

The Thermal Solution
Pyrolysis of a Luxembourg Oil Shale

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

Golden, Colorado

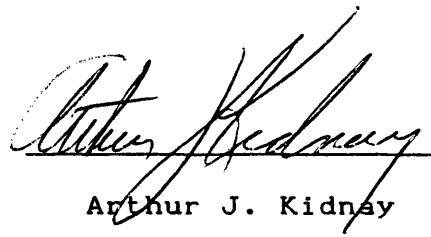
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DEDICATION

To my beautiful and loving wife Karen who gave me the motivation and support to finish and to my late grandfather Eugene A. Johnson for the inspiration to begin.

ABSTRACT

The pyrolysis and hydrolysis of a Luxembourg oil shale was carried out in a 1-liter stirred batch reactor in the presence of supercritical toluene solvent with and without the presence of gas phase molecular hydrogen and water. It was found that the conversion of organic carbon to oil products could be adequately modeled by a second order irreversible rate equation for reactions when no water was added to the reaction mixture. For the runs with small amounts of water added to the reaction mixture the results were unclear as to which kinetic model was most accurate for describing the system. Organic carbon conversions were greatest for the reactions where a hydrogen gas atmosphere with water was present. A temperature crossover effect was observed for the effect on organic carbon conversion of hydrogen gas. Five oil samples were characterized by open column chromatography and capillary column GC/MS to observe the effect of hydrogen gas and water on oil product chemistry.

TABLE OF CONTENTS

	Page
ABSTRACT	iv
LIST OF FIGURES	vii
LIST OF TABLES	ix
ACKNOWLEDGMENTS	x
INTRODUCTION	1
LITERATURE SURVEY	3
EXPERIMENTAL DESIGN	7
Phase One	7
Phase Two	9
Phase Three	9
EQUIPMENT AND MATERIALS	11
Oil Shale	11
Reactor System	11
Carbon Analyzer	14
Gas Product Analysis	14
Column Chromatography	15
GC/MS	15
ANALYTICAL AND EXPERIMENTAL PROCEDURES	17
Reactor Runs	17
Sample Preparation	18
Fractionation of Oil Samples	19

DATA ANALYSIS	26
Organic Carbon Conversion	26
Oil Selectivity	26
Kinetic Modeling	27
GC/MS Identification	29
RESULTS AND DISCUSSION	30
System Constraints and Data Errors	30
Phase One	35
Phase Two	39
Phase Three	60
CONCLUSIONS	84
RECOMMENDATIONS	86
LITERATURE CITED	87
APPENDIX A - Reactor Runs Data	92
APPENDIX B - Column Chromatography Data	128
APPENDIX C - Reactor Control Program	139

LIST OF FIGURES

Figure		Page
1	Reactor System	13
2	Extraction Scheme	20
3	Fractionation Scheme	25
4	Hydrogen Atmosphere Conversion Isotherms	36
5	375°C Isotherms	42
6	425°C Isotherms	43
7	Helium - 375°C	51
8	Helium - 425°C	52
9	Hydrogen - 375°C	53
10	Hydrogen - 400°C	54
11	Hydrogen - 425°C	55
12	Helium/Water - 375°C	56
13	Helium/Water - 425°C	57
14	Hydrogen/Water - 375°C	58
15	Hydrogen/Water - 425°C	59
16	Fischer Assay TIC - Fraction 2	67
17	Helium TIC - Fraction 2	68
18	Hydrogen TIC - Fraction 2	69
19	Helium/Water TIC - Fraction 2	70
20	Hydrogen/Water TIC - Fraction 2	71

21	Fischer Assay TIC - Fraction 4	73
22	Helium TIC - Fraction 4	74
23	Hydrogen TIC - Fraction 4	75
24	Helium/Water TIC - Fraction 4	76
25	Hydrogen/Water TIC - Fraction 4	77
26	Fischer Assay TIC - Fraction 6	79
27	Helium TIC - Fraction 6	80
28	Hydrogen TIC - Fraction 6	81
29	Helium/Water TIC - Fraction 6	82
30	Hydrogen/Water TIC - Fraction 6	83

