-
C/H Ratio	6.43(6.11) ²	6.54(6.24) ⁴	6.52(6.28) ²
Molar H/C Ratio	1.87	1.84	1.84

¹Huffman Laboratories
²Griswold
³Angelos
⁴Kavianian

EXPERIMENTAL APPARATUS

The overall experimental apparatus used in this study is essentially the same as in the previous studies (34,36, 37,38). The schematic of the system is presented in Figure 1. The system can be divided into three main parts:

1. Feed System
2. Reactor System
3. Cooling-Sampling System

Feed System:

Distilled water for generation of steam is pumped from 250 ml burets by a Lapp pump to a 24 inch section of 1 inch schedule-40, 304 stainless steel pipe packed with 3/8 inch Coors ceramic balls held by nichrome wire gauze inside a single zone Lindberg furnace with a controller that operates in the range of 200 to 1200 °C. The produced steam flows to the reactor inlet through a superheater of an 18 inch section of 1/4 inch O.D. 316 stainless steel tubing wrapped with a Briskeat heating tape and asbestos cloth insulation.

Shale oil is fed to the reactor inlet from 250 ml burets by a Lapp pump through 1/4 inch O.D. 316 stainless steel tubing. The oil is preheated by two tubing sections wrapped with Briskeat heating tape, the heating tapes are controlled with 7½ amp. rheostats for both steam and oil. Then the oil is mixed with steam in a tee junction at the

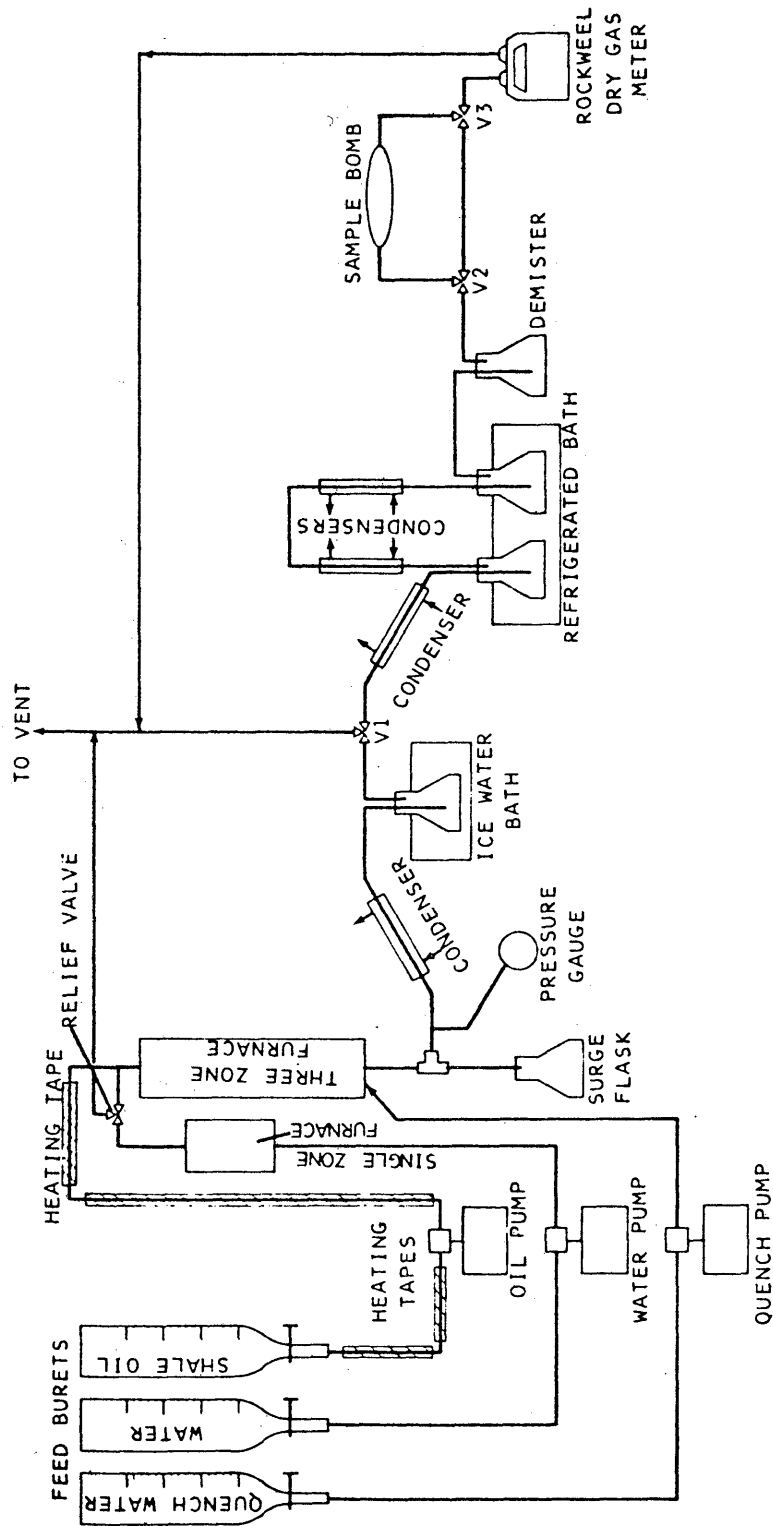


Figure 1.--Experimental apparatus for pyrolysis system.

reactor inlet. The temperatures of steam and oil inlet are measured by type K 1/8 inch O.D. 316 stainless steel sheathed ground thermocouples wired to an Omega 1695-automatic scanner and Omega 200 digital temperature indicator.

Reactor System:

A small unpacked reactor, 13-inch in length of 3/8 inch diameter schedule-40 Inconel Alloy 601 pipe was designed, constructed, and installed. The advantages of using the smaller reactor allows running with smaller feed volumes and thus more runs per sample can be made and allows for better temperature profile control. The disadvantage of the smaller reactor is the limitation on the size of liquid product sample that can be collected.

The temperature profile of the reactor during each run is monitored by a 1/4 inch O.D. 316 stainless tubing thermowell extending concentrically inside the reactor, containing nine type K 0.04 inch O.D. 316 stainless sheathed grounded thermocouples spaced at 2 inch intervals from the top to the bottom of the reactor for the first eight runs then replaced by nine other type K 0.04 inch O.D. Inconel 600 sheathed grounded thermocouples for the rest of the runs. The present arrangement of the centerline thermocouples is shown in Figure 2. These thermocouples are connected to an Omega automatic scanner and an Omega digital indicator. The desired

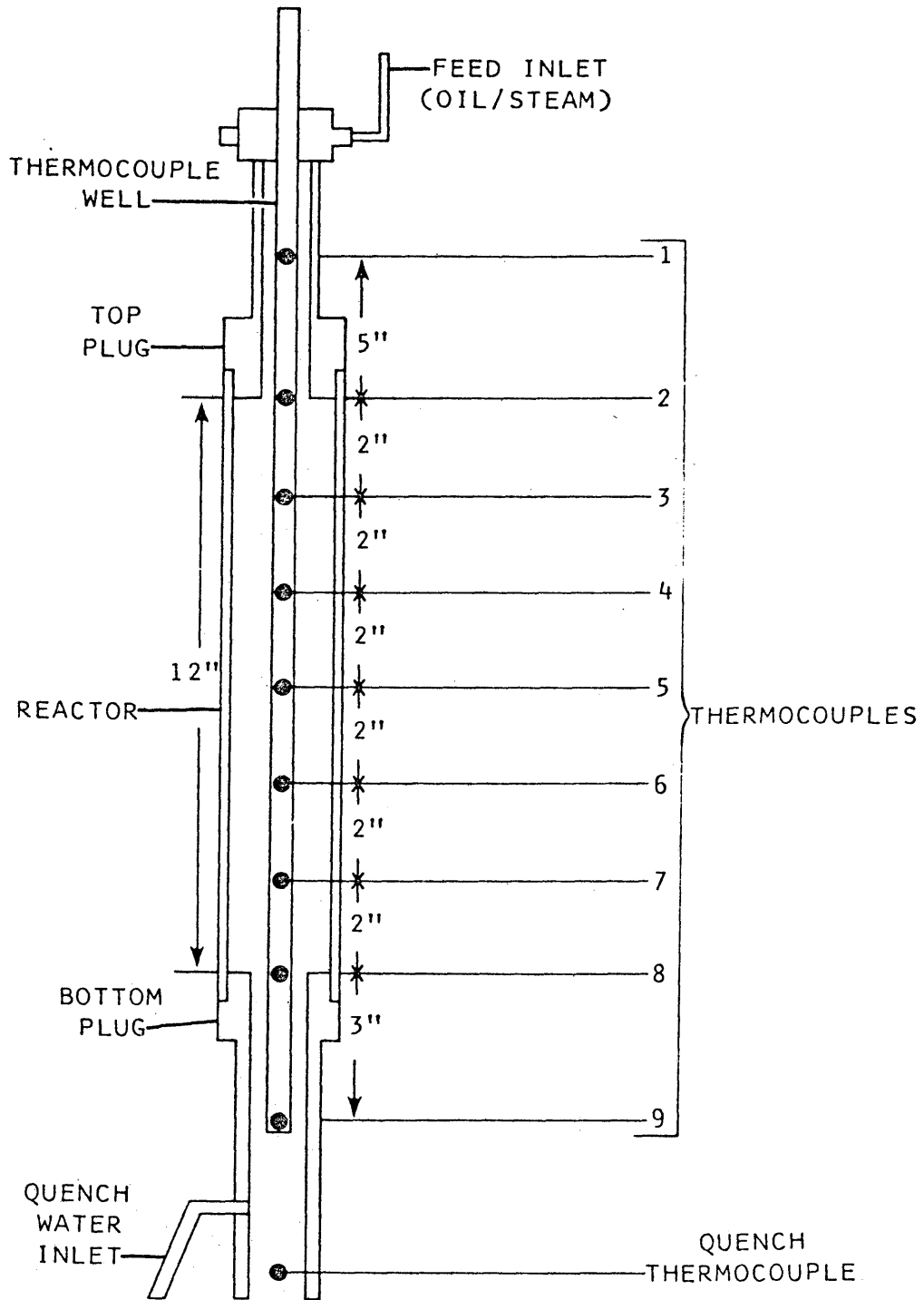


Figure 2.--Thermocouple location.

reactor temperature is reported as the mean average temperature of the temperature from position 2 to position 7. The reactor is heated by a Lindberg three-zone tube furnace with separate temperature controllers for each zone in the range of 200-1200 °C. The hot product gases flowing out of the reactor passes down through a 1 inch I.D. 316 stainless steel tube where they meet the distilled water quench stream which cools the products to about 500-700 °F. This has been found sufficient to stop the pyrolysis reactions.

The quench water is pumped by a liquid metronics pump from another 250 ml buret. A pressure gauge was used to measure the pressure of the system at the outlet of the reactor, normally 1-1.2 atmospheres.

Cooling-Sampling System:

The quenched vapor mixture flows into a 200 ml surge flask where the first gas-liquid separation takes place. The gas coming off the top of the surge flask passes through a 3/8 inch O.D. 316 stainless steel tube, where the gas is initially cooled by a single pipe condenser 18 inches long. The gas from the outlet of the condenser flows through a 1/4 inch O.D. 316 SS tubing to the next 1000 ml flask, which is cooled by an ice bath in which most of the liquids are condensed. The remaining gases pass through a two-way Whitey SS valve (V1), which can be switched to atmospheric

venting in case of an emergency when the pressure suddenly increases due to plugging in the system. The product gas flows through another single condenser, 16½ inches long, 1/2 inch O.D. for further cooling.

Additional cooling is obtained by passing the gases through two, 500 ml flasks, which are separated by two, 24 inch single pipe condensers 1/4 O.D. arranged vertically to drain back the liquids into the flasks. These flasks are cooled by an ethylene glycol/water refrigerated bath cooled to about -34°F.

Finally, the noncondensable gas flows through a 125 ml flask containing pyrex glass wool to remove entrained liquid, then to a Rockwell dry gas meter to measure the volume of the gas. Prior to the gas meter a parallel line is connected to the tubing by two Whitey two-way valves as shown in Figure 1 by V2 and V3 to allow venting the gases to the atmosphere outside of the laboratory or a sample of the product gas can be taken in a 300 ml or a 1000 ml, 316 SS sample bomb.

Calibration of Gas Meter:

A new simple and accurate method of calibrating laboratory gas meters is calibration by the aspirator or weighed-water method. This method was used to calibrate the gas meter instead of using the precision scientific wet test

meter which was used for the previous studies until problems occurred with the equipment due to long use. Figure 3 shows the inexpensive equipment for this method. The volume of gas drawn through the gas meter for a number of revolutions of the index is obtained from the corresponding weight of water displaced from the bottle (47).

Prior to every run, before making the calibration, the system should be operated several cycles to bring the temperatures of all parts as close together as possible. When temperatures are as nearly uniform, the water discharge is opened to discharge water into a waste bucket. As the index of the meter passes through zero position, the discharge tube is shifted to allow water to run into the weighing bucket. As soon as the meter index has made the required number of revolutions, the discharge tube is shifted back to the waste bucket just as the meter index passes through the zero position. The volume of the air which passed through the gas meter into the bottle is calculated corresponding to the weight of water displaced, i.e., equivalent volume (ft^3) is found, then from which the correction factor is calculated.

Safety Features:

- The pressure of the reactor is monitored at all times during the run. A 25 psig safety relief valve is connected to the steam feed line and vented to the atmosphere.

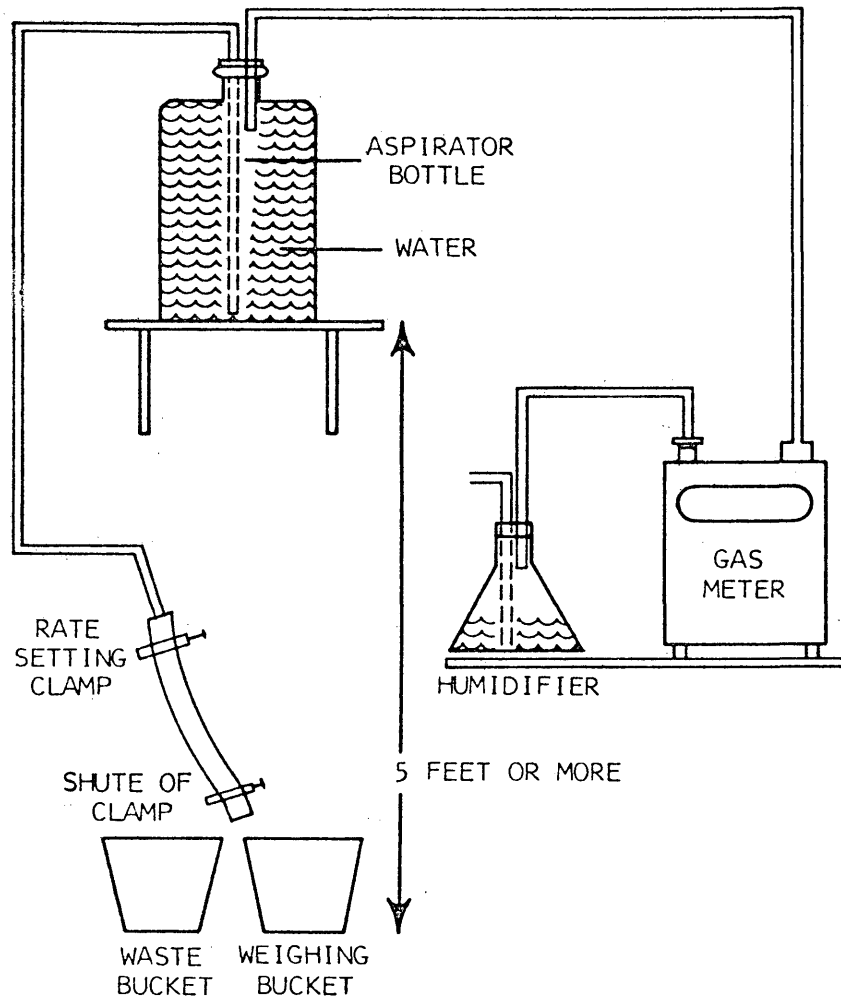


Figure 3.--Equipment for calibration of the gas meter by aspirator method.

- A combustible gas detection instrument of M-S-A series I-501 was used to continuously analyze the atmosphere to detect the presence of flammable gases or vapors up to their lower explosive limit in air and to an audio/visual alarm when a predetermined concentration is reached.
- The experimental apparatus is enclosed in a safety cage area to prevent the operator from hazardous gases and to protect the operator from contact with heated equipment and from any sudden explosion.
- The safety cage is equipped with a fan with duct work to help continuously exhaust the reactor area from the product gases.
- The emergency shutdown procedures is as follows:
 - If the pressure builds up, or if there is an emergency on the outside, shutoff the system, and switch valve V1 as shown in Figure 1 to vent and terminate the run.

EXPERIMENTAL PROCEDURE

Efforts of at least two people are required for the procedure. Prior to each run the following steps are necessary for each run.

1. Clean all lines in the condensing system and condensers with acetone then with compressed air, and weigh all four collection flasks.
2. Calibrate the Rockwell gas meter to obtain the correction factor by aspirator or weighed-water method as discussed in the previous section.
3. Set the controller of the refrigerator at the desired cooling temperature and turn it on about 12 hours before the run.
4. Set the controller at the desired reaction temperature on the three-zone Lindberg. The top of the reactor must be above the desired temperature and the bottom of the reactor somewhat below the desired temperature, and then turn the furnace on four to eight hours to get the desired temperature.
5. While the system is heating up, set the water and oil pumps to the desired flow rates. Fill oil, quench, and water burets, and then start up the Carle GC using the gas chromatograph method developed by Smith (33).

6. Shortly before the system reaches the desired temperature, the single-zone furnace, preheat oil, steam superheat rheostats, and the condenser coolant pump, are turned on. Then fill out the run data sheet with the required data.

7. When the reactor reaches the desired reaction temperature, record buret levels, attach surge flasks, and then record the temperature profile of the reactor and all other monitored temperatures using the Omega scanner indicator.

8. To start the run, turn valve V1 to condenser position, valve V3 to meter position, and then start the run by turning the oil, quench, and steam pumps simultaneously with stopwatch and record the time.

