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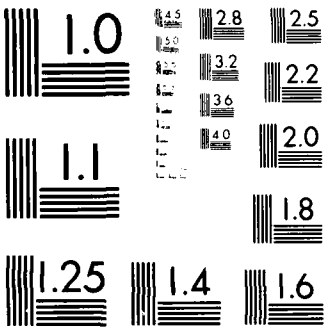

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Pyrolysis and Hydropyrolysis of Kentucky Oil Shale with Product Oil Characterization

CPT Jeff A. Manley
HQDA, MILPERCEN (DAPC-OPA-E)
200 Stovall Street
Alexandria, VA 22332

Final Report - 6 June 1985

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A thesis submitted to Colorado School of Mines, Golden, Colorado in partial fulfillment of the requirements for the degree of Master of Science (Chemical Engineering)

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Pyrolysis and Hydropyrolysis of Kentucky oil shale using supercritical toluene as the solvent was studied in a 300 c.c. stirred batch reactor. Organic carbon conversions in excess of 100% Fischer Assay were obtained in less than 30 minutes for these reactions occurring above 400°C with hydrogen atmospheres. It was found that the overall conversion of organic carbon to oil and gas products could be adequately modeled using a second order

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irreversible rate expression. Reactions occurring at 400 C and 300 psig hydrogen partial pressure could be considered instantaneous, yielding organic carbon conversions of 185% Fischer Assay. The effects of hydrogen partial pressure was found to be significant for reactions occurring above 400 degrees C. The selectivity for total carbon conversion to oil was shown to be high, however this value was dependent on the reaction temperature and reaction time. A characterization [illegible] is oil [illegible], and the oil produced from [illegible] run performed at 440 C for 10 minutes demonstrated that the oils were remarkably similar in their chemical make-up.

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Golden, Colorado

Date 6/11/85

Signed: _____

Jeff A. Manley

Approved: _____

Robert M. Baldwin
Thesis Advisor

Golden, Colorado

Date 6/11/85

_____

Arthur J. Kidnay
Chemical and Petroleum
Refining Engineering
Department Head

ABSTRACT

Pyrolysis and hydropyrolysis of Devonian oil shale from Kentucky (Cleveland Member) using supercritical toluene as the solvent was studied in a 300 c.c. stirred batch reactor. Organic carbon conversions in excess of 160% Fischer Assay were obtained in less than 30 minutes for those reactions occurring above 400 C with hydrogen atmospheres. It was found that the overall conversion of organic carbon to oil and gas products could be adequately modeled using a second order irreversible rate expression. Reactions occurring at 460 C and 300 psig hydrogen partial pressure could be considered instantaneous, yielding organic carbon conversions of 185% Fischer Assay. The effects of hydrogen partial pressure was found to be significant for reactions occuring above 400 degrees C. The selectivity for total carbon conversion to oil was shown to be high, however this value was dependent on the reaction temperature and reaction time. A characterization comparison between a pyrolysis oil produced by Dravo Engineers, Inc. and the oil produced from a run performed at 440 C for 10 minutes demonstrated that the oils were remarkably similar in their chemical make-up.

T-3097

DEDICATION

To Annie, Scott, Mom and Dad for your love and support.

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shale converted to oil. An additional objective, which was coupled with the determination of reaction parameter effects, was to determine an adequate model which described the reaction kinectics of this system.

The second objective of the study was to semi-quantitatively examine the nature of the oil products produced by the supercritical hydropyrolysis process and compare this to oil products generated by the Dravo Engineers Inc. traveling grate retort.

System Design Considerations

The system used in this study was designed to allow batch reactor data to be obtained. The batch reactor was operated in a semi-batch mode by the use of pressure assisted injection and withdrawl of slurry samples. This was done in order to facilitate data aquisition and to provide a means of obtaining meaningful kinetic data. in addition the system was designed to provide the following:

1) Rapid heating (3 minutes or less) of oil shale slurry samples to reaction temperatures in order to minimize the confounding effects of heat-up.

2) Isothermal operation (+/- 4 C) over the required time.

3) Rapid cooling of the reactor and contents after the required reaction time had elapsed in order quench the

EXPERIMENTAL DEVELOPMENT

Introduction

This study was undertaken with two principle objectives in mind. The primary objective was to investigate the effect of certain reaction parameters on the pyrolysis and hydropyrolysis of an Eastern Kentucky Devonian oil shale using supercritical toluene as the solvent. The term hydropyrolysis described in this study refers to the thermal decomposition and recovery of the oil shale kerogen in the presence of gas phase molecular hydrogen. The distinction between this study and other hydropyrolysis studies of Kentucky oil shale is the use of supercritical toluene as the solvent. The use of a dense gas medium as the extraction vehicle has been shown to be very effective in other oil shales (33) and is the basis for incorporating it into this study.

The reaction parameters studied in this investigation were reaction temperature, reaction time, and initial hydrogen partial pressure. The effect of each of these parameters was measured by respective variances in organic carbon conversion and oil selectivity. The term organic carbon conversion refers to conversion to oil plus gas of the non-carbonate carbon contained in the oil shale. Oil selectivity refers to the fraction of carbon in the feed

increasing the quality of the oil extracted from the shale.

Pyrolysis in supercritical fluids has proven to effective in other shales but the operating conditions for the production of oil from Kentucky shales still needs to be optimized for it to be a viable alternative to crude oil.

Finally, shale oil characterization is critical to the technological development in terms of required processing and refining. By specifying the major constituents of the shale oil it will be possible to determine possible end-use applications and any harmful effects that the processing and use of this particular shale oil might have on man and the environment.

pressure the solvent displayed increased extraction power. Maddox (32) reported that this phenomenon has been successfully applied to coal where high boiling coal components were extracted without significant degradation by using toluene at approximately 400 C. Baldwin (33) investigated using supercritical toluene in a hydrogen atmosphere to extract the organic material from Stuart A oil shale and reported achieving yields of 160 per cent of Fischer Assay. Scinta (34) and McKay (7,35) have investigated the use of supercritical extraction on eastern oil shales and Green River shales and reported the recovery of 75 to 85 percent of the organic carbon utilizing heptane, ethanol and water mixtures, and tetralin and water mixtures as the supercritical solvents.

Conclusion

The preceeding discussion and literature cited indicate the feasibility of organic carbon extraction from oil shale by contacting the shale with supercritical toluene in a hydrogen atmosphere. The supercritical fluid enables the extraction process to occur at much less severe conditions than those required for retorting, thus a decrease in gas production and an increase in oil formation is achieved. The hydrogen atmosphere acts as a free radical scavenger and inhibits cracking and condensation reactions, thus

Assay is a commonly referred to standard to measure the recoverable organic material in a shale.) Greene (24) was granted a patent for a process he developed in which a mixture of oil shale and tetralin was reacted in the presence of hydrogen at pressures from 10-200 atmospheres and temperatures of 300-650 C. Greene reported that high yields of liquid hydrocarbons boiling between 40 and 500 C were obtained and that hydrocarbon gas formation was reduced compared to conventional retorting. Gregoli (25) utilized a solids upflow fluidized bed reactor to study thermal solution at operating temperatures of 600 to 900 F, initial hydrogen pressures of 50 to 300 psig and residence times of 12 minutes to 2 hours. He reported an increased liquid product saturation and stability compared to conventional retort products.

Results on thermal solution applied to an Australian oil shale using tetralin and toluene have also been published by Baldwin (26,27), Frank (28), Bennett (29) and Winkler (30).

A variation of the thermal solution process receiving recent attention by researchers has been processes where the processing temperature exceeded the critical temperature of the solvent. Williams (31) observed that when certain solvents are used above their critical temperature and

solvents such as coal tar naptha, petroleum kerosene, tetralin, quinoline, and torbanite crude oil distillate.

Russian researcher D'yakova (19,20,21) studied the effects of various solvents on the thermal solution process and reported yields of 72 to 96 per cent of the organic material of seven different shales at temperatures between 380 and 430 C. The solvents utilized in his studies included anthracene oil, tetralin, petroleum fuel oil, diesel fuel, hydrogenated shale tars, and shale oil distillate.

Recently several researchers have explored the thermal solution process with simultaneous hydrogenation of extraction products. Jensen (22) conducted extensive bench scale studies in a batch reactor in which the thermal solution process was performed in the presence of hydrogen gas at pressures of 2000 psig. He was able to extract 100 per cent of the oil shale organic matter at temperatures of 650 F and reaction times of 110 minutes. The solvents utilized for his study included petroleum kerosene, quinoline, anthracene oil, and shale derived gas oil. Patzer (23) also studied the thermal solution process in a batch reactor. Utilizing organic solvents and shale oils at temperatures between 385 and 440 C, he reported organic conversions up to 138 per cent of Fischer Assay. (Fischer

benzene and chloroform.

Of the numerous patents granted in the early 1900's in the U.S. for work done on the thermal solution process those granted to Ryan, Day, and Hampton are the most noteworthy. Ryan (15) developed a process in which finely ground oil shale was digested in an oil bath at temperatures between 600 and 700 F. The temperatures employed in this study, although close to retorting temperatures, were considered low enough to avoid the problems of thermally degrading the extracted kerogen. The process developed by Day (16) was similar to Ryan's in that it utilized a heated oil bath to extract the kerogen from the oil shale, however it differed by the retorting of the spent shale. The process developed by Hampton (17) was also similar to Ryan's with the exception that steam was mixed with the oil bath vapors to allow the mixture to crack at temperatures above 700 F.

In the 1940's Australian and Russian researchers began publishing articles outlining their successes in extracting organic matter with various solvents from different forms of oil shale.

Dulhunty (18) reported his successes in the solvent processing of torbanite, which is a richly organic form of oil shale. He concluded that the thermal extraction of torbanite above 350 C was the most effective using aromatic

the gas phase molecular hydrogen acting as a free radical scavenger which significantly inhibits both reactions.

In an attempt to mitigate the inherent inefficiencies of the retorting processes, interest in the process of thermal solution has been renewed. Thermal solution could be considered a combination of both solvent extraction and pyrolysis because it is a process in which the oil shale is heated in the presence of a solvent and the solubilized conversion products are extracted. The main advantage that the thermal solution process presents over the retorting process is that the energy requirements for the process can be significantly less due to the lower operating temperatures characteristic of thermal solution processes.

The majority of the investigations dealing with the application of the thermal solution process to oil shale have been focused on determining the effects of varying operating conditions and solvents on the conversion of kerogen and the structure of resulting products.

Gavin and Aydelotte (8) reported that the organic matter in the oil shale could be extracted in high yield using several solvents at or near their boiling points in a Soxhlet extraction aparatus. Both polar and non-polar solvents were employed in their investigation and included carbon tetrachloride, carbon bisulfide, acetone, ether,

centuries, and involve heating the oil shale either directly or indirectly to temperatures in excess of 750 F in the absence of oxygen to allow the kerogen to pyrolize or thermally decompose. The retort product gases contain oil mist and vapors which are collected in an oil and gas recovery system. A variation of the basic retorting process has been the development of a process called hydrotorting. This involves retorting the oil shale in a hydrogen atmosphere and been shown for certain shales to produce higher oil yields than conventional retorting. Of the processes developed to date only the pyrolysis and hydropyrolysis processes have received the necessary attention required for developing them comercially (13). Unfortunately, due to the nature of the pyrolytic chemical reactions taking place, retorting processes are considered inefficient. Principally these inefficiencies result in low carbon conversions to oil due to free radical reactions, such as cracking and condensation. Cracking reactions result in the production of gas at the expense of oil formation while condensation reactions result in the undesireable formation of coke on the spent shale (14). However, in the presence of hydrogen oil shale pyrolysis has been shown to be less susceptible to these coke forming and cracking reactions. This thought to be the direct result of

deposition of organic rich sediments which were preserved in anaerobic and azoic conditions (4).

Currently, the biggest problem associated with exploiting these vast resources of oil shale has been the development of a process which can efficiently and economically convert the oil shale into useable petroleum products. The main objective of any conversion process is the efficient extraction of the organic material contained in the shale, commonly referred to as kerogen. Based on several studies it has been postulated that kerogen is:

> "an amorphous, highly disordered, cross-linked macromolecular complex in which the main elements are inherently cyclic in nature, with numerous primarily paraffinic cross links bridged to both organic and inorganic molecules." (6)

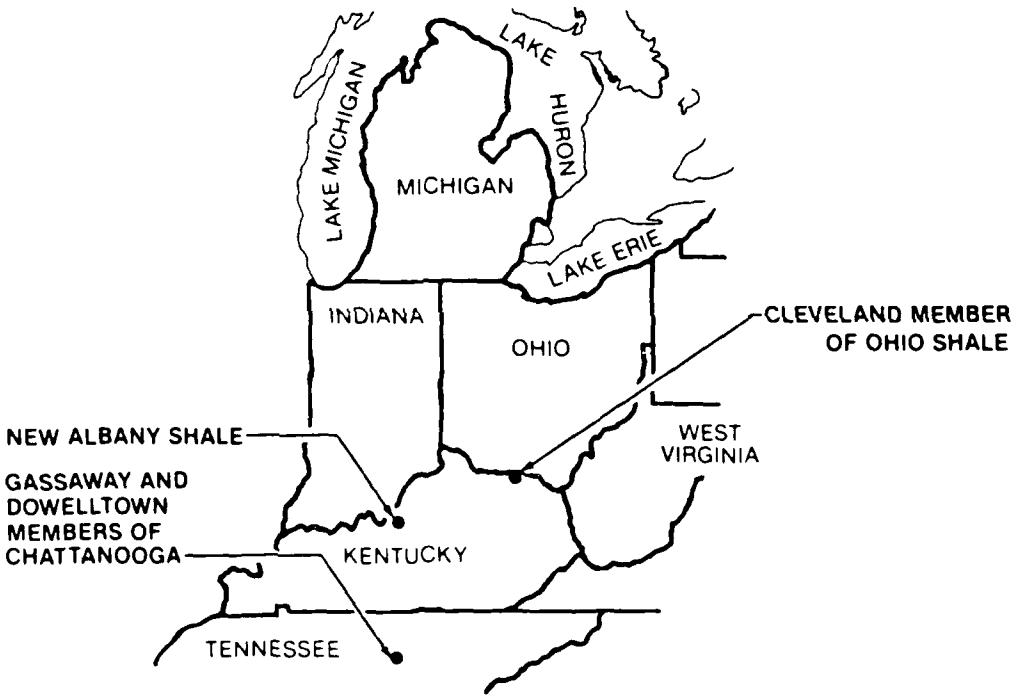
The processes which have been able to dislodge the kerogen with varying levels of success can be classified into the following main catagories, solvent extraction, retorting and thermal solution.

The solvent extraction process attempts to solubilize the kerogen away from the inorganic matrix in various solvents. Several attempts have been made to extract the kerogen with conventional organic solvents, both polar and non-polar, however the kerogen has been shown to have very low solubility at low temperatures (7,8,9,10,11,12).

Retorting processes have been known for over two

Figure 1

Location of Oil Shale Deposit



INTRODUCTION AND LITERATURE SURVEY

Oil shale is potentially one of the largest sources of recoverable hydrocarbons in the world today. In the United States alone it is estimated that there are resources of shale oil in excess of 85 trillion gallons (1). Of the known resources in the U.S., the U.S. Geological Survey has estimated that there are 400 billion barrels of recoverable shale oil in the eastern portion of the U.S., with figures as high as 2600 billion barrels for probable extensions of these known resources (2).

Of these eastern resources the black Devonian oil shales have received a great deal of interest for their potential as a viable source of petroleum feed stocks. Factors that have encouraged this interest include the vastness of the resource and its closeness to markets and supporting infrastructure (2). Of special interest to this thesis is the Devonian shale from the Cleveland Member of the Ohio Shale, Montgomery County, Kentucky. The location of this deposit is shown in Figure 1.

The oil shale contained in this deposit is of the late Devonian age and its sedimentary characteristics indicate it was deposited in an equatorial, inland epicontinental sea - the Chattanooga Sea (3,4,5). The organic material contained in the oil shale is thought to have been derived from the

ACKNOWLEDGEMENTS

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reaction.

Requirements

In order to accomplish the primary objective it was necessary to design an experimental program which established the impact of each of the aforementioned reaction parameters on the hydropyrolysis process. To accomplish the second objective it was necessary to formulate a technique to characterize each of the oil samples. The following criteria were used to develop the four phase experimental program:

1) Sufficient variation in the reaction parameters was necessary to observe a corresponding effect in the results obtained.

2) Operation at temperatures and pressures to insure that the toluene solvent was supercritical (T_c = 591.7 K, P_c= 40.6 atm).

3) The results must be reproducible.

Conditions

Phase One

Phase one of the experimental program was structured to accomplish three objectives. The first was to establish a standard operating procedure which would yield reproducible

results. Once the procedure was established it was necessary to determine the maximum and minimum temperatures to be investigated. The minimum temperature was established by determining the lowest temperature at which appreciable organic carbon conversion occurred. This was determined to be 350 C. The maximum temperature was established by determining both the point where organic carbon conversion dropped off with increased temperature and the point at which the toluene solvent became unstable. Toluene instability was of concern because it made oil selectivity calculations meaningless. Temperatures as high as 500 C were investigated, but in order to insure the above criteria the maximum temperature employed in the experimental program was 450 C. With this temperature range defined the three dimensional matrix shown in Table 1 was developed. By performing the experiments outlined in this matrix the final objective of Phase I, that of studying the effects of time, temperature and hydrogen partial pressure, was accomplished.

Phase Two

Phase two was performed to demonstrate the reproducibility of the organic carbon conversion data at elevated temperatures and short reaction times.

Table 1

Phase I Experimental Matrix

Reaction Temperature (C)	Reaction Time (min.) 10	60
350	300+	300
	800	800
450	300	300
	800	800

+ - initial pressure of hydrogen (psig) at room temperature

Phase Three

The goal of phase three was to determine the reaction conditions which optimized oil yield using the hydropyrolysis process. In addition phase three was executed to determine useful kinetic information for this process. In order to accomplish these goals the three dimensional matrix shown in Table 2 was developed and followed.

Phase Four

Phase four was carried out in order to facilitate a comparison between the oil produced by the supercritical hydropyrolysis process and the oil produced by the Dravo process. The procedure used to separate the product oils into concentrated fractions was a modification of the procedure developed for the chemical characterization of shale oil from Condor, Australia (36). Characterization of the oil samples was done by identifying the major constituents of the concentrated fractions using gas chromatography (G.C.) and gas chromatography/mass spectrometry (G.C./M.S.).

Table 2

Phase III Experimental Matrix

Reaction Temperature (C)	Reaction Time (min.) 0+	5	30
380	300	300	300
400	300	300/50[1]	300/50
420	300	300	300
440	300	300/50	300/50
460	300	300/50	300/50

1- Initial hydrogen partial pressure (psig) of reaction system. Those runs with an initial hydrogen partial pressure of 50 had an initial total pressure of 300 where the balance was helium.

APPARATUS AND MATERIALS

Apparatus

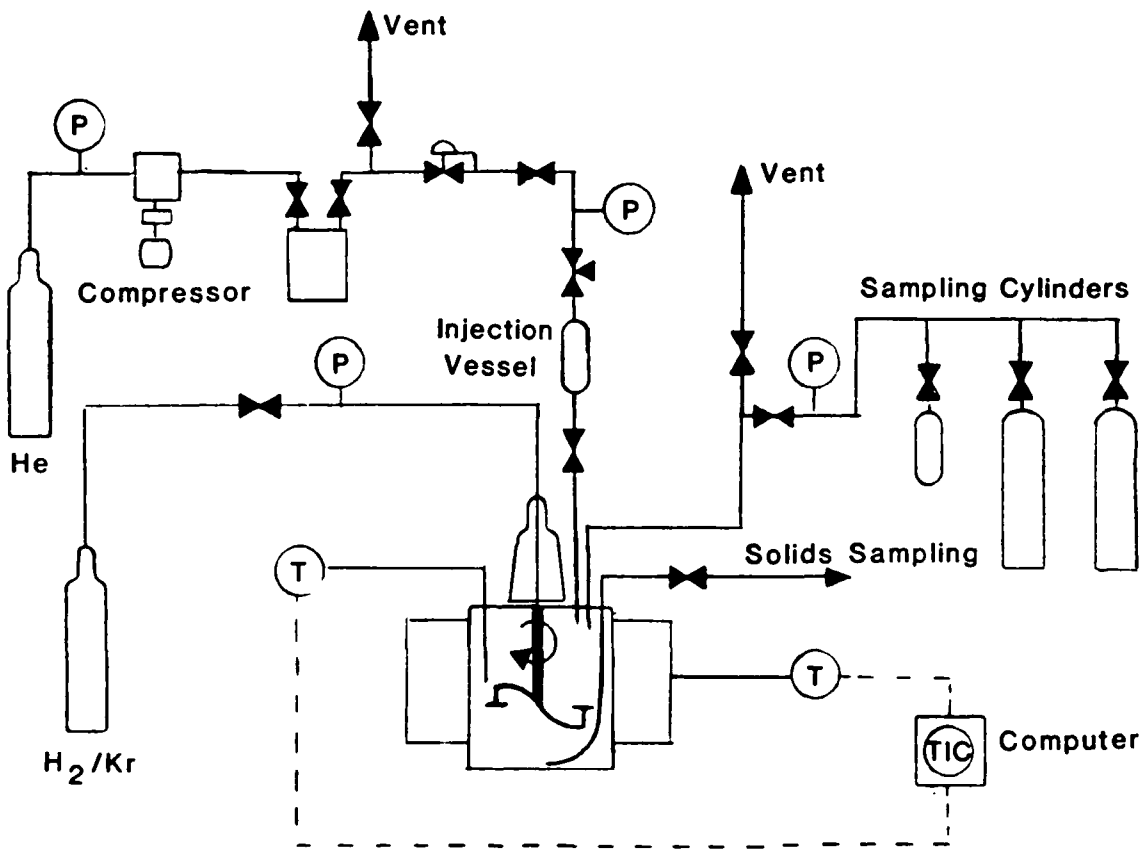
All experimental runs were performed in a 300 c.c., stirred, batch autoclave reactor, manufactured by Autoclave Engineers, Inc.. A variable speed stirrer, central baffle, coiling coil and thermowell extended into the reactor. The impeller was driven by a variable speed motor and monitored by a magnetic detection ring and tachometer. Connected to the reactor was a 75 c.c. injection vessel. Figure 2 shows a schematic of the reactor and associated piping used in all experimental runs.

The reactor temperature was monitored by a J-type thermocouple which was inserted into the reactor thermowell. It was connected to a Lawson Labs Model 20 Thermocouple Amplifier in combination with the Model 14 Analog Interface (A/D) card which allowed an Apple II computer to be used as a multi-channel thermometer. The A/D converter was able to resolve one millivolt signals throughout its range of -4.864 to 4.864 volts and was able to perform 12 conversions per second. The Thermocouple Amplifier was accurate to one degree C with the aid of a linearization program, written in basic, for the J-type thermocouple. See Appendix E for a copy of the linearization program.

The reactor was heated by a jacket type heater, which

Figure 2

Schematic of Reaction System



delivered 1.2 kw from a 115 A.C. electrical source and was manufactured by Autoclave Engineers, Inc.. The heater was raised and lowered by a Jaxline electonically controlled scissors jack manufactured by Precision Scientific Group.

The heater temperature was monitored by a J-type thermocouple connected to a Lawson Labs Model 24 Control Module in combination with the Model 14 A/D card and the Model 20 Thermocouple Amplifier.

The temperature in the reactor was monitored and controlled by the Apple computer. This was achieved by the automatic flow of cooling water through the reactor cooling coil when the reactor temperature exceeded an established setpoint and by controlling the voltage output to the heater with the aid of a computer program. See Appendix D for a listing of the program.

The gas delivery system consisted of cylinders of pure helium and a hydrogen/krypton (99%/1%) mixture, two pressure regulators, a reciprocating compressor, 316 stainless steel tubing (1/8 and 1/4 inch diameter), Whitey and 'Snotrik valves and Swagelok fittings. The hydrogen was used to flush air out of the system and to pressurize system to reaction conditions while the helium was used as the injection medium.

Reaction pressure was monitored by a Model AECI-5000

digital pressure indicator system, manufactured by Autoclave Engineers Inc.. The system used a standard transducer which had a pressure range of 0 to 5000 psig and displayed pressure readings in 1 psig increments.

The post-reaction gas sampling system consisted of an Ashcroft Maxisafe pressure gauge with a pressure range of 0-600 psig, Whitey valves, 316 stainless steel tubing, Swagelok fittings, one 500 c.c. stainless steel sample cylinder and two one gallon stainless steel sample cylinders.

Materials

Oil Shale

The oil shale used was from the Cleveland member of the Ohio Shale, Montgomery County, Kentucky. The shale was collected from a channel in a quarry face, and was about 25 feet below the top of the Cleveland Member. The weathered shale was first removed from the quarry face, the sample collected, immediately wrapped in plastic and placed in a water filled container. The oil shale was provided by Breckenridge Minerals, Inc., of Lexington, Kentucky.

The shale was vaccum dried at 100 C for one week and was then crushed progressively and screened to yield a -170 - +200 mesh (88 to 74 micron diameter) particle product.

The oil shale was then stored in a vaccum prior to use in an experimental run. The modified Fischer Assay of the feed shale used in this study is shown in Table 3. Table 4 gives the ultimate analysis of the same shale. Typical composition of the inorganic matter in Devonian shale is given in Table 5.

Shale Oil

The shale oil used for characterization was generated at 440 C, 300 psig of hydrogen, and reaction time of 10 minutes. The oil used for comparison was provided by Dravo Engineers Inc. and was generated using the Dravo traveling grate retort.

Solvents

The solvent used in the reaction process was toluene. Solvents used in the characterization/separation scheme included ether, chloroform, dichlorometane, hexane, methanol, n-pentane, and cyclohexane. A listing of the solvents used along with grade of purity and source is given in Table 6.

Table 3

Modified Fischer Assay of Kentucky Oil Shale

	Fischer Assay[1]				
%spent shale	%oil	%H_2O	%gas + oil	oil,GPT	O.C.C.[2]
91.6	4.6	1.5	2.3	11.6	31.6

1- Analysis by Commercial Testing and Engineering Co., Golden, Colorado.

2- % organic carbon conversion to oil by Fischer Assay procedure.

Table 4

Ultimate Analysis of Kentucky Oil Shale

Components in weight per cent				
Carbon	Hydrogen	Nitrogen	Sulfur	Ash
9.91	1.17	.268	2.15	83.96

Table 5

Typical Composition of the Inorganic Matter in Devonian Oil Shale

	Chemical formula	Mass %
Dolomite	$(Mg,Fe)Ca(CO_3)_2$	---
Calcite	$CaCO_3$	---
Quartz	SiO_2	28
Illite	Potassium aluminum silicates	40*
Albite	$NaAlSi_3O_6$	---
Feldspar	$KAlSi_3O_8$	12
Pyrite, Marcasite	FeS_2	14
Analcine	Sodium aluminum silicates	---
Other	---	6
	TOTAL	100

* - Includes kaolinite (hydrous aluminum silicates and muscovite (potassium aluminum silicates))

Table 6

List of Solvents used for Characterization/Separation

Type	Purity (%)	Source
Toluene	99.9	Fisher Scientific
Dichloromethane	99.9	Fisher Scientific
Cyclohexane	99.8	Fisher Scientific
Ethyl Ether	99.9	Fisher Scientific
Chloroform	99.9	Fisher Scientific
Methanol	99.9	Fisher Scientific
n-Pentane	99.0	Fisher Scientific
Hexane	97.5	Fisher Scientific

EXPERIMENTAL AND ANALYTICAL PROCEDURES

Run Procedure

The stirrer motor and pressure indicators were turned on and given time to warm up. Solvent (50 g) was weighed and charged into the reactor through the injection system and injection valve closed. The system was purged twice with 600 psig of the hydrogen gas mixture and then charged to the desired cold initial pressure. Next, the heater was raised, reaction set point entered into the computer, stirrer turned on to 200 rpm and temperature control system turned on.

Feed shale (25 g) and solvent (50 g) were weighed into a beaker and placed on magnetic drive stirrer to suspend the shale particles in slurry prior to injection. A sample (1-2 g) of the feed shale was placed in a sealed container for future analysis. The injection compressor was turned on and the injection surge tank was filled with high pressure helium.