LIST OF TABLES

Table	Page
1 Phase One Experimental Matrix	8
2 Phase Two Experimental Matrix	10
3 Modified Fischer Assay of Luxembourg Shale Oil	12
4 Chromatographic Separation of Shale Oil	16
5 Pure Component Fractionation	22
6 Chromatographic Elution Sequence	23
7 Phase One Results	38
8 Phase Two Results	41
9 Results of Hydrochloric Acid Experiments	47
10 Results of Kinetic Modeling	49
11 Phase Three Fractionation Results	61-62
12 Comparison of Heavy Polymers vs. Carbon Conversion.	64

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Lastly, the financial support provided by Southern Pacific Petroleum, N.L., is acknowledged.

INTRODUCTION

Vast resources of potential liquid fuel products exist in oil shale deposits located throughout the world. Dropping petroleum prices have resulted in diminished active exploitation of these reserves in the last several years. Despite this fact the search for more efficient processes for the conversion of the kerogen contained in oil shale continues. The impetus for this research is the inevitability of the long range depletion of crude oil reserves and the concurrent rise in their value.

The principal thrust in oil shale technology has been in retorting processes. Retorting however suffers from the liability of low conversions of kerogen to liquid products due to cracking and condensation reactions resulting in the production of gases and coke respectively.

Thermal solution techniques for the conversion of oil shale use a continuous fluid phase to solubilize products resulting from the degradation of the kerogen matrix. Much lower temperatures can be employed to effect conversions which can be significantly greater than those obtained by retorting. The use of hydrogen as a component of the fluid phase enhances the conversion according to Jensen (1). Work done in this laboratory by Briley (2) has shown that the

presence of water in the fluid phase decreases the consumption of hydrogen dramatically while maintaining high conversions of organic carbon to oil products.

The purpose of this research is to investigate the effect of water on the thermal solution pyrolysis of a Luxembourg oil shale by examining the conversion kinetics and the chemical composition of the products derived.

LITERATURE SURVEY

Oil shale is a fuel source found on all of the world's continents. Estimates of total world reserves range from 3,000 billion (3) to 2,000,000 billion (4) barrels of shale oil. Deposits in Europe account for approximately 12% of the known recoverable resources according to a U.S. Geological Survey study (5). The oil shale used in this study was from a deposit located in the European country of Luxembourg.

Processing of oil shale into a usable fuel source consists of converting the kerogen contained in the shale to liquid and gaseous products. Kerogen can be described as a three dimensional polymer, insoluble in conventional organic solvents, associated with small amounts of a benzene soluble material, bitumen (6).

There are several methods to recover oil shale kerogen as petroleum type feedstocks. The first technology to be employed was retorting. Retorting involves the thermal pyrolysis of the organic matter. The liquid and gaseous products are collected from the retort after cooling. Conventional retorting suffers from high gas production and low kerogen conversions (7). Of the several processes

T-3098

capable of producing shale oil only retorting has received the attention necessary to develop a commercial industry (8).

Hydroretorting is a variation of standard retorting where hydrogen gas is introduced. Hydroretorting can result in organic carbon recoveries 2.0 to 2.5 times those of a standard retort for some shales (9). Schlinger (10) found that the addition of water reduced the hydrogen consumption and the heat load necessary to produce shale oil under hydroretorting conditions.

An alternative to retorting for the recovery of shale oil is the thermal solution process. Thermal solution techniques consist of heating a shale/solvent slurry at temperatures generally lower than those in a conventional retort. Recovery of organics from oil shale by solvent extraction usually results in low yields at temperatures near the boiling point of the solvent (11). At higher temperatures the yields of products increase dramatically. D'yakova reports yields of 72 to 96 percent of organics extracted at temperatures from 385°C to 420°C (12,13,14), well below efficient retorting temperatures.

Results from an investigation on Green River oil shale by Jensen (1) also showed that high organic conversions could be obtained by thermal solution. The solvent role in thermal solution can include acting as a vehicle for

T-3098

hydrogen transfer (15). In a patent for a thermal solution process which was granted to Green (16) oil shale was reacted with tetralin in the presence of hydrogen at pressures from 10-200 atmospheres and at temperatures from 300-650°C. Green reported high yields of liquid hydrocarbons are obtained with reduced hydrocarbon gas yields compared to conventional retorting.