9. During each run, the temperature profile along the reactor is monitored and recorded at equal intervals of 10, 20, and 30 minutes. The flow rates of the gas, steam, and oil are recorded every five minutes to control the flow rates to the desired flow.

10. Gas samples are taken with two sample cylinder bombs of 300 cc and 1000 cc at 20, and 30 minutes from the start of the run. This time is believed to be sufficient for the system to reach steady state condition.

11. The run is terminated shortly after the second sample cylinder bomb is taken, by shutting off the steam, oil, and quench pumps simultaneously. Then turn off the Lindberg furnaces, superheater, oil preheat, and the refrigerated bath.

12. Record the gas meter reading, and the buret levels on the data sheets. Steam is allowed to flow a few more minutes to purge to remaining gases.

13. Allow the system to cool overnight, and disconnect the gas meter, then purge it with compressed air to flush out the remaining gases and the condensed liquid.

Gas Analysis System:

The gaseous products are analyzed by a Carle-Model III analytical gas chromatograph. The analysis is done by using a vacuum sampling system with a helium carrier gas to overcome the lack of enough pressure between the chromatograph and the gas bomb (33). For each run one test can be made on the 300 cc sample cylinder bomb and four tests on the 1000 cc sample cylinder bomb. The individual component peaks are determined by physically counting the traces, using a Houston instrument recorder #7302 omniscrite 1 mv complete with integrator. The chromatograph and its operation procedure has been described by Smith (33). The

components analyzed and the relative amounts of each compound from their peak area are calculated by the computer program PSY.FOR as shown in Appendix (C).

RESULT AND DISCUSSION

A series of experimental runs were made with the hydrogenated Paraho and Tosco II shale oils. A total of 16 runs were made; 7 runs for the Paraho and 7 for the Tosco II shale oils, and 2 additional runs to check the reproducibility of the pyrolysis system.

The two reaction variables--residence time, reaction temperature, were varied at constant steam to oil mass ratio to determine their relationship to gaseous product yields. The runs were attempted at temperatures of 1603, 1702, and 1775 °F and residence times of 0.05, 0.07, and 0.1 seconds, the steam to oil mass ratio was kept at about 1.0.

A summary of feedstock characteristics, reaction conditions, total gas and liquid products, molar H/C ratio, and C/H ratio of liquid products is given in Tables 10 and 11. Tables 12 and 13 are a compilation of selected product results of experimental runs on Paraho and Tosco II oils.

Detailed information of the product gas compositions, total gas and liquid yields, and the predicted molar H/C ratio and C/H ratio are listed in Appendix C. The computer program PSY.FOR and the equations used for calculating the product yields are given in Appendices A and B.

The experimental results to be discussed in the following sections will cover the following areas of investigations:

TABLE 10. EXPERIMENTAL PYROLYSIS SUMMARY OF HYDROGENATED PARAH OIL

Run No.	Oil Type	Wt. N	Wt. C	Wt. H	Reaction Temp (F)	Residence Time (sec)	Steam/oil Mass Ratio	Wt. gas Products	Wt. Liq. Products	Severity factor	C/H Ratio on Liq. Products	Molar H/C Ratio on Liq. Products
T1	6281	0.27	87.09	13.96	1605	0.100	1.015	60.76	39.24	1399.1	11.37	1.050
T2	6281	0.27	87.09	13.96	1604	0.069	0.997	72.91	27.09	1366.1	10.67	1.120
T3	6821	0.27	87.09	13.96	1608	0.050	0.996	76.60	23.40	1342.7	12.24	0.980
P1	6281	0.27	87.09	13.96	1702	0.100	0.933	58.68	41.32	1477.0	11.65	1.03
P2	6281	0.27	87.09	13.96	1773	0.100	1.107	61.79	38.21	1552.4	12.04	1.00
H1	3536	0.44	86.58	13.60	1611	0.101	0.997	64.84	35.16	1403.8	11.69	1.03
H2	6280	0.046	96.36	13.44	1607	0.106	0.976	60.79	39.21	1402.7	11.55	1.04
H3	6281	0.27	87.09	13.96	1706	0.093	0.991	59.04	40.96	1478.9	11.01	1.09

TABLE 11. EXPERIMENTAL PYROLYSIS SUMMARY OF HYDROGENATED TOSCO II

Run No.	Oil Type	Wt% N	Wt% C	Wt% H	Reaction Temp (°F)	Residence Time (sec)	Steam/Oil Ratio	Wt% Gas Products	Wt% Liq. Products	Severity Factor	C/H Ratio on Liq. Products	Molar H/C Ratio on Liq. Products
R1	6199	0.30	86.11	13.34	1610	0.105	1.040	53.46	46.54	1409.7	9.77	1.23
R2	6199	0.30	86.11	13.34	1604	0.071	0.966	69.58	30.42	1366.8	9.18	1.31
R3	6199	0.30	86.11	13.34	1609	0.050	0.994	69.95	30.05	1344.4	11.92	1.01
G1	6199	0.30	86.11	13.34	1705	0.105	0.999	51.53	48.47	1489.4	11.47	1.05
G2	6199	0.30	86.11	13.34	1775	0.099	0.987	53.93	46.07	1544.5	11.69	1.03
S1	6209	0.035	86.29	13.67	1611	0.101	0.984	62.99	37.01	1402.9	10.68	1.12
S2	6206	0.82	86.11	13.06	1606	0.100	0.966	59.43	40.57	1396.6	11.10	1.08
S3	6199	0.30	86.11	13.34	1603	0.101	0.986	53.33	46.87	1395.9	9.37	1.28

- A. The effects of the reaction variables on the product yield, the investigations take two directions:
1. Short residence time pyrolysis
 2. High temperatures pyrolysis
- B. The effects of feed composition and nitrogen level on product distribution and yields.
- C. Comparison of the results of steam pyrolysis of hydrogenated shale oil with other studies of shale pyrolysis of conventional shale oil feedstocks.

A. Effect of the Reaction Variables:

1. Short Residence Time

A series of experimental runs were made on the Paraho and Tosco II hydrogenated samples to study the effect of short residence time on the yield of valuable gaseous products. This effect was investigated at 0.05, 0.069, and 0.10 seconds times at average temperature about 1606 °F and a steam to oil mass ratio at about 1.0. A summary of the experimental results on the pyrolysis of different severity for hydrogenated Paraho and Tosco II shale oils can be found in Tables 12 and 13.

The weight percent of feedstock converted to different gaseous products is plotted as a function of residence time in Figures 4 and 5. And the volumetric gaseous product

TABLE 12. SUMMARY OF RESULTS FOR STEAM PYROLYSIS OF HYDROGENATED PARAFFIN OIL

Run No.	Oil Type	Reaction Temp.(°F)	Residence Time(sec)	Steam/oil Mass Ratio	Gas Product Composition (mole Gas)					Gas Product Yields (wt% Feed)				
					C ₂ H ₄	C ₃ H ₆	C ₄ H ₆	C ₄ H ₈ 's	Total Olefin	C ₂ H ₄	C ₃ H ₆	C ₄ H ₆	C ₄ H ₈ 's	Total Olefin
T1	6281	1605	0.100	1.015	23.07	4.91	1.88	1.18	31.04	20.83	6.65	3.27	2.13	32.88
T2	6281	1604	0.069	0.997	24.93	7.12	2.36	1.21	35.62	24.02	10.29	4.39	2.32	41.02
T3	6281	1608	0.050	0.996	31.04	9.69	2.79	2.59	46.11	28.57	13.39	4.95	4.76	51.67
P1	6281	1702	0.100	0.933	12.64	1.47	1.30	0.12	15.53	14.03	2.56	2.91	0.28	20.38
P2	6281	1773	0.100	1.107	9.01	0.85	0.2	0.07	10.13	11.86	1.69	0.51	0.19	14.25
H1	3536	1611	0.101	0.997	33.19	8.01	2.48	1.41	45.09	26.66	9.65	3.85	2.27	42.43
H2	6280	1607	0.106	0.976	13.23	2.69	0.92	0.41	17.25	14.58	4.45	1.96	0.93	21.92
H3	6281	1706	0.093	0.991	14.01	1.79	1.34	0.22	17.36	15.45	2.95	2.84	0.46	21.70

TABLE 13. SUMMARY OF RESULTS FOR STEAM PYROLYSIS OF HYDROGENATED IOSCO LI OIL

Run No.	Oil Type	Reaction Temp.(°F)	Residence Time(sec)	Steam/oil Mass Ratio	Gas Product Composition(Mole Gas)					Gas Product Yields (wt% Feed)				
					C ₂ H ₄	C ₃ H ₆	C ₄ H ₆	C ₄ H ₈ 's	Total Olefin	C ₂ H ₄	C ₃ H ₆	C ₄ H ₆	C ₄ H ₈ 's	Total Olefins
R1	6199	1610	0.105	1.046	30.99	7.92	2.45	1.67	43.03	21.39	8.21	3.26	2.31	35.17
R2	6199	1604	0.071	0.966	28.74	9.05	2.88	2.18	42.85	23.30	11.00	4.50	3.54	42.34
R3	6199	1609	0.050	0.994	38.81	10.81	3.11	3.05	55.78	30.15	12.60	4.66	4.74	52.15
G1	6199	1705	0.105	0.999	21.47	3.64	0.93	0.47	26.51	18.48	4.70	1.54	0.81	25.53
G2	6199	1775	0.099	0.987	10.08	1.57	0.47	0.33	12.45	11.27	2.64	1.87	0.58	16.36
S1	6209	1611	0.101	0.984	25.35	6.05	2.03	0.92	34.35	22.52	8.06	3.47	1.63	35.68
S2	6206	1606	0.100	0.966	31.53	8.77	2.67	1.66	44.63	23.02	9.60	3.76	2.42	38.80
S3	6199	1603	0.101	0.986	34.25	7.97	2.70	1.45	46.37	23.10	8.06	3.51	1.95	36.82

yields are plotted as a function of residence time in Figures 6 and 7.

Paraho Shale Oil:

Experimental runs were made with the medium severely hydrogenated Paraho shale oil (Sample #6281, 0.27 wt.% nitrogen), the runs were attempted at constant average temperature (1609 °F). As can be seen from Figure 4, lowering residence time from 0.1 to 0.05 seconds results in increased weight percent of feed converted to total gas, total olefin, ethylene, pyrolylene, and 1,3 butadiene. The total gas yield increased gradually from 60.76 wt.% of feed (12.42 SCF/#feed) to 72.09 wt.% of feed (13.24 SCF/#feed) then increases slowly to a maximum of 76.60 wt.% of feed (12.65 SCF/#Feed) at 1608 °F. The yield of ethylene exhibits a maximum of 28.57 wt.% of feed (3.93 SCF/#Feed) at 0.050 second and 1608 °F. The results show also a decreasing in the yields of hydrogen, carbon monoxide, and methane as the residence time decreased from 0.100 to 0.05 seconds. A summary of the more important results is given in Tables 10 and 12.

Tosco II Oil:

Effect of 0.05, 0.071, and 0.105 seconds residence time were examined at an average temperature (1608 °F) and steam to oil mass ratio about 1.0. The experimental results

HYDROGENATED PARAHO OIL #6281
(AVERAGE TEMP. :1606 DEG.F)

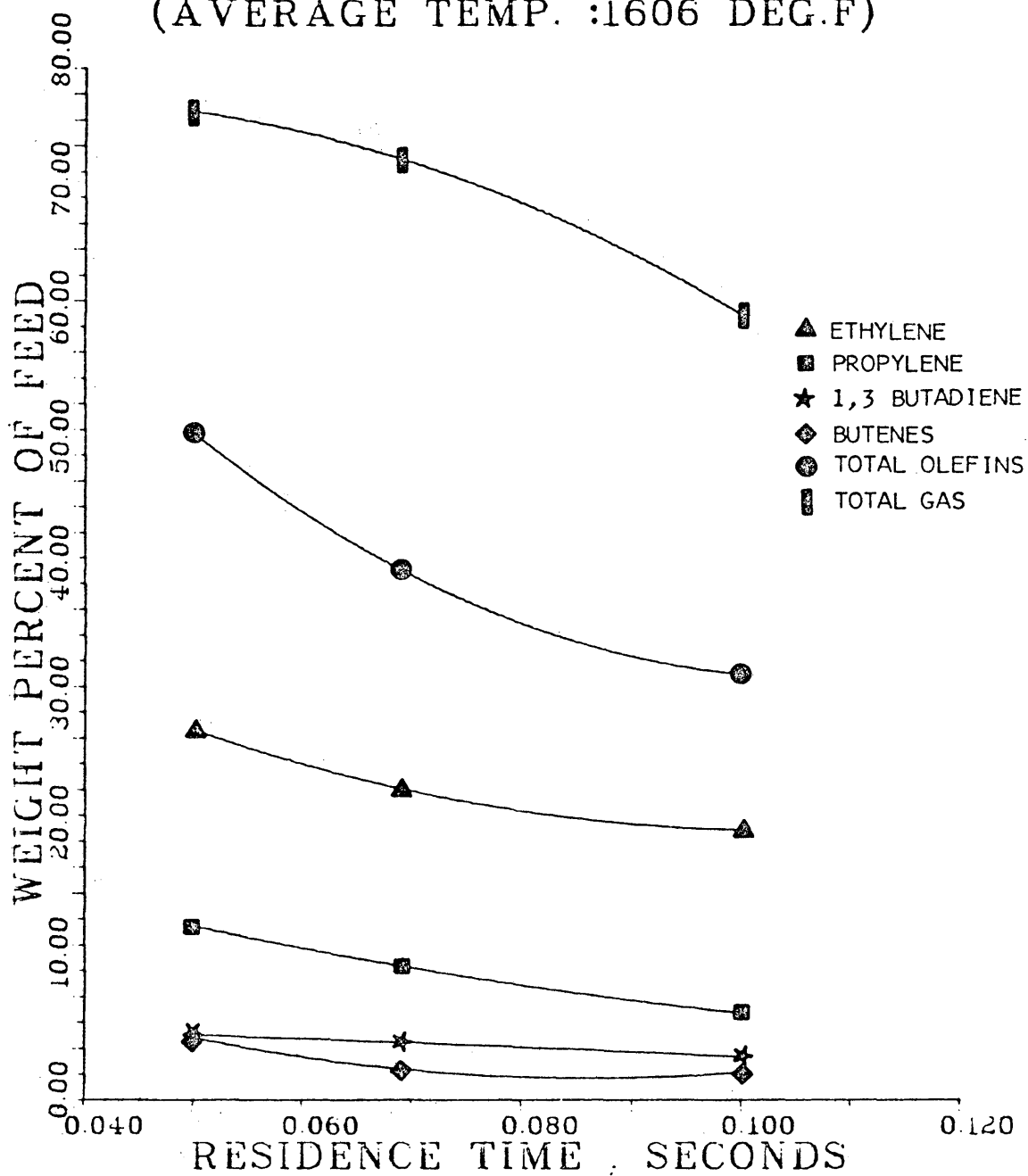


Figure 4.--Effect of Residence Time on product yields

HYDROGENATED TOSCO II #6199
(AVERAGE TEMP. :1607 DEG. F)

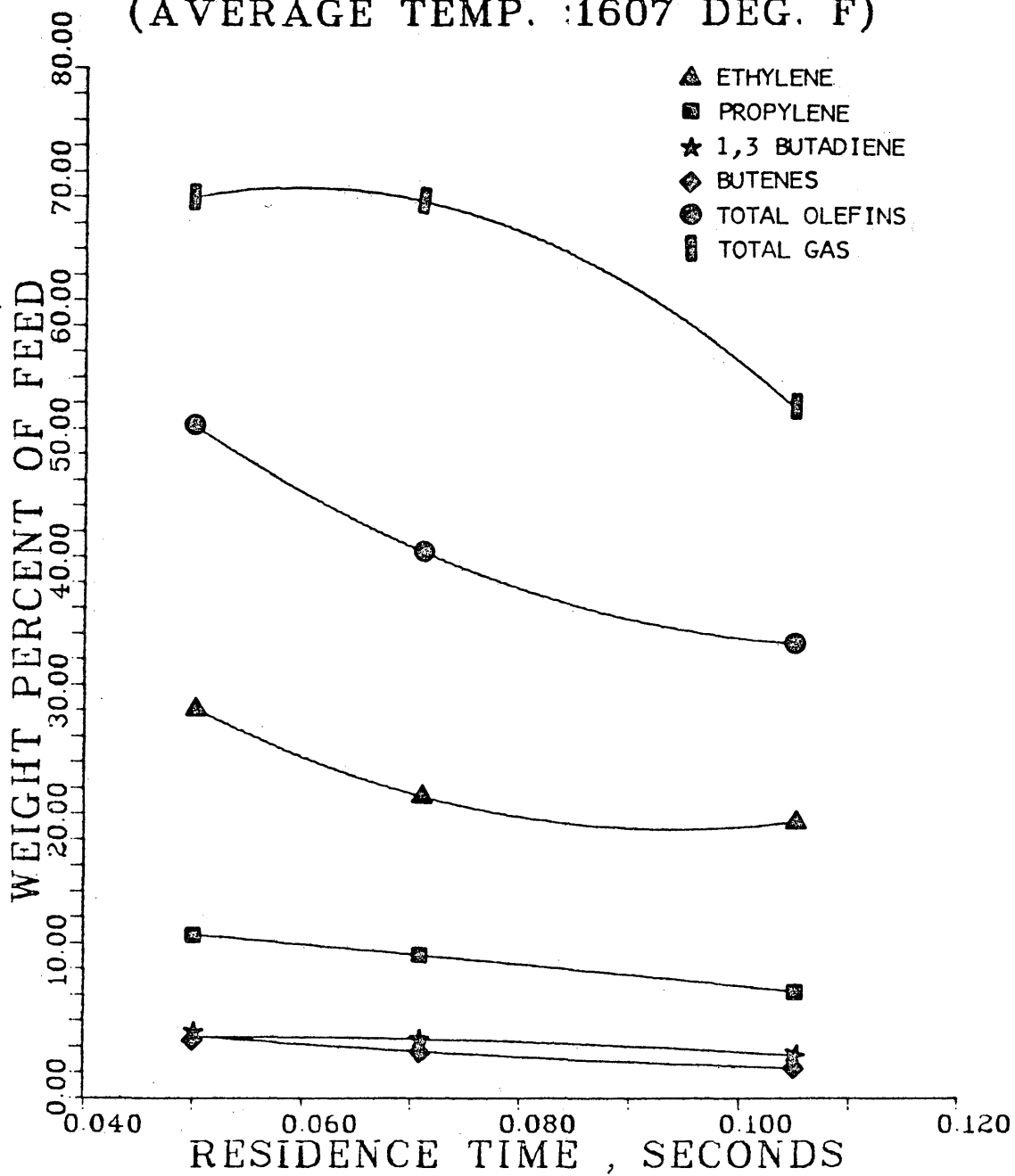


Figure 5.--Effect of Residence Time on product yields

HYDROGENATED PARAHO OIL #6281
(AVERAGE TEMP. : 1606 DEG. F)