When the reactor reached reaction temperature the slury was poured into the injection vessel. The injection vessel was sealed and purged twice with 500 psig of helium. The injection system pressure regulator was set to 1650 psig, which was sufficient to provide adequate injection overpressure for all reaction temperatures investigated.

Figure 9

Typical Mass Spectrum Output of a Gas Spectrum

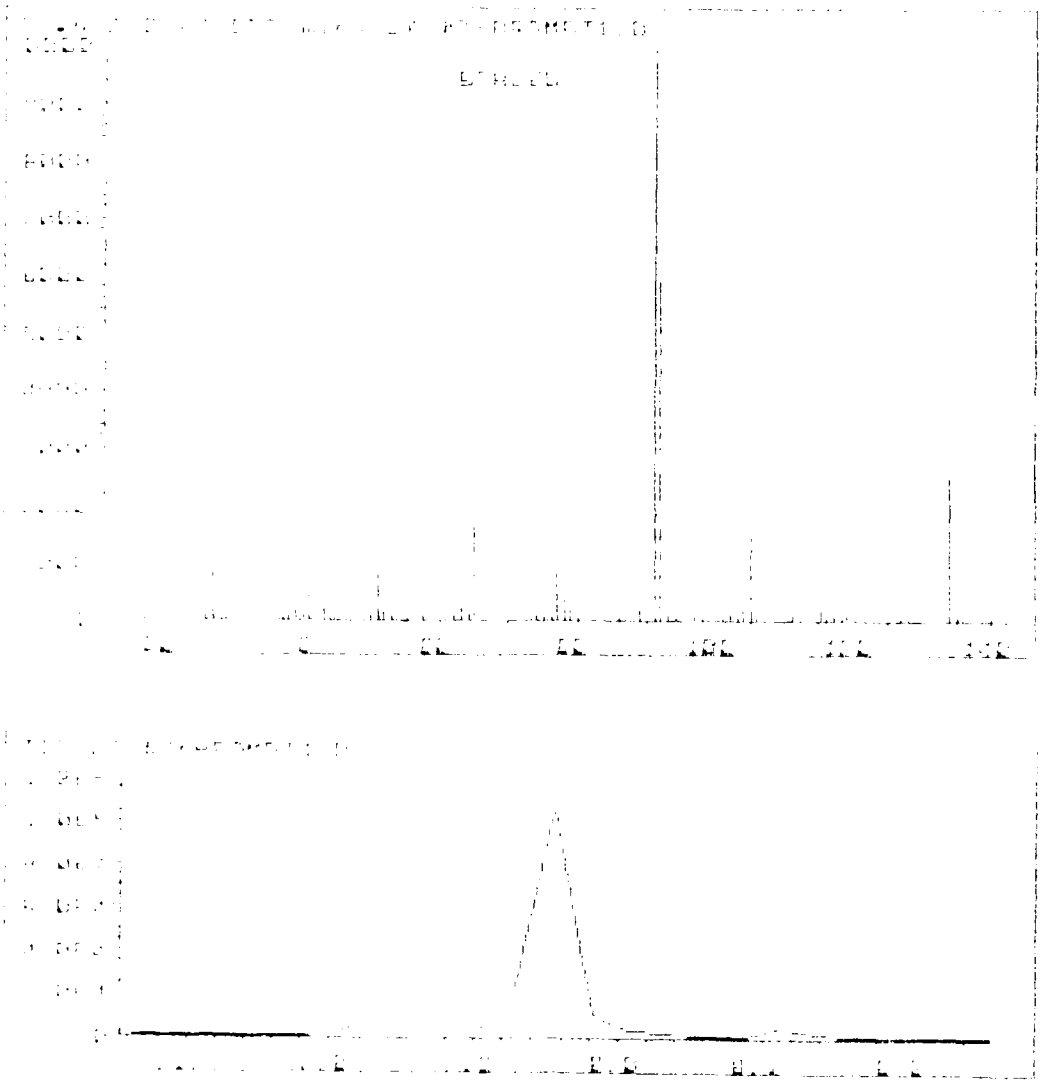


Figure 8

Typical Total Ion Chromatogram Output

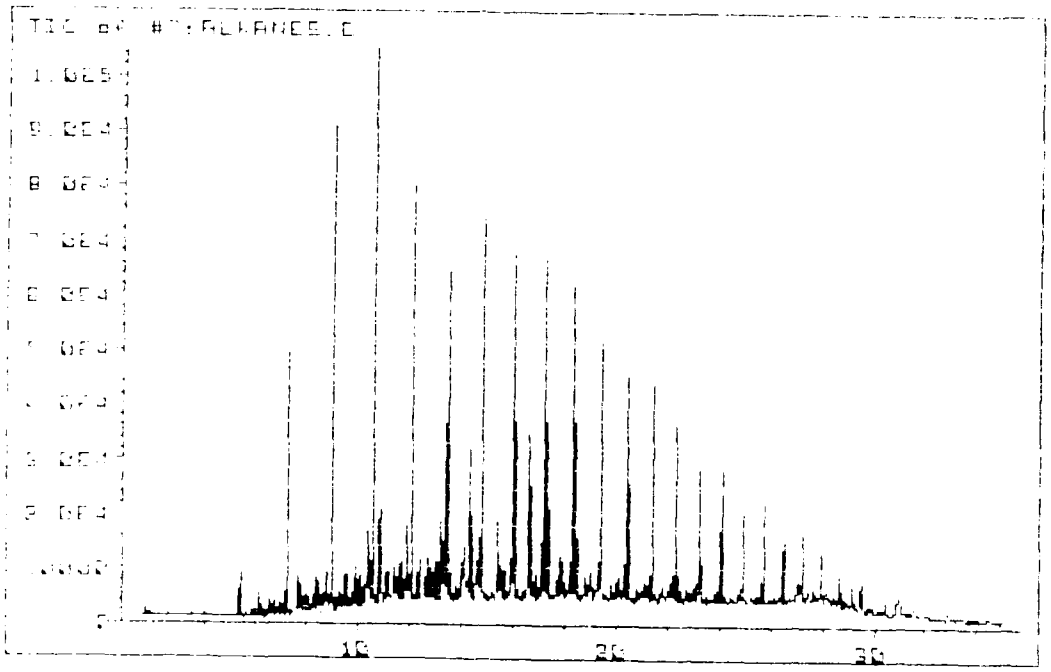
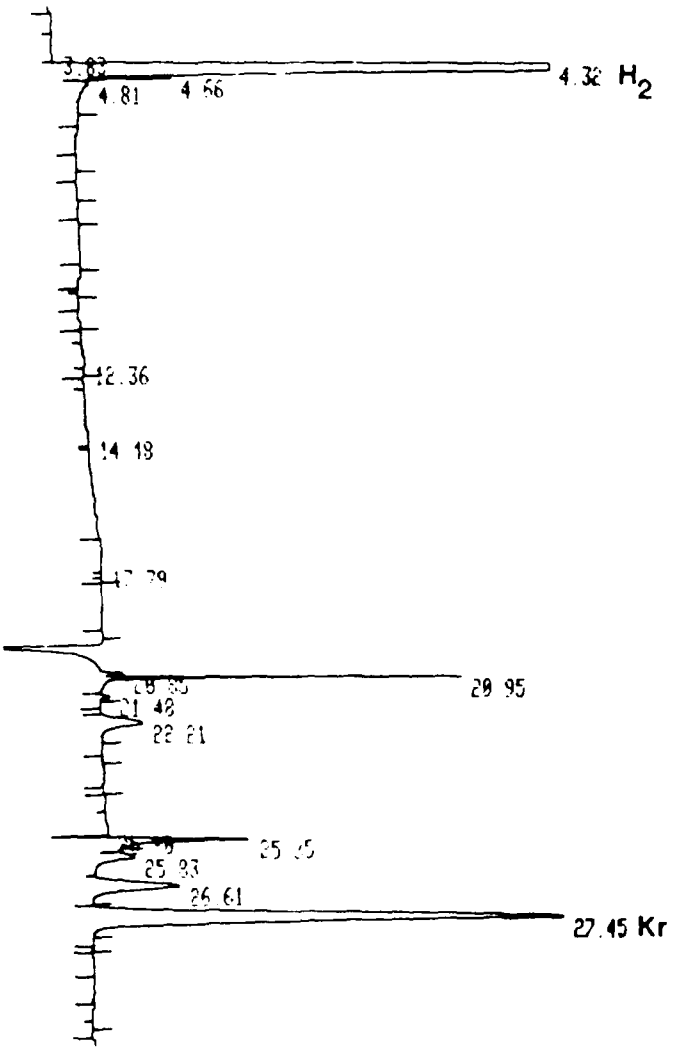


Figure 7

Typical 2 Component Calibration Gas Results



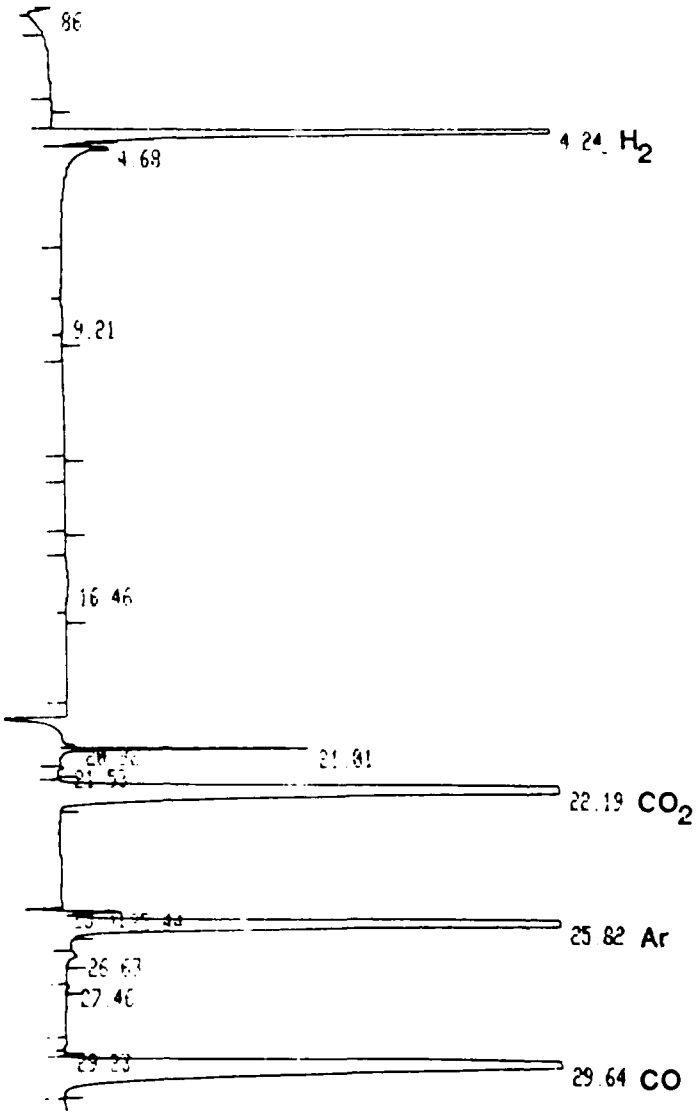
RT	AREA	TYPE
0.85	9922	BB
3.83	3420	VP
4.32	4620100	PB
4.66	6893 D	BB
4.81	3070	BB
12.36	3337	VV
14.48	3194	VV
17.79	3488	PV
20.85	242950	BV
20.95	46561	VB
21.48	1752	BB
22.21	36597	BB
25.20	89464	VP
25.35	73746	PB
25.83	9063	BP
26.61	76314	PB
27.45	507340	BB
31.16	1006	PB
31.28	3106	PB
31.51	6583	PV
31.91	16565	VV

Response Factors

CAL#	RT	AMT	AMT/AREA
1R	4.33	9.9000E+01	2.1514E-05
2	27.47	1.0000E+00	1.9938E-06

Figure 6

Typical 4 Component Calibration Gas Results



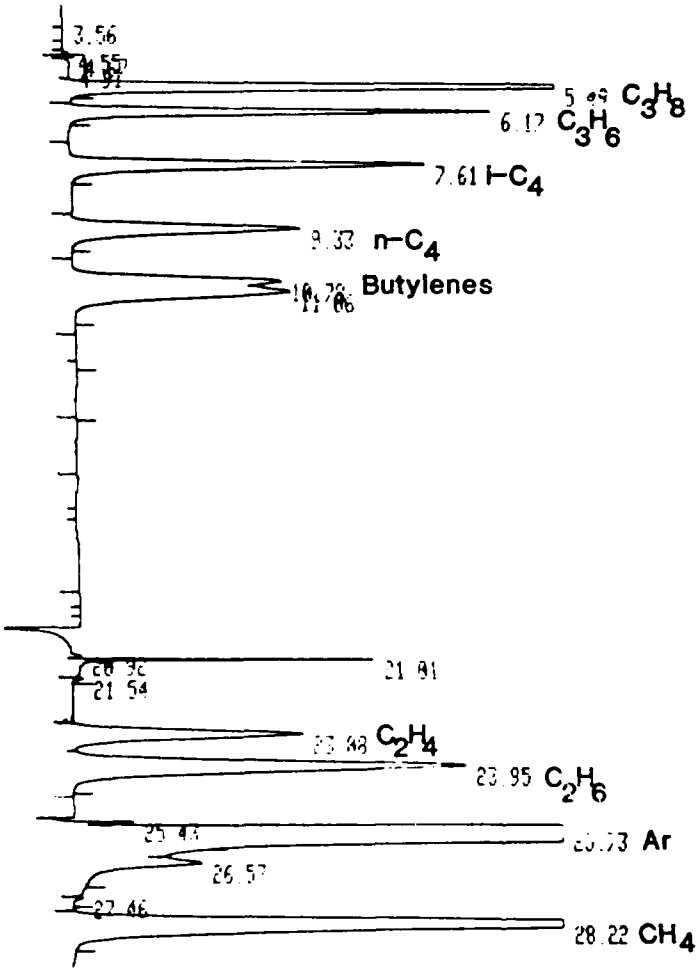
RT	AREA	TYPE
0.86	10947	VB
4.24	3919300	PB
4.68	14472	PB
9.21	6725	PV
16.46	7493	PP
20.92	254150	PV
21.01	58437	VB
21.53	1447	BB
22.19	2549800	PB
25.31	8927	D BP
25.44	58086	PV
25.82	2227300	VB
26.63	8692	BB
27.46	2693	BB
29.23	206	PB
29.64	1830900	BB
31.30	1398	PB
31.41	3309	PP
31.55	5004	PB

Response Factors

CAL#	RT	AMT	AMT/AREA
1R	4.24	8.4600E+01	2.1586E-05
2	22.19	5.5000E+00	2.1570E-06
3	25.82	4.8100E+00	2.1596E-06
4	29.64	5.0900E+00	2.7800E-06

Figure 5

Typical 10 Component Calibration Gas Results



AREA%

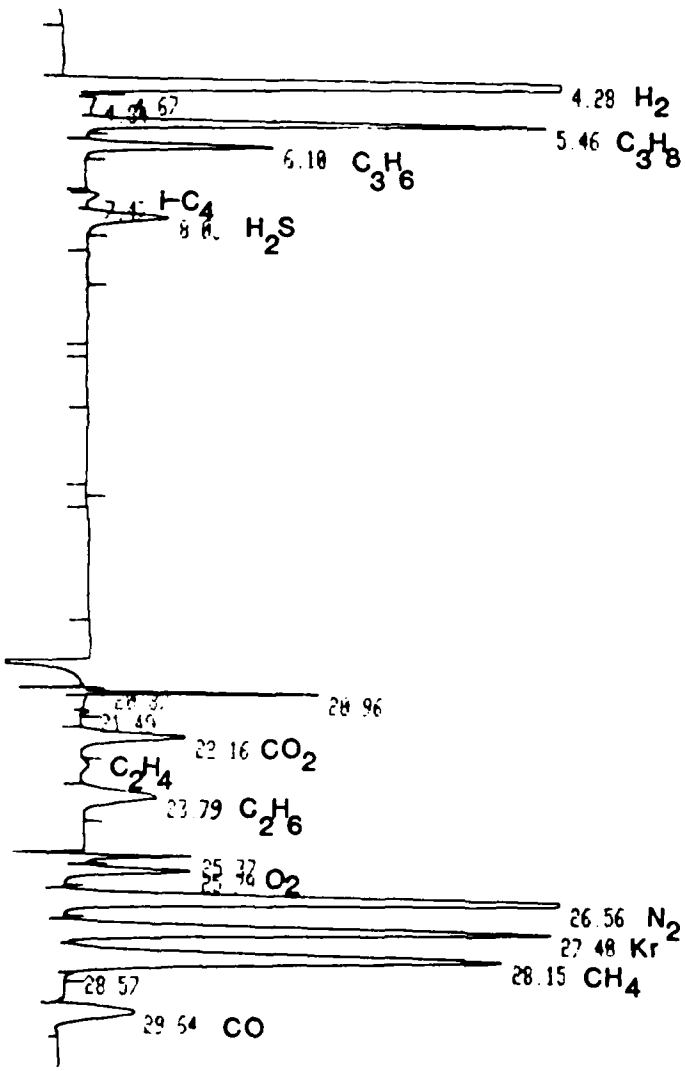
RT	AREA	TYPE
3.56	15686	BV
4.55	1017	PB
4.67	2320	BP
4.91	13152	PV
5.49	1178000	VB
6.17	538170	BB
7.61	624440	PB
9.33	488150	BB
10.78	433550	BV
11.06	546570	VB
20.92	213210	PV
21.01	67380	VB
21.54	2490	BB
23.08	490090	BV
23.95	1029800	VB
25.43	36286	PV
25.73	3.5774E+07	VB
26.57	19521	BB
27.46	0	BB
28.22	1832900	BB
31.28	754	PB
31.39	2909 D	BP
31.48	2931	PB

Response Factors

CAL#	RT	AMT	AMT/AREA
1R	5.49	1.9980E+00	1.6960E-06
2	6.17	9.9600E-01	1.8507E-06
3	7.61	9.9700E-01	1.5966E-06
4	9.33	9.9900E-01	2.0465E-06
5	10.78	9.9900E-01	2.3042E-06
6	11.06	9.9700E-01	1.8241E-06
7	23.08	1.0030E+00	2.0466E-06
8	23.95	1.9920E+00	1.9343E-06
9	25.73	8.5012E+01	2.3764E-06
10	28.22	5.0070E+00	2.7318E-06

Figure 4

Typical Gas Chromatogram of Experimental Run



AREA% RT	AREA	TYPE
4.28	4337700	PB
4.67	2644	D BP
4.84	7148	PV
5.46	254350	VB
6.10	115530	PB
7.47	8357	BP
8.05	76608	PB
20.87	15872	PV
20.96	34416	VB
21.49	1805	PB
22.16	91330	BB
23.79	95141	BB
25.37	57345	BB
25.79	68334	BB
26.56	576600	PB
27.40	463040	BV
28.15	535550	VV
28.57	2004	VB
29.64	102090	BB

components with their respective peak areas and area percentages. Figure 4 shows a typical printout of the gas product generated in an experimental run.

The mole percentages of the component gases were calculated using the respective component response factors. Response factors were determined with the use of standard calibration gases. Figure 5,6, and 7 show typical calibration results.

Liquid Products

The fractionated oil samples generated during the separation procedure were analyzed with equipment manufactured by Hewlett Packard. A Model HP 5970A Mass Selective Detector in conjunction with a Model 5890 Gas Chromatograph was utilized to perform M.S. (Mass Spectrometry) and G.C. (Gas Chromatography) on each of the liquid fractions. These were interfaced to an HP 9133 computer equipped with a 15 megabyte hard disk and the HP 59974 GC/MS-MSD Operating Software. The major constituents of each of the liquid fractions were identified by utilizing the HP 59973 NBS Mass Spectral Library. Figure 8,9, and 10 show typical printouts of the analyses performed by the system.

Instrumental Analysis

Solid Products

Carbon analysis of the all feed and spent shale samples was performed with equipment manufactured by Coulometrics, Inc.. A Model 5010 carbon dioxide coulometer in conjunction with a Model 5030 carbonate carbon (CO_2) apparatus and Model 5020 total carbon analyzer were used to measure the inorganic and total carbon contents.

Ash content was determined for all feed and spent shale samples by a variation of the ASTM procedure D3174-82. A weighed sample was placed in a cold muffle furnace, heated to 800 C and ashed for 3-4 hours. The ash content was calculated by the dividing net weight of the shale sample after ashing by the net weight of the sample prior to ashing which is in accordance with the accepted ASTM procedure listed above.

Gas Products

Analysis of the gaseous reaction products was performed with a Carle Model 111-H gas chromatograph equipped with a Hewlett Packard Model 3390A integrator. The gases that were quantified included hydrogen, krypton, hydrocarbon gases (through C4), hydrogen sulfide and carbon oxide gases. The integrator output identified the above

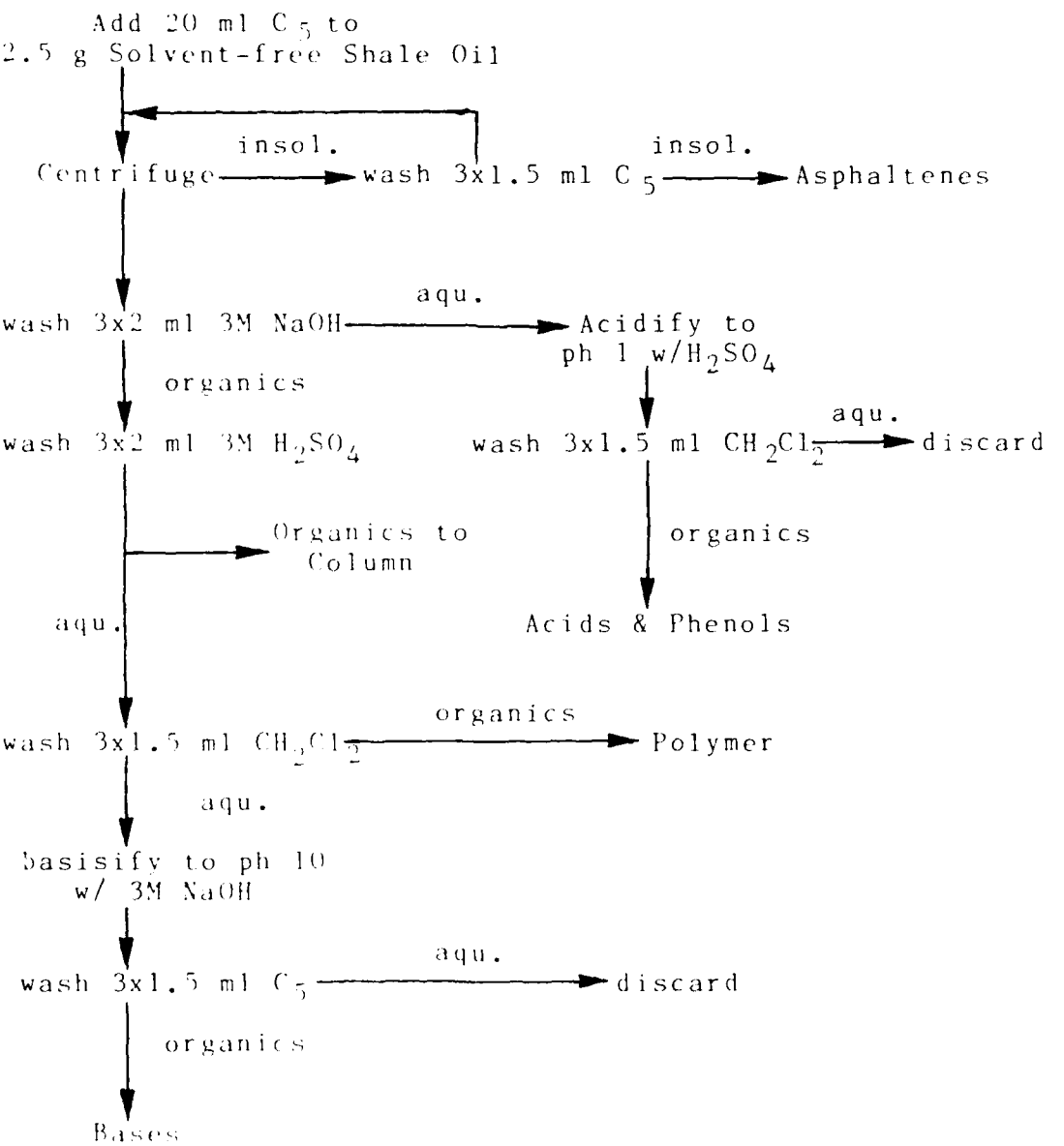
Table 7

Open Column Chromatography Elution Scheme with 23 grams of Alumina on top of 58 grams of Silica Gel

Fraction #	Solvent	Volume (ml)	Group
1	C_6	125	Void Volume
2	C_6	35	Alkanes & Napthenes
3	C_6	10	
4	C_6	35	Alkenes
5	C_6	40	Dienes
6	C_6	100	Start of Aromatics
7	C_6	85	
8	C_6	50	
9	C_6	50	
10	C_6	100	
11	C_6/CH_2Cl_2(9:1)	30	
12	C_6/CH_2Cl_2(9:1)	20	
13	C_6/CH_2Cl_2(4:1)	30	End of Aromatics
14	C_6/CH_2Cl_2(4:1)	20	
15	CH_2Cl_2	50	Nitriles
16	$CH_2Cl_2/CHCl_3$(9:1)	50	Ketones
17	$CHCl_3$/Diethyl ether (9:1)	30	Start of Polymeric Material
18	$CHCl_3$/Diethyl ether (9:1)	20	
19	Diethyl ether	50	
20	CH_3OH	50	End of Polymeric Material

Figure 3

Extraction Scheme



The technique utilized was a slightly modified version of the separation procedure used by Rovere (36) to characterize the shale oil from Condor, Australia. A flow chart of the extraction scheme is provided in Figure 3, while Table 7 outlines the elution scheme.

pentane/oil mixture was then decanted into sealed containers for future analysis.

The spent oil shale was washed with excess dichloromethane, sonicated for 5 minutes, centrifuged for 5 minutes at 5000 rpm and the dichloromethane was decanted. This procedure was performed twice. After the second washing the spent shale was Soxhlet extracted in dichlorometane in order to wash any residual oil from the shale. The shale was washed three times in this system. The washed shale was then placed in an oven and dried for 24 hours at 100 C and ambient pressure. The resultant solid product was fine-ground and retained in a sealed container for future analysis.

The reactor system was eventually cleaned by flushing the system with acetone until there was less than one hundreth of a gram of shale left in the reactor system.

Shale Oil Separation Procedure

From previous attempts at characterizing shale oils by other researchers it has been documented that separating the parent oil into its component fractions was necessary to effectively identify the compounds present in the oil. For this reason the parent oil was separated into the following fractions, acids/phenols, bases, alkanes/napthenes, alkenes, dienes, aromatics, nitriles, ketones and polymeric material.

after the initiation of cooling. This was determined to be the temperature at which little or no reaction occurred. When the reaction system had completely cooled and reached thermal equilibrium with the surroundings, the pressure and temperature were noted prior to gas sampling. The gas sampling system was connected after the three sample cylinders had been evacuated. The gas sampling valve was opened and the gas product was allowed to expand into the increased volume of the sample cylinders. The sampling volume was designed to be large enough to force the equilibrium pressure to be atmospheric. After equilibration the pressure was noted and the 500 cc sample cylinder was sealed and set aside for future analysis.

The reactor was then charged with helium (50-70 psig) in order to force the reacted slurry out of the reactor. The resultant slurry product was then collected and centrifuged for 5 minutes at 5000 rpm.