Patzer (17) examined the shale oil products from thermal solution and reported an increase in asphaltenes and aromatics compared to oil produced by retorting.

Williams (18) observed that when certain solvents are employed in thermal solution extraction, the yields are increased significantly when the solvent is above its critical temperature and critical pressure. This phenomenon was also observed by Maddox (19) for the extraction of organics from coal using toluene as a solvent. Baldwin (20) has investigated the supercritical extraction of an Australian shale with toluene in a hydrogen atmosphere and reported yields 160 percent above Fischer Assay. McKay (21) investigated the supercritical extraction of Green River oil shale and found a polar methanol/water fluid effective for recovering high yields of organic matter at a reaction temperature of 400°C. A tetralin/water system was also found to give conversions greater than tetralin alone (22).

Briley (2) has found that the addition of water

significantly reduced the hydrogen consumption in a supercritical thermal solution process using tetralin solvent.

The literature cited above indicate the feasibility of obtaining high yields of organic carbon products using the thermal solution process. Concurrent hydrogenation with the presence of water has also been shown to be effective in increasing yields and decreasing hydrogen consumption.

EXPERIMENTAL DESIGN

Phase I

The primary objective of the first phase of this project was to determine a range of temperatures which gave experimentally valuable results for modeling the kinetics of conversion. A standard reaction mixture was chosen and temperatures from 300°C to 450°C were investigated. The standard reaction mixture chosen consisted of 25 grams of oil shale which had been sized to -200 mesh and dried for 48 hours at 125°C. 200 ml of reagent grade toluene was charged to the reactor as the fluid phase and 300 psia cold charge hydrogen was added after the reactor had been purged with helium. The toluene and hydrogen were heated to 25°C above the desired reaction temperature and the shale along with 100 ml additional toluene were injected into the reactor from a helium-gas-propelled addition vessel. The reactor reached the desired isothermal temperature within one minute after injection of the shale slurry. Samples withdrawn from the reactor during the run were analyzed for conversion.

Table 1
Phase One Experimental Matrix

Reaction Temperature(^o C)	Sample Times (min.)
300	10, 30, 60
375	10, 30, 60
425	10, 30, 60
450	5, 10, 30, 60

- all runs with 300 psia initial hydrogen pressure at room temperature.

Phase II

Objectives for the next phase were to examine the effects upon the conversion of kerogen by the addition of water to the system. The amount of water added, the effect of pH and the simultaneous presence or absence of molecular hydrogen were chosen as reaction parameters to be examined. After examining the effects of water, an additional goal was to model the kinetics of conversion. The models examined were for the irreversible conversion of kerogen to gas and oil products.

Phase III

Characterization of the liquid products formed from selected reaction conditions was the purpose of the third phase of this project. It was hoped that this would result in some observable effect on product composition from varying those reaction parameters which had been previously examined for their effect upon the reaction kinetics.

Table 2
Phase Two Experimental Matrix

Reaction Conditions	Reaction Temperature ($^{\circ}\text{C}$)
Helium	375, 425
Hydrogen	375, 400, 425
Hydrogen (200 psia)	400
Helium/Water	375, 425
Helium/Water (20 ml)	375
Hydrogen/Water	375, 425, 450

- unless indicated all runs were with an initial gas pressure of 300 psia at room temperature.

- unless indicated the amount of water used was 2.0 ml.

T-3098

EQUIPMENT AND MATERIALS

Oil Shale

The Luxembourg deposit shale was supplied by Southern Pacific Petroleum, N.L. in the form of large solid pieces 1 to 3 inches in size. This material was ground wet with water at the C.S.M.R.I. to a granular consistency. This slurry was dried in an oven at 115°C and reduced further to -200 mesh with a mortar and pestle. This served as the raw shale used in all reactor runs. Fisher Assay results for this shale are provided in Table 3.