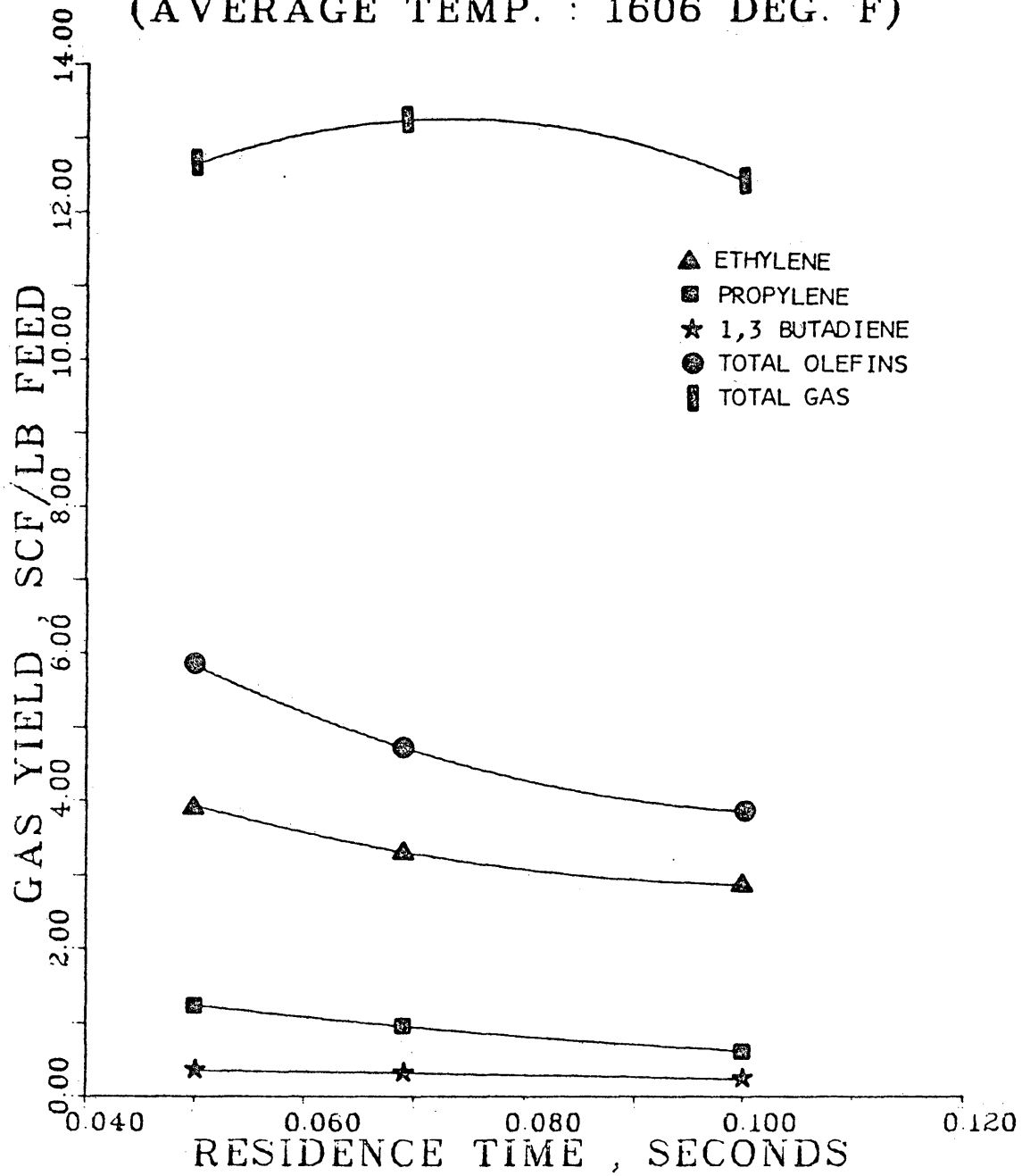


Figure 6.--Effect of Residence Time on Volumetric product yields

HYDROGENATED TOSCO II OIL #6199
(AVERAGE TEMP. : 1607 DEG. F)

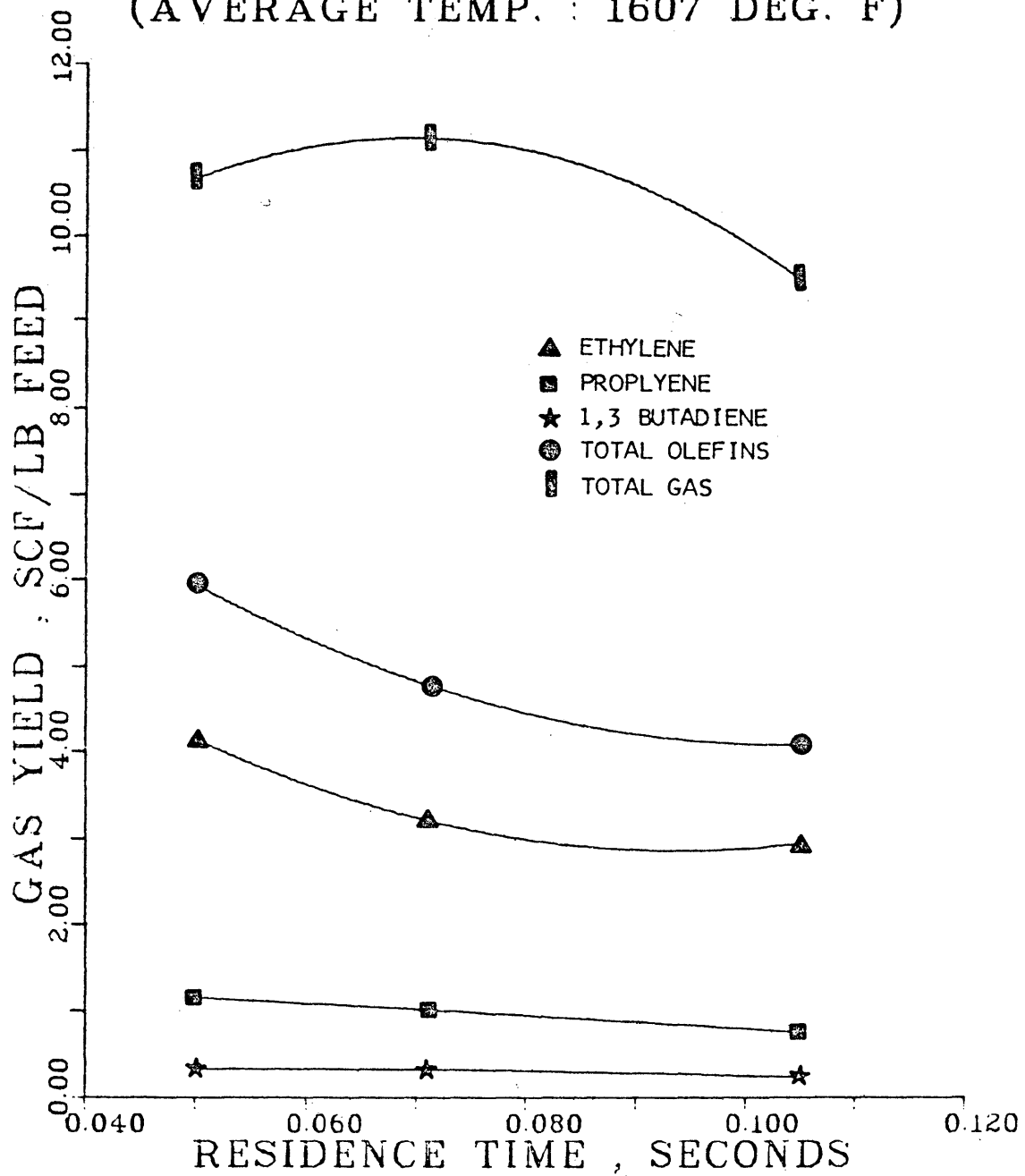


Figure 9.--Effect of Residence Time on volumetric product yield

for medium severity hydrogenated Tosco II shale oil (Sample #6199, 0.3 wt.% nitrogen) show that, decreasing the residence time results in increased weight percent of total gas, total olefin, ethylene, propylene, 1,3 butadiene as shown in Figure 5. The yield of the ethylene increased from 21.39 wt.% of feed (2.94 SCF/#Feed) at 1610 °F and 0.105 sec. to a maximum of 30.15 wt.% of feed (4.14 SCF/#Feed) at 1609 °F and 0.050 sec. as shown in Figure 5 and 7, which is higher than the ethylene yield found at the same condition from medium severity hydrogenated Paraho oil. The yields of total olefin is increased from 35.17 wt.% to 52.15 wt.% of feed. The yields of total gas increased sharply at first from 53.46 wt.% of feed (9.49 SCF/#Feed) at 0.05 second to 69.58 wt.% of feed (11.14 SCF/#Feed) at 0.071 second then become constant above 0.071 second. The yields of hydrogen and carbon monoxide decreased from 1.10 and 5.01 wt.% to 0.77 and 4.49 wt.% of feed respectively.

2. High Reaction Temperature:

Tests for high temperature effects were made at average temperatures of 1600, 1700, 1775 °F for 0.100 second residence time and about 1.0 steam to oil mass ratio. The results of these tests are given in Tables 12 and 13. The weight percent of valuable products and the volumetric

gaseous product yields are plotted as a function of temperature in Figures 8, 9, 10, and 11 respectively for hydrogenated Paraho and Tosco II oils

Paraho Oil:

As shown in Figures 8 and 10, an increase in the temperature causes a decrease in total olefin, ethylene, propylene, and 1,3 butadiene. The ethylene production decreased from 20.83 wt.% of feed (2.86 SCF/#Feed) at 1605 °F and 0.1 second to 11.86 wt.% of feed (1.63 SCF/#Feed) at 1773 °F and 0.100 second for medium severely hydrogenated Paraho oil (Sample #6281, 0.27 wt.% nitrogen), at corresponding temperatures propylene decreased from 6.65 wt.% of feed (0.61 SCF/#Feed) to 1.69 wt.% of feed (0.15 SCF/#Feed), and 1,3 butadiene decreased from 3.27 wt.% of feed (0.23 SCF/#Feed) to 0.51 wt.% of feed (0.04 SCF/#Feed). The yield of total gas is almost constant, while the yield of hydrogen increased from 1.96 wt.% of feed (3.75 SCF/#Feed) to 5.09 wt.% of feed (9.73 SCF/#Feed), which indicate the medium severely hydrogenated Paraho oil will undergo steam reforming and gasification takes place over the range of temperatures studied. More of the gaseous products were converted to hydrogen, carbon monoxide, and methane; this maybe attributed to secondary reaction and condensing to monoaromatics at the high temperature involved (16,14,50).

A possible cause of this reforming which must be considered is the possibility of catalytic activity or surface reaction within the reactor system, which will be discussed later.

Tosco II Oil:

Test at average residence time of 0.1 seconds and an average steam to oil mass ratio of 1.0 were made at 1610, 1705, and 1775 °F for medium severely hydrogenated Tosco II oil (Sample #6199, 0.3 wt.% nitrogen). The results of these tests are plotted in Figures 9 and 11. As can be seen from these figures, the yields of ethylene, propylene and 1,3 butadiene were decreased as the temperature is increased. The yield of ethylene decreased from 21.39 wt.% of feed (2.94 SCF/#Feed) at 1610 °F to 11.29 wt% of feed (1.55 SCF/#Feed) at the same conditions propylene from 8.21 to 2.64 wt% of feed, and 1,3 butadiene decreased from 3.26 to 1.87 wt% of feed. The yield of total gas is almost constant as shown in Figure 9. While the hydrogen yield increased from 1.10 wt% (2.11 SCF/#Feed) to 4.29 wt% of feed (8.01 SCF/#Feed) and carbon monoxide increased also from 5.02 wt% (0.69 SCF/#Feed) to 22.37 wt% of feed (3.08 SCF/#Feed) as can be seen in Appendix C for runs R1 and G2, which indicates also that the medium severely hydrogenated Tosco II shale oil gasified over the high temperature range studied as the hydrogenated Paraho oil.

HYDROGENATED PARAHO OIL #6281
(AV. RESIDENCE TIME:0.100 SEC)

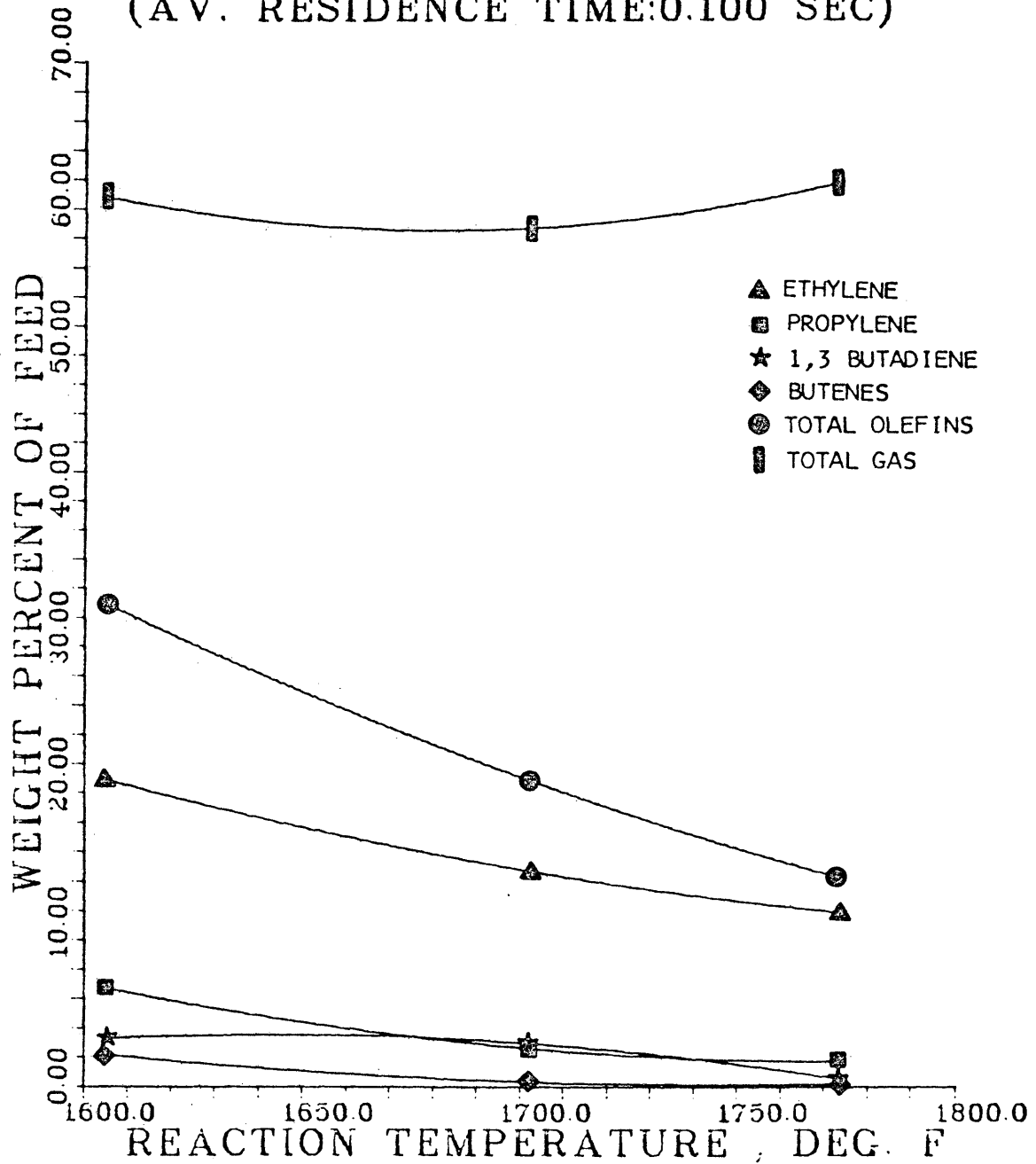


Figure 8.--Effect of Reaction Temperature on product yields

HYDROGENATED TOSCO II OIL #6199 (AV. RESIDENCE TIME :0.103 SEC.)