After centrifugation the toluene/oil products solution was decanted and evaporated on a rotary evaporation system at 70 C and a vaccum until all recoverable toluene was removed. The distillate from the evaporation was collected and a sample was placed in a sealed container for future analysis. The oil product which remained was then washed in n-pentane to separate the oils from the asphaltenes. The n-

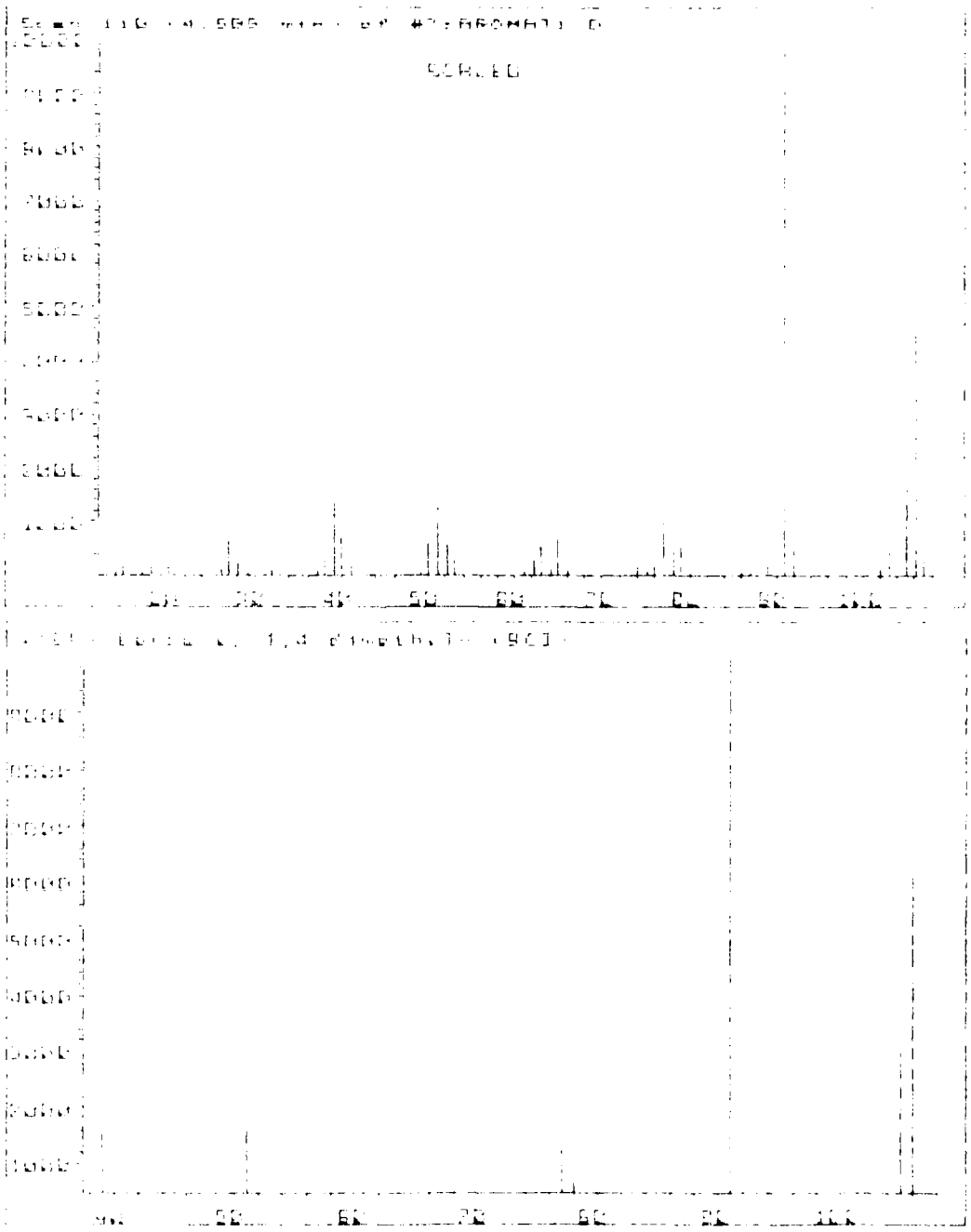
After the injection system was pressurized the injection valve was opened and the slurry was forced into the reactor. The injection valve was closed and the stirrer was turned up to 1000 rpm. Due to the cooler temperature of the slurry, the temperature of the reactor spiked down but re-equilibrated within 3 minutes. After injection the temperature and pressure of the system were recorded every minute until the reactor temperature incresed to within 10 degrees of the desired reaction temperature.

While the reaction progressed the injection vessel was disconnected from the system and was washed with acetone to remove all uninjected slurry. This uninjected shale was collected, centrifuged, decanted, dried and weighed.

Reaction time began when the reaction sytem reached 10 degrees below the desired reaction temperature. This was done to minimize the effects of heat up time on the conversion to products. After the desired reaction time had elapsed forced convection was used to quickly cool the reactor in order to stop the reaction. The heater was lowered, a high speed fan turned on and a new set point entered into the computer. The new set point automatically turned on the cooling water through the coils in the reactor and turned off the voltage output to the heater. The system was cooled to at least 350 C within a minute and a half

Figure 10

Typical Output of NBS Library Search of Mass Spectrum

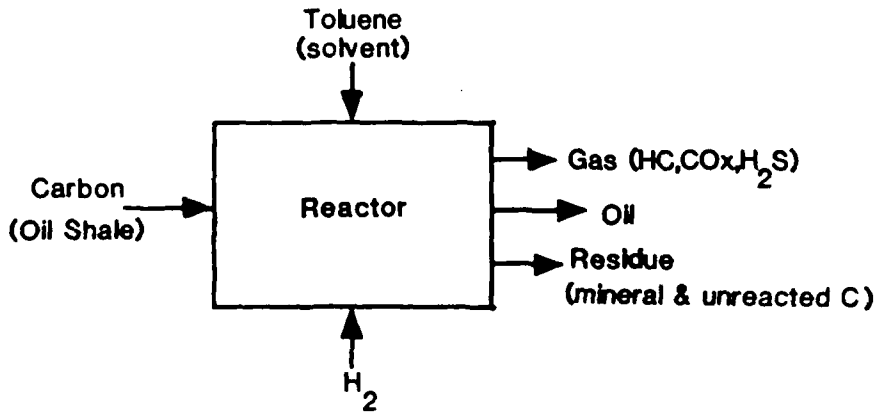


DATA ANALYSIS

The data used for analysis was obtained after the feed shale and spent shale for each experimental run was analyzed for carbon content, both total and inorganic. From this carbon content information and ash contents of the feed and spent shale total and organic carbon conversions were determined. The gas samples taken after each run were used to determine the extent of production and characterization of the reaction gases. The organic carbon conversion and gas production or oil selectivity calculations were performed with the aid of a computer program originally developed by Dr. R. Baldwin. See Appendix F for a listing of the program.

Organic Carbon Conversion

By performing a mass balance on the following reaction system;



the organic carbon conversion can be calculated. The mass balance calculations are dependent on two key assumptions;

1) the ash contained in the shale is non-reactive, 2) the solvent does not degrade under the reaction conditions. The assumption concerning the reactivity of the ash is considered a good one since it has been shown that ash remains relatively unchanged during a thermal solution process (22). The assumption about the solvent is also valid because it was shown that toluene did not degrade appreciably up to 500 C (38).

Utilizing the first assumption, a forced ash balance is peformed on the reaction system yielding the following expression for the mass of product in terms of the mass of the feed:

$$\text{mass of product} = \text{mass of feed} \times \frac{(\ \%\ \text{ash in feed}\ )}{(\ \%\ \text{ash in product}\ )}$$

This is useful because the mass of the product cannot be accurately measured.

The definition used for the organic carbon conversion was :

$$\text{OCC} = \frac{\text{organic carbon in feed} - \text{organic carbon in products}}{\text{organic carbon in feed}}$$

The organic carbon in the feed shale and spent shale is determined by the following expressions:

organic C in feed=(%total C - %inorganic C)(mass of feed)

organic C in spent=(%total C - %inorganic C)(mass of spent)

All the above expressions were combined which simplified the organic carbon conversion expression to the following:

$$OCC = \frac{(\%\ \text{organic C of feed}) - \frac{(\%\ \text{feed ash})}{(\%\ \text{spent ash})}(\%\ \text{organic C in spent})}{(\%\ \text{organic carbon of feed})}$$

Oil Selectivity

The mass of carbon in the gaseous products is the basis for the oil selectivity calculations. The mass of carbon in the product gases was determined by using the ideal gas law and by analyzing the gas chromatogram of the reaction gases.

The ideal gas law was used to calulate the total number of moles of tracer gas, krypton, in the system given the volume, initial temperature and initial pressure. By analyzing the gas chromatograms the mole percentages of all identifiable species were calculated by the following

expression:

gmoles carbon out=(moles Kr)(area of component i)(RRF)(B)

where;

$$RRF = \frac{\text{Response factor of component i}}{\text{Response factor of krypton}}$$

$$B = \frac{\text{gmoles of carbon}}{\text{gmoles of component i}}$$

The identifiable peaks of the chromatograms were hydrogen, hydrogen sulfide, hydrocarbon gases (through C4), carbon monoxide, carbon dioxide, nitrogen, oxygen, and krypton. The total number of grams of carbon in the reaction gases was calcualted by summing the total gmoles of carbon in the gases and multiplying this value by the molecular weight of carbon.

The next step was to calculate the total mass of carbon converted to either oil or gaseous products. This was done by the following expression:

mass of carbon converted=(mass of shale in)(% total C) - (mass of shale out)(% total C)

The final calculation used to determine the oil selectivity was the following:

$$\text{\% oil selectivity} = \frac{\text{mass of C converted - mass of C in gas}}{\text{mass of C converted}}$$

Kinetic Modeling

It was desired to develop a kinetic expression which related organic carbon conversion to time where conversion was defined as the fraction of the organic carbon which reacted to form either oil or gas.

In order to develop the kinetic expression it was necessary to determine a kinetic model which adequately described the experimental rate data. It has been shown previously that various irreversible models have been used to adequately describe the reaction kinetics of oil shale pyrolysis (37). The following three irreversible batch reactor models were investigated:

	Mass balance	Integrated form
1st order in X:	$\frac{dX}{dt} = k\,(a - X)$	$X = a - a\,e^{-kt}$
3/2's order in X:	$\frac{dX}{dt} = k\,(a - X)^{\frac{3}{2}}$	$X = a - (\frac{1}{2}kt + a^{\frac{-1}{2}})$
2nd order in X:	$\frac{dX}{dt} = k\,(a - X)^{2}$	$X = \frac{kta^2}{kta + 1}$

where;

X = OCC - Organic Carbon Conversion

t = reaction time

a = psuedo equilibrium OCC at infinite time

k = rate constant (ko exp (-Ea/RT))

The procedure used to determine the adequacy of each model was to first examine the low temperature data and attempt to fit this data to each of the models. This was done because low temperature data is easiest to fit relative to high temperature data. This is true because the changes in conversion versus time are far less extreme. By linearizing the integrated forms of the rate expressions, the adequacy of each model was ascertained by how well the data fit a straight line. The following linearized expressions were used:

$$\text{1st order:} \quad -\ln(a - x) = kt$$

$$\text{3/2's order:} \quad 2\left(\frac{1}{(a - x)} - a^{-\frac{1}{2}}\right) = kt$$

$$\text{2nd order:} \quad \left(\frac{1}{(a - x)} - \frac{1}{a}\right) = kt$$

As a result of the temperature dependency of the rate constant it was necessary to insure that the data was isothermal prior to evaluating each model. The only data points considered non-isothermal were the 0+ data points because of the heat-up time associated with these data points. This being the case it was necessary to correct these points so the carbon conversion results would reflect isothermal results. The procedure for correcting the 0+

data points is outined in Appendix A.

With the aid of the MINITAB computer program developed at Pennsylvania State University the rate constants were evaluated by linear regression of the data using the method of least squares. A sample of the input and output for the MINITAB program can be seen in Appendix G.

To complete the kinetic expression an Arrhenius plot was prepared to determine values for the apparent frequency factor (ko) and apparent activation energy (Ea) for the reaction. These values were obtained by linear regression of the best fit rate constants using the method of least squares. The slope and the y-intercept of the best fit line are the source for the activation energy and frequency factor respectively.

DISCUSSION OF RESULTS

Introduction

Detailed results for all experimental runs are summarized in Appendix C. Some of the results presented in this appendix have been omitted from the discussion for reasons that are presented below. It will become evident as the discussion of the results continues that the results from the first sixteen experimental runs were selectively excluded from the data analysis. The reason for their exclusion is due to the reconfiguration of the reactor system and modification of the experimental procedure which occurred after KY-16. It was after KY-16 that the batch reactor system was reconfigured to operate as a semi-batch reactor in order to avoid having to reseal the reactor after each experimental run. This reconfiguration eliminated problems of small leaks in the system which effected the reproducibility of data and significantly reduced turn around time between runs. Since the runs prior to KY-16 had been operated in the true batch mode, these results were not included in the discussion of the semi-batch results. The only result used from these initial runs was the result of KY-14 which determined the organic carbon conversion at 500 C and 800 psig of hydrogen partial pressure. This result was used only for the determination of the upper

temperature limit and was not used for any comparative analysis. All the results from KY-17 to the end of the experimental program are discussed even though minor modifications were made to the system and procedure as the experimental program progressed. The minor modifications to the system, the time of occurrance (experiment number) and impact on previous results are discussed below.

The first modification after converting the system to the semi-batch mode was interfacing the computer to control the voltage output to the heater. This was done after KY-21 and provided more efficient temperature control during the reaction. The modification had no impact on the previous runs because temperature control had previously been very good. The next modification occurred after KY-38 when the gas sampling procedure was changed. The procedure was changed to force the final gas sample pressure to be atmospheric by expanding the reaction gases into a sufficiently large volume to achieve the desired condition. This was done to insure that the samples taken were accurate representatives of the product gases and eliminated the possibility of gas solubility problems on the gas analysis. The impact of this modification is seen only in the oil selectivity calculation. It is difficult to ascertain the impact on the oil selectivity results of experiments prior

to KY-38 and compare them to experiments after because of the differences in the run conditions between Phase I and Phase III experiments. Since the runs in Phase I did not utilize the atmospheric gas sampling procedure, analysis of oil selectivity results for each phase has been done independently and any comparisons were avoided. The final modification to the reaction system occurred after KY-46 when the tracer gas was changed from argon to krypton. This was done in an attempt to facilitate accounting for the fate of any oxygen that happened to be introduced into the system and to improve the reproducibility of hydrogen consumption results. Since the gas chromatograph was unable to separate argon and oxygen in the gas samples it was necessary to change the tracer gas to krypton, which could be separated from all other components present in the product gas. Once again the impact of this modification was seen in the oil selectivity results. Prior to KY-46 it was assumed that the oxygen contribution to the argon peak of the chromatograms was a specifed fraction. Since the area of the tracer peak was used to calculate the mole percentages of component gases it was imperative to know its true size. After switching to the krypton tracer it was determined that the size of the oxygen contribution varied as a function of temperature. This result indicated that the little oxygen

present in the reaction system was being consumed in the reaction and that the contribution of oxygen to the argon peak varied. Since this was the case, only those runs performed in Phase III which had krypton as the tracer gas had their oil selectivity results analyzed.

Processing Errors

The processing variables of temperature, pressure and reaction time accounted for most of the experimental errors experienced.

Temperature fluctuations in the reaction system were minimized by interfacing with the Apple computer. This enabled the system to be kept within +/- 2 degrees of the desired reaction temperature once the injected samples had reached thermal equilibrium with the reactor.

The final system pressure varied significantly when the injection procedure was incorporated which was another source of error. This variation was due to the inability to control the rate of slurry injection. The rate at which the slurry was injected directly effected the amount of cold helium that was allowed into the reactor, which had a significant impact on the final system pressure. Since organic carbon conversion and oil selectivity results for similar runs with different final system pressures were very reproducible, it was concluded that the final system

pressure had little effect on the final results.

The final source of experimental error was the reaction time. The reaction time of the system was defined as the time interval between injection and the onset of cooling. This interval was timed fairly accurately (+/- 10 seconds). The major contribution of this factor to the error was connected to the time required to heat up the slurry to reaction conditions once it was injected. Temperature versus time profiles were obtained for each of the reaction temperatures in Phase III only once, and it was assumed that heat up times for all other runs were consistent. Other causes for variation in reaction time were the time required to lower the heater, turn on the cooling fan and re-establish the cooling setpoint into the computer.

Phase One

The principle objective of the experiments performed in phase one was to determine the effect of temperature, reaction time, and hydrogen partial pressure on the organic conversion and oil selectivity during the hydropyrolysis of the Kentucky oil shale under investigation. The results of the phase one experiments are summarized in Table 8.

The preliminary work in phase one established the maximum and minimum operating temperatures to be 450 and 350

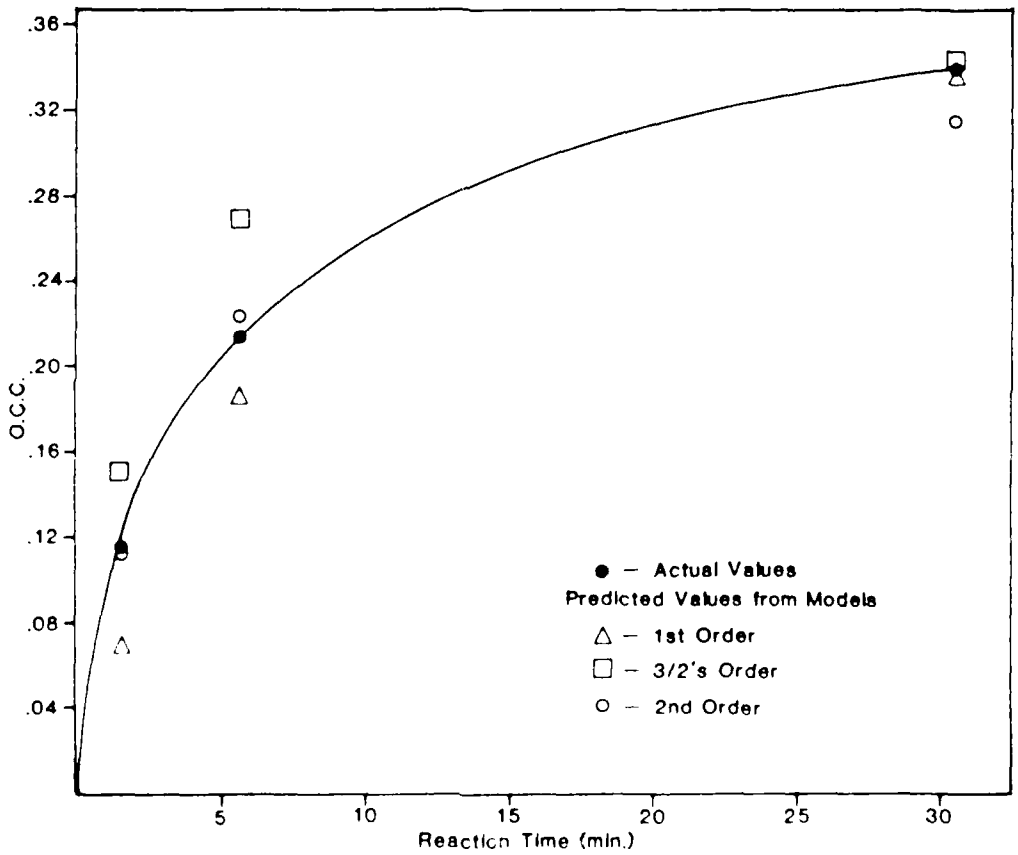
Table 8

Summary of Results for Phase I Experimental Runs

Run #	Temp (C)	Time (min)	Press (H_2) (psig)	O.C.C. %	% Oil Selectivity
KY 19	350	60	300	17.00	98.1
KY 20	350	10	300	7.22	97.3
KY 21	350	10	800	7.20	91.8
KY 22	450	60	300	61.90	92.5
KY 23	450	60	800	74.00	93.8
KY 24	450	10	800	70.80	94.6
KY 25	450	10	300	64.80	97.6
KY 26	350	60	800	18.90	98.0
KY 33	450	10	0	57.56	----

Figure 13

Predicted Organic Carbon Conversions versus Reaction Time



increased dramatically. This result reinforces the conclusion that the rates of the gas forming reactions are slow relative to the oil forming reactions. From this result it was indicated that the reaction time should be less than 5 minutes in order to limit excessive gas production.

The final parameter of hydrogen partial pressure had a significant effect on the organic conversion but did not have a significant impact on the oil selctivity results. The most significant result was the increased amounts of methane in the product gases at the low hydrogen partial pressure. This indicated that the reaction system should be run with sufficient amounts of hydrogen in order to promote high organic carbon conversions and inhibit the undesirable production of methane.

From the results presented it is concluded that of the conditions investigated the optimum was at a reaction temperature of 460 C, reaction time of 0+, and an initial hydrogen partial pressure of 300 psig. These conditions maximized the oil products while minimizing the formation of gas products and reaction time.

Kinetic Modeling

Using the kinetic expressions developed from the MINITAB program it was possible to prepare a plot comparing

Therefore, the impact of reaction temperature, reaction time, and hydrogen partial pressure on the production of gaseous products was examined to establish an optimum set of operating conditions. It should be understood that no attempt is being made to establish the optimum set of conditions for this process because of the limited conditions that were investigated.

Examining the results in Table 10 it is clearly shown that temperatures of at least 420 C are necessary to obtain appreciable conversion to oil products. However, as is demonstrated in Figure 12 the selectivity to oil over gas production decreases as the temperature increases. This result is once again explained by the fact that gas forming reactions have higher activation energies and proceed more rapidly at elevated temperatures. In addition, by examining the mole percentages of the reaction gases presented in Appendix C, the amount of methane gas produced increased with increased temperature for similar reaction times. For example, comparing the 460 and 440 experiments the methane mole percentages were 4.73 and 1.56 for the 30 minute runs, while the percentages were 1.17 and .749 for the 5 minute runs.

Reaction time had a similar effect in that as time increased oil selectivity decreased and methane production

Figure 12

Oil Selectivity versus Reaction Time

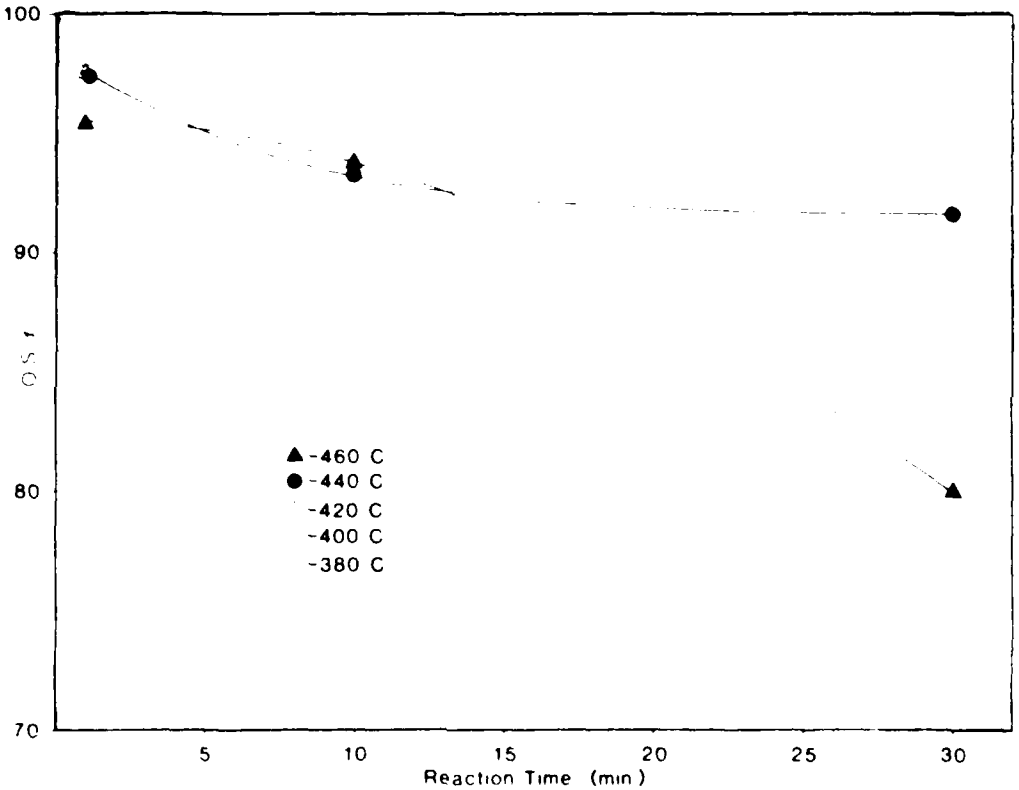


Figure 11A

Organic Carbon Conversion versus Reaction Time Isotherms with Low Initial Hydrogen Partial Pressure Isotherms

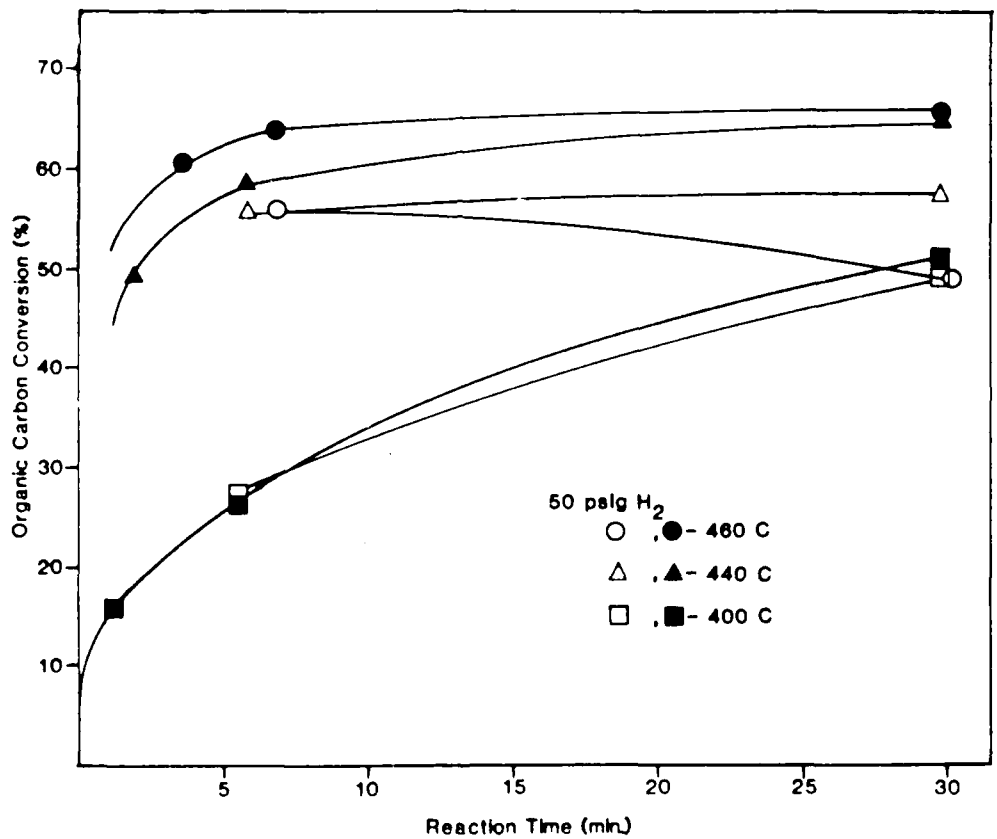


Figure 11

Organic Carbon Conversion versus Reaction Time Isotherms

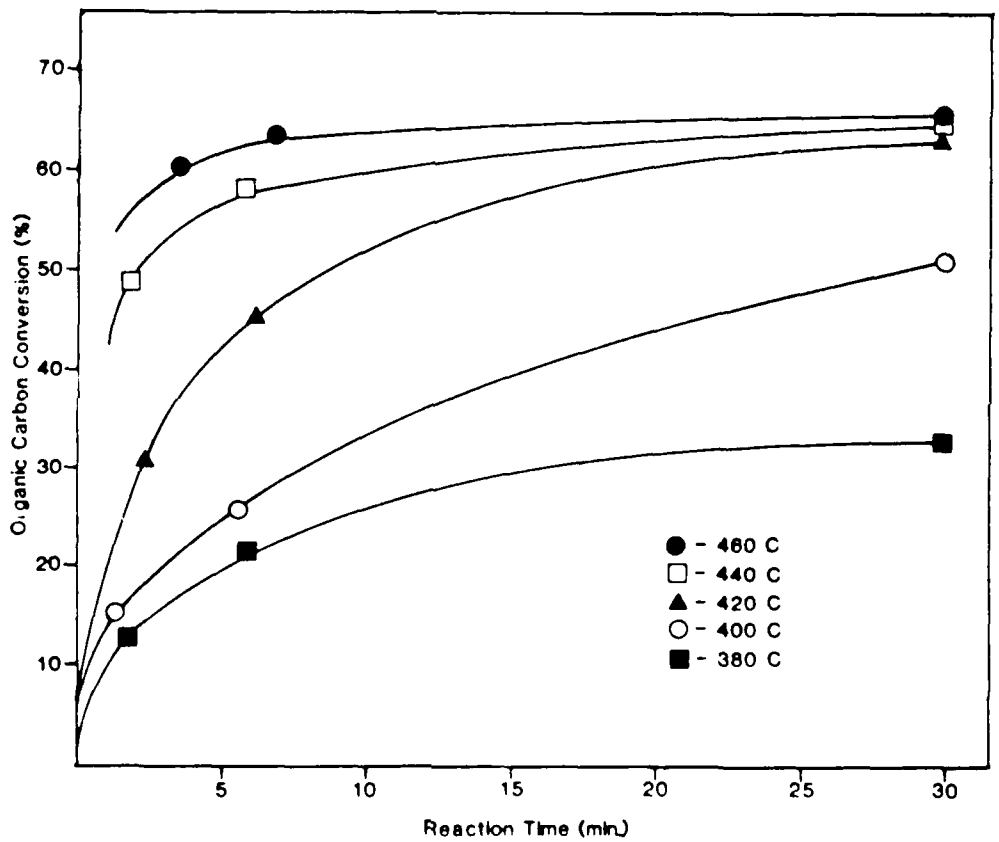


Table 10
Summary of Results for Phase III Experimental Runs

Temp (C)	Press (psig)	Run #	Time (min)	O.C.C.[1] %	O.S.[2] %	O.Y.[3] %	%FA[4]
460	300	KY 35	30	72.61	---	---	---
		KY 38	30	64.14	---	---	---
		KY 48	30	63.60	79.95	50.85	160.9
		KY 46	5	63.91	---	---	
		KY 47	5	62.67	93.85	58.82	186.1
		KY 59	0+(3.31)	61.25	95.60	58.56	185.3
	50	KY 53	30	50.96	87.83	44.76	141.6
		KY 56	5	54.47	96.75	52.70	166.8
440	300	KY 37	30	67.12	---	---	---
		KY 50	30	65.10	90.46	58.89	186.3
		KY 51	30	66.10	91.16	60.26	190.7
		KY 52	30	65.96	93.29	61.53	194.7
		KY 45	5	60.06	---	---	---
		KY 49	5	55.4	93.52	51.81	164.0
		KY 60	0+(1.74)	48.40	97.68	47.28	149.6
	50	KY 54	30	57.01	95.31	54.33	172.0
		KY 57	5	54.31	97.90	53.17	168.3
420	300	KY 39	30	63.90	---	---	---
		KY 44	5	45.70	---	---	---
		KY 62	0+(2.30)	30.25	97.69	29.55	93.5
400	300	KY 40	30	51.20	---	---	---
		KY 43	5	26.60	---	---	---
		KY 63	0+(1.32)	14.00	98.27	13.76	43.5
	50	KY 55	30	49.09	97.61	47.92	151.6
		KY 58	5	27.79	99.04	27.52	87.1
380	300	KY 41	30	33.80	---	---	---
		KY 42	5	21.40	---	---	---
		KY 61	0+(1.65)	11.55	96.60	11.16	35.3

1-Organic Carbon Conversion
2-Oil Selectivity or per cent of OCC to oil
3-Oil Yield or product of OCC and OS
4-Per cent of Fischer Assay based on an assay of 31.6%

the reaction temperature as well as an increase in conversion at higher hydrogen partial pressures. In addition the effect of reaction time was the same in that organic carbon conversions increased with increased reaction time. The only exception to this was seen by comparing the results of KY-53 and KY-56 where there was a decrease in conversion associated with an increase in reaction time. The decrease in conversion for the longer time can be explained by the onset of regressive coke forming reactions at such an elevated temperature (460 C) and low hydrogen partial pressure (50 psig initial pressure).