Reactor System

The reactions were performed in a 1-liter batch autoclave reactor manufactured by Autoclave Engineers Inc.. A schematic of the reactor system is shown in Figure 1. The computer control program used to monitor and adjust the temperature of the reactor is included in Appendix D. The reactor was constructed of 316 S.S. and rated to 10,000 psi. There was a centrally mounted impeller and a baffle to provide agitation. Heat was supplied by an electric resistance jacket and cooling by an internal coil supplied with tap water. A stainless-steel cylinder with connection

Table 3
Modified Fischer Assay of Luxembourg Oil Shale

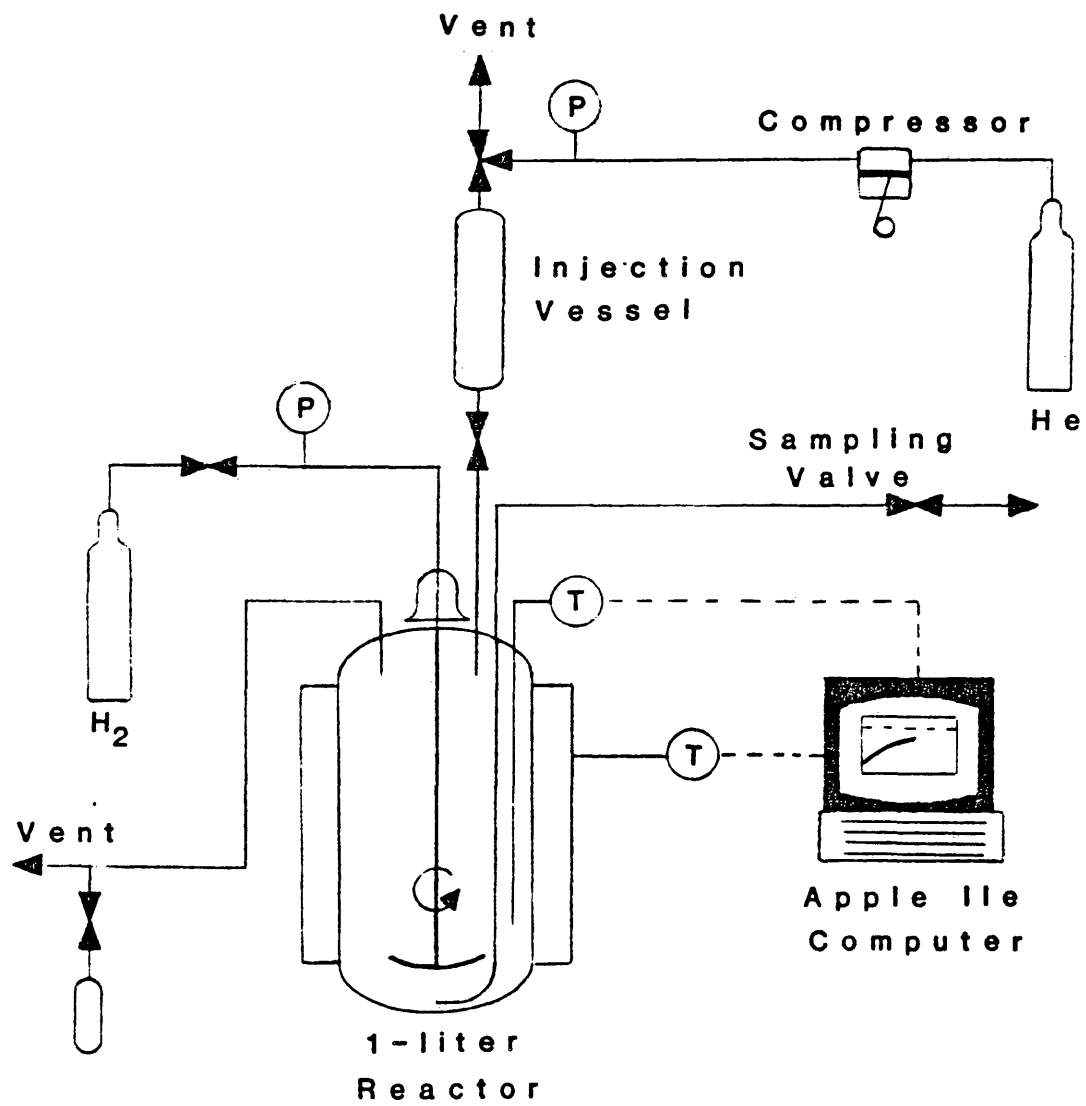
	Yield (wt. %)
Oil	3.6
Gas	1.3
Water	3.4
Spent Shale	91.7

Organic Carbon Conversion - 45.2 %

- results are for conversion to oil and gas products

- analysis performed by J&A Associates of Golden, Colorado.