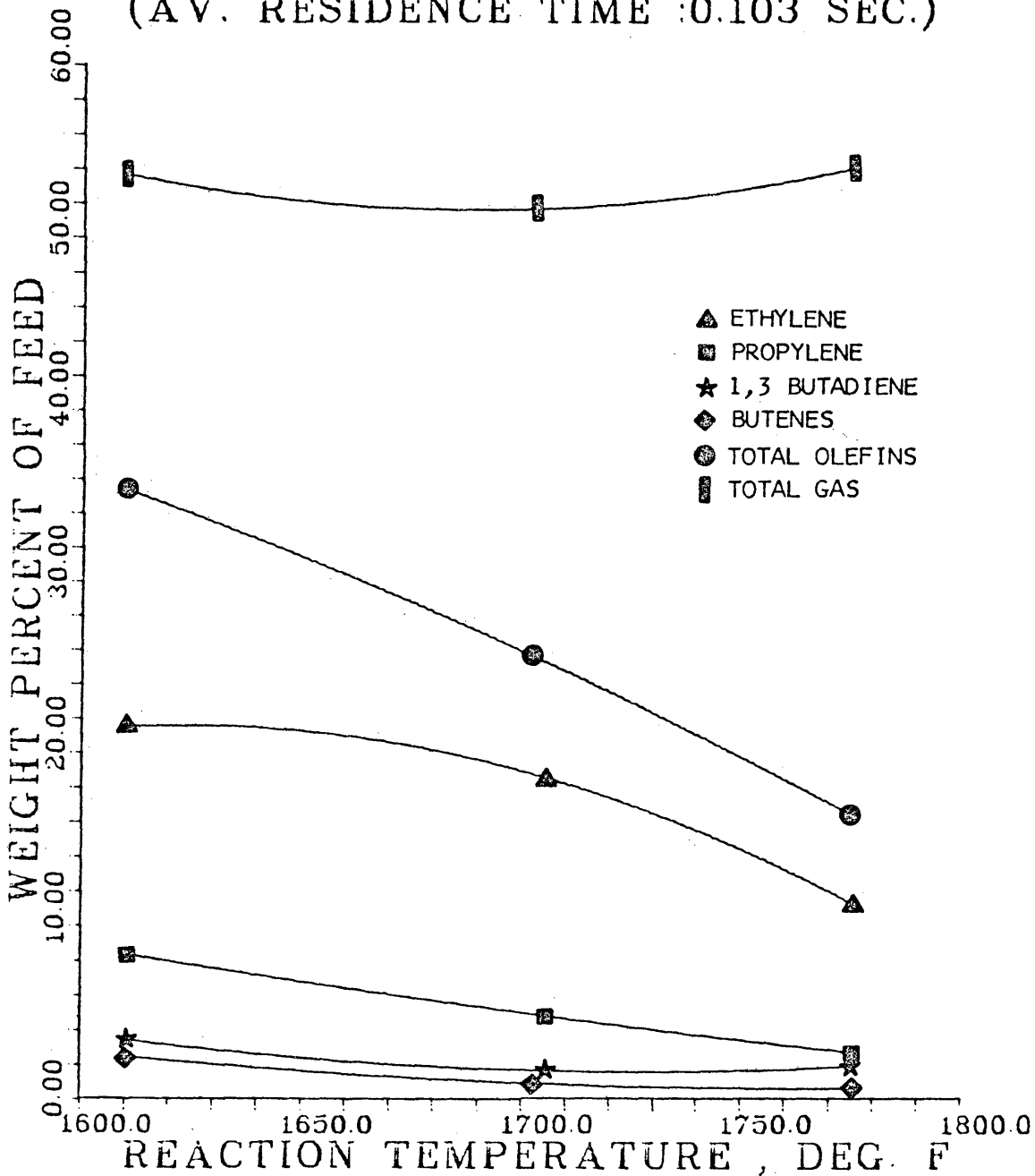


Figure 9.--Effect of Reaction Temperature on product yields

HYDROGENATED PARAHO OIL #6281
(AV. RESIDENCE TIME : 0.100 SEC.)

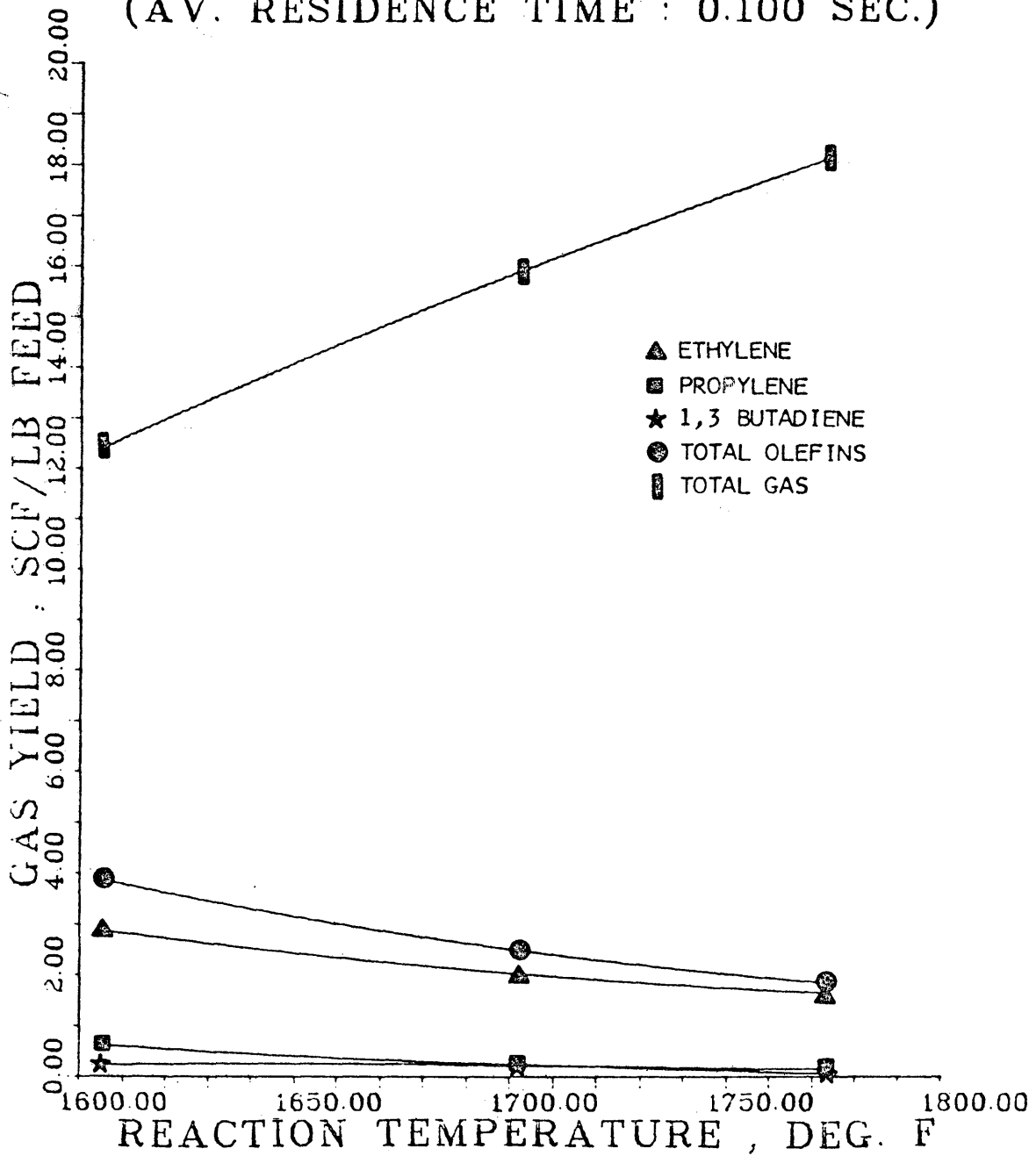


Figure 10.--Effect of Reaction Temperature on volumetric product yields

HYDROGENATED TOSCO II OIL #6199
(AV. RESIDENCE TIME: 0.103 SEC.)

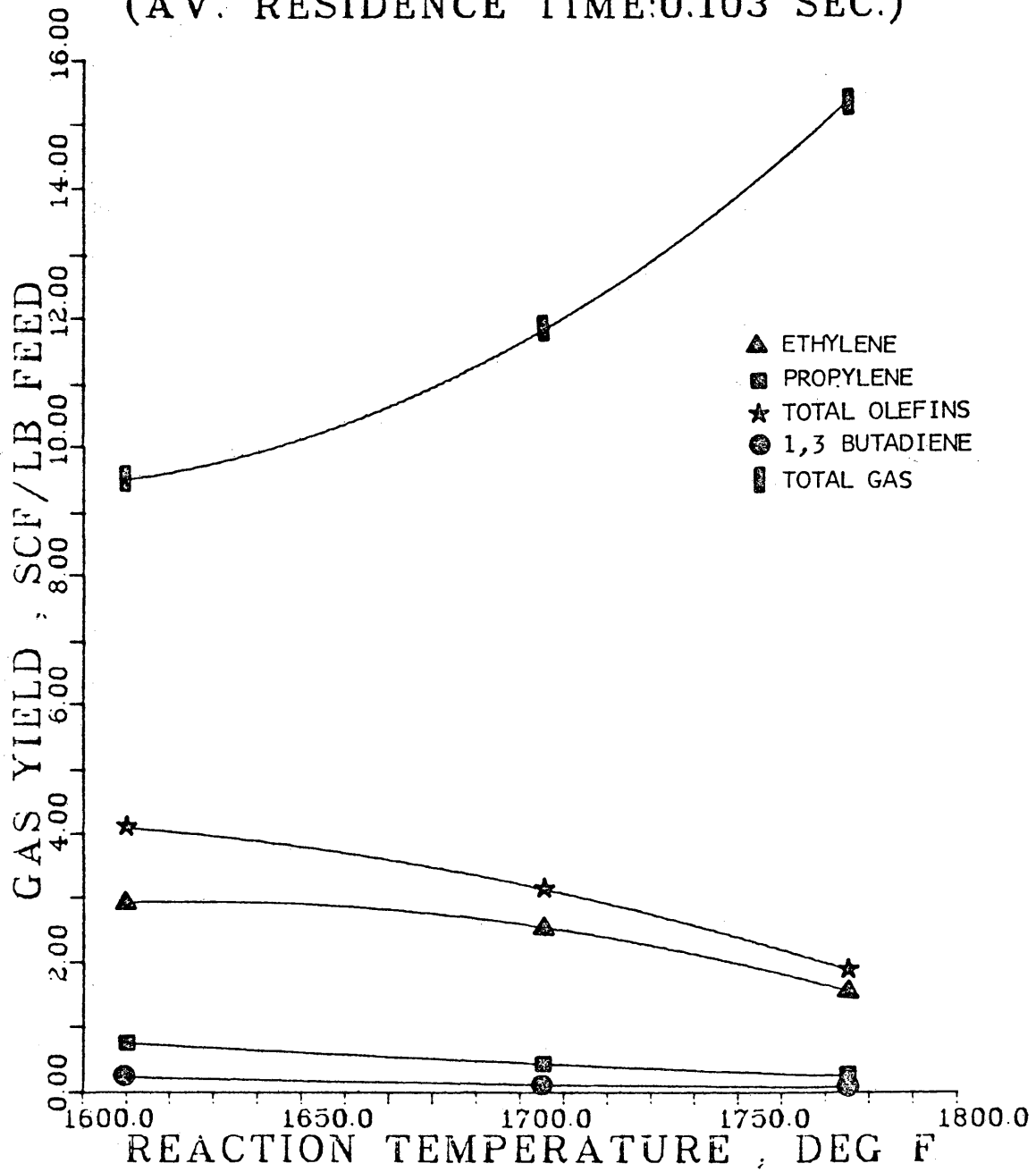


Figure 11.--Effect of Reaction Temperature on volumetric product yields

3. Effect of Severity

The severity factor is a reaction parameter that combines the effect of operating conditions such as reaction temperature and residence time, into a single variable which can be used to correlate yield data (20, 39, 42, 43, 15). Several severity factors have been developed or utilized for correlating pyrolysis results, the common form of the severity factor (S) is that used by the IGT (20) is

$$S = T\theta^{0.06}$$

Figure 12 and 13 show the weight percent of the gas product yield as a function of severity for hydrogenated Paraho and Tosco II respectively. As the severity rises, ethylene yield decreased from 28.57 to 11.86 wt.% of feed for Paraho oil and from 30.15 to 11.27 wt% of feed for Tosco II oil. The yield of 1,3 butadiene is decreased slightly until the severity is above 1477 it begins more decrease for Paraho oil, but above 1489.4 begins to increase for Tosco II. The yield of total gas for both oils decreased rapidly in the severity range 1366 to 1400 and then decreased slightly until severity is above 1480 it begins increasing steadily with severity. The yield of hydrogen and carbon monoxide are generally increased with increased severity for both oils.

HYDROGENATED PARAHO OIL (SAMPLE # 6281)

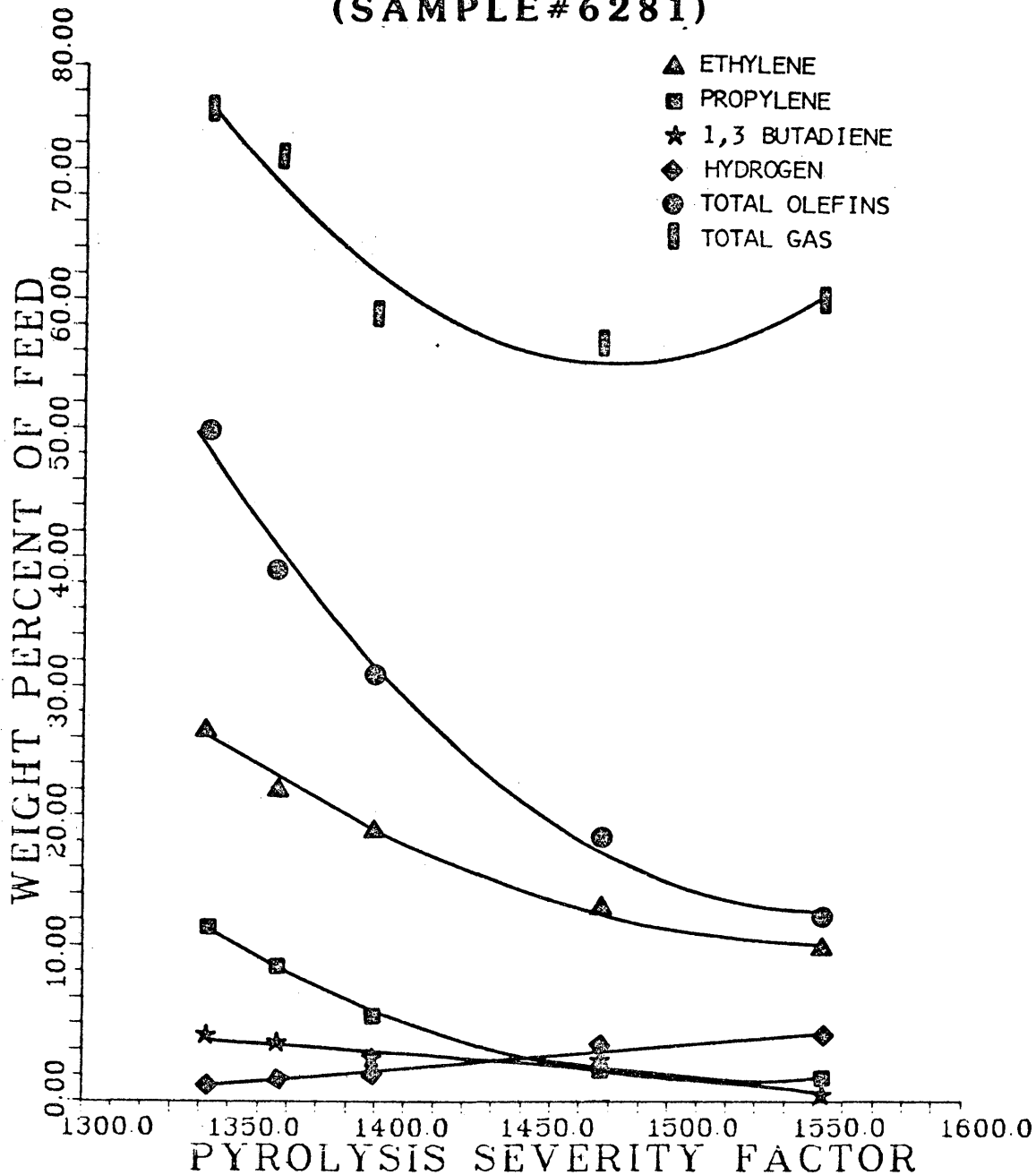


Figure 12.--Effect of Severity factor on weight percent yields

HYDROGENATED TOSCO II OIL (SAMPLE # 6199)

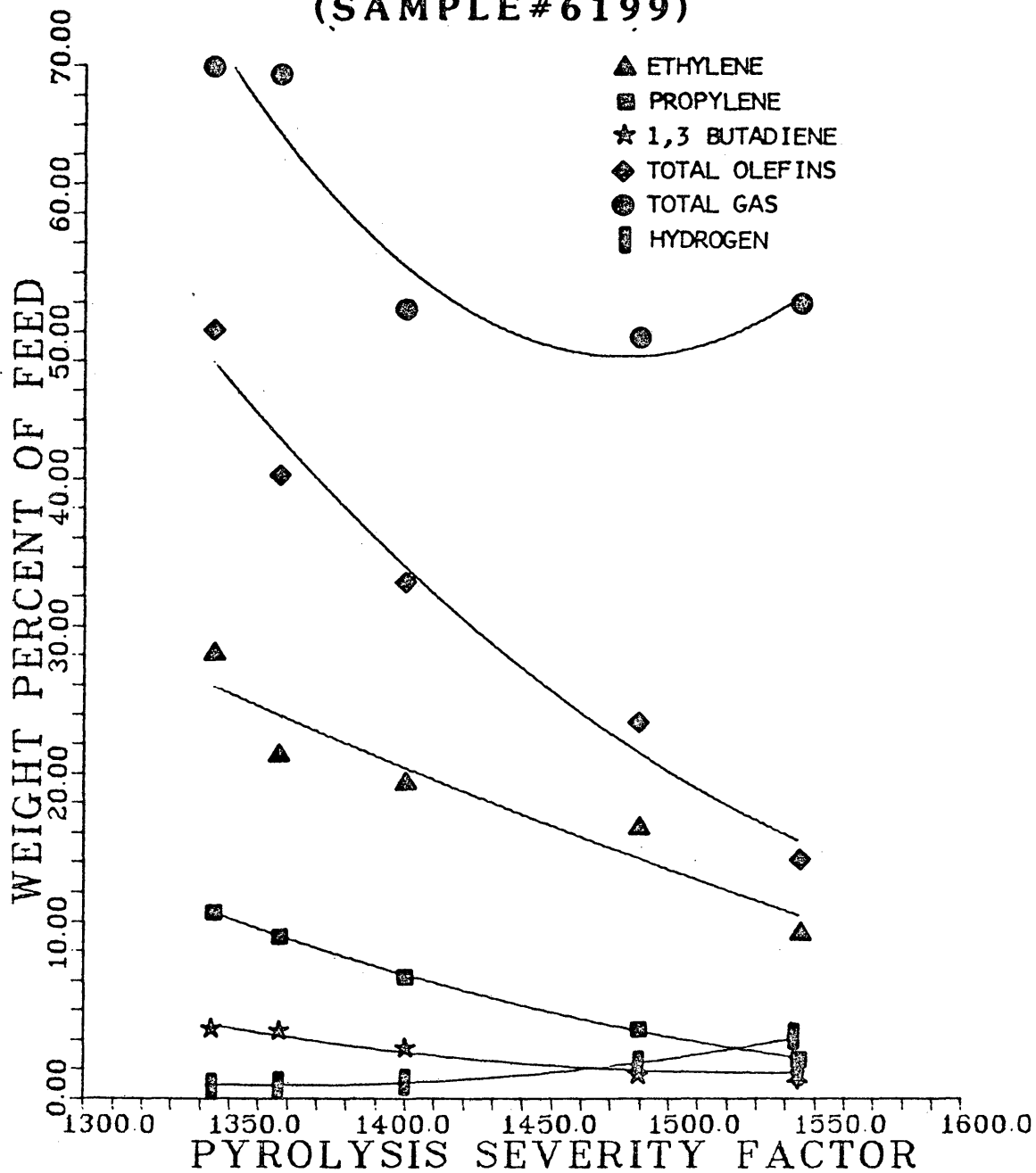


Figure 13.--Effect of Severity factor on weight percent yields

B. The Effect of Feed Composition and Nitrogen Level on the Product Yield

Griswold (38) reported that the tendency of severely hydrogenated shale oil to undergo steam reforming at high reaction temperature appeared at first to be a qualification to the potential advantages of using shale oil as a petrochemical feedstock. To investigate the causes of gasification, the effect of feedstock composition and reactor metallurgy will be discussed respectively. The analysis of feedstock effects on steam reforming during steam pyrolysis was made by selecting two different types of hydrogenated shale oil feedstocks from Paraho and Tosco II shale oils. Three levels of hydrogenation were selected for pyrolysis runs, indicated by nitrogen content 0.048, 0.27, and 0.44 wt.% of feed nitrogen for hydrogenated Paraho oil and 0.035, 0.30, and 0.82 wt% of feed nitrogen for Tosco II oil. Figures 14 and 15 show the effect of hydrotreating (nitrogen content) on the product yields for hydrogenated Paraho and Tosco II oils respectively.