The basis for establishing an optimum set of reaction conditions was to determine which set produced the most oil, while at the same time minimized gas production, hydrogen requirements, reaction time, and reaction temperature. Of the parameters needing to be minimized, by far the most important was to minimize gas production. This is true because the most likely source of hydrocarbon gases present in the reaction system comes from cracking reactions involving the oil produced from the pyrolytic process. It is diffiult to assign relative importance to the remaining minimization parameters because it would require an economic analysis of the associated hydrogen costs, energy costs, and operating costs, which is beyond the scope of this paper.

Table 9

Summary of Results for Phase II Experimental Runs

Reaction Temp: 450 C H_2 Press: 300 psig Run Time: 10 min.

Run Number	Organic Carbon Conversion	Oil Selectivity	Maximum Reaction Pressure
KY 25	64.78	97.60	1760
KY 27	63.50	96.20	1627
KY 28	59.13	96.26	1950
KY 29	66.70	97.13	2205
KY 30	64.00	98.10	2500
KY 31	67.00	-----	2830
KY 34	64.63	-----	3510
KY 36	67.50	-----	2530

OCC = 64.64 ± 2.67%

KY-23 and KY-25 it is seen that similar amounts of oil can be produced by using less hydrogen, which from an economic standpoint is desirable.

Phase Two

The Phase II results are used to demonstrate the reproducibility of the organic carbon conversions and oil selectivity at elevated temperatures and short residence times to help validate the results of Phase I. As can be seen from Table 9 the results are very reproducible. The results indicate an average organic carbon conversion value of 64.64% +/-2.678% and over 92% oil selectivity would be expected for the hydropyrolysis of Kentucky oil shale in supercritical toluene for 10 minutes, at 450 C.

Phase Three

The objectives of phase three experiments were to determine optimum reaction conditions and to develop a kinetic expression which adequately described the reaction system.

The results are summarized in Table 10 and are graphically displayed in Figures 11,11A, and 12. As expected the results demonstrate the same trends as those experiments performed in phase one. There was an increase in organic carbon conversion associated with an increase in

effect of reaction time. From the results it is clear that at the high temperature the organic carbon conversions were not significantly increased by allowing the reaction to proceed longer than 10 minutes, indicating high reaction rates. It is interesting to note that there was an adverse effect on the carbon conversion and oil selectivity results at the lower hydrogen partial pressures by allowing the reaction to proceed for the additional 50 minutes. This result is mostly likely explained by noting that at the lower partial pressure condensation reactions are more probable relative to higher partial pressures. This being the case, the longer the reaction is allowed to proceed the more coking that occurs resulting in lower carbon conversions. In addition the oil selectivity differences indicate that the oil forming reactions occur faster at this temperature than do the gas make reactions.

The results from Phase I experiments indicate that organic carbon conversions in excess of 190% of Fischer Assay can be achieved using the supercritical toluene hydropyrolysis process at a temperature of 450 C. In addition by reducing the reaction time from 60 minutes to 10 minutes similar organic organic carbon conversions are obtained and undesireable gas forming reactions are minimized. Finally, by comparing the oil yield values of

hydrogen partial pressure is lowered from 800 to 300 psig, while the oil selectivity was effectively the same, 93.8% to 92.5%. At the shorter residence time a similar trend is seen but the difference is less pronounced; 70.8% to 64.8%, while the oil selectivities were similar; 97.6% to 94.6% for the 800 and 300 psig runs respectively. The increase in organic carbon conversions associated with the increase in hydrogen partial pressure is most likely due to the necessity for gas phase molecular hydrogen in the reaction system. The need for hydrogen to produce elevated organic carbon conbversions is clearly seen when comparing the organic carbon conversion results of an experimental run performed in pure helium; 57.6%, to those in which hydrogen was present. Once again the explanation comes from an understanding of the chemistry of the oil forming reactions. What is most likely occurring is that the free radicals formed during the homolysis of the bonds holding the kerogen in the inorganic matrix of the oil shale react by "capping" reactions in the presence of the free radical scavanging hydrogen molecules. Higher hydrogen concentrations in the system provides an environment which was more effective at inhibiting condensation or coking reactions which leads to the decrease in carbon conversion observed.

The final reaction parameter investigated was the

organic carbon conversion rises rapidly with increasing temperature while oil selectivity declines from 98% at 350 C to 93% at 450 C. The rapid increase in the organic carbon conversion values can be explained by the chemistry of the reactions most likely taking place. Oil forming reactions most probably proceed via free radical chemistry, involving homolysis of bonds in the kerogen matrix resulting in the formation of high molecular weight free radical species. By inreasing the reaction temperature the rate of bond scission reactions is accelerated thus promoting kerogen pyrolysis and organic carbon conversion. The decline in oil selectivity with increasing temperature is most likely due to the fact that the gas formation reactions have reasonalby high activation energies and require elevated temperatures in order to proceed.

The effect of hydrogen partial pressure is also consistent with previous results (33) in that a system utilizing a non-donor solvent such as toluene requires a source of hydrogen in order to achieve elevated carbon conversions. As shown in Table 8 carbon conversions are significantly effected by the initial hydrogen partial pressure at the elevated temperature while at the low temperature there is very little effect. In the 450 C, 60 minute runs carbon conversions drop from 74% to 61.9% when

C respectively. The minimum temperature of 350 C was selected because as can be seen from the results in Table 8 the organic carbon conversions were low enough to be easily differentiated from the results at higher temperatures. There were two reasons for selecting a maximum temperature of 450 C. First, the organic carbon conversion of 58.7% resulting from the experimental run performed at 500 C (KY-14) was considerably lower than the results obtained for runs at 450 C (65-70%) indicating the possibility of a maximum conversion existing between 450 and 500 C. The drop off in conversion can best be explained by the onset of condensation reactions which lead to the formation of coke on the surface of the spent shale. These reactions are those in which the pyrolyzed kerogen molecules react regressively on the surface of the spent oil shale, and remain with the shale particles. This is an undesireable result since the objective is to produce the maximum amount of organic carbon from the shale. The second reason for choosing 450 C as the upper limit was the fact that thermal stability studies performed on toluene at 450 C had demonstrated that toluene was stable at this temperature.

The results from the Phase I experimental matrix shown in Table 8 demonstrate expected trends in organic carbon conversion and oil yield s a function of temperature. The

the predicted values of the organic carbon conversion versus time for each of the three models attempted. Figure 13 compares the predicted values to the original experimental values of the 380 C isotherm. From this figure it can clearly be seen that the second order model best fits the data. As a result the 1st and 3/2's order models were eliminated from further consideration as adequate models for this particular pyrolysis reaction. The next step in the analysis was to determine whether the second order irreversible model adequately described the reaction kinetics for the remaining temperatures investigated. Figures 14,15,16,17, and 18 show the best fit conversion versus time plots with associated r^2 values. From these figures it was determined that second order irreversible kinetics adequately modeled the particular hydropyrolysis mechanism proposed.

The next step in the development of a suitable kinetic expression was the preparation of an Arrhenius plot to determine the activation energy and frequency factor. In order to obtain rate constants independent of the psuedo equilibrium conversion, "a", it was necessary to slightly modify the rate model and eliminate the dependence by letting "a" equal one. The rate constants for each isotherm were re-evaluated by re-regressing the raw data with the

Figure 14

Linear Fit of 380 C Organic Carbon Conversion Data to 2nd Order Model

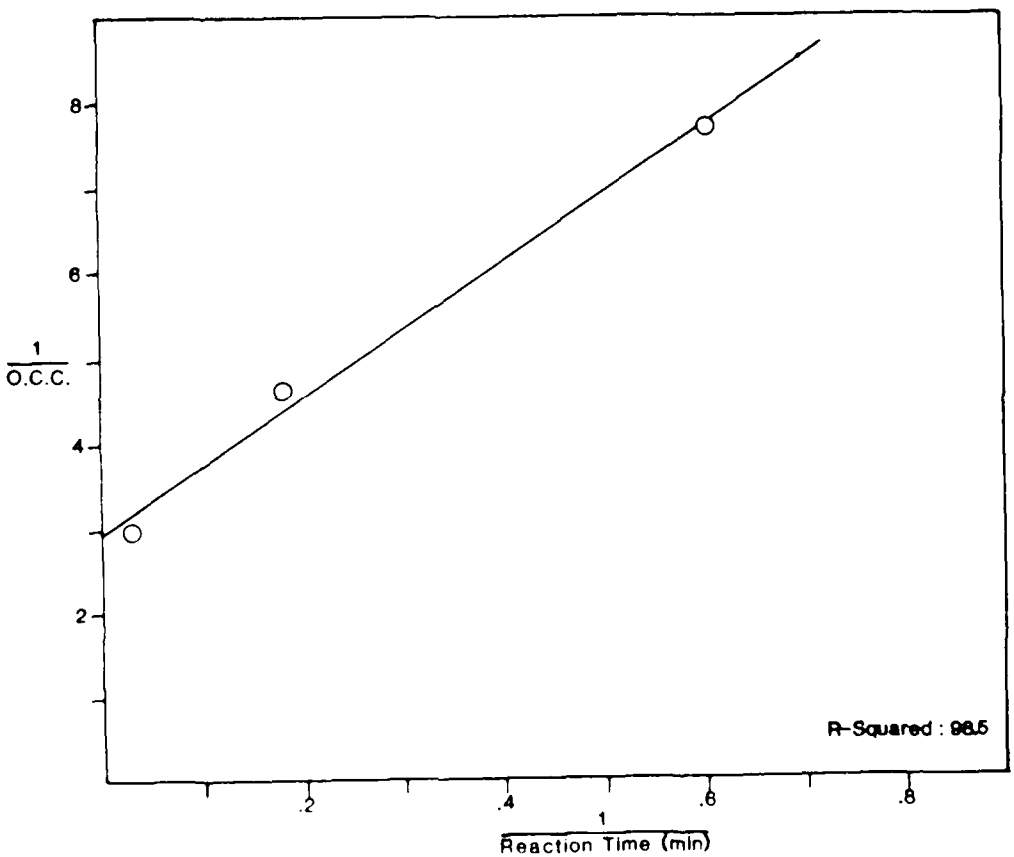


Figure 15

Linear Fit of 400 C Organic Carbon Conversion Data to 2nd Order Model

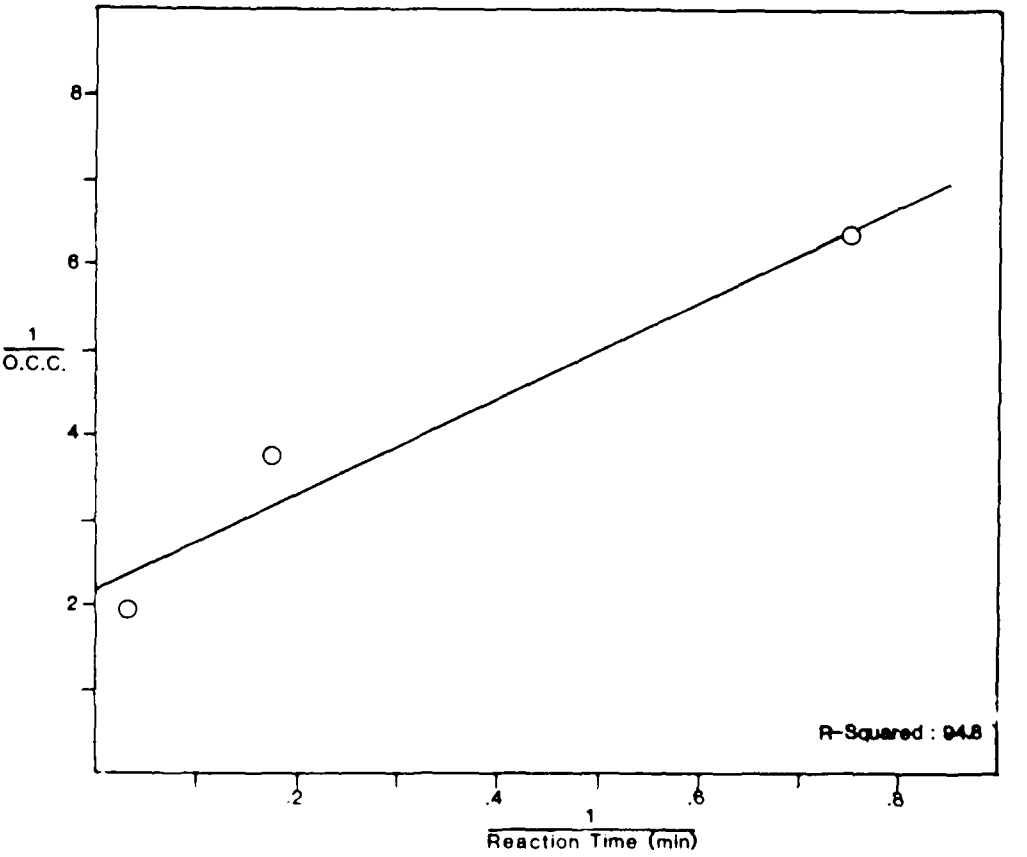


Figure 16

Linear Fit of 420 C Organic Carbon Conversion Data to 2nd Order Model

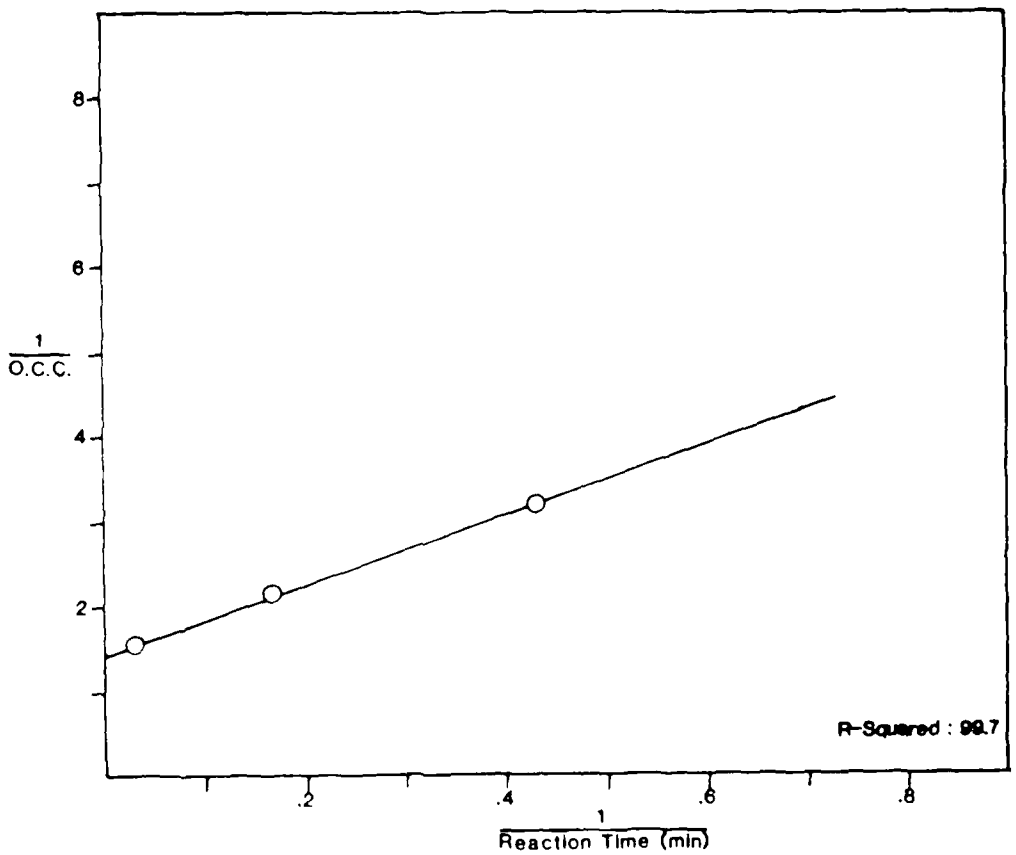


Figure 17

Linear Fit of 440 C Organic Carbon Conversion Data by 2nd Order Model

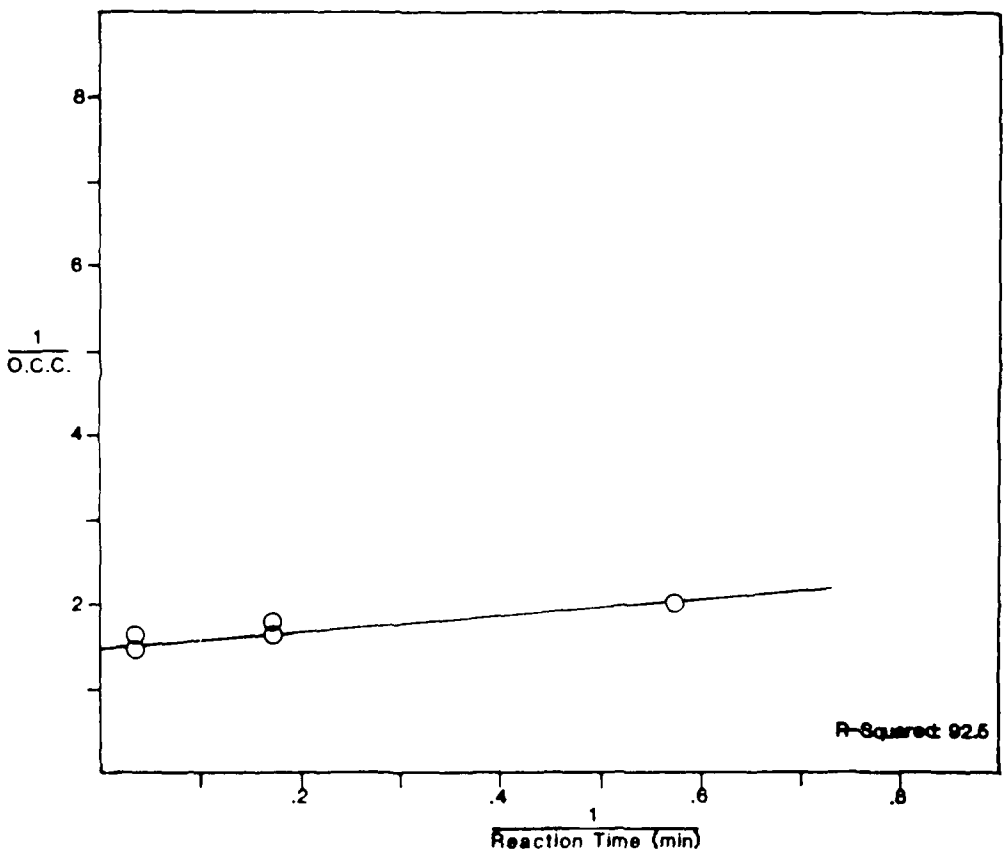
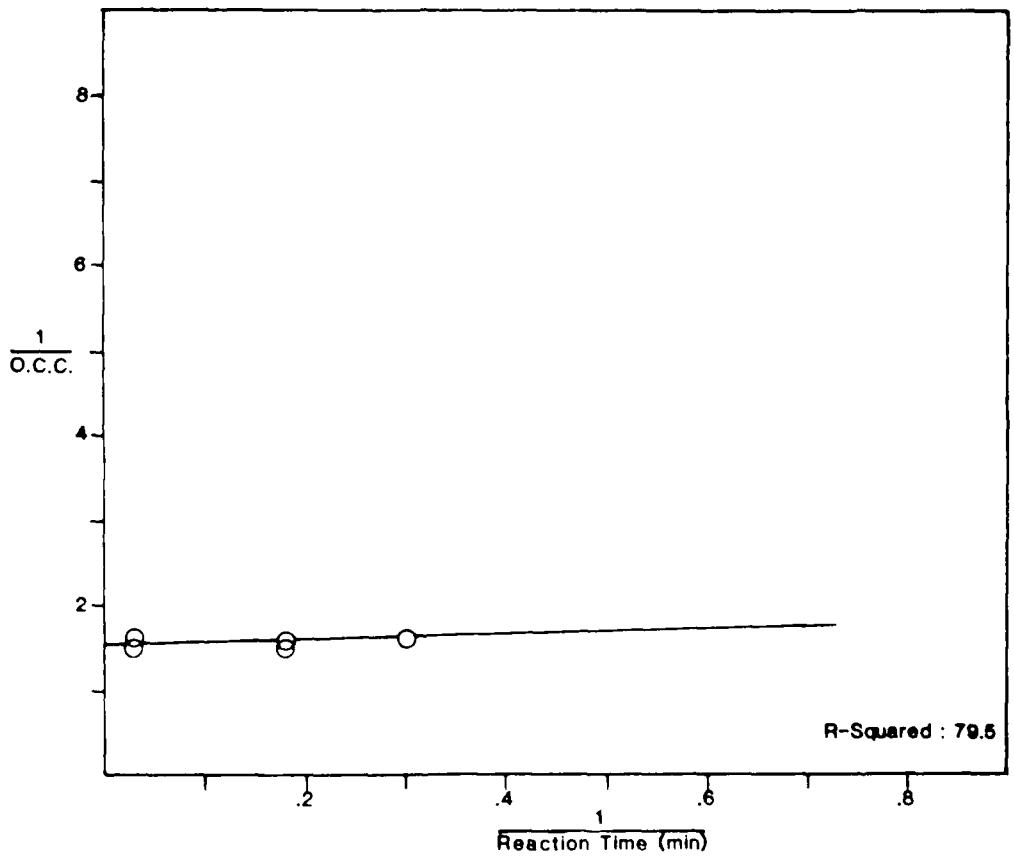


Figure 18

Linear Fit of 460 C Organic Carbon Conversion Data by 2nd Order Model



second order model. The new rate constants are shown in Table 11 along with additonal Arrhenius plot information. From the Arrhenius plot shown in Figure 19 the apparent activation energy was found to be 28.48 ± 1.97 kcal/gmole and the frequency factor was $5.941 \pm 1.48 \times 10^{7}$. The activation energy value is in good agreement with the values obtained by Winkler for the hydropyrolysis of Stuart A oil shale, 31.07 kcal/gmole.

There are two possible interpretations for the break in the Arrhenius plot associated with the rate constants at 440 and 460 C. The first is the existence of a controlling transport resistance, either heat or mass, which dominates over the rate of chemical reaction. A change in slope of the Arrhenius plot would indicate there was a change in mechanism at the elevated temperatures. Since the slope at high temperature is nearly zero, one conclusion is that transport rates become dominant at these temperatures. The second interpretation is that the reaction system cannot be adequately described at these temperatures utilizing a second order model. A more adequate high temperature model could be developed with shorter residence time data.