Paraho Oil #6281 (0.27 Wt% N)

Tests were made at temperatures of 1605, 1702, and 1773 °F and about 0.100 second. The results show that the hydrogen and carbon monoxide dominated the gas product

yield with corresponding low olefin content as shown in Appendix C for runs T1, P1, and P2. Figures 6 and 10 show that the light olefin yields decreased as the temperature is increased. The ethylene is decreased rapidly to 11.83 wt% of feed (2.86 SCF/#feed) but the hydrogen and carbon monoxide increased up to 5.09 wt% of feed (9.73 SCF/#feed) and 28.62 wt% of feed (3.94 SCF/# feed) respectively.

Paraho Oil #3536 (0.44 Wt.% N)

For further investigation if a less severely hydrogenated oil would gasify, a run at 1611 °F and 0.101 sec. was made. The results given in Table 12 showed no apparent gasification, the yield of ethylene is 26.66 wt.% of feed (3.66SCF/# Feed), propylene yield is 9.65 wt% of feed (0.88 SCF/# Feed), 1,3 butadiene yield is 3.85 wt.% of feed (0.27 SCF/# Feed), and the yield of total olefins 42.43 wt.% of feed (4.98 SCF/ # Feed), while the yield of hydrogen is very low 0.94 wt.% of feed compared to the yield of hydrogen for medium severely and high severely as we can see later.

Paraho Oil # 6280 (0.048 Wt.% N)

A run at 1607 °F and 0.106 sec was made with the most severely hydrogenated Paraho oil. The results indicate that a gasification took place. As shown in Appendix C, and

Run H2, the product gas was extremely high in hydrogen and carbon monoxide content. The yield of hydrogen was extremely high about 45.91 mole % gas (6.95 SCF/# Feed) and carbon monoxide exhibits about 19.97 mole % (3.03 SCF/# Feed), where the yield of ethylene is about 14.58 wt.% of feed (2.00 SCF/# Feed) which is less than the ethylene yield of the medium severely Paraho oil at the same condition. This demonstrates that the most severely hydrogenated Paraho oil will undergo steam reforming in the reactor system used over the range of temperature studied.

Tosco II Oil #6199 (0.27 Wt.% N)

For further analysis of feedstock composition and property effects another kind of shale oil was selected. As discussed previously, the runs exhibited the same gasification observed for medium severely hydrogenated Paraho oil at the high temperature range studied. The hydrogen weight percent of the product yield increased rapidly to 4.19 wt.% (52.20 mole % gas) and the carbon monoxide increased to 22.37 wt.% of feed (20.05 mole % gas) while the weight percent of ethylene, propylene, 1,3 butadiene, and total olefin decreased.

Tosco II Oil #6206 (0.82 Wt.% Nitrogen)

The less severely hydrogenated Tosco II oil was pyrolyzed

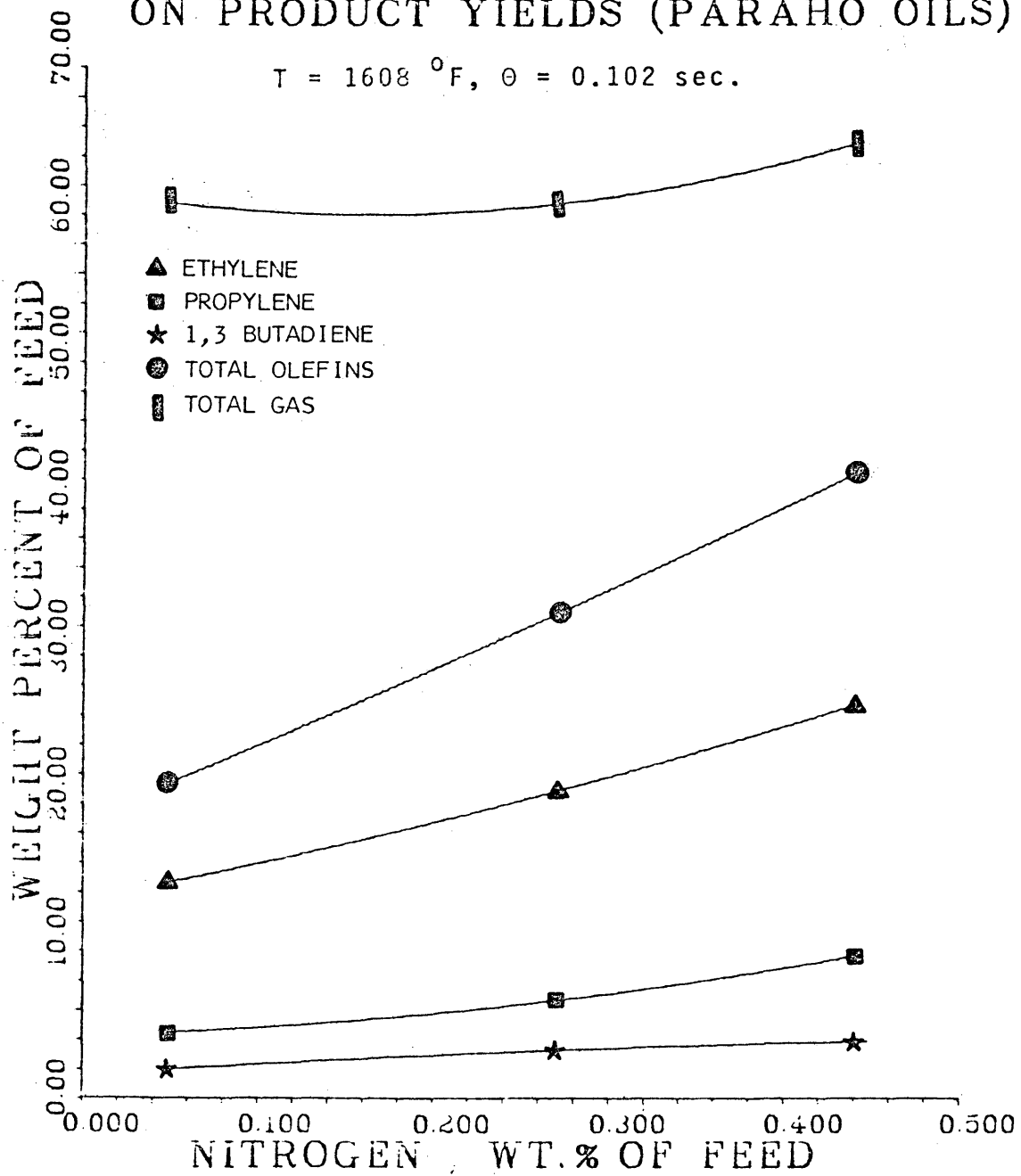
at 1606 °F and 0.100 second, the results show no apparent gasification. Table 13 is a compilation of selected yields. The yield of ethylene is 23.02 wt% of feed (3.16 SCF/#Feed) which is comparable with ethylene yield from Paraho feedstock of less severely hydrogenated oil.

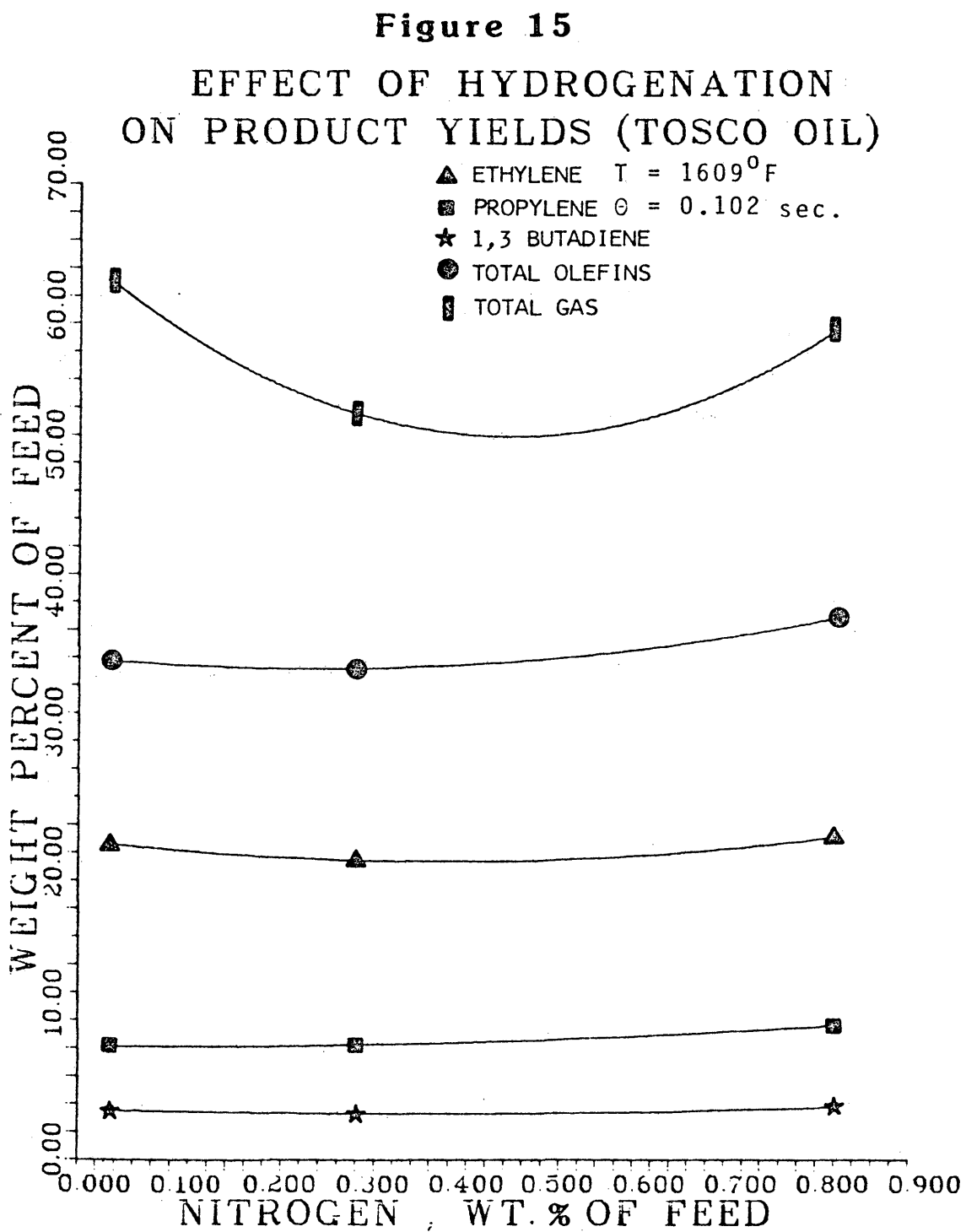
Tosco II Oil #6209 (0.035 wt% Nitrogen)

To analyze if the high severity hydrogenated Tosco II oil would gasify at the same condition, a run was made at 1611 °F and 0.101 second. The yield of ethylene exhibits a maximum of 23.02 wt% (3.16 SCF/#Feed), and the hydrogen yield is 0.93 wt% (1.77 SCF/#Feed), which indicates that less severely hydrogenated Tosco II did not gasify over the range studied with ethylene, propylene, 1,3 butadiene, and total olefins higher than high severity Paraho oil and comparable with yields from medium and less severely Tosco II oil.

To determine the hydrotreating (nitrogen content) effect on product yields the nitrogen weight percent on feed oils is plotted versus the weight percent of valuable products at approximate equivalent severities of 1399-1404 for Paraho oils and 1397-1409 for Tosco II oils as given by Figures 14 and 15. Figure 14 clearly shows that as the degree of hydrogenation decreases (nitrogen content

Figure 14

EFFECT OF HYDROGENATION
ON PRODUCT YIELDS (PARAHO OILS) $T = 1608^{\circ}\text{F}$, $\theta = 0.102 \text{ sec.}$ 



increases) the yields of valuable products of Paraho oils increase, which is an unusual result. The yield of ethylene increased from 14.59 wt% of feed at 0.048 wt% nitrogen to 26.66 wt% of feed at 0.44 wt% nitrogen. The yield of total olefins increased also from 21.92 wt% at 0.048 wt% of nitrogen to 42.43 wt% at 0.44 wt% nitrogen. There is little increase in the yield of total gas, propylene, and 1,3 butadiene. For Tosco II oils the effect of hydrotreating is very small as shown in Figure 15 compared to Paraho oils. There is little increase in the yield of ethylene, propylene, 1,3 butadiene, and total olefins. The yield of total gas is first decreased from 62.99 wt% of feed at 0.035 wt% of nitrogen to 53.46 wt% of feed at 0.30 wt% nitrogen then increased up to 57.43 wt% of feed at 0.44 wt% nitrogen. This indicates that low nitrogen shale oil will undergo steam reforming in this reactor system for both oils.

Reactor Metallurgy

A possible cause of the gasification which may be considered is the possibility of catalytic activity or surface reaction within the reactor system. The significance of surface reaction in laboratory pyrolysis is greater than for commercial units, because the pyrolysis laboratory

units use much smaller diameter reactors with greater surface area/volume ratio, and frequently they operate at lower pressures.

The undesirable by-products of coke and carbon oxides are produced via surface reaction with the steam which is used as a feedstock diluent. This phenomena will occur in metal reactors using steam since at pyrolysis conditions, steam reacts with nickel, iron, and chromium to form oxides of these metals. These undesired products reduce the yields of desired products (18). The pyrolysis run of this study were made in 3/8 inch diameter schedule 40 Inconel Alloy 601 pipe (high nickel), the composition of this kind of reactor is given in Table 14. Chambers and Potter (51) reported high nickel alloys are utilized in commercial pyrolysis units if the temperature used exceeds 1500 °F. Thus, this study necessitated using the high nickel alloys to provide superior corrosion resistance as well as high resistance. As previously discussed, the gasification occurrence at high temperature range studied demonstrates that a high metal surface of nickel within the reactor will enhance production of hydrogen and carbon monoxide as shown in Appendix C for high temperature range.

TABLE 14 COMPOSITION OF THE REACTOR USED
IN THE PYROLYSIS SYSTEM (52)

Kind of the reactor: Inconel Alloy 601 Pipe
Melting Range: 2375-2495 °F, 1300-1370 °C
Density: 8.05 g/cu cm

<u>Nominal Composition</u>	<u>Wt. %</u>
Ni	60.5
Cr	23.0
Co	-
Al	1.40
Fe	14.0
Mn	0.5
Si	0.2
C	0.05
Cb	-
Ti	-

C-Comparison With Other Studies: The runs H1, S2, T2, and H2 were compared with Kavianian's (37) studies and Griswold's (38) studies on hydrogenated Tosco II and Paraho oils. The comparison was made at approximate equivalent (C/H) carbon to hydrogen ration on liquid products as presented in Tables 15, 16, 17, and 18.

As can be seen from these tables, the shorter the residence time the greater the yield of ethylene and total olefins for severely and medium hydrogenated Paraho oils as indicated by Table 17 and 18. For low severely hydrogenated Tosco II and Paraho oils, the shorter the residence time the greater the yield of ethylene and a little bit less total olefins as indicated by Tables 15 and 16. The product yields proved to be comparable to values in Kavianian's (37) and Griswold's (38) studies, with higher ethylene yield and lower propylene, 1.3 butadiene and butenes and with comparable total olefins yields.