Phase Four

The results from the separation procedure indicated

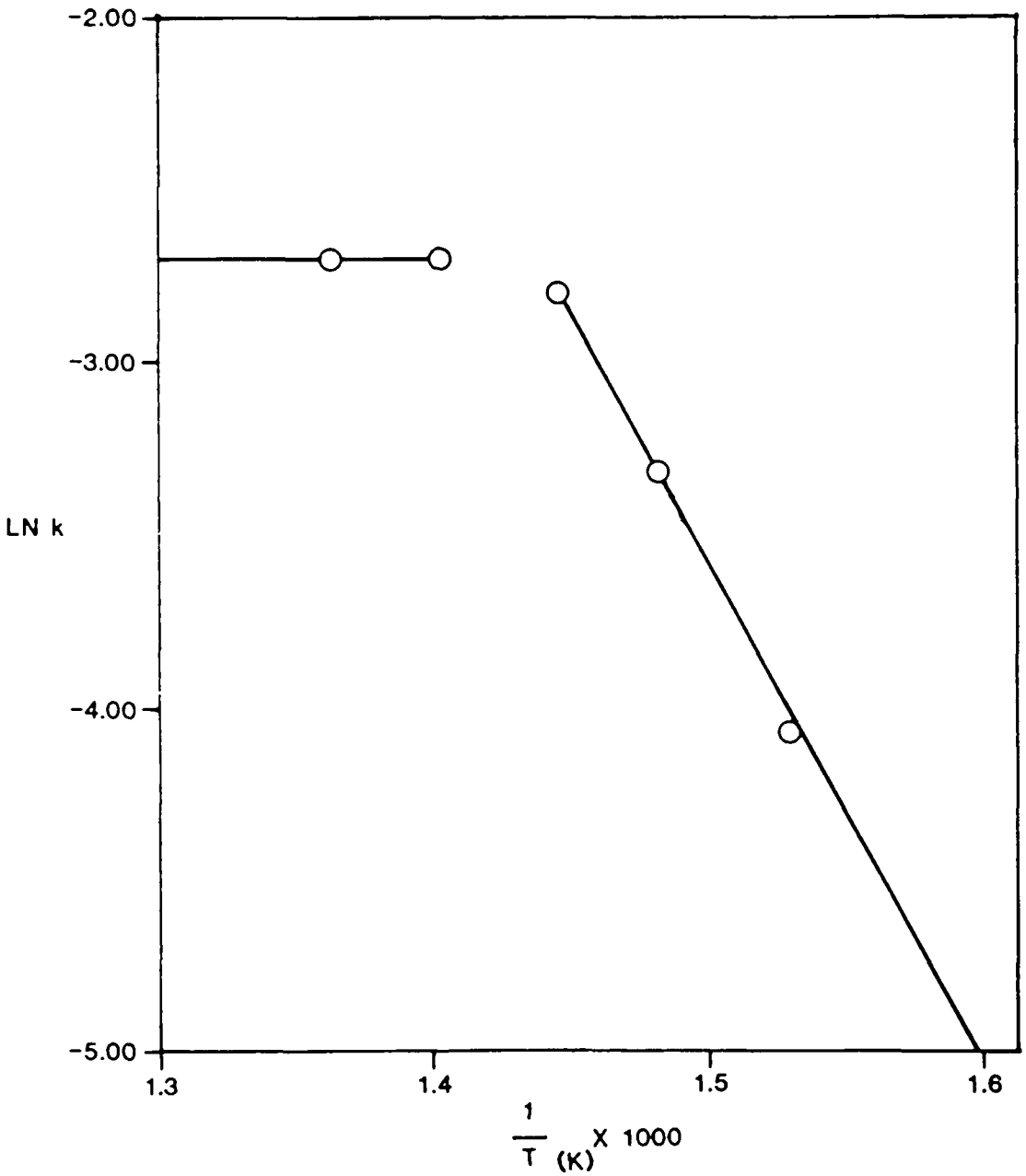
Table II

Arrhenius Plot Data

Temperature (C)	k (min^{-1})	1/T X 1000 (1/K)	Ln k
380	.0173 ±.00486	1.531	-4.06
400	.0354 ±.00491	1.486	-3.34
420	.0608 ±.0130	1.443	-2.80
440	.0665 ±.0108	1.403	-2.71
460	.0664 ±.0249	1.346	-2.71

Figure 19

Arrhenius Plot

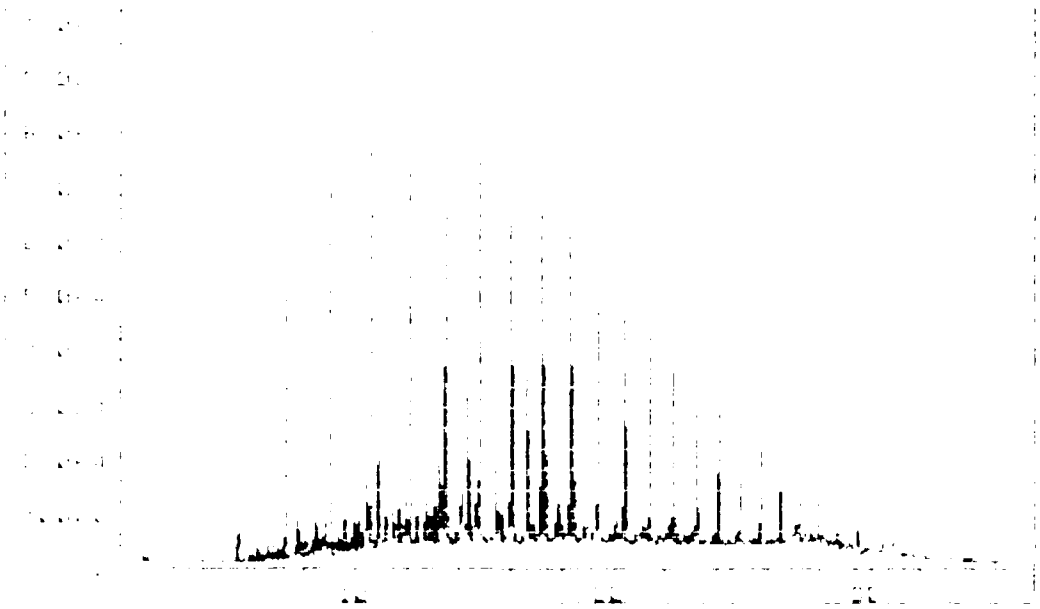


that the elution scheme employed was very effective in separating the oils into component fractions. Figure 20 shows the total ion chromatograms of the alkane fractions for both the hydropyrolysis oil and the Dravo oil. The major peaks were identified as the homologus series of normal parafins with carbon numbers ranging from C9 to C30. The chromatograms of the remaining fractions are contained in Appendix D. Even though the oils were produced at radically different conditions, a comparison of the chromatograms demonstrated that the chemical make-up of the product oils was remarkably similar.

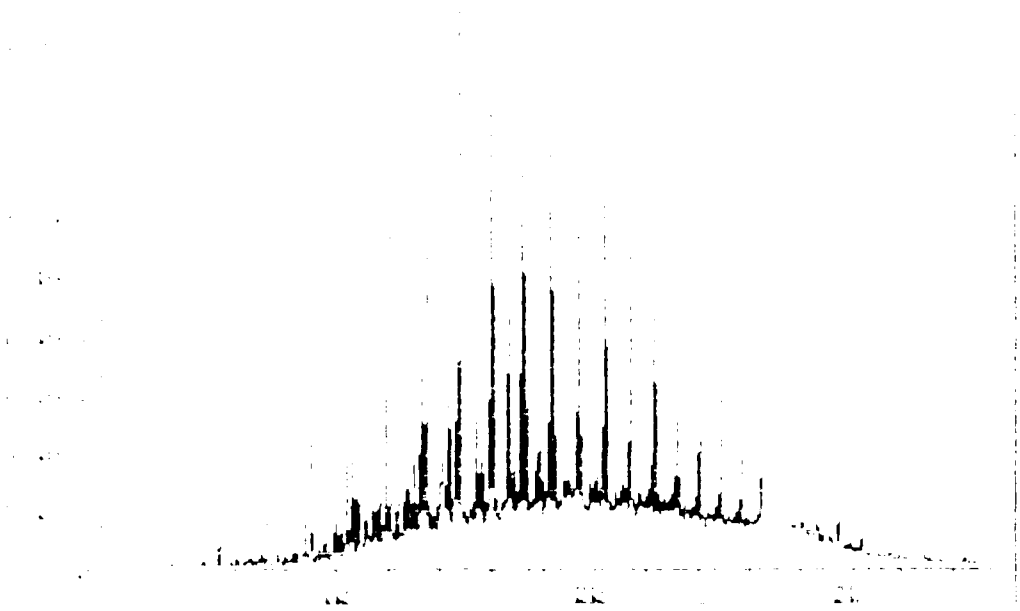
Figure 20

Total Ion Chromatograms of the Alkane Fractions

Hydropyrolysis Oil



Dravo Oil



CONCLUSIONS

The conclusions which follow pertain exclusively to the experimental system employed for this research. The following conclusions were drawn:

1. It is possible to obtain high organic carbon conversions utilizing a hydropyrolysis process employing supercritical toluene as the extraction vehicle.

2. Utilizing this process oil yields in excess of 185% Fischer Assay can be obtained for temperatures greater than 420 C and run times of 30 minutes.

3. The presence of gas phase molecular hydrogen enhances the conversion of organic carbon to oil products. In addition, the hydrogen improves the selectivity of oil products over gaseous products. For the vast majority of reaction conditions investigated the oil selectivity was in excess of 90%.

4. The gas make of the reaction system yielded primarily H_2S, CO, CO_2, and hydrocarbon gases, C1-C4.

5. The production of hydrocarbon gases dramatically decreases by decreasing the reaction time at temperatures in excess of 440 C.

6. An irreversible second order model adequately describes the reaction kinetics and predicts an apparent activation energy 28.48 kcal/gmole.

7. The separation process employed was successful in separating Kentucky shale oil into its component fractions.

8. The product oils from the hydropyrolysis process and the Dravo process are remarkably similar even though they were produced at dramatically different conditions.

RECOMMENDATIONS

The following are presented as recommendations for future work in the hydropyrolysis of Kentucky oil shale.

1. In order to elucidate the fate of hydrogen in the reaction system, in terms of consumption and/or generation, isotope tracer studies could be employed. Utilizing deuterium in the gas phase of system one could determine how the molecular hydrogen is incorporated in the pyrolyzed kerogen matrix. In addition this procedure could provide some information about the reaction mechanism of this complex reaction system.

2. Perform a more detailed characterization, ie. qualitative analysis of the compounds present in each of the separated fractions which might also provide information regarding the reaction mechanism.

3. A more descriptive kinetic model could be developed by perform[illegible] a more detailed mass balance of the reaction system, [illegible] accurately measuring the weights of all products.

AD-A156 884 PYROLYSIS AND HYDROPYROLYSIS OF KENTUCKY OIL SHALE WITH PRODUCT OIL CHARACTERIZATION(U) ARMY MILITARY PERSONNEL CENTER ALEXANDRIA VA J A MANLEY 06 JUN 85 2/2

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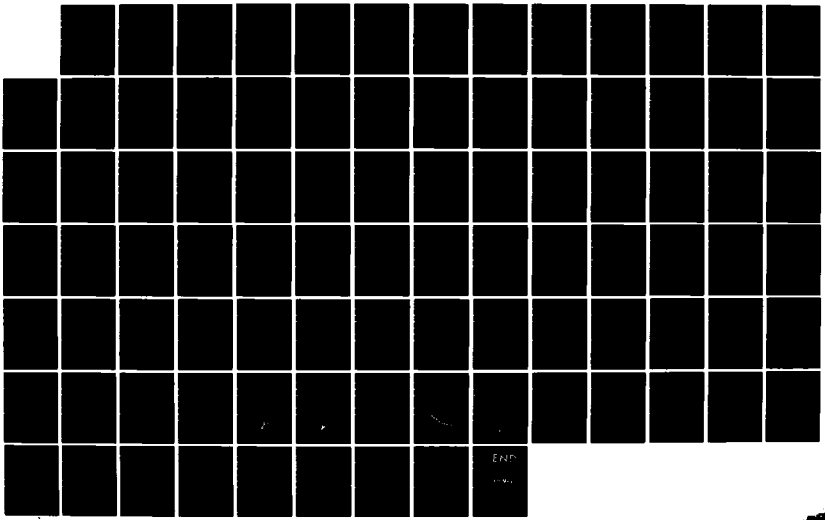

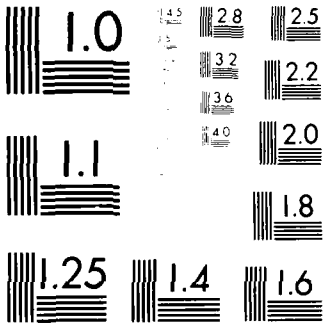

MICROCOPY RESOLUTION TEST CHART

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APPENDIX A

DATA CORRECTION PROCEDURE

Data Correction

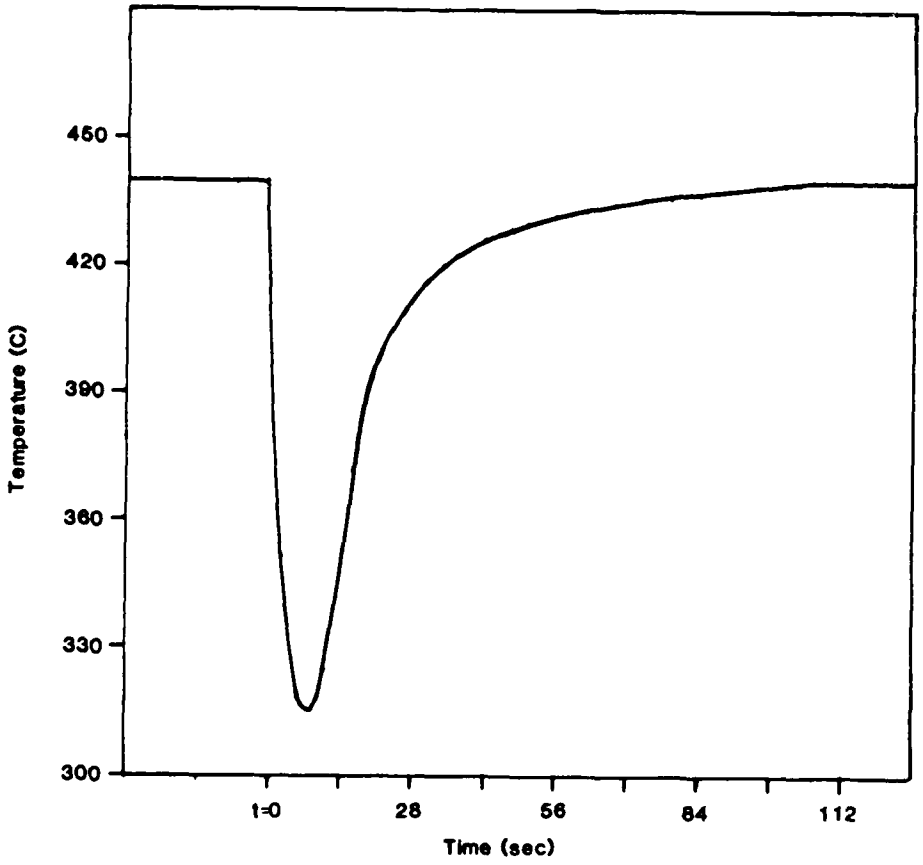
In order to account for the fact that the 0+ data points were not isothermal it was necessary to correct them so they could be used in the kinetic analysis. The approach taken to correct the points was to first establish the temperature versus time profile the injected slurry experienced at each of the reaction temperatures. This was done with the aide of the Apple computer which was programed to take temperature data points every 1.4 seconds after injection. Figure 21 shows a representative profile. The interval between the injection time and the time it took the slurry to reach the desired reaction temperature was taken to be the reaction time. With the reaction time established the following integral involving the temperature profile was evaluated numerically using Simpson's rule to determine the average temperature experienced by the injected shale:

$$\langle T \rangle = \frac{1}{t} \int_{0}^{t} T(t)\, dt$$

The organic carbon conversion calculated for each of the 0+ points was the conversion associated with the average temperature. As a result it became necessary to correct the organic carbon conversions to reflect the conversion that would have resulted had the slurry reacted under true isothermal conditions. The corection of the

Figure 21

Typical Post Injection Temperature versus Time Profile



organic carbon conversions depended upon which model was chosen to adequately describe the reaction kinetics. This being the case the O+ data points were corrected for each of the three models attempted using the following expressions (See Appendix B for the development of the 2nd order correction term):

1st order in X: $$Xc = 1 - \exp(- (- \ln(1 - X))^{\langle T\rangle/T}$$

3/2's order in X: $$Xc = 1 - ((\frac{1}{(1 - X)} - 1)^{\langle T\rangle/T} + 1)^{-2}$$

2nd order in X: $$Xc = 1 - ((\frac{1}{(1 - X)} - 1)^{\langle T\rangle/T} + 1)^{-1}$$

where;

Xc = the corrected value for O.C.C.

$\langle T\rangle$ = average temperature

X = known O.C.C.

T = equilibrium temperature

The organic carbon conversions for the 5 and 30 minute runs were not corrected because the difference between the average temperature and equilibrium temperature would be negligible resulting in little or no correction to the conversions. The reaction time however, was slightly adjusted by adding the heating time required to get ten degrees below the equilibrium temperature in order to have the same time basis for kinetic data.

APPENDIX B

SAMPLE CALCULATION

Correction for Xc for 2nd order kinetics

Begining with the second order mass balance expression:

$$\frac{dX}{dt} = k\ (1 - X)^2$$

Separating and integrating using the initial condition; X = 0 at t = 0 results in the following:

$$\frac{1}{(1 - X)} - 1 = kt$$

Ratioing the expression for Xc and X at <T>:

$$\frac{\left(\frac{1}{(1 - X)} - 1 \right)_c}{\left(\frac{1}{(1 - X)} - 1 \right)_{\langle T \rangle}} = \frac{ko\ \exp\ (- Ea/RT)}{ko\ \exp\ (- Ea/R\langle T \rangle)}$$

Taking the natural logrithm of both sides and simplifying:

$$\left(\frac{1}{(1 - X)} - 1 \right)_c = \left(\frac{1}{(1 - X)} - 1 \right)_{\langle T \rangle}^{\langle T \rangle / T}$$

The final expression for X ;

$$Xc = 1 - \left(\left(\frac{1}{(1 - X)} - 1 \right)^{\langle T \rangle / T} + 1 \right)^{-1}$$

APPENDIX C

RAW DATA

Run Number: KY 1

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale (Vaccum Dried)
Weight of Solvent-Toluene	: 100 gr.	
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 794 psig	
Initial Temperature	: 19 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2268 psig	
Post Reaction Temp.+Press.	: 25 C - 713 psig	
Gas Sample Temp. + Press.	: -- C - --- psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.92	10.22	.032	10.19
Spent	94.00	2.89	.061	2.83

Calculated Yields

Organic Carbon Conversion	: 75.20	%
Oil Yield	: -----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	-----
n-C4	-----	C2H4	-----
i-C4	-----	CH4	-----
C3H8	-----	CO2	-----
C3H6	-----	CO	-----
Ar	-----	Kr	-----
H2S	-----		

* - Mole fractions calculated on air free basis

Run Number: KY 21

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 802 psig	
Initial Temperature	: 35 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 350 C	
Maximum Pressure	: 1974 psig	
Post Reaction Temp.+Press.	: 34 C - 879 psig	
Gas Sample Temp. + Press.	: 28 C - 248 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	86.06	9.22	.003	9.22
Spent	87.85	8.72	.006	8.71

Calculated Yields

Organic Carbon Conversion:	7.190 %
Oil Yield :	91.81 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	93.42	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	.025
C3H8	.026	CO2	.048
C3H6	.044	CO	----
Ar	6.42	Kr	----
H2S	.018		

* - Mole fractions calculated on air free basis

Run Number: KY 20

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 25 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 350 C	
Maximum Pressure	: 1370 psig	
Post Reaction Temp.+Press.	: 34 C - 465 psig	
Gas Sample Temp. + Press.	: 34 C - 126 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.68	9.22	.031	9.19
Spent	86.61	8.75	.015	8.73

Calculated Yields

Organic Carbon Conversion:	7.220 %
Oil Yield :	97.31 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	93.66	C2H6	.005
n-C4	----	C2H4	----
i-C4	----	CH4	.060
C3H8	.007	CO2	.083
C3H6	.014	CO	----
Ar	6.09	Kr	----
H2S	.085		

* - Mole fractions calculated on air free basis

Run Number: KY 19

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 42 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 350 C	
Maximum Pressure	: 1620 psig	
Post Reaction Temp.+Press.	: 31 C - 646 psig	
Gas Sample Temp. + Press.	: 29 C - 186 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	87.55	9.10	.007	9.09
Spent	88.70	7.66	.022	7.64

Calculated Yields

Organic Carbon Conversion:	17.04 %
Oil Yield :	98.05 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	93.74	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	.075
C3H8	.009	CO2	.118
C3H6	----	CO	----
Ar	6.06	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 15

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 800 psig	
Initial Temperature	: 28 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 500 C	
Maximum Pressure	: 1760 psig	
Post Reaction Temp.+Press.	: 27 C - 371 psig	
Gas Sample Temp. + Press.	: 26 C - 117 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.81	9.62	.019	9.60
Spent	92.00	4.32	.026	4.29

Calculated Yields

Organic Carbon Conversion:	57.80	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	65.13	C2H6	2.46
n-C4	.011	C2H4	.029
i-C4	.025	CH4	25.89
C3H8	.556	CO2	.102
C3H6	.017	CO	----
Ar	6.04	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 13

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale (Vaccum Dried)
Weight of Solvent-Tetralin	: 100 gr.	
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 27 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 425 C	
Maximum Pressure	: 506 psig	
Post Reaction Temp.+Press.	: 30 C - 228 psig	
Gas Sample Temp. + Press.	: 25 C - --- psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.90	9.45	.006	9.44
Spent	92.89	3.60	.059	3.54

Calculated Yields

Organic Carbon Conversion:	66.13	%
Oil Yield :	94.51	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	92.26	C2H6	.422
n-C4	.038	C2H4	.059
i-C4	.008	CH4	1.25
C3H8	.126	CO2	.112
C3H6	.086	CO	----
Ar	4.33	Kr	----
H2S	1.313		

* - Mole fractions calculated on air free basis

Run Number: KY 12

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 797 psig	
Initial Temperature	: 26 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 475 C	
Maximum Pressure	: 2274 psig	
Post Reaction Temp.+Press.	: 27 C - 703 psig	
Gas Sample Temp. + Press.	: 25 C - 214 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.22	9.52	.009	9.51
Spent	94.66	2.37	.200	2.17

Calculated Yields

Organic Carbon Conversion	: 79.70	%
Oil Yield	: 90.64	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	91.01	C2H6	.406
n-C4	.015	C2H4	.010
i-C4	.006	CH4	2.33
C3H8	.195	CO2	.045
C3H6	.013	CO	----
Ar	5.76	Kr	----
H2S	.219		

* - Mole fractions calculated on air free basis

Run Number: KY 11

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H_2/Ar	
Initial Gas Pressure	: 797 psig	
Initial Temperature	: 22 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 2180 psig	
Post Reaction Temp.+Press.	: 30 C - 751 psig	
Gas Sample Temp. + Press.	: 30 C - 232 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	82.70	9.46	.069	9.39
Spent	92.82	2.77	.197	2.57

Calculated Yields

Organic Carbon Conversion:	75.59 %
Oil Yield :	95.05 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H_2	92.55	C_2H_6	.196
n-C4	.007	C_2H_4	.011
i-C4	.004	CH_4	1.02
C_3H_8	.114	CO_2	.025
C_3H_6	.028	CO	----
Ar	5.70	Kr	----
H_2S	.229		

* - Mole fractions calculated on air free basis

Run Number: KY 10

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Ar	
Initial Gas Pressure	:	800 psig	
Initial Temperature	:	22 C	
Reaction Time	:	60 min.	
Reaction Temperature	:	425 C	
Maximum Pressure	:	1500 psig	
Post Reaction Temp.+Press.	:	22 C - 780 psig	
Gas Sample Temp. + Press.	:	21 C - 248 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.60	9.62	.032	9.59
Spent	93.31	3.24	.112	3.13

Calculated Yields

Organic Carbon Conversion:	70.75	%
Oil Yield :	96.17	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	93.47	C2H6	.132
n-C4	.006	C2H4	.007
i-C4	.003	CH4	.369
C3H8	.179	CO2	.033
C3H6	.053	CO	----
Ar	5.65	Kr	----
H2S	.093		

* - Mole fractions calculated on air free basis

Run Number: KY 8

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Ar	
Initial Gas Pressure	:	800 psig	
Initial Temperature	:	23 C	
Reaction Time	:	60 min.	
Reaction Temperature	:	425 C	
Maximum Pressure	:	2054 psig	
Post Reaction Temp.+Press.	:	25 C - 447 psig	
Gas Sample Temp. + Press.	:	19 C - 143 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.55	9.7[illegible]	.042	9.71
Spent	9[illegible].70	3.06	.174	2.88

Calculated Yields

Organic Carbon Conversion	:	73.24 %
Oil Yield	:	98.11 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	9[illegible].61	C2H6	.111
[illegible]	.002	C2H4	.010
[illegible]	----	CH4	.391
[illegible]	.02[illegible]	CO2	.018
[illegible]	.00[illegible]	CO	.018
Ar	[illegible]	Kr	----
[illegible]	.[illegible]		

Mole [illegible] calculated on air free basis

Run Number: KY 5

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vacuum Dried)
Atmosphere	:	H_2/Ar	
Initial Gas Pressure	:	800 psig	
Initial Temperature	:	22 C	
Reaction Time	:	60 min.	
Reaction Temperature	:	425 C	
Maximum Pressure	:	1043 psig	
Post Reaction Temp.+Press.	:	29 C - 74 psig	
Gas Sample Temp. + Press.	:	23 C - 20 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.85	9.63	.047	9.58
Spent	91.66	4.18	.113	4.07

Calculated Yields

Organic Carbon Conversion	:	6[illegible].67 %
Oil Yield	:	91.40 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H_2	91.32	C_2H_6	.383
n-C4	.028	C_2H_4	.042
i-C4	----	CH_4	1.050
C_3H_8	.127	CO_2	.187
C_3H_6	.046	CO	----
Ar	5.76	Kr	----
H_2S	1.044		

* - Mole fractions calculated on air free basis

Run Number: KY 4

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Ar	
Initial Gas Pressure	:	800 psig	
Initial Temperature	:	21 C	
Reaction Time	:	57 min.	
Reaction Temperature	:	425 C	
Maximum Pressure	:	2152 psig	
Post Reaction Temp.+Press.	:	25 C - 639 psig	
Gas Sample Temp. + Press.	:	25 C - 637 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.43	9.71	.038	9.67
Spent	93.10	3.12	.263	2.86

Calculated Yields

Organic Carbon Conversion:	73.50	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	92.36	C2H6	.101
n-C4	.004	C2H4	.010
i-C4	----	CH4	.497
C3H8	.027	CO2	.014
C3H6	.008	CO	----
Ar	6.77	Kr	-----
H2S	.205		

* - Mole fractions calculated on air free basis

Run Number: KY 2

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 804 psig	
Initial Temperature	: 21 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2149 psig	
Post Reaction Temp.+Press.	: 25 C - 646 psig	
Gas Sample Temp. + Press.	: -- C - --- psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.92	10.22	.032	10.19
Spent	93.58	3.32	.074	3.25

Calculated Yields

Organic Carbon Conversion:	71.30	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	-----
n-C4	-----	C2H4	-----
i-C4	-----	CH4	-----
C3H8	-----	CO2	-----
C3H6	-----	CO	-----
Ar	-----	Kr	-----
H2S	-----		

* - Mole fractions calculated on air free basis

Run Number: KY 22

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 30 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 1553 psig	
Post Reaction Temp.+Press.	: 35 C - 297 psig	
Gas Sample Temp. + Press.	: 31 C - 87 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	86.00	9.47	.049	9.42
Spent	93.14	3.92	.034	3.89

Calculated Yields

Organic Carbon Conversion:	61.90 %
Oil Yield :	92.45 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	88.47	C2H6	.360
n-C4	.017	C2H4	----
i-C4	.011	CH4	2.92
C3H8	.442	CO2	.198
C3H6	.156	CO	----
Ar	7.01	Kr	----
H2S	.433		

* - Mole fractions calculated on air free basis

Run Number: KY 23

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 807 psig	
Initial Temperature	: 25 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 3115 psig	
Post Reaction Temp.+Press.	: 26 C - 807 psig	
Gas Sample Temp. + Press.	: 26 C - 223 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	85.35	9.30	.034	9.27
Spent	96.39	2.76	.038	2.72

Calculated Yields

Organic Carbon Conversion:	73.99 %
Oil Yield :	93.80 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	90.90	C2H6	.174
n-C4	.004	C2H4	----
i-C4	.002	CH4	1.81
C3H8	.119	CO2	.050
C3H6	.017	CO	.049
Ar	6.87	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 24

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 803 psig	
Initial Temperature	: 26 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 2520 psig	
Post Reaction Temp.+Press.	: 32 C - 729 psig	
Gas Sample Temp. + Press.	: 29 C - 198 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.52	9.36	.038	9.32
Spent	94.89	3.08	.027	3.05

Calculated Yields

Organic Carbon Conversion: 70.83 %
Oil Yield : 94.66 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	91.70	C2H6	.088
n-C4	----	C2H4	.016
i-C4	----	CH4	.732
C3H8	.177	CO2	.076
C3H6	.169	CO	----
Ar	6.73	Kr	----
H2S	.309		

* - Mole fractions calculated on air free basis

[illegible]

Run Number: KY [illegible]

Conditions:

Weight of Shale	:	[illegible] gr.	Fentuccy [illegible]
Weight of Solvent-Toluene	:	[illegible] gr.	[illegible]
Atmosphere	:	[illegible] Ar	
Initial Gas Pressure	:	[illegible] psi.	
Initial Temperature	:	[illegible]	
Reaction Time	:	[illegible] min.	
Reaction Temperature	:	[illegible]	
Maximum Pressure	:	[illegible] psi.	
Post Reaction Temp.+Pressure	:	[illegible]	
Gas Sample Temp.+Pressure	:	[illegible] psi.	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	[illegible]	[illegible]	[illegible]	[illegible]
Spent	[illegible]	[illegible]	[illegible]	[illegible]

Calculated Yield

Organic Carbon Conversion	:	[illegible] %
Oil Yield	:	[illegible] %

Gas Analysis

Component	Mole %	Component	Mole %
H2	91.91	C2H6	[illegible]
n-C4	----	C2H4	[illegible]
i-C4	.001	CH4	[illegible]
C3H8	.070	CO2	[illegible]
C3H6	.059	CO	----
Ar	6.54	Fr	----
H2S	[illegible]		

% - Mole fractions calculated on air free basis

[illegible] KY 27

[illegible]:

[illegible]	: [illegible] gr.	Kentucky Shale
[illegible] Ivent-Toluene	: 10[illegible] gr.	(Vacuum Dried)
[illegible]	: H2/Ar	
[illegible] Pressure	: [illegible] psig	
[illegible] Temperature	: [illegible] C	
[illegible]	: 10 min.	
[illegible] Temperature	: 450 C	
[illegible] Pressure	: [illegible] psig	
[illegible] Temp.+Press.	: [illegible] C - 31[illegible] psig	
[illegible] Temp. + Press.	: 30 C - 84 psig	

[illegible]

[illegible]	% A.F.	% Total C	% Inorganic C	% Organic C
[illegible]	[illegible].41	9.67	.028	9.64
[illegible]	[illegible].11	[illegible].96	.077	3.88

[illegible]

[illegible] Conversion:	63.50	%
[illegible] :	96.28	%

[illegible]

[illegible]	Mole %*	Component	Mole %*
[illegible]	91.84	C2H6	.110
[illegible]	.002	C2H4	.022
[illegible]	.002	CH4	.784
[illegible]	.115	CO2	.112
[illegible]	.159	CO	.159
[illegible]	6.70	Kr	----
[illegible]	---		

* [illegible] calculated on air free basis

Run Number: KY 28

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 301 psig	
Initial Temperature	: 22 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 1983 psig	
Post Reaction Temp.+Press.	: 28 C - 247 psig	
Gas Sample Temp. + Press.	: 28 C - 68 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.19	9.84	.035	9.81
Spent	93.00	4.50	.020	4.48

Calculated Yields

Organic Carbon Conversion	: 59.13	%
Oil Yield	: 96.27	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	90.71	C2H6	.640
n-C4	----	C2H4	.020
i-C4	.001	CH4	1.42
C3H8	.188	CO2	.224
C3H6	.066	CO	.459
Ar	6.81	Kr	----
H2S	.004		

* - Mole fractions calculated on air free basis

Run Number: KY 29

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 21 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 2256 psig	
Post Reaction Temp.+Press.	: 39 C - 397 psig	
Gas Sample Temp. + Press.	: 35 C - 110 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.90	9.65	.001	9.64
Spent	92.34	3.56	.003	3.56

Calculated Yields

Organic Carbon Conversion:	66.70	%
Oil Yield :	97.14	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	91.78	C2H6	.190
n-C4	.001	C2H4	----
i-C4	.002	CH4	1.26
C3H8	.176	CO2	.240
C3H6	.095	CO	.317
Ar	5.73	Kr	----
H2S	.213		

* - Mole fractions calculated on air free basis

Run Number: KY 30

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Ar	
Initial Gas Pressure	:	303 psig	
Initial Temperature	:	30 C	
Reaction Time	:	10 min.	
Reaction Temp rature	:	450 C	
Maximum Pressure	:	2532 psig	
Post Reaction Temp.+Press.	:	31 C - 433 psig	
Gas Sample Temp. + Press.	:	35 C - 113 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.40	9.34	.004	9.34
Spent	92.36	3.70	.021	3.68

Calculated Yields

Organic Carbon Conversion	:	63.97 %
Oil Yield	:	98.10 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	92.32	C2H6	.167
n-C4	.010	C2H4	----
i-C4	.003	CH4	1.58
C3H8	.102	CO2	.222
C3H6	.056	CO	----
Ar	5.54	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 31

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 301 psig	
Initial Temperature	: 22 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 2897 psig	
Post Reaction Temp.+Press.	: 26 C - 549 psig	
Gas Sample Temp. + Press.	: 25 C - 119 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.24	9.35	.030	9.32
Spent	92.82	3.39	.032	3.36

Calculated Yields

Organic Carbon Conversion:	67.28	%
Oil Yield :	97.11	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 32

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 20 C	
Reaction Time	: 60 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 2800 psig	
Post Reaction Temp.+Press.	: 25 C - 523 psig	
Gas Sample Temp. + Press.	: 25 C - 120 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.36	9.83	.020	9.81
Spent	91.04	4.71	.023	4.69

Calculated Yields

Organic Carbon Conversion	: 56.26	%
Oil Yield	: -----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 33

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	He	
Initial Gas Pressure	:	301 psig	
Initial Temperature	:	20 C	
Reaction Time	:	10 min.	
Reaction Temperature	:	450 C	
Maximum Pressure	:	3540 psig	
Post Reaction Temp.+Press.	:	25 C - 607 psig	
Gas Sample Temp. + Press.	:	25 C - 140 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.00	9.75	.020	9.73
Spent	90.39	4.47	.027	4.44

Calculated Yields

Organic Carbon Conversion	:	57.56 %
Oil Yield	:	----- %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 34

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 302 psig	
Initial Temperature	: 19 C	
Reaction Time	: 10 min.	
Reaction Temperature	: 450 C	
Maximum Pressure	: 3587 psig	
Post Reaction Temp.+Press.	: 24 C - 500 psig	
Gas Sample Temp. + Press.	: 24 C - 102 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.20	9.75	.026	9.72
Spent	91.75	3.82	.028	3.79

Calculated Yields

Organic Carbon Conversion: 64.63 %
Oil Yield : ----- %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* Mole fractions calculated on air free basis

Run Number: KY 35

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 22 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 3099 psig	
Post Reaction Temp.+Press.	: 25 C - 611 psig	
Gas Sample Temp. + Press.	: 25 C - 142 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	82.86	9.76	.019	9.74
Spent	93.19	3.02	.019	3.00

Calculated Yields

Organic Carbon Conversion:	72.61	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 49

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 299 psig	
Initial Temperature	: 20 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 2702 psig	
Post Reaction Temp.+Press.	: 27 C - 499 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.45	10.04	.023	10.02
Spent	91.42	4.84	.006	4.84

Calculated Yields

Organic Carbon Conversion:	55.40 %
Oil Yield :	93.50 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	97.28	C2H6	.092
n-C4	----	C2H4	----
i-C4	----	CH4	.749
C3H8	.174	CO2	.344
C3H6	.222	CO	.079
Ar	----	Kr	.931
H2S	.130		

* - Mole fractions calculated on air free basis

Run Number: KY 48

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 296 psig	
Initial Temperature	: 25 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2748 psig	
Post Reaction Temp.+Press.	: 31 C - 471 psig	
Gas Sample Temp. + Press.	: 26 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.17	10.00	.016	9.98
Spent	93.10	4.04	.012	4.03

Calculated Yields

Organic Carbon Conversion:	63.60 %
Oil Yield :	80.00 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	91.71	C2H6	.433
n-C4	----	C2H4	----
i-C4	.038	CH4	4.73
C3H8	.639	CO2	.883
C3H6	.185	CO	.452
Ar	----	Kr	.926
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 47

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 302 psig	
Initial Temperature	: 21 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2432 psig	
Post Reaction Temp.+Press.	: 27 C - 408 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.17	10.01	.016	9.99
Spent	92.33	4.16	.008	4.09

Calculated Yields

Organic Carbon Conversion	:	62.70 %
Oil Yield	:	93.83 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	97.14	C2H6	.131
n-C4	----	C2H4	.019
i-C4	----	CH4	1.17
C3H8	.111	CO2	.255
C3H6	.099	CO	.106
Ar	----	Kr	.821
H2S	.145		

* - Mole fractions calculated on air free basis

Run Number: KY 46

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 24 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2413 psig	
Post Reaction Temp.+Press.	: 27 C - 381 psig	
Gas Sample Temp. + Press.	: 25 C - 5 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.90	9.86	.015	9.85
Spent	92.58	3.91	.012	3.90

Calculated Yields

Organic Carbon Conversion:	63.91	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 45

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 25 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 2463 psig	
Post Reaction Temp.+Press.	: 25 C - 482 psig	
Gas Sample Temp. + Press.	: 25 C - 1 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.90	9.31	.014	9.30
Spent	92.41	4.06	.019	4.04

Calculated Yields

Organic Carbon Conversion:	60.06	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 44

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 21 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 420 C	
Maximum Pressure	: 2435 psig	
Post Reaction Temp.+Press.	: 30 C - 542 psig	
Gas Sample Temp. + Press.	: 25 C - 1 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.90	9.31	.014	9.30
Spent	89.54	5.34	.016	5.32

Calculated Yields

Organic Carbon Conversion:	45.70	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 43

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 24 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 400 C	
Maximum Pressure	: 2105 psig	
Post Reaction Temp.+Press.	: 34 C - 513 psig	
Gas Sample Temp. + Press.	: 27 C - 3 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.29	10.09	.008	10.08
Spent	87.48	7.77	----	7.77

Calculated Yields

Organic Carbon Conversion: 26.60 %
Oil Yield : ----- %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 42

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 25 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 380 C	
Maximum Pressure	: 2194 psig	
Post Reaction Temp.+Press.	: 25 C - 631 psig	
Gas Sample Temp. + Press.	: 25 C - 3 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.29	10.09	.008	10.08
Spent	86.62	8.26	.010	8.25

Calculated Yields

Organic Carbon Conversion:	21.40	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: [illegible]

Conditions:

Weight of Shale	:	[illegible] gr.
Weight of Solvent-Toluene	:	100 gr.
Atmosphere	:	H_2/Ar
Initial Gas Pressure	:	300 psig
Initial Temperature	:	21 C
Reaction Time	:	30 min.
Reaction Temperature	:	380 C
Maximum Pressure	:	2061 psig
Post Reaction Temp.+Press.	:	25 C - 551 psig
Gas Sample Temp. + Press.	:	25 C - 2 psig

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.29	10.09	.008	10.08
Spent	87.30	7.00	.005	6.99

Calculated Yields

Organic Carbon Conversion:	33.80	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

[illegible]

[illegible]:

Weight of Shale	:	[illegible] gr.	Kentucky Shale
Weight of [illegible]	:	[illegible] gr.	(Vacuum Dried)
Atmosphere	:	[illegible]	
Initial Gas Pressure	:	[illegible] psig	
Initial Temperature	:	[illegible]	
Reaction Time	:	[illegible] min.	
Reaction Temperature	:	[illegible]	
Maximum Pressure	:	[illegible] psig	
[illegible]	:	[illegible] psig	
[illegible]	:	[illegible] psig	

[illegible]

[illegible]	[illegible]	[illegible] Total C	[illegible] Inorganic C	[illegible] Organic C
[illegible]	[illegible]	[illegible]	.018	9.53
[illegible]	[illegible]	[illegible]	[illegible]	4.98

[illegible]

[illegible]	:	[illegible]
[illegible]	:	-----

[illegible]

[illegible]	Mole [illegible]	Component	Mole [illegible]
[illegible]	-----	C_2H_6	----
[illegible]	----	C_2H_4	----
[illegible]	----	CH_4	----
[illegible]	----	[illegible]	----
[illegible]	----	[illegible]	----
[illegible]	----	[illegible]	----
[illegible]	----		

Mole fractions calculated on air free basis

I-[illegible]

Run Number: KY [illegible]

Conditions:

Weight of Shale	:	[illegible] gr.	[illegible]
Weight of Solvent-Toluene	:	[illegible] gr.	[illegible]
Atmosphere	:	H_2 Ar	
Initial Gas Pressure	:	[illegible]	
Initial Temperature	:	[illegible]	
Reaction Time	:	[illegible] min.	
Reaction Temperature	:	[illegible]	
Maximum Pressure	:	[illegible]	
Post Reaction Temp.+Press.	:	[illegible]	
Gas Sample Temp. + Press.	:	[illegible]	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.21	9.41	[illegible]	[illegible]
Spent	91.46	3.76	[illegible]	[illegible]

Calculated Yields

Organic Carbon Conversion: [illegible]
Oil Yield : ----

Gas Analysis

Component	Mole %	Component	Mole %
H_2	-----	C_2H_6	[illegible]
n-C_4	--	C_2H_4	
i-C_4	----	CH_4	
C_3H_8	----	[illegible]	
C_3H_6	----	[illegible]	
Ar	----	[illegible]	
H_2S	----		

* - Mole fractions calculated on air free [illegible]

Run Number: KY 38

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Ar	
Initial Gas Pressure	: 301 psig	
Initial Temperature	: 21 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2565 psig	
Post Reaction Temp.+Press.	: 26 C - 490 psig	
Gas Sample Temp. + Press.	: -- C - --- psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.80	9.45	.030	9.42
Spent	92.96	3.75	.047	3.70

Calculated Yields

Organic Carbon Conversion:	64.14	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 37

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Ar	
Initial Gas Pressure	:	300 psig	
Initial Temperature	:	21 C	
Reaction Time	:	30 min.	
Reaction Temperature	:	440 C	
Maximum Pressure	:	2740 psig	
Post Reaction Temp.+Press.	:	26 C - 607 psig	
Gas Sample Temp. + Press.	:	-- C - --- psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.93	9.62	.039	9.58
Spent	92.73	3.53	.050	3.48

Calculated Yields

Organic Carbon Conversion:	67.18	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 36

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Ar	
Initial Gas Pressure	:	301 psig	
Initial Temperature	:	23 C	
Reaction Time	:	10 min.	
Reaction Temperature	:	450 C	
Maximum Pressure	:	2512 psig	
Post Reaction Temp.+Press.	:	26 C - 466 psig	
Gas Sample Temp. + Press.	:	-- C - --- psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	82.68	9.79	.022	9.77
Spent	93.21	3.60	.020	3.58

Calculated Yields

Organic Carbon Conversion:	67.49	%
Oil Yield :	-----	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	-----	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	----	CO2	----
C3H6	----	CO	----
Ar	----	Kr	----
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 50

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 27 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 2896 psig	
Post Reaction Temp.+Press.	: 24 C - 588 psig	
Gas Sample Temp. + Press.	: 25 C - 3 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	74.45	10.04	.023	10.02
Spent	93.08	3.86	.014	3.85

Calculated Yields

Organic Carbon Conversion:	65.20	%
Oil Yield :	90.46	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	95.81	C2H6	.201
n-C4	----	C2H4	----
i-C4	----	CH4	1.77
C3H8	.460	CO2	.428
C3H6	.189	CO	.118
Ar	----	Kr	.904
H2S	.116		

* - Mole fractions calculated on air free basis

Run Number: KY 51

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 22 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 2259 psig	
Post Reaction Temp.+Press.	: 29 C - 380 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.77	10.25	.023	10.23
Spent	93.73	3.89	.010	3.88

Calculated Yields

Organic Carbon Conversion:	66.11 %
Oil Yield :	91.15 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	96.04	C2H6	.190
n-C4	----	C2H4	----
i-C4	.013	CH4	1.56
C3H8	.405	CO2	.377
C3H6	.208	CO	.126
Ar	----	Kr	.961
H2S	.116		

* - Mole fractions calculated on air free basis

Run Number: KY 52

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vacuum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 301 psig	
Initial Temperature	: 26 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 3066 psig	
Post Reaction Temp.+Press.	: 26 C - 671 psig	
Gas Sample Temp. + Press.	: 25 C - 7 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.04	10.27	.013	10.26
Spent	92.92	3.87	.010	3.86

Calculated Yields

Organic Carbon Conversion	:	65.96 %
Oil Yield	:	93.30 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	96.69	C2H6	.163
n-C4	----	C2H4	----
i-C4	----	CH4	1.46
C3H8	.258	CO2	.308
C3H6	.106	CO	.066
Ar	----	Kr	.872
H2S	.081		

* - Mole fractions calculated on air free basis

Run Number: KY 53

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 50 psig	
Initial Temperature	: 23 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2348 psig	
Post Reaction Temp.+Press.	: 26 C - 422 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.81	9.77	----	9.77
Spent	91.52	5.17	----	5.17

Calculated Yields

Organic Carbon Conversion:	50.96	%
Oil Yield :	87.84	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	86.08	C2H6	.455
n-C4	----	C2H4	----
i-C4	----	CH4	9.87
C3H8	.694	CO2	1.96
C3H6	.208	CO	.656
Ar	----	Kr	.737
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: [illegible]

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 50 psig	
Initial Temperature	: 25 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 2838 psig	
Post Reaction Temp.+Press.	: 28 C - 513 psig	
Gas Sample Temp. + Press.	: 25 C - 4 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	84.04	9.65	----	9.65
Spent	91.77	4.53	----	4.53

Calculated Yields

Organic Carbon Conversion: 57.01 %
Oil Yield : 95.31 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	88.44	C2H6	.962
n-C4	----	C2H4	----
i-C4	----	CH4	6.03
C3H8	.565	CO2	1.64
C3H6	.186	CO	.111
Ar	----	Kr	1.11
H2S	.945		

* - Mole fractions calculated on air free basis

Run Number: KY 55

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 50 psig	
Initial Temperature	: 24 C	
Reaction Time	: 30 min.	
Reaction Temperature	: 400 C	
Maximum Pressure	: 2245 psig	
Post Reaction Temp.+Press.	: 25 C - 474 psig	
Gas Sample Temp. + Press.	: 25 C - 1 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.20	9.71	----	9.71
Spent	89.54	5.32	----	5.32

Calculated Yields

Organic Carbon Conversion:	49.09	%
Oil Yield :	97.61	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	95.79	C2H6	.250
n-C4	----	C2H4	----
i-C4	----	CH4	1.31
C3H8	.116	CO2	.861
C3H6	.118	CO	----
Ar	----	Kr	.715
H2S	.832		

* - Mole fractions calculated on air free basis

Run Number: KY 56

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 50 psig	
Initial Temperature	: 25 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2709 psig	
Post Reaction Temp.+Press.	: 28 C - 479 psig	
Gas Sample Temp. + Press.	: 25 C - 6 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.74	9.46	----	9.46
Spent	91.19	4.69	----	4.69

Calculated Yields

Organic Carbon Conversion:	54.47 %
Oil Yield :	96.75 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	94.13	C2H6.	.473
n-C4	----	C2H4	----
i-C4	----	CH4	3.13
C3H8	.167	CO2	.885
C3H6	.116	CO	.194
Ar	----	Kr	.867
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 57

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 50 psig	
Initial Temperature	: 23 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 440 C	
Maximum Pressure	: 2650 psig	
Post Reaction Temp.+Press.	: 25 C - 517 psig	
Gas Sample Temp. + Press.	: 25 C - 2 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.74	9.46	----	9.46
Spent	91.06	4.70	----	4.70

Calculated Yields

Organic Carbon Conversion:	54.31 %
Oil Yield :	97.92 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	95.76	C2H6	.316
n-C4	----	C2H4	----
i-C4	----	CH4	1.94
C3H8	.152	CO2	.629
C3H6	.109	CO	.125
Ar	----	Kr	.963
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 58

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 50 psig	
Initial Temperature	: 26 C	
Reaction Time	: 5 min.	
Reaction Temperature	: 400 C	
Maximum Pressure	: 2360 psig	
Post Reaction Temp.+Press.	: 28 C - 544 psig	
Gas Sample Temp. + Press.	: 25 C - 1 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.84	9.74	----	9.74
Spent	86.78	7.28	----	7.28

Calculated Yields

Organic Carbon Conversion:	27.79 %
Oil Yield :	99.04 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	98.47	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	.339
C3H8	.723	CO2	.444
C3H6	----	CO	----
Ar	----	Kr	.723
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 59

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 23 C	
Reaction Time	: 0+ min.	
Reaction Temperature	: 460 C	
Maximum Pressure	: 2331 psig	
Post Reaction Temp.+Press.	: 28 C - 402 psig	
Gas Sample Temp. + Press.	: 26 C - 1 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.30	9.81	----	9.81
Spent	91.82	4.19	----	4.19

Calculated Yields

Organic Carbon Conversion	: 61.25	%
Oil Yield	: 95.60	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	97.76	C2H6	.084
n-C4	----	C2H4	----
i-C4	----	CH4	.803
C3H8	.093	CO2	.144
C3H6	.141	CO	.054
Ar	----	Kr	.924
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 60

Conditions:

Weight of Shale	:	25 gr.	Kentucky Shale
Weight of Solvent-Toluene	:	100 gr.	(Vaccum Dried)
Atmosphere	:	H2/Kr	
Initial Gas Pressure	:	300 psig	
Initial Temperature	:	27 C	
Reaction Time	:	0+ min.	
Reaction Temperature	:	440 C	
Maximum Pressure	:	2180 psig	
Post Reaction Temp.+Press.	:	28 C - 406 psig	
Gas Sample Temp. + Press.	:	27 C - 1 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.11	9.88	----	9.88
Spent	89.67	5.50	----	5.50

Calculated Yields

Organic Carbon Conversion: 48.40 %
Oil Yield : 97.68 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	98.63	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	.288
C3H8	.035	CO2	.109
C3H6	.060	CO	.005
Ar	----	Kr	.863
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 61

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 29 C	
Reaction Time	: 0+ min.	
Reaction Temperature	: 380 C	
Maximum Pressure	: 2222 psig	
Post Reaction Temp.+Press.	: 25 C - 576 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.52	9.74	----	9.74
Spent	85.60	8.83	----	8.83

Calculated Yields

Organic Carbon Conversion: 11.55 %
Oil Yield : 96.60 %

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	98.90	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	.100
C3H8	.011	CO2	.078
C3H6	.015	CO	----
Ar	----	Kr	.803
H2S	.093		

* - Mole fractions calculated on air free basis

Run Number: KY 62

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 300 psig	
Initial Temperature	: 23 C	
Reaction Time	: 0+ min.	
Reaction Temperature	: 420 C	
Maximum Pressure	: 2548 psig	
Post Reaction Temp.+Press.	: 28 C - 548 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	83.71	9.62	----	9.62
Spent	87.95	7.05	----	7.05

Calculated Yields

Organic Carbon Conversion:	30.25	%
Oil Yield :	97.69	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	98.70	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	.098
C3H8	.037	CO2	.086
C3H6	.048	CO	----
Ar	----	Kr	.813
H2S	----		

* - Mole fractions calculated on air free basis

Run Number: KY 63

Conditions:

Weight of Shale	: 25 gr.	Kentucky Shale
Weight of Solvent-Toluene	: 100 gr.	(Vaccum Dried)
Atmosphere	: H2/Kr	
Initial Gas Pressure	: 313 psig	
Initial Temperature	: 30 C	
Reaction Time	: 0+ min.	
Reaction Temperature	: 400 C	
Maximum Pressure	: 2562 psig	
Post Reaction Temp.+Press.	: 25 C - 599 psig	
Gas Sample Temp. + Press.	: 25 C - 0 psig	

Chemical Analysis

Shale	% Ash	% Total C	% Inorganic C	% Organic C
Feed	82.64	9.86	----	9.86
Spent	85.80	8.80	----	8.80

Calculated Yields

Organic Carbon Conversion	: 14.04	%
Oil Yield	: 98.27	%

Gas Analysis

Component	Mole %*	Component	Mole %*
H2	98.95	C2H6	----
n-C4	----	C2H4	----
i-C4	----	CH4	----
C3H8	.008	CO2	.080
C3H6	.029	CO	----
Ar	----	Kr	.927
H2S	----		

* - Mole fractions calculated on air free basis

```
570  VTAB 23: HTAB 16: PRINT  SPC( 4);: HTAB 34: PRINT SPC(4)
;: VTAB 23: HTAB16: PRINT TEMP;: HTAB 34: PRINT HE;
580  IF TEMP > 740 THEN  GOSUB 720
590  PRINT
600  GOTO 320
605   REM  :  LINEARIZATION SUBPROGRAM  FOR  CALCULATION  OF
HEATER TEMPERATURE IN DEGREES C FOR A J-TYPE THERMOCOUPLE
610  IF V < 411 THEN T = C + V / 5.2: RETURN
620  IF V < 2738 THEN T = C + 79 + (V - 411) / 5.527
630  RETURN
640  END
645   REM  :  LINEARIZATION SUBPROGRAM TO CALCULATE  REACTOR
TEMPERATURE IN DEGREES C FOR A J-TYPE THERMOCOUPLE
650  IF V < 326 THEN T = C + V / 4.07: RETURN
660  IF V   654 THEN T = C + 80 + (V - 326) / 4.11: RETURN
670  IF V   1137 THEN T = C + 160 + (V - 654) / 4.02: RETURN
680  IF V < 1935 THEN T = C + 280 + (V - 1137) / 4.2: RETURN
690   IF  V   2932 THEN T = C + 470 + (V  - 1935)  /  4.26:
RETURN
700   IF  V   3614 THEN T = C + 704 + (V  - 2932)  /  4.11:
RETURN
710   IF  V   4276 THEN T = C + 870 + (V  - 3614)  /  3.94:
RETURN
715  REM : AUTOMATIC ALARM IF HEATER TEMPERATURE EXCEEDS 740
C
720  FOR BEEP = 1 TO 100
730 SOUND =  PEEK ( - 16336)
740  NEXT BEEP: RETURN
745  REM : OPEN AND CLOSES DATA FILE FOR TEMPERATURE PROFILE
750 D$ =  CHR$ (4)
760  PRINT D$;"OPEN ";F$;",L10"
770 WR$ = D$ + "WRITE " + F$ + ",R"
780  FOR J = 1 TO FL: PRINT WR$;J: PRINT X(J): NEXT
790  PRINT WR$;0: PRINT FL
800  PRINT D$;"CLOSE"
810  END
```

```
270 V = (V(N) - V(0)) * G: IF N = 1 THEN  GOSUB 610
280  IF N = 2 THEN  GOSUB 650
290 TEMP =  INT (T + .5)
300  IF N = 1 THEN  GOTO 330
310  IF N = 2 THEN  GOTO 570
320  NEXT N
325  REM : OUTPUTS CURRENT REACTOR TEMPERATURE
330  VTAB 22:  HTAB 16:  PRINT  SPC( 4):  VTAB 22:  HTAB 16:
PRINT TEMP
335  REM :  COMPUTER SEARCHES KEYBOARD TO DETERMINE THE LAST
KEYSTROKE  IN  ORDER TO DETERMINE WHETHER OR NOT  IT  SHOULD
BEGIN TAKING DATA; S(83 OR 211) STARTS DATA AQUISITION, Q(81
OR 209) QUITS TAKING DATA,  C(195) RESETS SET POINT TO 25 C,
E(198) ENDS PROGRAM AND CLOSES DATA FILE FOR TEMPERATURE
340  IF FD = 1 THEN KK = KK + 1
350  IF J = 500 THEN FL = J: GOTO 750
360 ZZ =  PEEK (49152)
370  IF ZZ = 197 THEN  PRINT  CHR$ (7);  CHR$ (7); CHR$ (7):
GOTO 750
380  IF ZZ <  > 209 AND ZZ <  > 81 THEN 400
390   IF FD(1) = 0 THEN FL = J:FD(1) = 1:  PRINT  CHR$  (7);
CHR$ (7):FD = 0
400   IF ZZ = 195 AND FD(2) = 0 THEN TSET = 25:  PRINT  CHR$
(7):FD(2) = 1
410  IF ZZ <  > 211 AND ZZ <  > 83 THEN 430
420  IF FD = 0 THEN  PRINT  CHR$ (7); CHR$ (7):FD = 1
430  IF FD = 1 AND KK = 2 THEN J = J + 1:X(J) =  TEMP:  VTAB
22: HTAB 34: PRINT JKK = 0
435  REM : CALCULATES DIFFERENCE BETWEEN REACTOR TEMPERATURE
AND  SET  POINT IN ORDER TO DETERMINE IF IT IS NECESSARY  TO
OPEN VALVE CONTROLLING COOLING WATER
440 I = I + 1:TP = 159 - (T / 3.3)
450  IF T >  TSET THEN Q = 4
460  IF T <  TSET THEN Q = 0
470  IF I >  258 THEN I = 1
480  HCOLOR= 0: HPLOT I,Y(I)
490  HCOLOR= 3:Y(I) = TP: HPLOT I,Y(I)
495   REM  :   CALCULATES  DIFFERENCE  BETWEEN  THE  REACTOR
TEMPERATURE AND SET POINT,THEN ESTAPLISHES HEATER OUTPUT.
500 DT = TSET - T
510  IF DT <  0 THEN HE = 0: GOTO 310
520  IF DT >  12.6 THEN  GOTO 550
530 HE =  INT (DT * 5)
540  GOTO 310
550 HE = 63
560  GOTO 310
565   REM  :  OUTPUTS  THE REACTOR  TEMPERATURE  AND  HEATER
TEMPERATURE
```