TABLE 15 COMPARISON WITH OTHER STUDIES
(TOSCO II OIL)

<u>Investigator</u>	<u>Author</u>	<u>Kavianian</u>
Run #	S2	H22
Oil #	6206	6206
Nitrogen wt% of feed	0.82	0.82
Reaction Time, Sec.	0.100	0.743
Reaction Temp., °F	1606	1301
Steam-oil Ratio	0.966	0.820
C/H Ratio (Feed)	6.59	6.67
<u>Yields, wt% of Feed</u>		
C ₂ H ₄	23.02	22.48
C ₃ H ₆	9.60	11.30
C ₄ H ₆	3.76	4.14
C ₄ H ₈ 's	2.42	5.07
Total Olefins	38.80	42.99
C/H Ratio of (Liq. Products)	11.10	10.86

TABLE 16 COMPARISON WITH OTHER STUDIES
(PARAHO OIL)

<u>Investigator</u>	<u>Author</u>	<u>Griswold</u>
Run #	H1	G16
Oil #	P-3536	P-3536
Nitrogen, wt% Feed	0.44	0.44
Reaction Time, Sec.	0.101	0.41
Reaction Temp., °F	1611	1351
Steam-Oil Ratio	0.997	0.971
C/H Ratio (Feed)	6.37	6.37
<u>Yields, wt% of Feed</u>		
C ₂ H ₄	26.66	21.58
C ₃ H ₆	9.65	13.83
C ₄ H ₆	3.85	4.98
C ₄ H ₈ 's	2.27	5.97
Total Olefins	42.43	46.36
C/H Ratio of (Liq. Products)	11.69	11.24

TABLE 17 COMPARISON WITH OTHER STUDIES
(PARAHO OIL)

<u>Investigator</u>	<u>Author</u>	<u>Kavianian</u>
Run #	T2	K-13
Oil #	6281	6281
Nitrogen wt% Feed	0.27	0.27
Reaction Time, Sec.	0.069	0.100
Reaction Temp., °F	1604	1397
Steam-Oil Ratio	0.997	1.03
C/H Ratio (Feed)	6.24	6.24
<u>Yields, wt% of Feed</u>		
C ₂ H ₄	24.02	16.36
C ₃ H ₆	10.29	11.52
C ₄ H ₆	4.39	4.44
C ₄ H ₈ 's	2.32	5.11
Total Olefins	41.02	37.43
C/H Ratio of (Liq. Products)	10.67	10.99

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TABLE 18 COMPARISON WITH OTHER STUDIES
(PARAHO OIL)

<u>Investigator</u>	<u>Author</u>	<u>Griswold</u>
Run #	H2	G7
Oil #	6280	6280
Nitrogen, wt% Feed	0.048	0.048
Reaction Time, Sec	0.106	0.411
Reaction Temp., °F	1607	1493
Steam-Oil (Feed)	0.976	0.984
C/H Ratio (feed)	6.43	6.20
<u>Yields, wt% of Feed</u>		
C ₂ H ₄	14.58	11.59
C ₃ H ₆	4.45	4.40
C ₄ H ₆	1.96	1.71
C ₄ H ₈ 's	0.93	0.96
Total Olefins	21.92	18.66
C/H Ratio of (Liq. Products)	11.55	11.70

Reproducibility and Discussion of Error

Determining the reproducibility of the reaction system is extremely difficult, because exact reproductions of oil, steam flow rates, and temperature profiles along the reactor were hard to obtain. Possible errors encountered in the gas product analysis came from those errors within the chromatography analysis.

To check the consistency of the experimental results obtained in this study, additional runs H3 and S3 were made in an attempt to duplicate runs P1 and R1 respectively. The reaction conditions for each run are given in Tables 10 and 12 for Paraho oil and Tables 11 and 13 for Tosco II oil. Tables 19 and 20 show the percent deviations in the yield of ethylene, propylene, 1,3 butadiene, total olefins, and total gas, for Paraho and Tosco II oils respectively. Good agreement was obtained with maximum percent deviation of about 7% for Paraho oil as indicated in Table 19, and with maximum percent deviation of about 4% for Tosco II oil as shown in Table 20.

TABLE 19 PARAHO SHALE OIL (SAMPLE # 6281)

<u>Component</u>	<u>Wt% of Feed</u>		<u>\bar{X}</u>	<u>% Deviation</u>
	<u>Run #H3 (S.F. 1478.9)</u>	<u>Run #P1 (S.F. 1477)</u>		
Ethylene	15.45	14.63	15.04	2.73
Propylene	2.95	2.56	2.80	6.96
1,3 Butadiene	2.84	2.91	2.88	1.22
Total Olefin	21.7	20.38	21.04	3.14
Total Gas	59.04	58.68	58.86	0.31

TABLE 20 TOSCO II SHALE OIL (SAMPLE # 6199)

<u>Component</u>	<u>Wt% of Feed</u>		<u>\bar{X}</u>	<u>% Deviation</u>
	<u>Run #R1 (S.F. 1409.7)</u>	<u>Run #S3 (S.F. 1395J)</u>		
Ethylene	21.39	23.10	22.250	3.84
Propylene	8.21	8.06	8.140	0.92
1,3 Butadiene	3.26	3.51	3.380	3.69
Total Olefin	35.17	36.62	35.895	2.09
Total Gas	53.46	53.33	53.395	1.13

Overall Mass Balance:

Overall mass balances were made for all experimental runs in this study as an important criterion in establishing the validity for the experimental data. The mass balances for each run calculated from the total oil, water, and quench water inputs and the total outputs which calculates from the collection flask weighings and the amount of feed out as a gas.

The result of the overall mass balance are given in Table 21. The percent of mass balance recovery ranges from a high of 105.0 percent to a low of 92.56 percent. The spreads are due the error involved in neglecting the amount of coke solids. But for the size of the system used in this study, the percent recovery range shows an acceptable result.

TABLE 21. OVERALL MASS BALANCE

Run No. Paraho	IN			OUT		Total In	Total Out	%Total Out/ Total In
	Oil	H ₂ O	Quench	Gas	Liquid			
T1	139	118	170	84.5	361.70	427	446.20	104.5
T2	157	132	163	114.5	358.08	452	472.58	105.0
T3	219	184	165	167.75	371.9	568	539.67	95.01
P1	91	84	169	56.23	276.1	344	332.33	96.60
P2	127	100	158	74.53	282.3	385	356.83	92.68
H1	108	92	130	70.03	269.8	330	339.83	102.98
H2	123	100	153	72.62	286.5	376	359.12	95.51
H3	146	125	170	86.19	346.3	441	432.49	98.10
<u>Tosco II</u>								
R1	100	88	156	53.46	258.2	338	311.7	92.21
R2	160	130	162	111.33	321.4	452	432.73	95.74
R3	220	184	173	153.89	380.2	577	534.09	92.56
G1	100	84	137	51.53	258.5	321	310.03	96.58
G2	106	88	175	57.17	321.7	369	378.87	102.67
S1	119	97	237	74.96	354.2	453	429.16	94.74
S2	110	91	210	65.37	316.8	411	382.17	92.99
S3	111	92	165	59.19	289.8	368	348.99	94.83

SUMMARY AND CONCLUSIONS

1. Steam pyrolysis characteristics at short residence times of hydrogenated Paraho and Tosco II shale oils were studied in a bench-scale unpacked tubular reactor. The results were reasonably successful and indicate that hydrogenated Paraho and Tosco II shale oils should make excellent feedstocks for production of ethylene by steam pyrolysis. The maximum ethylene production and total olefins for hydrogenated Paraho oil are respectively 28.57 weight percent of feed at a severity factor of 1342.7 and 51.65 weight percent of feed.

For hydrogenated Tosco II oil a maximum of 30.15 weight percent of feed was converted to ethylene at a severity factor of 1344.4 and 52.15 weight percent of feed was converted to total olefins.

At high pyrolysis severity of 1552.4, gasification tendencies were observed with most severely hydrogenated Paraho oil, hydrogen and carbon monoxide dominated the gas product yields with corresponding low olefin content.

2. Within the ranges studied, the decrease in residence time resulted in an increase in overall conversion and the yields of valuable products. The increase in reaction temperature or with increase in the residence

time resulted in decrease in the yield of ethylene and total olefins.

3. Increasing the severity of the operation resulted in decreased weight percent of ethylene, propylene, and total olefins. The hydrogen and carbon monoxide yields are gradually increased, while the yield of 1,3 butadiene is slowly increased. Also as the severity is increased the weight percent of total gas is sharply decreased at first, and then levels off slightly, and then gradually increases above the severity factor of 1480.

4. The liquid product carbon to hydrogen and molar hydrogen to carbon ratios predicted from the carbon and hydrogen percentages in the feed and product gas for all the runs show that fairly representative liquid products was obtained and the hydrogenated shale oils feedstocks were pyrolyzed at optimum conditions. The molar H/C range obtained is 0.98 to 1.31 which shows an acceptable reactor severity was obtained. King and Glidden (1), reported that a value of 1 or greater for molar H/C ratio of the liquid products is desired in pyrolysis operation and cracking. Severity is adjusted to meet this criterion. The product yields proved to be comparable to values reported in other studies (37,38), with higher ethylene yield and slightly lower propylene, 1,3 butadiene and butenes.

RECOMMENDATION

A. Further study of product composition and yields of the valuable components of steam pyrolysis of shale oil at high temperature and short residence time is needed.

Also, reactor performance can be enhanced and the type of reactor improved by better control of the temperature profile and reduction of the catalytic activity or surface reaction within the reactor, by the following means:

1. New and unique reactors from Coors alumina ceramics that combine the desirable properties of metals (high strength, hardness and high temperature resistance, and chemical resistance).

2. A new furnace, with more heating elements with separate controls for tighter temperature control along the reactor.

3. A better steam superheat system to obtain higher steam temperature to eliminate heat losses and to help the temperatures in the reactor to rise to a desired operating temperature.

B. Further study to investigate the effect of hydrotreating on product yields is in order, to study why hydrogenated Paraho oil is affected by nitrogen level, and hydrogenated Tosco II is not.

REFERENCES CITED

1. Glidden, H. J., and C. F. King, "Light Olefines from Shale Oil," Chemical Engineering Progress, V. 76, No. 12, Dec. 1980, p. 47.
2. Cameron Engineers, "Stuatus of Synfuels Projects," Synthetic Fuels, V. 12, No. 3, 1975, p. 1-3.
3. Zdonik, S. B., E. J. Bassber, and L. P. Hallee, "How Feedstocks Affects Ethylene," Hydrocarbon Processing, V. 53, No. 2, Feb. 1974, p. 73.
4. Ponder, T. C., "Trends in Petrochemical Feedstocks," Hydrocarbon Processing, V. 56, No. 12, 1977, p. 111.
5. Maples, R. E., and P. Adler, "Options for Olefin Feedstocks," Hydrocarbon Processing, V. 57, No. 7, 1978, p. 171.
6. Hatch, L. F. and S. Mator, "From Hydrocarbon to Petrochemicals (part 9)," Hydrocarbon Processing, V. 57, No. 3, 1978, p. 129.
7. Montgomery, D. F., "Refining of Pyrolytic Shale Oil," I&EC Produced Research and Development, V. 7, No. 4, 1968, p. 274-282.
8. Dinneen, G. U., J. S. Ball, and H. M. Thorne, "Composition of Crude Shale Oils," I&EC., V. 44, No. 11, Nov. 1952, p. 2632-2635.
9. Schora, F. C., P. B. Tarman, and H. L. Feldkirchner, "State-of-the-art-above Ground Shale Processing," Hydrocarbon Processing, V. 56, No. 2, 1977, p. 113-119.
10. William E. Cady, and Herman S. Seelig, "Composition of Shale Oil," I&EC., V. 44, No. 11, Nov. 1952, p. 2636-2641.
11. Poulson, R. E., H. B. Jensen, and G. L. Gook, "Nitrogen Bases in Shale-Oil Light Distillate," ACS Division of Petroleum Chemistry, V. 16, No. 1, 1971, p.A49-A55.
12. Gary, L. F, and G. E. Handwerk, "Petroleum Refining," Technology and Economics, Marcel Decker, New York, 1975.

13. Atwood, M. T., Raw Shale Oil Inspection, The Oil Shale Corporation, Golden, Colorado, 1975.
14. Sullivan, R. F., "Catalytic Hydroprocessing of Shale Oil to Product Distillate Fuels," ACS Div. of Petroleum Chemistry Preprints, V. 22, No. 3, 1977, p. 998.
15. Farrell, T. J., and H. S. Davis, "An Approach to Obtaining First Order Rate Contents for the Pyrolysis of Pure Components in Mixed Liquid Feedstocks," ACS Division of Petroleum Chemistry Preprints, V. 17, No. 2, 1972, p. B72.
16. Sakai, T., K. Soma, Y. Sasaki, H. Tominaga, and T. Kunugi, "Secondary Reaction of Olefins in Pyrolysis of Petroleum Hydrocarbon," ACS Division of Petroleum Chemistry Preprints, V. 14, No. 4, 1969, p.D40.
17. Sakai, T., and D. Nohara, "A Kinetic Study of the Formation of Aromatics during Pyrolysis of Petroleum Hydrocarbon," Industrial and Laboratory Pyrolysis, ACS Symposium Series, No. 32, 1976, p. 152.
18. Hurd, C. D., "McGraw-Hill Encyclopedia of Science and Technology," New York, McGraw-Hill Book Company, V. 11, 1977, p. 122.
19. Sohns, H. W., E. E. Jukkola, and W. I. Murphy, "Development and Operation of an Experimental Entrained-Solids-Oil Shale Retort," U. S. Bureau of Mines, RI5522, 1959, p.45.
20. Shultz, E. B., J. J. Guyer, and H. R. Linden, "Pyrolysis of Crude Shale Oil," I&EC, V. 47, No. 12, 1955, p. 2479-2482.
21. Williamson, K. D., and H. C. Davis, "Mechanistic Studies of Methane Pyrolysis at Low Pressures," Industrial and Laboratory Pyrolysis, ACS Symposium Series, No. 32, 1976, p. 51.
22. Harauachi, T., F. Nakashie, and W. Sakai, "Kinetics of Pyrolysis of Propane-Propylene Mixtures," Industrial and Laboratory Pyrolysis, ACS Symposium Series, No. 32, 1976, p. 99.

23. Rice, F. O., "Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicles," J. Am. Chem. Soc., V. 55, No. 7, 1933, p. 3035.
24. Gates, B. C., J. R. Katzer, and G. C. Schmit, "Chemistry of Catalytic Processes," McGraw-Hill Book Company, 1979, p. 8-10.
25. King, C. F, and H. J. Glidden, "Light Olefin from Shale Oil Distillates," ACS Division of Petroleum Chemistry Preprints, V. 25, No. 3, 1980, p 616.
26. Thorne, H. M., "Retort Oil Shale for Chemical," Petroleum Refiner, V. 35, No. 7, 1956, p. 155.
27. Ruderhausen, C. G., and J. B. Thompson, "Feedstocks from Paraho Shale Oil," ACS Advanced Chemistry Series, No. 183, 1979, p. 91.
28. Adams, C. T., and C. A. Trevine, "Pyrolysis Gasoline/Gas Hydrotreating," Industrial and Laboratory Pyrolysis, ACS Symposium Series, No. 32, 1976, p. 412.
29. Brantely, F. E., R. J. Cox, H. W. Johns, W. I. Barnet, and W. I. R. Murphy, "High Temperature Shale Oil-Production and Utilization," I&EC, V. 44, No.11, Nov. 1952, p. 2641.
30. Dickson, P. F., and V. F. Yesavage, "Shale Oil as a Feedstock for Petrochemical Intermediate Production," Colorado School of Mines, Golden, Colorado, Nov. 20, 1978.
31. Griswold, C. F., "Steam Pyrolysis of Tosco II Shale Oil for Production of Chemical Intermediates," Master's Thesis, 1976, Colorado School of Mines, Golden, Colorado.
32. Fritzler, E. A., "Steam Pyrolysis of Tosco II and Simulated In situ Shale Oil for Chemical Intermediated Production," Master's Thesis, 1977, Colorado School of Mines, Golden, Colorado.
33. Smith, P. D., "Steam Pyrolysis of Tosco II and Simulated In situ Shale Oil Vacuum Distillates for Production of Petrochemical Intermediates," Master's Thesis, 1977, Colorado School of Mines, Golden, Colorado.

34. Kavianian, H. R., "Aromatic Formation and Distribution of Sulfur and Nitrogen in the Liquid Products of Steam Pyrolysis of Petrochemical Intermediates," Master's Thesis, 1978, Golden, Colorado.
35. Angelos, C. P., "Production of Commercial Monoaromatics by Steam Pyrolysis of Hydrogenated Paraho Shale Oils," Master's Thesis, 1981, Colorado School of Mines, Golden, Colorado.
36. Ballut, A. A., "An Experimental and Theoretical Study of Steam Pyrolysis of Shale Oil Feedstocks for Petrochemical Intermediates," Ph.D. Thesis, 1979, Colorado School of Mines, Golden, Colorado.
37. Kavianian, H. R., "A Simulation Model for the Steam Pyrolysis of Shale Oil for Production of Chemical Intermediates," Ph.D. Thesis, 1979, Colorado School of Mines, Golden, Colorado.
38. Griswold, C. F., "Utilization of Shale Oil Feedstocks for Petrochemical Production," Ph.D. Thesis, Colorado School of Mines, Golden, Colorado.
39. Vanderkooi, W. N., "Pyrolysis Experimentation and Computation," ACS Div. of Petroleum Chemistry Preprints, V. 19, No. 1, 1974, p. 125-139.
40. Leftin, H. P., D. S. Newsome, and T. J. Wolff, "Pyrolysis of Naphtha and Kerosene in the Kellogg Millisecond Furnace," Industrial and Laboratory Pyrolysis, ACS Symposium Series, No. 32, 1976, p. 373.
41. McConaghy, J. S., and R. N. Moore, "The Mechanism of Aromatic Formation in Hydrocarbon Pyrolysis," ACS Div. of Petroleum Chemistry Preprints, V. 16, No. 1, 1971, p B88.
42. Chambers, L. E., and W. S. Potter, "Design of Ethylene Furnaces," Part No. 1, Maximum Ethylene, Hydrocarbon Processing, V. 53, No. 1, 1974, p 121-126.
43. Chambers, L. E., and W. S. Potter, "Design of Ethylene Furnaces," Part No. 2, Maximum Olefins, Hydrocarbon Processing, V. 53, No. 3, 1974, p. 95-100.

44. Kamptner, H. K., "Theory and Technique of the High Temperature of Petroleum Hydrocarbons and Their Influence on Some Manufacturing Processes," ACS Div. of Petroleum Chemistry Preprints, V. 13, No. 4, 1968, p.A23-A35.
45. Zdonik, S. B., and E. J. Green, "Function of Dilution Steam in Cracking," Oil and Gas Journal, May 27, 1968, p. 103-108.
46. Woolcock, J. W., "Cracking Processes for Olefins," Introduction to Petroleum Chemicals, Pergaman Press, New York, 1961, pp. 1-13.
47. American Society for Testing and Materials, "1980 Annual Book of ASTM Standards," Philadelphia, PA, Part 26, D1071.
48. Korosi, A., Halla, L. P., and P. S. Virk, "Steam Cracking of Colorado Shale Oil and Athabasca Bitumen Feedstocks for Petrochemicals," ACS Div. of Petroleum Chemistry Preprints, V. 25, No. 3, 1980, p. 621.
49. Rudershausen, C. G., and J. B. Thompson, "Feedstocks from Processing of Shale Oils," ACS Div. of Petroleum Chemistry Preprints, V. 23, No. 1, 1978, p. 241.
50. Kamptner, H. K., "Theory and Technique of the High Temperature Pyrolysis of Petroleum Hydrocarbons and Their Influence on Some Manufacturing Processes," ACS Div. of Petroleum Chemistry Preprints, V. 13, No. 4, 1968, p. A23.
51. Chambers, L. E. and W. S. Patter, "Design of Ethylene Furnaces," Part 3. Furnace Costs, Hydrocarbon Processing, V. 53, No. 8, 1974, p. 90.
52. The International Nickel Company, Inc., "High Temperature - High Strength Nickel Base Alloys," New York, 3rd. Edition, July 1977, Table 11, p. 16.

APPENDIX A
COMPUTER PROGRAM LISTING AND NOTATION
(PSY.FOR)

NOTATION

Arrays

- ATEN(I) - Standard component chromatograph attenuation on Carle GC.
- CFR(I) - Component mass fraction of carbon.
- CMWT(I) - Component molecular weight.
- CMLPC(I) - Component mole percent of product gas.
- CVOL(I) - Component volume in product gas, ScF/#-Feed.
- CPA(I) - Component chromatograph peak area at standard attenuation.
- HFR(I) - Component mass fraction of hydrogen.
- RF(I) - Component chromatograph response factor of Carle GC relative to methane standard.
- WTPCF(I) - Component weight percent on feed oil.
- WTPCG(I) - Component weight percent on product gas.

Variables

- ACH₄ - Chromatograph methane calibration area.
- AMWT - Molecular Weight of feed oil.
- AVMWT - Average molecular of product gas.
- CFVOL - Total volume of product gas made during run, FT³.
- CHR - Carbon/hydrogen ratio of liquid products calculated by gas yield difference.
- LRTIME - Length of run, minutes.

- MHCR - Molar hydrogen/carbon ratio of liquid products calculated by gas yield difference.
- MOF - Mass of oil feed flowed, g.
- NITC - Weight percent of nitrogen content in feed oil.
- OILNUM - Number of the feed oil.
- OILSV - Specific volume of feed oil at average reactor temperature cm^3/g .
- PCL - Liquid weight percent of feed.
- PRS - Atmospheric pressure, Torr.
- PCGF - Gas weight percent of feed.
- PYRSF - Pyrolysis severity factor.
- Ratio - Steam-hydrocarbon mass ratio.
- RUNNUM - Run number.
- SPFG - Specific gravity of feed oil.
- STMSV - Specific volume of steam at average reactor temperature cm^3/g .
- SUMX - Sum of all mole fraction of gas products.
- TAV - Mean average reactor temperature, $^{\circ}\text{F}$.
- TAU - Reactor residence time at average reactor temperature, sec.
- TOTVF - Total volume of steam and oil vapor, cm^3 .
- TPG - Temperature of product gas, $^{\circ}\text{F}$.
- TVPG - Total volume of product gas, $\text{ScF}/\#$ -Feed.
- VOIL - Actual liquid volume of oil feed used in the run, ml.

VOF	- Volume of oil vapor flowed, Cm^3 .
VSF	- Volume of steam flowed, Cm^3 .
VSTM	- Actual liquid volume of water used in the run, ml.
WCH	- Weight percent hydrogen on feed oil.
WCC	- Weight percent carbon on feed oil.
WPGAS	- Weight of gas product, g.
WTPC	- Weight percent carbon of feed oil in product gas.
WTPH	- Weight percent hydrogen of feed oil in product gas.

The Components Analyzed Are:

1. Hydrogen
2. Carbon monoxide
3. Carbon dioxide
4. Methane
5. Ethylene
6. Ethane
7. Propylene
8. Propane
9. 1-Butene
10. Trans-Butene
11. CIS-2 Butene
12. 1,3 Butadiene
13. N-Butane
14. I-Butane


```

C *****COMPUTER PROGRAM*****
C
C          ABDALLAH S. ELKABULE
C
C          MASTER THESIS                      FEB.,1982
C *****
C THE FOLLOWING COMPUTER PROGRAM CALCULATES THE STEAM PYROLYSIS
C PRODUCT COMPOSITION AND YIELD FOR EACH COMPONENT IN PRODUCT
C GAS AND PREDICTS THE LIQUID PRODUCTS YIELD, MOLAR HYDROGEN-
C CARBON RATIO, AND CARBON HYDROGEN RATIO OF LIQUID PRODUCTS .
C *****
REAL MOF,LRTIME,MHCR
DIMENSION RF(14),CPA(14),ATEN(14),CMWT(14),CMLPC(14)
DIMENSION WTPCG(14),WTPCF(14),CVOL(14),HFR(14),CFR(14)
DATA(RF(I),I=1,8)/0.0,9285,7411,1.0,713,6556,.58,.5684/
DATA(RF(I),I=9,14)/.4497,4652,3781,541,4712,.488/
DATA(ATEN(I),I=1,8)/1.5,128,8,512,258,32,128,.8/
DATA(ATEN(I),I=9,14)/32,8,8,32,8,8,8,8/
DATA(CMWT(I),I=1,7)/2.016,28.01,44.01,16.04,28.05,30.07,42.08/
DATA(CMWT(I),I=8,14)/44.10,3*56.11,54.09,2*58.12/
DATA(HFR(I),I=1,8)/1.0,0.0,0.0,0.25,0.143,0.2,0.143,.182/
DATA(HFR(I),I=9,14)/7.143,0.143,0.143,1.11,1.72,0.0/
DATA(CFR(I),I=1,8)/0.0,0.439,0.273,0.45,0.857,0.8,0.857,.818/
DATA(CFR(I),I=9,14)/.857,.858,.857,.889,.828,0.0/
100 READ(4,100)FEED
    FORMAT(10A5)
150 READ(4,200)OILNUM
    FORMAT(4I)
200 READ(4,300)NITC
    FORMAT(F)
250 READ(4,400)LRTIME,VOIL,VSTM,TAV,PRS
    FORMAT(5F)
300 READ(4,500)CFVOL,TPG,AMWT,SPFG,ACH4,WCH,WCC
    FORMAT(7F)
350 READ(4,600)CPA
    FORMAT(14F)
400 MOF=VOIL*SPFG
    OILSV=(TAV+460.)*34634.44/(PRS*AMWT)
    STMSV=(TAV+460.)*34634.44/(PRS*18.)
    VOF=OILSV*MOF
    VSF=STMSV*VSTM
    TOTVF=VOF+VSF
    TAU=30.196/(TOTVF/(LRTIME*60.0))
    RATIO=VSTM/(SPFG*VOIL)
    SUMX=0.0
    CMLPC(1)=CPA(1)
    DO 10 I=2,14
    CH4=ACH4*1024.
10  CMLPC(I)=RF(I)*CPA(I)*ATEN(I)/CH4
    DO 20 I=1,14
20  SUMX=SUMX+CMLPC(I)
    DO 30 I=1,14
30  CMLPC(I)=CMLPC(I)/SUMX*100
    AVMWT=0.0
    DO 40 I=1,14
40  AVMWT=AVMWT+CMWT(I)*CMLPC(I)/100.0

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```

WPGAS=PRS*CFVOL*AVMWT/(TPG+460.)
PCGF=(WPGAS/(1.223*SPFG*VOIL))*100.
PCL=100.0-PCGF
DO 50 I=1,14
50 WTPCG(I)=CMLPC(I)*CMWT(I)/AVMWT
WTPCF(I)=PCGF*WTPCG(I)/100.0
WTPH=0.0
WTPC=0.0
DO 60 I=1,14
60 WTPH=WTPH+WTPCF(I)*HFR(I)
WTPC=WTPC+WTPCF(I)*CFR(I)
MHCR=(WCH-WTPH)*12./(WCC-WTPC)
CHR=(WCC-WTPC)/(WCH-WTPH)
TVPG=0.0
DO 70 I=1,14
70 CVOL(I)=3.855*WTPCF(I)/CMWT(I)
TVPG=TVPG+CVOL(I)
PYRSF=TAV*TAU*0.06
WRITE(4,145) FEED
WRITE(6,145) FEED
WRITE(4,147) OILNUM
WRITE(6,147) OILNUM
WRITE(4,148) NITC
WRITE(6,148) NITC
WRITE(4,150) TAV,TAU,RATIO,PYRSF,PCGF,TVPG
WRITE(6,150) TAV,TAU,RATIO,PYRSF,PCGF,TVPG
WRITE(4,106)
WRITE(6,106)
WRITE(4,151) (CMLPC(I),WTPCG(I),WTPCF(I),CVOL(I),I=1,14)
WRITE(6,151) (CMLPC(I),WTPCG(I),WTPCF(I),CVOL(I),I=1,14)
WRITE(4,155) PCL,MHCR,CHR
WRITE(6,155) PCL,MHCR,CHR
150 FORMAT(14X, REACTION TEMPERATURE, F7.1, ' DEG F'
1/14X, REACTION TIME, F6.3, ' SEC'
1/14X, STEAM-OIL RATIO, F6.3
1/14X, PYROLYSIS SEVERITY FACTOR, F7.1
1//14X, GASEOUS PRODUCTS
1/16X, ' WT % OF FEED', F6.2
1/16X, ' SCF/LB OF FEED', F6.2)
106 FORMAT(15X, ' COMPONENT', 12X, ' MOL % GAS', 3X, ' WT % GAS', 3X
1, ' WT % FEED', 3X, ' SCF/# FEED'
1/15X, '-----' 12X, '-----' 3X, '-----' 3X
1, '-----' 3X, '-----' )
151 FORMAT(16X, ' HYDROGEN', 8X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' CARBON MONOXIDE', 1X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' CARBON DIOXIDE', 2X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' METHANE', 9X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' ETHYLENE', 8X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' ETHANE', 10X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' PROPYLENE', 7X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' PROPANE', 9X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' 1-BUTENE', 8X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' TRANS-BUTENE', 4X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' CIS-2BUTENE', 5X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' 1,3-BUTADIENE', 3X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' N-BUTANE', 8X, 2(6X, F5.2), 2(7X, F5.2)
1/16X, ' I-BUTANE', 8X, 2(6X, F5.2), 2(7X, F5.2)
155 FORMAT(14X, ' LIQUID PRODUCTS', 15X, ' WT % OF FEED', F6.2
1//14X, ' H/C MOLAR RATIO ON LIQ. PRODUCT', F6.2
1//14X, ' C/H RATIO ON LIQ. PRODUCT', F6.2)

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145 FORMAT(15X,RUN NUMBER : 'A5)  
147 FORMAT(14X, OIL TYPE : TOSCO OIL# 'I4)  
148 FORMAT(14X, NITROGEN WT.%='F5.3)  
STOP  
END
```

APPENDIX B
SAMPLE CALCULATION

SAMPLE CALCULATION

A. Reactor Volume Calculation

$$\text{Pipe Volume: } (\pi/4)(0.493 \text{ in})^2(13 \text{ in})\left(\frac{2.54 \text{ Cm}}{\text{In}}\right)^3 = 40.67 \text{ Cm}^3$$

$$\text{Thermocouple Well Volume: } (\pi/4)(1/4 \text{ in})^2(13 \text{ in})\left(\frac{2.54 \text{ Cm}}{\text{In}}\right)^3 = 10.47 \text{ Cm}^3$$

$$\text{Reactor Volume: } 40.67 - 10.47 = 30.196 \text{ Cm}^3$$

B. Computer Program Calculation

1. Reaction parameters:

$$\text{Average reactor Temperature } T_c = \frac{\sum T_{Tc}}{8} = 2 T_{Tc}/7$$

where TC = Thermocouple

$$\text{Specific Volume of Steam} = \frac{RT_{\text{reactor}}}{P(18)}$$

$$\text{Specific volume of oil vapor} = \frac{RT_{\text{reactor}}}{P \text{ MWT}_{\text{oil}}}$$

$$\text{Total Vapor Volume flow} = (\text{specific vol. of oil vapor})(\text{mass of oil flowed})$$

$$+ (\text{specific vol. of steam})(\text{mass of water flowed})$$

$$\text{Volumetric flow rate} = \frac{\text{Total vapor Vol. flow}}{\left[1 + \frac{(\text{ratio})}{(\text{MWT}_{\text{oil}})/18}\right]}$$

$$\text{Volumetric flow rate of Steam} = (\text{Total vapor vol. flow}) - (\text{Volumetric flow rate of oil vapor})$$

$$\text{Residence time} = \frac{(\text{Reactor volume})(\text{Elapsed Time})}{\text{Total vapor volume flow}}$$

$$\text{Steam-hydrocarbon ratio} = \frac{\text{Mass of water flowed}}{\text{Mass of oil flowed}}$$

2. Product Gas Composition

$$\text{Mole fraction of comp. "i" on product gas} = \frac{(\text{Peak area})(\text{attenuation})(\text{sensitivity})}{(\text{Methane standard area})(1024)}$$

$$\text{Corrected Mole fraction of comp "i" on product gas} = \frac{\text{Mole fraction of comp. "i" on product gas}}{\text{Sum of all mole fraction of gas products}}$$

$$\text{Average molecular weight of product gas} = (\text{corrected mole fraction}) (\text{molecular weight of comp. "i"})$$

$$\text{Mass of product gas} = (P/RT_{PG})(MWT_{PG})(\text{Volume of product gas})$$

where T_{PG} = Temp. of product gas and MWT_{PG} = Molecular weight of product gas.

$$\text{Component Weight of product gas} = \frac{(\text{Corrected mole fraction})(\text{molecular weight of comp "i"})}{\text{molecular weight of product}} \times 100$$

$$\text{Carbon/hydrogen ratio of liquid product} = \frac{(\text{weight\% carbon in liquid})}{(\text{weight\% hydrogen in liquid})}$$

4. Pyrolysis Severity Factor = (reaction temperature)
(residence time)^{0.06}

REACTION CONDITIONS AND PRODUCT ANALYSIS
ON THE SAMPLES OF HYDROGENATED PARAH0 OILS
(RUNS T1 THORUGH H3)

APPENDIX C
COMPUTER PROGRAM PSY.FOR OUTPUT

RUN NUMBER : T1
 OIL TYPE : PARHO OIL#6281
 NITROGEN WT.% : .270
 REACTION TEMPERATURE 1605.0DEG F
 REACTION TIME 0.100 SEC
 STEAM -OIL RATIO 1.015
 PYROLYSIS SEVERITY FACTOR 1399.1

GASEOUS PRODUCTS
 WT % OF FEED 60.76
 SCF/LB OF FEED 12.41

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	30.23	3.56	1.945	3.75
CARBON DIOXIDE	10.49	15.59	1.646	1.30
METHANE	1.17	2.79	1.24	1.18
ETHYLENE	25.65	34.28	2.83	2.86
ETHANE	23.07	21.28	1.65	1.65
PROPYLENE	1.20	1.94	1.03	0.60
PROPANE	4.91	10.05	0.32	0.09
1-BUTENE	0.73	2.15	1.70	0.05
TRANS-2-BUTENE	0.39	1.18	0.33	0.13
CIS-2-BUTADIENE	0.06	0.39	0.17	0.00
1,3-BUTADIENE	1.88	5.13	0.27	0.20
N-BUTANE	0.20	0.61	0.00	0.00
I-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED 39.24

H/C MOLAR RATIO ON LIQ. PRODUCT 1.05

C/H RATIO ON LIQ. PRODUCT 11.37

RUN NUMBER : T2
 OIL TYPE : PARAH OIL#6281
 NITROGEN WT.% : 270
 REACTION TEMPERATURE 1604.0DEG F
 REACTION TIME 0.069 SEC
 STEAM-OIL RATIO 0.997
 PYROLYSIS SEVERITY FACTOR 1366.1

GASEOUS PRODUCTS
 WT % OF FEED 72.91
 SCF/LB OF FEED 13.24

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED	WT % FEED
HYDROGEN MONOXIDE	26.03	2.47	1.80	3.45	1.80
CARBON MONOXIDE	14.10	18.60	13.56	1.87	13.56
CARBON DIOXIDE	2.48	4.97	3.28	1.03	3.28
METHANE	20.93	15.47	11.20	2.30	11.20
ETHYLENE	24.14	32.94	24.18	3.00	24.18
ETHANE	1.12	1.61	1.29	0.00	1.29
PROPYLENE	7.02	10.54	9.34	0.00	9.34
PROPANE	0.85	2.78	1.57	0.00	1.57
1-BUTADIENE	0.30	0.78	0.51	0.00	0.51
TRANS-2-BUTADIENE	0.06	0.16	0.11	0.00	0.11
CIS-3-BUTADIENE	2.20	6.03	4.39	0.00	4.39
1-BUTANE	0.20	0.55	0.40	0.00	0.40
I-BUTANE	0.00	0.00	0.00	0.00	0.00

LIQUID PRODUCTS 27.09

H/C MOLAR RATIO ON LIQ. PRODUCT 1.12

C/H RATIO ON LIQ. PRODUCT 10.67

RUN NUMBER : T3
 OIL TYPE : PARAH OIL#6281
 NITROGEN WT.% : 0.270
 REACTION TEMPERATURE 1608.0DEG F
 REACTION TIME 0.050 SEC
 STEAM -OIL RATIO 0.996
 PYROLYSIS SEVERITY FACTOR 1342.7

GASEOUS PRODUCTS
 WT % OF FEED 76.60
 SCF/LB OF FEED 12.65

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED	WT % FEED
HYDROGEN MONOXIDE	20.74	11.79	1.37	2.62	1.37
CARBON MONOXIDE	10.12	12.15	1.378	1.16	1.378
CARBON DIOXIDE	1.23	13.78	1.56	1.54	1.56
METHANE	20.05	13.30	1.57	2.33	1.57
METHYLENE	31.04	17.37	1.53	1.19	1.53
ETHYLENE	1.53	17.48	1.39	1.33	1.39
PROPYLENE	9.69	10.05	1.04	1.00	1.04
PROPANE	0.03	4.99	0.82	0.26	0.82
1-BUTENE	2.08	4.00	0.77	0.00	0.77
TRANS-BUTENE	0.42	1.00	0.17	0.00	0.17
CIS-2-BUTADIENE	0.09	6.23	0.95	0.00	0.95
1,3-BUTADIENE	2.79	0.48	0.36	0.00	0.36
N-BUTANE	0.19	0.00	0.00	0.00	0.00
I-BUTANE	0.00	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED 23.40