Computer listing for program utilized for temperature control of reactor

```
5  REM :  DIMENSION DATA FILE ARRAY X(I) AND GRAPHICS  ARRAY
Y(I)
10  DIM X(500),Y(259):J = 0:KK = 0
20  FOR I = 1 TO 259:Y(I) = 189: NEXT
25   REM :  DEFINES FUNCTION USED TO PERFORM A/D CONVERSIONS
FOR TERMOCOUPLE THERMOMETER
30  DEF  FN V(X) = (44 -  PEEK (1146)) * ( PEEK (1274) * 256
+  PEEK (1402))
35  REM : INPUT RUN PARAMETERS
40   INPUT  "DATA  FILE  NAME:   ";F$50   INPUT  "SET  POINT
(DEGREES):";TSET: HOME
55   REM  :  INSTRUCTIONS  TO  PRINT  HEADINGS  FOR  REACTOR
TEMPERATURE,  HEATER  TEMPERATURE,  DATA  POINT  NUMBER  AND
HEATER OUTPUT
60   VTAB 22:  HTAB 1:  PRINT "REACTOR TEMP = ";:  HTAB  26:
PRINT "POINT #"
70  VTAB 23: HTAB 2: PRINT "HEATER TEMP = ";: HTAB 25: PRINT
"OUTPUT = "
80 TX = 159 - TSET / 3.3
85   REM  :  INSTRUCTIONS TO DRAW  GRAPHICS  FOR  MONITORING
REACTOR TEMPERATURE
90  HGR : HCOLOR= 3: HPLOT 0,0 TO 0,159 TO 279,159
100  FOR N = 0 TO 260 STEP 5: HPLOT N,TX TO N + 1,TX: NEXT N
110 I = 0
120  FOR N = 0 TO 128 STEP 32
130  FOR M = 0 TO 260 STEP 10
140  HPLOT M,N TO M + 5,N: NEXT M: NEXT N
145  REM :  ESTABLISH PARAMETERS FOR DETERMINING TEMPERATURE
OF  REACTOR(  K  AND  G ARE CONSTANTS UNIQUE  FOR  A  J-TYPE
THERMOCOUPLE  NECESSARY  FOR  A/D  CONVERSIONS  TO  DEGREES
CELCIUS) AND MAXIMUM OUTPUT OF HEATER( HE )
150 K = 11.77:G = .809:Q = 0:HE = 63
160 Z = 0
165  REM : COMPUTER'S ADDITIONAL A/D & D/A CARDS ARE ACESSED
TO CALCULATE REACTR TEMPERATURE AND HEATER OUTPUT
170  POKE 49314,Q
180  POKE 49400,HE
190  FOR N = 0 TO 3
200  CALL 49664: IF N = 3 GOTO 220
210  POKE 49314,N + 1 + Q
220 V(N) =  FN V(X)
230  NEXT N
240 C = (V(3) - V(0)) / K - 273
250  FOR N = 1 TO 3
260  IF N = 3 THEN  GOTO 170
```

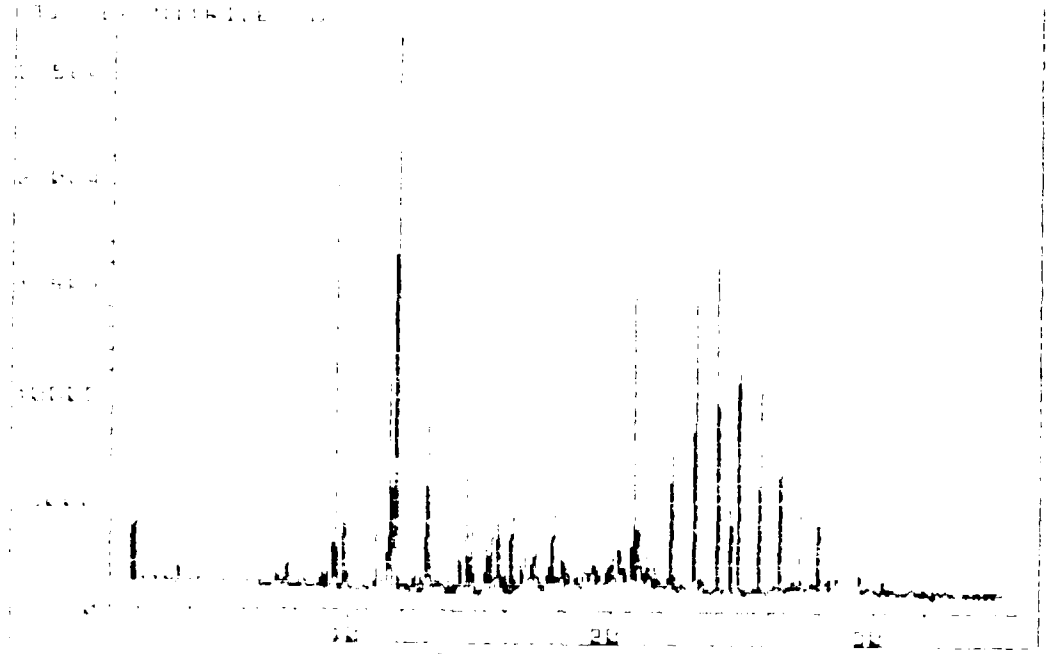
APPENDIX E

TEMPERATURE CONTROL PROGRAM LISTING

Figure 30

Total Ion Chromatograms of the Nitrile and Ketone Fractions of the Hydropyrolysis Oil

Nitriles



Ketones

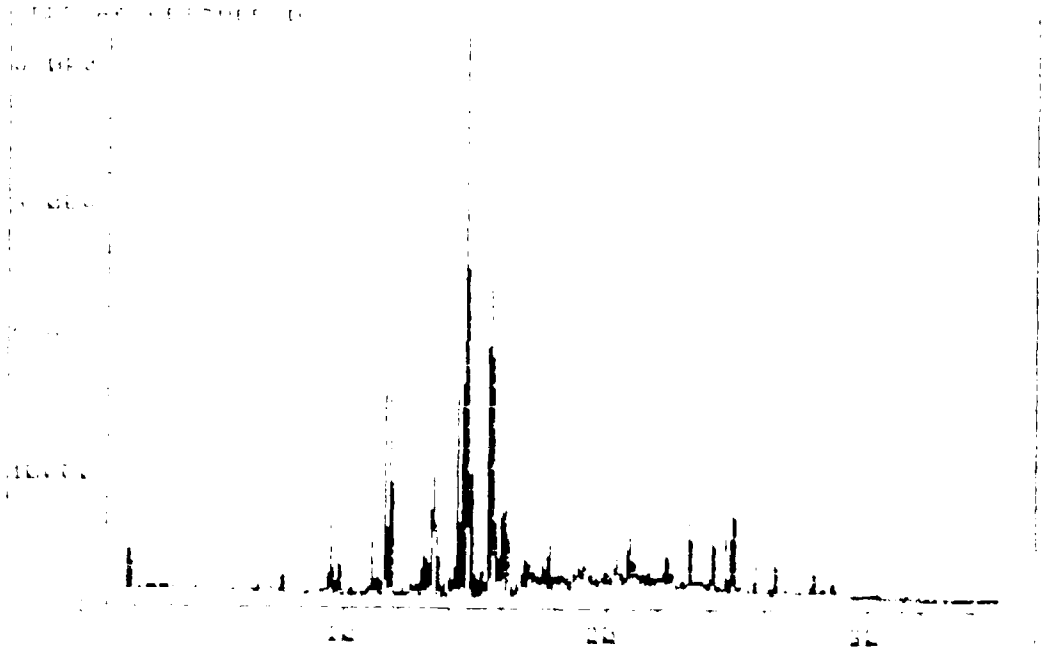
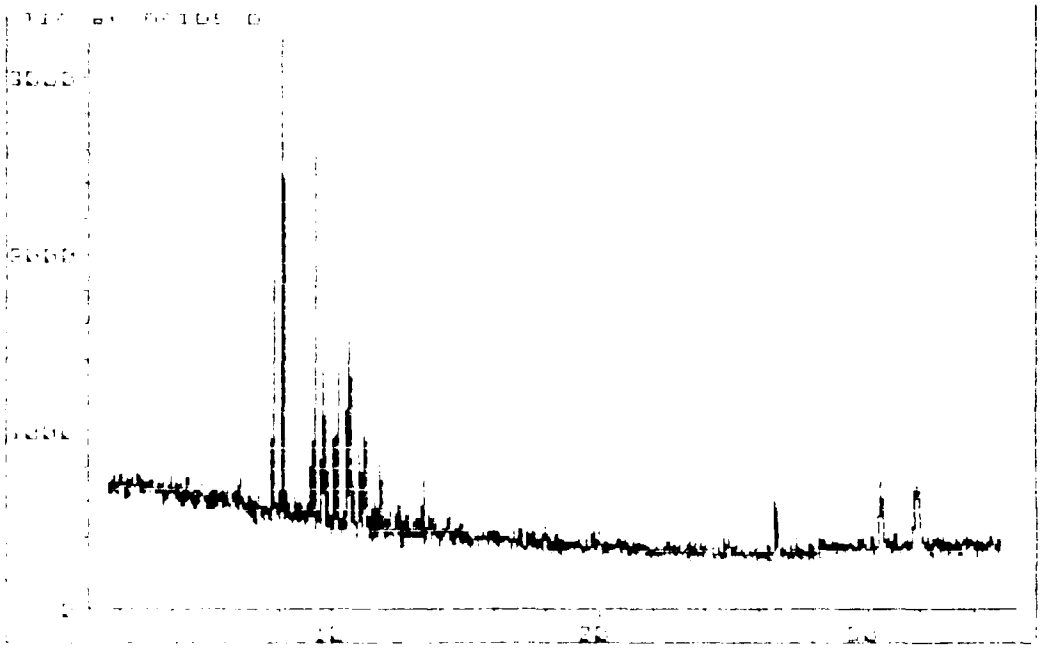


Figure 29

Total Ion Chromatograms of the Acid/Phenol Fractions

Hydropyrolysis Oil



Dravo Oil

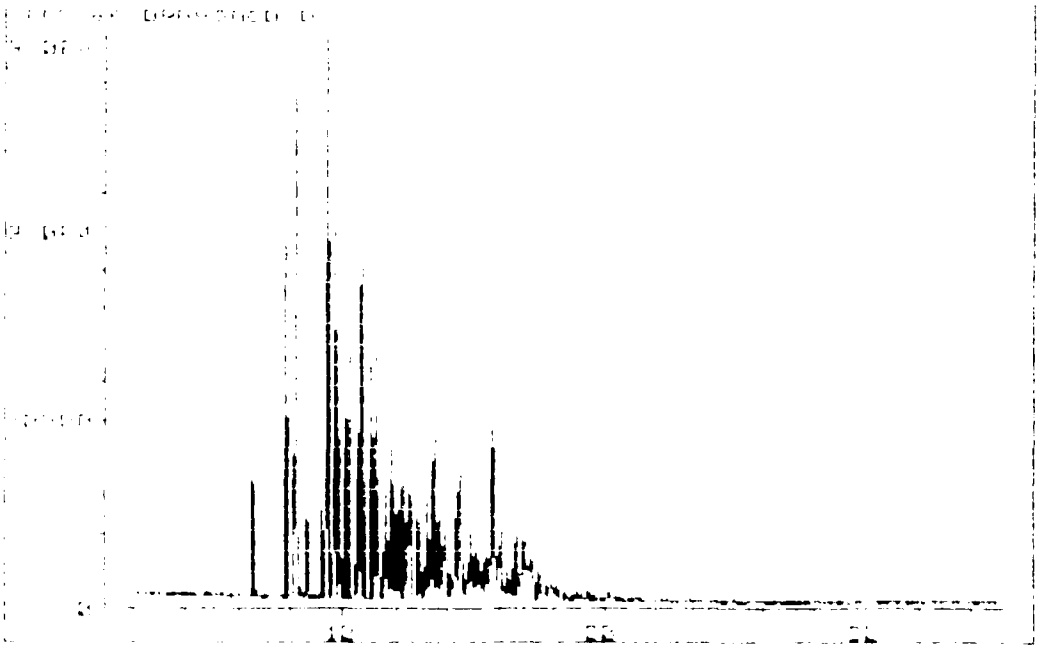
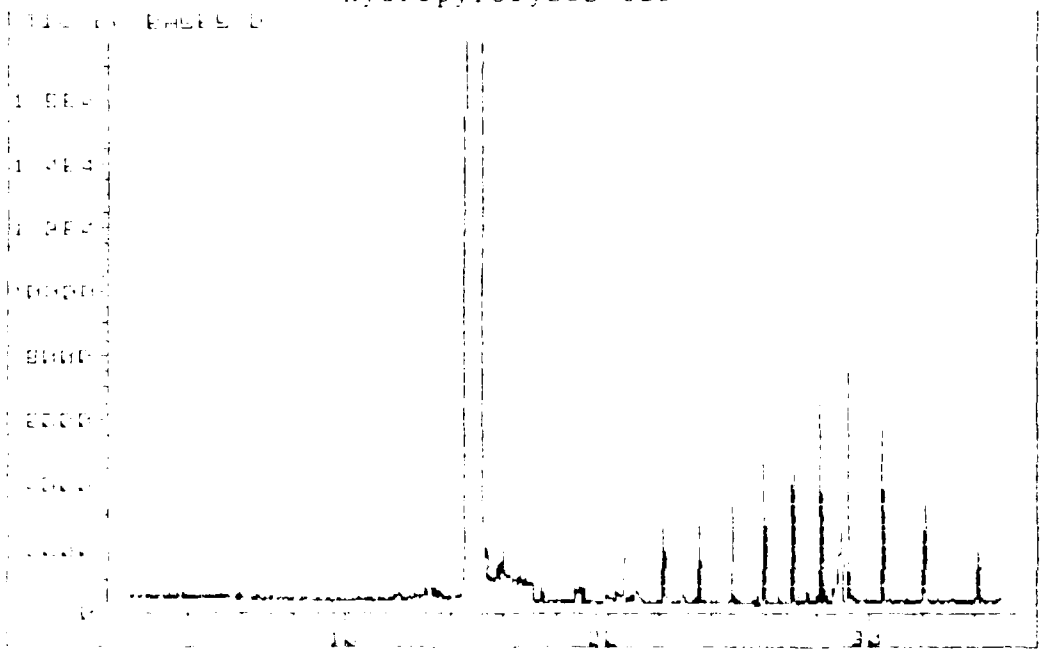


Figure 28

Total Ion Chromatograms of the Base Fractions

Hydropyrolysis Oil



Dravo Oil

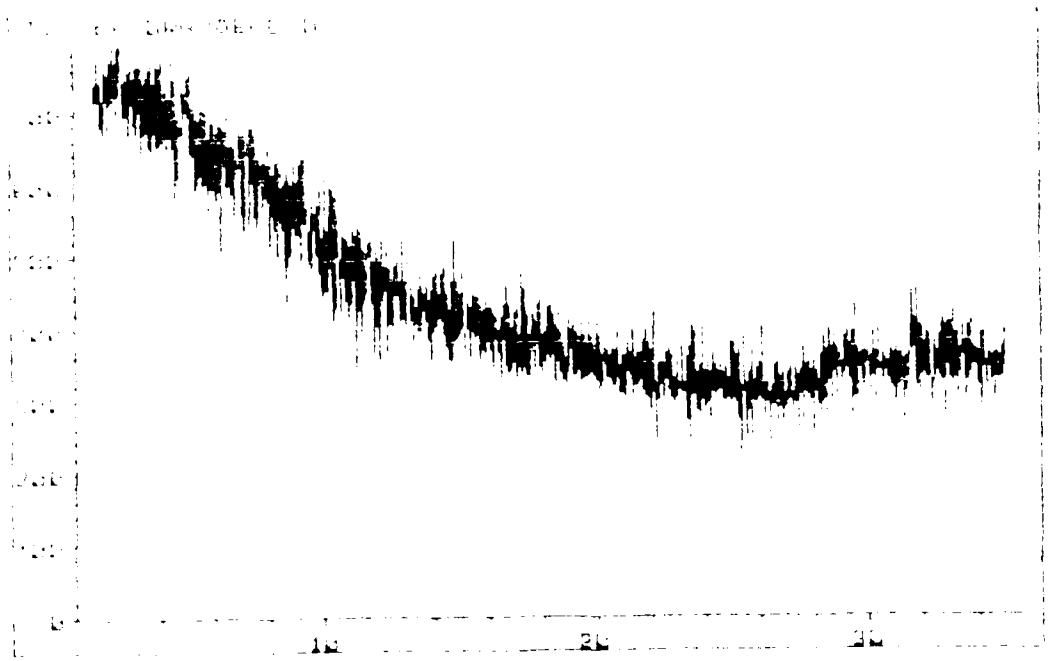
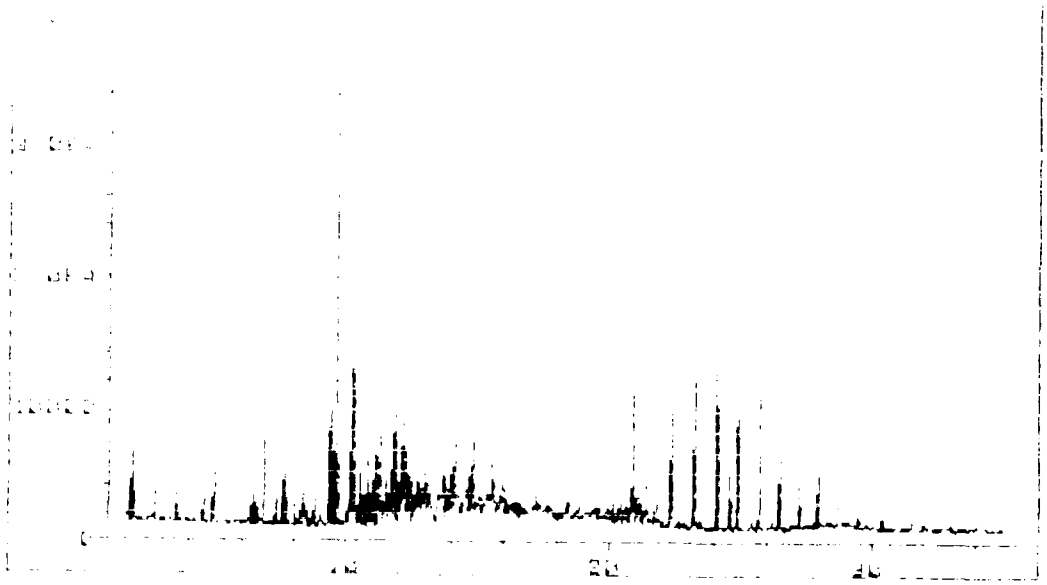


Figure 27

Total Ion Chromatograms of the Fourth Aromatic Fractions

Hydropyrolysis Oil



Dravo Oil

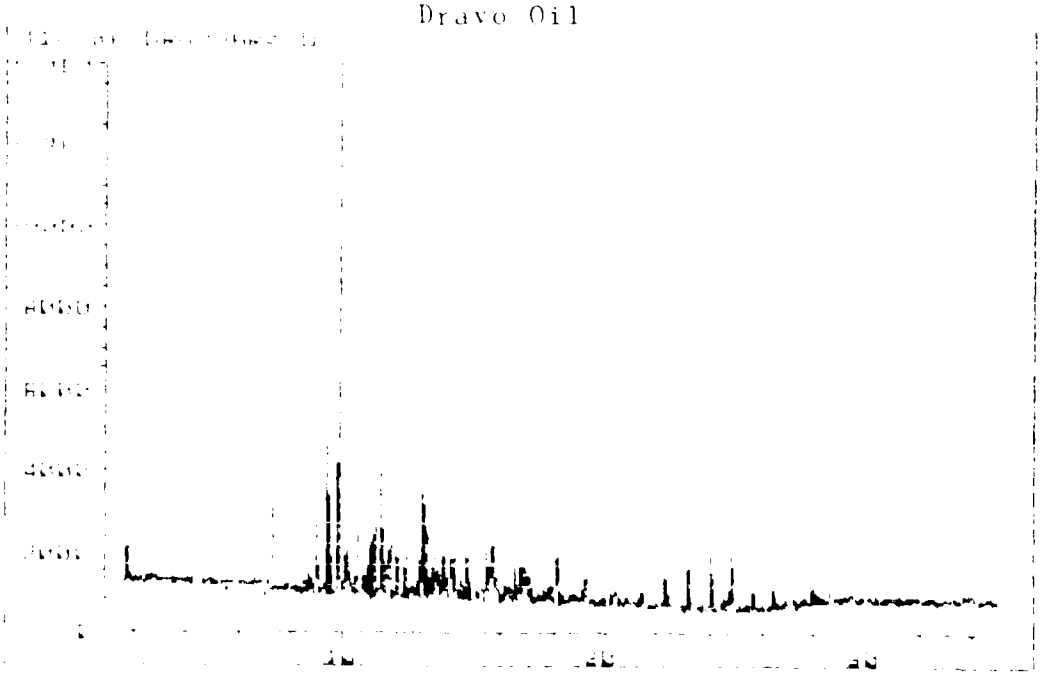
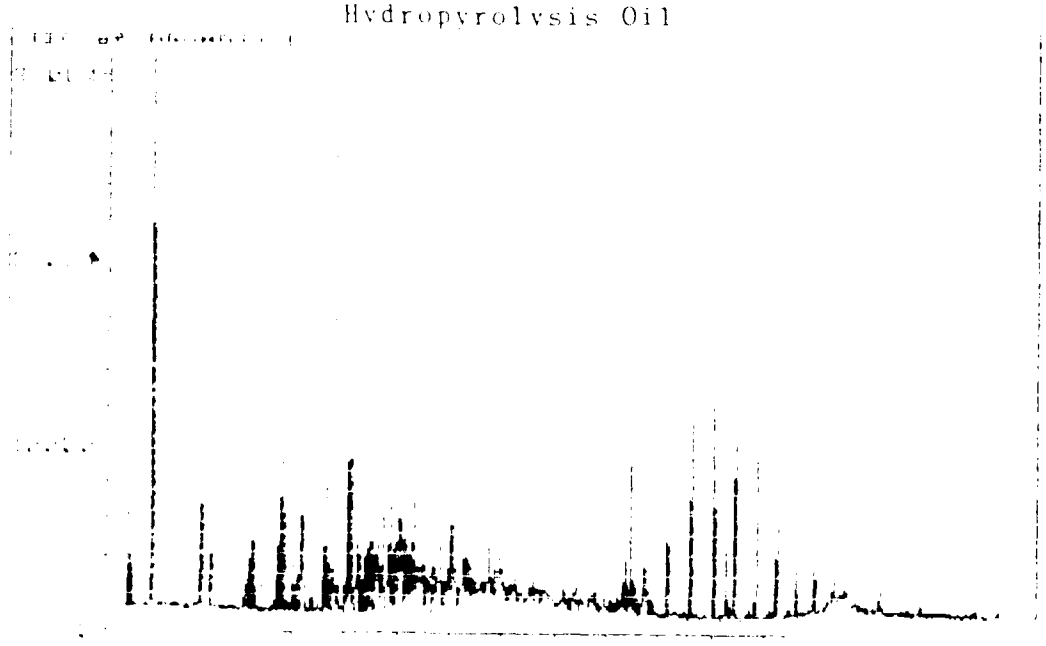


Figure 26

Total Ion Chromatograms of the Third Aromatic Fractions

Hydropyrolysis Oil



Dravo Oil

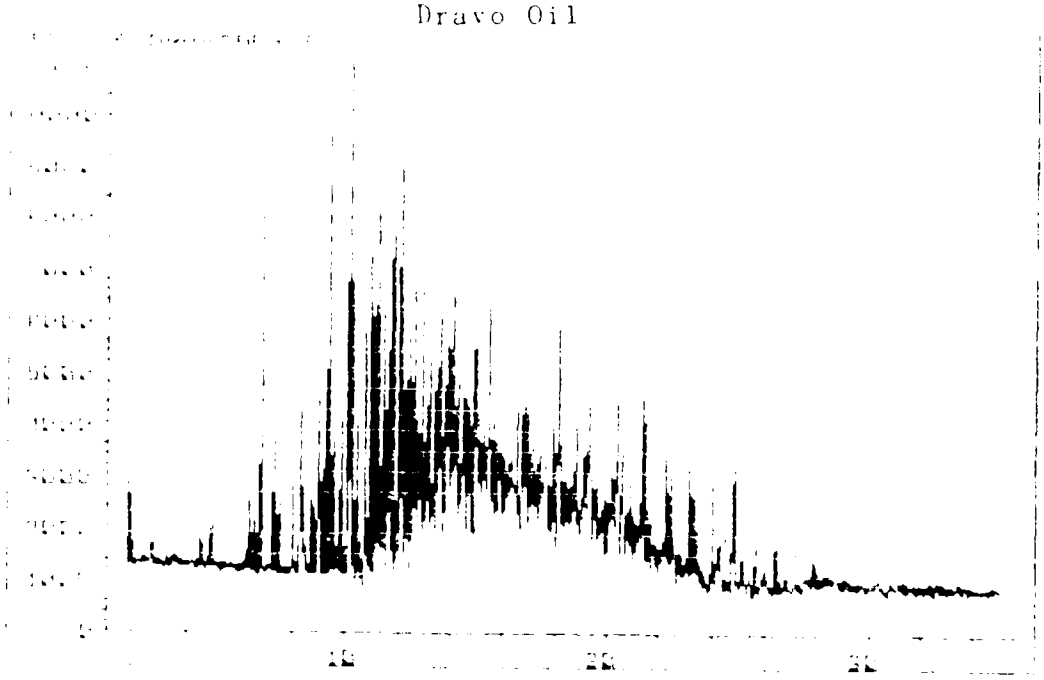
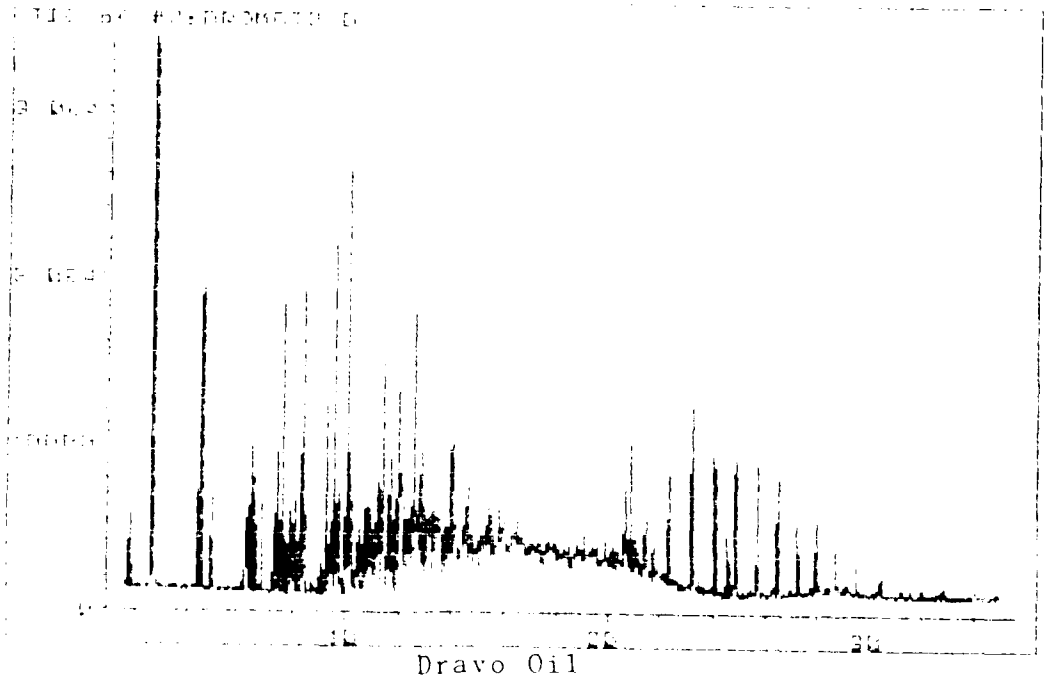