H/C MOLAR RATIO ON LIQ. PRODUCT 0.98

C/H RATIO ON LIQ. PRODUCT 12.24

RUN NUMBER : P1
 OIL TYPE : PARHO OIL#6281
 NITROGEN WT.% = 270
 REACTION TEMPERATURE 1702.0DEG F
 REACTION TIME 0.100 SEC
 STEAM-OIL RATIO 0.933
 PYROLYSIS SEVERITY FACTOR 1477.0

GASEOUS PRODUCTS
 WT % OF FEED 58.68
 SCF/LB OF FEED 15.90

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	49.26	6.98	4.10	7.83
CARBON DIOXIDE	18.53	36.48	21.41	20.95
CARBANE	11.26	16.88	9.91	20.38
METHYLENE	14.97	24.92	14.63	20.01
ETHYLENE	12.64	4.83	2.45	20.03
PROPYLENE	1.47	0.00	0.00	0.00
PROPANE	0.00	0.00	0.00	0.00
1-BUTENE	0.12	0.48	0.28	0.02
TRANS-BUTENE	0.00	0.00	0.00	0.00
CIS-2-BUTADIENE	1.30	4.96	2.91	0.01
1-3-BUTANE	0.05	0.22	0.10	0.00
N-BUTANE	0.00	0.00	0.00	0.00
I-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
WT % OF FEED 41.32

H/C MOLAR RATIO ON LIQ. PRODUCT 1.03

C/H RATIO ON LIQ. PRODUCT 11.65

RUN NUMBER : P2
 OIL TYPE : PARAH OIL#6281
 NITROGEN WT.% = .270
 REACTION TEMPERATURE 1773.0DEG F
 REACTION TIME 0.100 SEC
 STEAM-OIL RATIO 1.107
 PYROLYSIS SEVERITY FACTOR 1552.4

GASEOUS PRODUCTS
 WT % OF FEED 61.79
 SCF/LB OF FEED 18.10

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	53.75	8.23	5.09	9.73
CARBON DIOXIDE	21.76	47.03	28.62	30.38
METHANE	11.93	14.54	8.98	2.16
ETHYLENE	9.01	19.20	11.86	1.63
ETHANE	0.29	0.67	1.41	0.55
PROPYLENE	0.85	2.73	1.69	0.15
PROPANE	0.00	0.00	0.00	0.00
1-BUTENE	0.07	0.31	0.19	0.01
TRANS-2BUTENE	0.00	0.00	0.00	0.00
CIS-2BUTADIENE	0.20	0.82	0.51	0.04
1,3-BUTADIENE	0.03	0.15	0.00	0.01
N-BUTANE	0.00	0.00	0.00	0.00
I-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED 38.21

H/C MOLAR RATIO ON LIQ. PRODUCT 1.00

C/H RATIO ON LIQ. PRODUCT 12.04

RUN NUMBER : H1
 OIL TYPE : PARAH OIL#3536
 NITROGEN WT.% : 440
 REACTION TEMPERATURE 1611.0DEG F
 REACTION TIME 0.101 SEC
 STEAM-OIL RATIO 0.997
 PYROLYSIS SEVERITY FACTOR 1403.8

GASEOUS PRODUCTS
 WT % OF FEED 64.84
 SCF/LB OF FEED 11.04

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED	WT % FEED
HYDROGEN MONOXIDE	16.36	1.46	0.94	1.81	1.81
CARBON MONOXIDE	17.44	1.20	0.96	1.82	1.82
CARBON DIOXIDE	0.55	1.07	0.69	0.00	0.00
METHANE	29.04	10.57	3.34	3.33	3.33
ETHYLENE	33.19	24.17	16.66	3.66	3.66
PROPYLENE	1.29	1.72	1.15	0.00	0.00
PROPANE	8.01	14.88	9.15	0.00	0.00
1-BUTENE	0.82	0.01	0.01	0.00	0.00
TRANS-BUTENE	0.58	2.03	1.32	0.00	0.00
CIS-2BUTADIENE	0.08	1.20	0.82	0.00	0.00
1,3-BUTADIENE	2.48	5.93	3.13	0.00	0.00
1-BUTANE	0.21	0.55	0.36	0.00	0.00
2-BUTANE	0.00	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
WT % OF FEED 35.16

H/C MOLAR RATIO ON LIQ. PRODUCT 1.03

C/H RATIO ON LIQ. PRODUCT 11.69

RUN NUMBER : H2
 OIL TYPE : PARAH OIL#6280
 NITROGEN WT % : 0.48
 REACTION TEMPERATURE 1607.0DEG F
 REACTION TIME 0.106 SEC
 STEAM-OIL RATIO 0.976
 PYROLYSIS SEVERITY FACTOR 1402.7

GASEOUS PRODUCTS
 WT % OF FEED 60.79
 SCF/LB OF FEED 15.15

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	45.91	5.98	3.64	6.95
CARBON MONOXIDE	19.97	36.16	21.98	3.03
CARBON DIOXIDE	1.90	5.40	3.28	0.24
METHANE	14.23	14.68	8.58	2.10
ETHYLENE	13.69	23.99	14.58	2.00
ETHYLENE	2.69	7.35	4.45	0.41
PROPYLENE	0.03	1.32	0.85	0.04
PROPANE	0.24	0.88	0.54	0.04
TRANS-BUTENE	0.15	0.56	0.34	0.02
CIS-2BUTADIENE	0.02	0.08	0.05	0.00
1,3-BUTANE	0.92	3.20	1.96	0.14
N-BUTANE	0.00	0.30	0.18	0.00
I-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED 39.21

H/C MOLAR RATIO ON LIQ. PRODUCT 1.04

C/H RATIO ON LIQ. PRODUCT 11.55

RUN NUMBER : H3
 OIL TYPE : PARAFFIN OIL#6281
 NITROGEN WT% : 270
 REACTION TEMPERATURE 1706.0 DEG F
 REACTION TIME 0.093 SEC
 STEAM-OIL RATIO 0.991
 PYROLYSIS SEVERITY FACTOR 1478.9

GASEOUS PRODUCTS
 WT % OF FEED 59.04
 SCF/LB OF FEED 15.15

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	46.42	6.23	3.68	7.03
CARBON MONOXIDE	17.97	35.36	19.16	2.28
CARBON DIOXIDE	11.83	17.06	3.08	0.42
METHANE	15.98	26.17	15.43	2.16
ETHYLENE	14.01	0.73	0.95	0.20
PROPYLENE	1.79	5.01	2.00	0.20
PROPANE	0.00	0.11	0.00	0.01
1-BUTENE	0.06	0.25	0.12	0.02
TRANS-2-BUTENE	0.16	0.50	0.34	0.02
CIS-2-BUTADIENE	0.00	0.82	0.04	0.00
1,3-BUTADIENE	1.34	4.83	2.00	0.20
1-BUTANE	0.09	0.34	0.20	0.00
2-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
WT % OF FEED 40.96

H/C MOLAR RATIO ON LIQ. PRODUCT 1.09

C/H RATIO ON LIQ. PRODUCT 11.01

REACTION CONDITONS AND PRODUCT ANALYSIS
ON THE SAMPLES OF HYDROGENATED TOSCO II OILS
(RUNS R1 THROUGH S3)

RUN NUMBER : R1
 OIL TYPE : TOSCO OIL#6199
 NITROGEN WT.% : 300
 REACTION TEMPERATURE 1610.0DEG F
 REACTION TIME 0.105 SEC
 STEAM-OIL RATIO 1.046
 PYROLYSIS SEVERITY FACTOR 1409.7

GASEOUS PRODUCTS
 WT % OF FEED 53.46
 SCF/LB OF FEED 9.49

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	22.21	2.06	1.10	2.11
CARBON MONOXIDE	27.29	9.49	5.02	0.69
CARBON DIOXIDE	0.98	1.58	1.06	0.39
METHANE	25.16	18.02	9.33	2.94
ETHYLENE	30.99	40.02	21.77	3.10
ETHAPYLENE	7.04	1.43	0.71	0.15
PROPANE	1.92	1.35	0.21	0.00
1-BUTENE	0.02	0.04	0.45	0.10
TRANS-2BUTENE	1.05	2.70	1.00	0.15
CIS-2BUTENE	0.55	1.42	0.76	0.00
1,3-BUTADIENE	0.07	0.19	0.10	0.00
N-BUTANE	2.45	6.10	3.26	0.23
I-BUTANE	0.27	0.71	0.38	0.00

LIQUID PRODUCTS
 WT % OF FEED 46.54

H/C MOLAR RATIO ON LIQ. PRODUCT 1.23

C/H RATIO ON LIQ. PRODUCT 9.77

RUN NUMBER : R2
 OIL TYPE : TOSCO OIL#6199
 NITROGEN WT.% : 300
 REACTION TEMPERATURE 1604.0DEG F
 REACTION TIME 0.071 SEC
 STEAM-OIL RATIO 0.966
 PYROLYSIS SEVERITY FACTOR 1366.8

GASEOUS PRODUCTS
 WT % OF FEED 69.58
 SCF/LB OF FEED 11.14

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	16.82	1.41	0.98	1.87
CARBON DIOXIDE	17.71	20.60	14.33	1.97
CARBON MONOXIDE	20.82	11.49	1.04	1.09
METHANE	28.74	13.58	9.45	2.27
ETHYLENE	1.19	33.48	23.30	3.20
ETHYLENE	9.05	1.49	1.00	0.13
PROPANE	0.63	15.82	11.00	1.01
1-BUTENE	1.47	0.80	0.03	0.08
TRANS-2-BUTENE	0.88	3.09	2.76	0.15
CIS-3-BUTADIENE	2.88	1.19	0.13	0.01
1-BUTANE	0.21	6.46	4.50	0.32
I-BUTANE	0.01	0.51	0.02	0.00

LIQUID PRODUCTS
 WT % OF FEED 30.42

H/C MOLAR RATIO ON LIQ. PRODUCT 1.31

C/H RATIO ON LIQ. PRODUCT 9.18

RUN NUMBER : R3
 OIL TYPE : OSO OIL#6199
 NITROGEN WT.% : 300
 REACTION TEMPERATURE 1609.0DEG F
 REACTION TIME 0.050 SEC
 STEAM-OIL RATIO 0.994
 PYROLYSIS SEVERITY FACTOR 1344.4

GASEOUS PRODUCTS
 WT % OF FEED 69.95
 SCF/LB OF FEED 10.68

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED	# FEED
HYDROGEN MONOXIDE	13.75	1.10	0.77	1.47	1.47
CARBON DIOXIDE	16.38	7.02	4.95	0.68	0.68
METHANE	0.75	1.81	0.88	0.08	0.08
ETHYLENE	21.81	13.10	9.66	2.34	2.34
PROPYLENE	1.36	1.62	1.15	1.15	1.15
PROPANE	10.37	18.06	12.60	1.05	1.05
1-BUTENE	2.55	0.52	0.68	0.05	0.05
TRANS-2-BUTENE	0.13	0.29	0.80	0.00	0.00
CIS-2-BUTENE	3.11	1.66	0.26	0.00	0.00
1-BUTANE	0.23	0.52	4.00	0.33	0.33
I-BUTANE	0.01	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
WT % OF FEED 30.05

H/C MOLAR RATIO ON LIQ. PRODUCT 1.01

C/H RATIO ON LIQ. PRODUCT 11.92

RUN NUMBER : G1
 OIL TYPE : TOSCO OIL#6199
 NITROGEN WT.% = .300
 REACTION TEMPERATURE 1705.0 DEG F
 REACTION TIME 0.105 SEC
 STEAM-OIL RATIO 0.999
 PYROLYSIS SEVERITY FACTOR 1489.4

GASEOUS PRODUCTS
 WT % OF FEED 51.53
 SCF/LB OF FEED 11.83

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/#	FEED
HYDROGEN MONOXIDE	36.63	4.40	2.27	4	33
CARBON MONOXIDE	10.84	18.58	9.34	10	163
CARBON DIOXIDE	1.36	23.87	1.78	2	54
METHANE	23.93	35.04	18.48	20	43
ETHYLENE	21.47	19.12	4.70	0	0
PROPYLENE	3.64	0.55	0.18	0	0
ISOBUTENE	0.16	0.09	0.03	0	0
TRANS-BUTENE	0.29	0.05	0.03	0	0
CIS-2-BUTADIENE	0.02	0.00	0.00	0	0
1,3-BUTADIENE	0.93	2.99	1.54	0	0
I-BUTANE	0.14	0.48	0.20	0	0
N-BUTANE	0.00	0.00	0.00	0	0

LIQUID PRODUCTS
WT % OF FEED 48.47

H/C MOLAR RATIO ON LIQ. PRODUCT 1.05

C/H RATIO ON LIQ. PRODUCT 11.47

RUN NUMBER : G2
 OIL TYPE : TOSCO OIL#6199
 NITROGEN WT% : 300
 REACTION TEMPERATURE : 1775.0DEG F
 REACTION TIME : 0.099 SEC
 STEAM-OIL RATIO : 0.987
 PYROLYSIS SEVERITY FACTOR : 1544.5

GASEOUS PRODUCTS
 WT % OF FEED : 53.93
 SCF/LB OF FEED : 15.36

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	52.20	7.77	4.19	8.01
CARBON MONOXIDE	20.05	41.47	22.09	3.07
CARBON DIOXIDE	1.76	15.78	8.51	2.05
METHANE	13.32	20.89	11.27	1.55
ETHYLENE	10.08	20.89	10.43	0.20
ETHANE	1.36	4.89	2.64	0.24
PROPYLENE	1.57	0.80	0.04	0.00
PROPANE	0.02	0.08	0.02	0.00
1-BUTENE	0.12	0.48	0.06	0.00
TRANS-BUTENE	0.00	0.02	0.01	0.00
CIS-BUTENE	0.47	0.87	1.01	0.07
1,3-BUTADIENE	0.05	1.21	0.11	0.01
N-BUTANE	0.00	0.00	0.00	0.00
I-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED : 46.07

H/C MOLAR RATIO ON LIQ. PRODUCT : 1.03

C/H RATIO ON LIQ. PRODUCT : 11.69

RUN NUMBER : S1
 OIL TYPE : TOSCO OIL#6209
 NITROGEN WT.% = .035
 REACTION TEMPERATURE 1611.0DEG F
 REACTION TIME 0.101 SEC
 STEAM-OIL RATIO 0.984
 PYROLYSIS SEVERITY FACTOR 1402.9

GASEOUS PRODUCTS
 WT % OF FEED 62.99
 SCF/LB OF FEED 12.21

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN MONOXIDE	28.19	2.86	1.80	3.44
CARBON MONOXIDE	13.00	18.31	11.54	1.59
CARBON DIOXIDE	10.97	22.10	11.37	0.73
METHANE	25.38	18.05	11.37	2.73
ETHYLENE	25.35	35.73	22.52	3.11
PROPYLENE	0.05	1.79	0.87	0.11
PROPANE	6.01	12.03	8.06	0.74
1-BUTENE	0.49	10.03	0.62	0.00
TRANS-BUTENE	0.38	1.09	0.88	0.05
CIS-2BUTENE	0.03	1.04	0.69	0.01
1,3-BUTADIENE	2.03	5.52	3.47	0.20
I-BUTANE	0.19	0.56	0.35	0.00
N-BUTANE	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED 37.01

H/C MOLAR RATIO ON LIQ. PRODUCT 1.12
 C/H RATIO ON LIQ. PRODUCT 10.68

RUN NUMBER : S2
 OIL TYPE : TUSCO OIL#6206
 NITROGEN WT.% = 820
 REACTION TEMPERATURE 1606.0 DEG F
 REACTION TIME 0.100 SEC
 STEAM -OIL RATIO 0.966
 PYROLYSIS SEVERITY FACTOR 1396.6

GASEOUS PRODUCTS
 WT % OF FEED 59.43
 SCF/LB OF FEED 10.03

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED
HYDROGEN	17.56	1.56	0.93	1.77
CARBON MONOXIDE	8.58	10.37	6.25	0.86
CARBON DIOXIDE	0.71	1.37	0.81	0.07
METHANE	26.88	18.88	11.22	2.70
ETHYLENE	31.53	38.73	23.92	3.16
PROPYLENE	1.24	1.64	0.97	0.12
1-BUTENE	8.77	16.16	9.60	1.88
2-BUTENE	0.08	0.55	0.37	0.01
1,3-BUTADIENE	1.50	2.23	1.57	0.15
ISOBUTANE	0.08	1.21	0.93	0.01
N-BUTANE	2.67	6.33	4.76	0.27
I-BUTANE	0.00	0.67	0.40	0.00

LIQUID PRODUCTS
WT % OF FEED 40.57

H/C MOLAR RATIO ON LIQ. PRODUCT 1.08

C/H RATIO ON LIQ. PRODUCT 11.10

RUN NUMBER : S3
 OIL TYPE : TOSCO OIL#6199
 NITROGEN WT.% : 300
 REACTION TEMPERATURE 1603.0DEG F
 REACTION TIME 0.101 SEC
 STEAM -OIL RATIO 0.986
 PYROLYSIS SEVERITY FACTOR 1395.9

GASEOUS PRODUCTS
 WT % OF FEED 53.33
 SCF/LB OF FEED 9.27

COMPONENT	MOL % GAS	WT % GAS	WT % FEED	SCF/# FEED	WT % FEED
HYDROGEN MONOXIDE	21.68	1.97	1.05	2.01	0.61
CARBON DIOXIDE	7.22	1.12	4.86	0.09	0.08
METHANE	0.45	1.89	1.66	2.08	0.17
ETHYLENE	34.25	16.24	18.10	3.10	0.74
ETHANE	1.07	4.32	23.78	0.00	0.00
PROPYLENE	7.97	15.46	8.06	0.00	0.00
PROPANE	0.02	1.14	0.23	0.00	0.00
1-BUTENE	0.91	5.04	1.23	0.00	0.00
TRANS-2-BUTENE	0.47	2.18	0.09	0.00	0.00
CIS-2-BUTENE	0.07	1.18	0.51	0.00	0.00
1,3-BUTADIENE	2.70	6.59	3.33	0.00	0.00
N-BUTANE	0.24	0.62	0.33	0.00	0.00
I-BUTANE	0.00	0.00	0.00	0.00	0.00

LIQUID PRODUCTS
 WT % OF FEED 46.67

H/C MOLAR RATIO ON LIQ. PRODUCT 1.28

C/H RATIO ON LIQ. PRODUCT 9.37