Figure 25

Total Ion Chromatograms of the Second Aromatic Fractions

Hydropyrolysis Oil



Dravo Oil

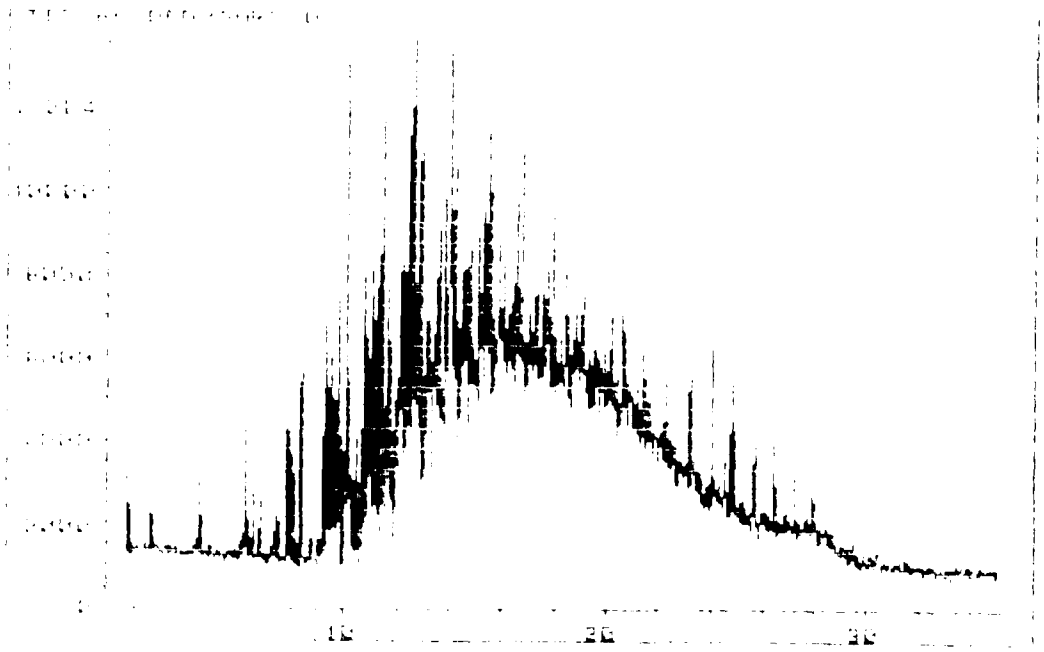
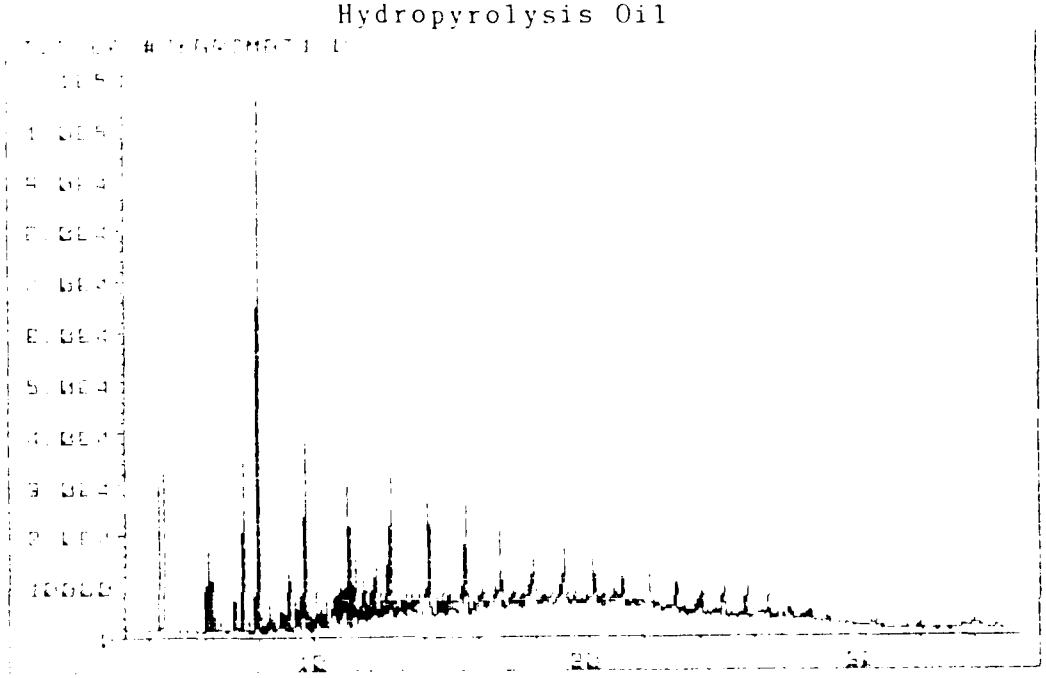


Figure 24

Total Ion Chromatograms of the First Aromatic Fractions

Hydropyrolysis Oil



Dravo Oil

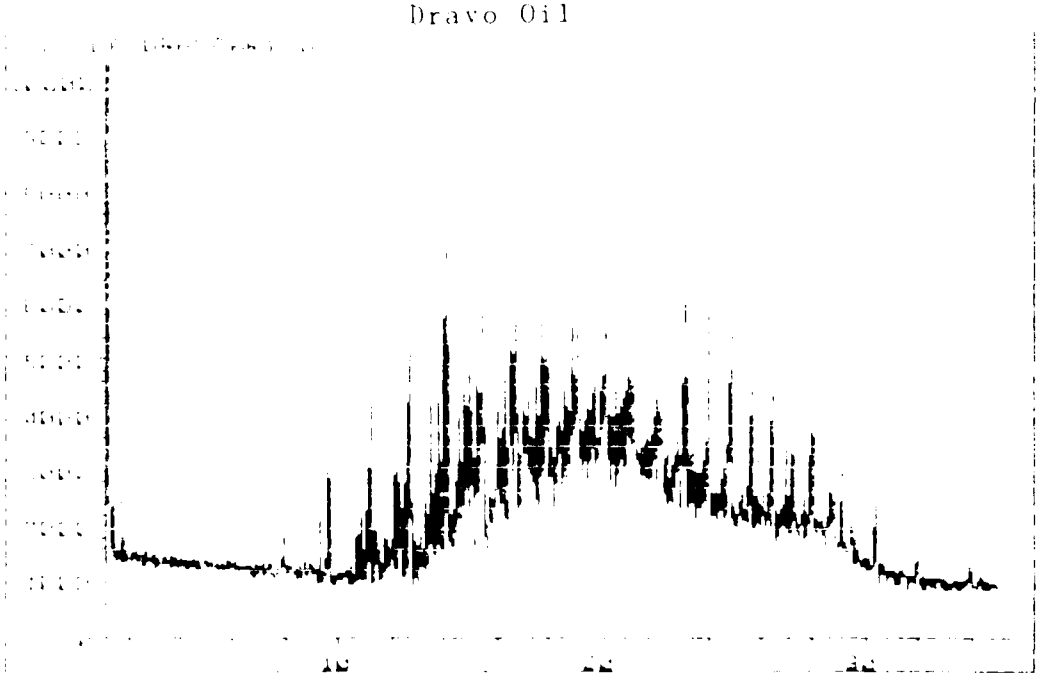
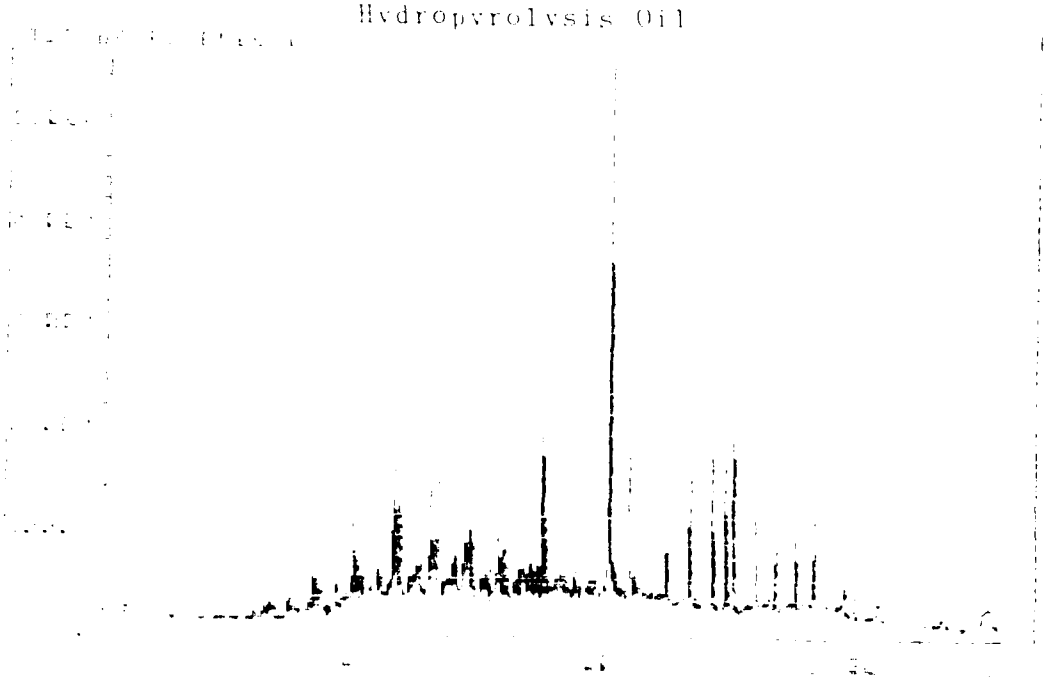


Figure 24

Total Ion Chromatograms of the Alkene Fractions

Hydropyrolysis Oil



Bravo Oil

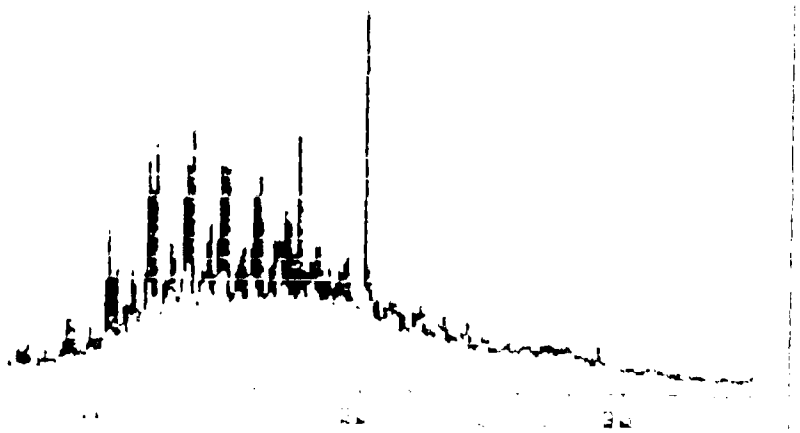
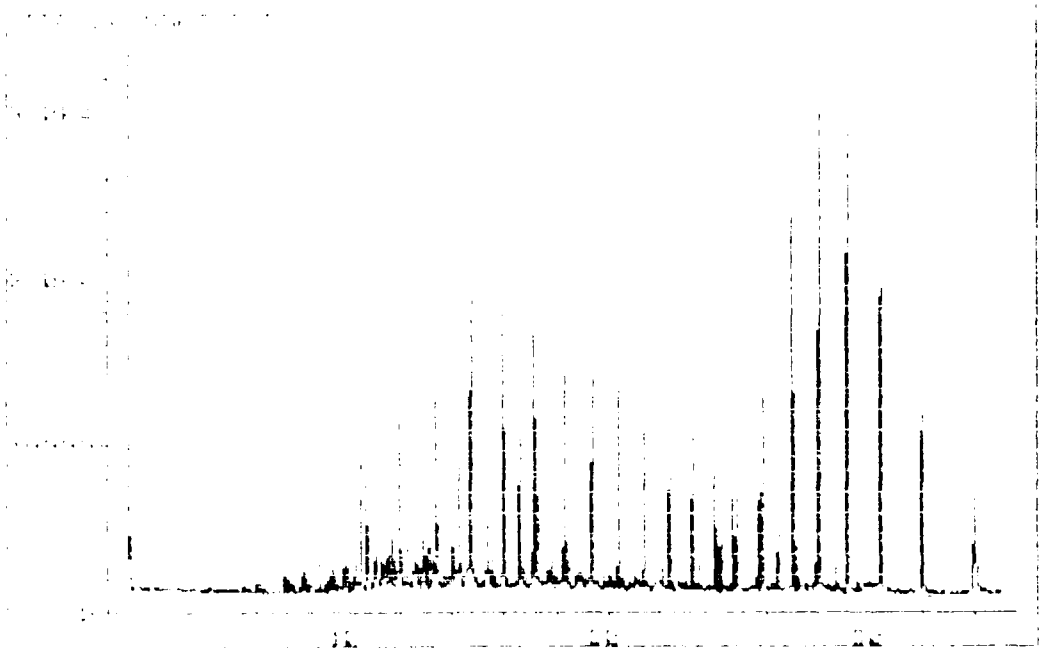


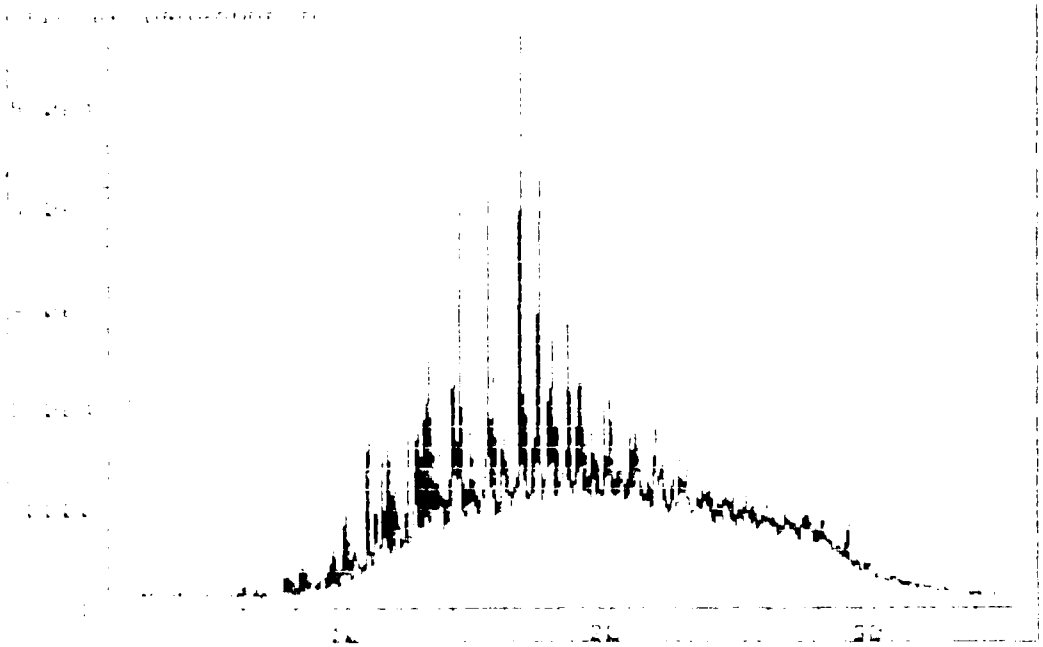
Figure 22

Total Ion Chromatograms of the Napthene Fractions

Hydropyrolysis Oil



Dravo Oil



APPENDIX D

TOTAL ION CHROMATOGRAMS OF SEPARATED FRACTIONS

APPENDIX F

ORGANIC CARBON CONVERSION AND OIL SELECTIVITY PROGRAM LISTING

Computer listing of the program devoloped to calculate organic carbon conversion and oil selectivity

```
5  INPUT T$
7  IF T$ =  CHR$ (89) THEN 12
9  IF T$ =  CHR$ (78) THEN 86
10  IF T$ =  CHR$ (81) THEN 1600
11  GOTO 3
12  PRINT D$;"PR#1"
13   PRINT "THIS PROGRAM IS DESIGNED TO CALCULATE THE CARBON
CONVERSION AND"
15  PRINT "OIL YIELD.   ALSO,  A HYDROGEN BALANCE AND CARBON
BALANCE ARE CALCULATED"
17  PRINT "INPUT TO THE PROGRAM SHOULD BE AS FOLLOWS:"
19  PRINT "  "
21  PRINT "      1)  RUN INDENTIFICATION"
23  PRINT "      2)  ABSOLUTE RESPONSE FACTORS IN THIS ORDER:
25  PRINT "           H2 = 1       i-C4 = 5     C2H4 =  9"
27  PRINT "           KR = 2       H2S = 6      C2H6 = 10"
29  PRINT "         C3H8 = 3       n-C4 = 7     CH4 = 11"
31  PRINT "         C3H6 = 4       CO2 = 8      CO = 12"
33  PRINT "      3)  MOLE FRACTION HYDROGEN IN FEED GAS"
35  PRINT "      4)  MOLE FRACTION KRYPTON IN FEED GAS"
37  PRINT "      5)  INITIAL PRESSURE (psig)"
39  PRINT "      6)  INITIAL TEMPERATURE (DEGREES C)"
41  PRINT "      7)  MOLE FRACTION NAPHTHALENE IN "
43  PRINT "      8)  MOLE FRACTION NAPHTHALENE OUT"
45  PRINT "      9)  GRAMS SOLVENT IN "
47  PRINT "     10)  GRAMS SHALE IN "
49  PRINT "     11)  WEIGHT FRACTION OF CARBON IN"
51  PRINT "     12)  WEIGHT FRACTION CARBON OUT"
53  PRINT "     13)  WEIGHT FRACTION ASH IN"
55  PRINT "     14)  WEIGHT FRACTION ASH OUT"
57  PRINT "     15)  WEIGHT FRACTION ORGANIC CARBON IN"
59  PRINT "     16)  WEIGHT FRACTION ORGANIC CARBON OUT"
61  PRINT "     17)  H2 AREA "
63  PRINT "     18)  KRYPTON AREA"
65  PRINT "     19)  N2 AREA"
67  PRINT "     20)  C3H8 AREA"
69  PRINT "     21)  C3H6 AREA"
71  PRINT "     22)  i-C4 AREA"
73  PRINT "     23)  H2S AREA"
75  PRINT "     24)  n-C4 AREA"
77  PRINT "     25)  CO2 AREA"
79  PRINT "     26)  C2H4 AREA"
81  PRINT "     27)  C2H6 AREA"
83  PRINT "     28)  CH4 AREA"
```

```
82  PRINT "     29)  CO AREA"
83  FOR I = 1 TO 32
84  PRINT " "
85  NEXT I
86  PRINT D$;"PR#0"
87   INPUT "INPUT TODAY'S DATE USING THIS  FORMAT  05/30/84:
";B$
88  PRINT "INPUT THE ABSOLUTE RESPONSE FACTORS"
89  FOR I = 1 TO 13
91  PRINT "R("I") = "
92  INPUT R(I)
93  NEXT I
94  FOR I = 1 TO 13
95  PRINT "R("I") = ";R(I)
96  NEXT I  PRINT "IS INPUT CORRECT (Y=YES; N=NO)?"
99  INPUT T$
101  IF T$ =  CHR$ (89) THEN 113
103  IF T$ =  CHR$ (78) THEN 107
105  GOTO 97
107   INPUT  "INPUT THE NUMBER OF THE RESPONSE FACTOR TO  BE
CORRECTED:  ";I
109  INPUT "INPUT THE NEW VALUE:  ";R(I)
111  GOTO 97
113  INPUT "RUN IDENTIFICATION = ";A$
115  FOR I = 1 TO 27
117  PRINT "C("I") = "
118  INPUT C(I)
119  NEXT I
120  FOR I = 1 TO 27
121  PRINT "C("I") = ";C(I)"    C("I + 1") = ";C(I + 1)
122 I = I + 1
123  NEXT I
124  PRINT "IS ALL THE INPUT CORRECT (Y=YES; N=NO)"
125  INPUT T$
127  IF T$ =  CHR$ (89) THEN 141
129  IF T$ =  CHR$ (78) THEN 133
131  GOTO 124
133   INPUT  "INPUT  THE  NUMBER OF THE  DATA  POINT  TO  BE
CORRECTED:  ";J
135  INPUT "INPUT THE NEW VALUE:  ";C(J)
137  GOTO 124
141 PE = R(1) / R(2)
320 AP = (C(3) / 12.3) + 1.0
330 BT = C(4) + 273.15
335   REM  :NOTE THAT THE FOLLOWING STATEMENT ASSUMES A  GAS
HEAD SPACE OF 0.22927 LITERS
340 TM = (AP * 0.22927) / (.08205 * BT)
350 HM = TM * C(1)
```

```
360 AM = TM * C(2)
370  REM :  CALCULATE GAS COMPOSITIONS
440 O2 = C(17) * 0.19
450 C2 = C(16) - O2
460 NH = AM * (C(15) / C2) * PR
470 DL = HM - NH
475 D2 = DL * 2
550 MT = C(7) / 132
560 NM = (MT) * (C(6) - C(5))
570 NS = NM * 2
580 N2 = NS * 2
590 GC = D2 + N
600  REM : PART II - YIELD CALCULATIONS
890 R(1) = 3
895 H(1) = 8
900 R(2) = 3
905 H(2) = 6
910 R(3) = 4
915 H(3) = 10
917 R(4) = 0
918 H(4) = 2
920 R(5) = 4
925 H(5) = 1
930 R(6) = 1
935 H(6) = 0
940 R(7) = 2
945 H(7) = 4
950 R(8) = 2
955 H(8) = 6
960 R(9) = 1
965 H(9) = 4
970 R(10) = 1
975 H(10) = 0
980 ML = 0.
985 MH = 0
987  FOR I = 1 TO 10
988  IF I = 6 THEN 997
989  IF I = 10 THEN 998
990 ML = ((AM * C(I + 17) * R(I + 3) * B(I)) / (C2 *  R(3)))
+ ML
995  MH = ((AM * C(I + 17) * R(I + 3) * H(I)) / (C2 * R(3)))
+ MH
996  GOTO 1000
997 ML = ((AM * C(I + 17) * R(I + 3) * B(I)) / (C2 *  R(2)))
+ ML
998  MH = ((AM * C(I + 17) * R(I + 3) * B(I)) / (C2 * R(2)))
+ MH
1000  NEXT I
```

```
1010 CG = 12.01115 * ML
1020 HG = 1.0079 * MH
1025  CI = ((C(27) * B(10) * R(13) + C(23) * B(6) * R(9))  *
AM) / (C2 * R(3))
1027 CC = 12.01115 * CL
1040  REM : CALCULATE OIL YIELD
1150 SO = C(8) * (C(11) / C(12))
1160 CN = (C(8) * C(9)) - (SO * C(10))
1170 OY = ((CN - CG) / CN) * 100.
1180  REM : CALCULATE ORGANIC CARBON CONVERSION
1230 PO = (1 - ((SO * C(14)) / (C(8) * C(13)))) * 100.
1240  REM : CALCULATE PERCENT HYDROGEN CONSUMPTION
1250 OP = (CN - CG) / .83
1260 PH = (GC / OP) * 100
1265 WW = ((GC - HG) / OP) * 100
1270 SF = (350 * .9 * 359 * .5 * PH) / 100
1275 YY = (350 * .9 * 359 * .5 * WW) / 100
1277  PRINT D$;"PR#1"
1278  GOTO 1416
1279  PRINT "THE OUTPUT IS AS FOLLOWS:"
1280  PRINT : PRINT "RUN IDENTIFICATION= ";A$
1290  PRINT "GRAMS OF HYDROGEN CONSUMED, GAS PHASE =";D2
1300  PRINT "GRAMS OF HYDROGEN CONSUMED, SOLVENT =";N2
1305   PRINT "GRAMS OF HYDROGEN ACCOUNTED FOR IN H2S AND  HC
GASES=";HG
1310  PRINT "TOTAL GRAMS OF HYDROGEN CONSUMED =";GC
1315  PRINT "TOTAL GRAMS OF HYDRO
GEN CONSUMED BY OIL=";GC - HG
1320  PRINT "GRAMS OF CARBON IN COX GASES =";CC
1340  PRINT "GRAMS OF CARBON IN TOTAL GASES =";CG
1350  PRINT "OIL YIELD, % =";OY
1360  PRINT "ORGANIC CARBON CONVERSION,% =";PO
1370  PRINT "HYDROGEN CONSUMED,% =";PH
1375  PRINT "HYDROGEN CONSUMED BY OIL,%=";WW
1383  FOR I = 1 TO 12
1384  PRINT
1385  NEXT I
1386  PRINT D$;"PR#0"
1387   PRINT  "IS  ANOTHER RUN WITH THE  SAME  DATA  DESIRED
(Y=YES; N=NO)?"
1388  INPUT T$
1389  IF T$ =  CHR$ (89) THEN 141
1390  IF T$ =  CHR$ (78) THEN 1394
1391  GOTO 1387
1394   PRINT "IS ANOTHER ANALYSIS TO BE PERFORMED  WITH  THE
SAME RESPONSE FACTORS? (Y=YES; N=NO)"
1395  INPUT T$
1400  IF T$ =  CHR$ (89) THEN 113
```

```
1405  IF T$ =  CHR$ (78) THEN 1411
1410  GOTO 1390
1411   PRINT  "WOULD YOU LIKE TO CHANGE A FEW OF  THE  DATA?
(Y=YES; N=NO)"
1412  INPUT T$
1413  IF T$ =  CHR$ (89) THEN 120
1414  IF T$ =  CHR$ (78) THEN 1600
1416  PRINT " "; TAB( 60);B$
1417  PRINT
1418  PRINT
1419   PRINT "BELOW ARE THE DATA USED TO GENERATE THE OUTPUT
FOR"
1420  PRINT
1425  PRINT "            FEED GAS COMPOSITION"
1430   PRINT "MOLE FRACTION H2 "C(1)"     MOLE  FRACTION  Ar
"C(2)
1432  PRINT
1435  PRINT "           INITIAL CONDITIONS"
1440  PRINT "TEMP. "C(4)" DEGREES C","PRESSURE "C(3)" psig"
1445  PRINT "GRAMS SHALE "C(8),"GRAMS SOLVENT "C(7)
1447  PRINT
1450  PRINT "                  WEIGHT FRACTIONS"
1455   PRINT "          CARBON";  TAB(  27);"ASH";  TAB(  41)
;"ORGANIC"
1460  PRINT "IN        "C(9); TAB( 26);C(11); TAB( 41);C(13)
1465  PRINT "OUT       "C(10); TAB( 26);C(12); TAB( 41);C(14)
1470  PRINT
1475  PRINT "COMPONENT       AREA         RESPONSE FACTOR"
1480  PRINT "  H2",C(15); TAB( 33);R(1)
1483  PRINT " Kr",C(16); TAB( 33)
;R(2); TAB( 52);R(3)
1486  PRINT "C3H8",C(18),R(4)
1489  PRINT "C3H6",C(19),R(5)
1492  PRINT "i-C4",C(20),R(6)
1495  PRINT " H2S",C(21),R(7)
1498  PRINT "n-C4",C(22),R(8)
1501  PRINT " CO2",C(23),R(9)
1504  PRINT "C2H4",C(24),R(10
1507  PRINT "C2H6",C(25),R(11)
1510  PRINT " CH4",C(26),R(12)
1513  PRINT "  CO",C(27),R(13)
1515  FOR I = 1 TO 4
1518  PRINT
1521  NEXT I
1524  GOTO 1279
1600  END
```

APPENDIX G

MINITAB INPUT AND OUTPUT

Sample input and output for the MINITAB program

```
MINITAB RELEASE 81.1 *** COPYRIGHT - PENN STATE UNIV. 1981
JUNE 10, 1983 *** Colorado School of Mines * DECsystem-1091
STORAGE AVAILABLE  19800

*** THIS RELEASE OF MINITAB IS OBSOLETE ***

-- READ C1,C2

-- 7.657,.6079

-- 4.6729,.1745

-- 2.959,.0325

-- BRIEF

-- CONSTANT

-- REGRESS ; C1 1 C2

THE REGRESSION EQUATION IS
Y =     2.96 +  7.87 X1

                                          ST. DEV.     T-RATIO =
        COLUMN      COEFFICIENT           OF COEF.     COEF/S.D.
        --              2.9599             0.3748          7.90
X1      C2               7.865             1.025           7.67

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.4346
WITH (    3- 2) =    1 DEGREES OF FREEDOM

R-SQUARED - 98.3 PERCENT
R-SQUARED = 96.7 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

 DUE TO      DF            SS        MS=SS/DF
REGRESSION    1        11.1157        11.1157
RESIDUAL      1         0.1888         0.1888
TOTAL         2        11.3045
```

END

FILMED

8-85

DTIC