Figure 1
Reactor System



T-3098

to high pressure helium was used as an injection vessel to the reactor. Temperature was monitored by a thermowell into the reactor internals and pressure by electronic transducer.

Carbon Analyzer

The analysis of total and inorganic carbon on feed and spent shale samples was performed on a Model 5020 carbon dioxide coulometer manufactured by Coulometrics Inc.. The amount of organic carbon was calculated by difference. Samples were performed in triplicate and results averaged for both total and inorganic carbon. Calcium carbonate was used as a control standard for both analyses.

Gas Products Analysis

The reaction gases were analyzed on a Carle Model 111-H gas chromatograph. An inert argon tracer gas was used as internal standard for quantifying hydrocarbon and carbon oxide gases. Results were retrieved on a HP Model 3390A integrator/printer.

Column Chromatography

Selected oils were fractionated on a Fischer Porter 15 mm O.D. glass open column chromatography column. The packing used was 23 grams alumina over 58 grams activated silica gel. The column was run isothermally with gravity fed elution of the oil by chromatographic grade solvents. The chemical groups extracted for each fraction collected from the column are shown in Table 4. The column was cleaned and repacked with fresh asbestos after each run.

GC/MS

The fractions from the open column chromatography were further characterized by running them on a HP 5890 gas chromatograph coupled to a HP 5790A ion selective detector. Operating software allowed the individual peaks from these runs to be identified by comparison with compounds in the NBS Mass Spectral Library.

Table 4
Chromatographic Separation of Shale Oil

Fraction #	Chemical Group
1	Void Volume
2	Alkanes and Naphthenes
3	
4	Alkenes
5	Dienes
6	Start of Aromatics
7-12	
13	End of Aromatics
14	
15	Nitriles
16	Ketones
17-21	Polymeric Material

ANALYTICAL AND EXPERIMENTAL PROCEDURES

Reactor Runs

250 ml of toluene was charged to the clean reactor. The stirrer was turned on and maintained at 1500 rpm. The reactor was sealed and then purged twice with 300 psia of helium gas. After purging, the desired cold initial pressure of either hydrogen or helium was charged. The heater was raised into position and the computer program run to heat the reactor contents to a temperature 25°C above the desired run temperature.

While the reactor heated up, 25 grams of shale was slurried with 100 ml of toluene on a magnetic stirrer. When the reactor temperature reached 25°C above the desired run temperature, the shale slurry was charged to the injection vessel along with water if desired. The injection vessel was sealed and purged twice with helium. The injection vessel was then pressurized with 1700 psia of helium and the valve between the reactor and the injection vessel was opened.

The run clock was started when the desired run temperature was reached, generally within 1.5 minutes after injection of the slurry. As the reaction proceeded a time/temperature plot was recorded on the computer CRT. Samples were removed from the reactor at appropriate times

T-3098

during the run through the sample collection valving. Sample sizes were approximately 5 ml in volume containing less than 1 gram of shale.

When the run was completed, the heater was turned off and lowered. The cooling water was turned on along with an external fan. When the reactor temperature reached 25°C a reaction gas sample was taken for analysis of carbon oxides and hydrocarbon gases.

The remaining gas was vented and helium was used to force the remaining slurry out of the reactor through the sample collection system. The injection vessel was removed and cleaned of any remaining uninjected shale slurry. The reactor was rinsed with aliquots of solvent until all remaining slurry was removed and then dried with a compressed air gas stream.

Sample Preparation

Solids

Slurry samples removed during the reactor run were collected in 500 ml clean glass centrifuge bottles labeled with the appropriate run number and reaction time.

These samples were washed and centrifuged twice with 50 ml of toluene and again twice with methylene chloride. The resulting solvent washed shale samples were dried at 125°C

T-3098

for 24 hours in an oven. The dried samples were collected in 20 ml glass sample vials to await carbon analysis.

Oils

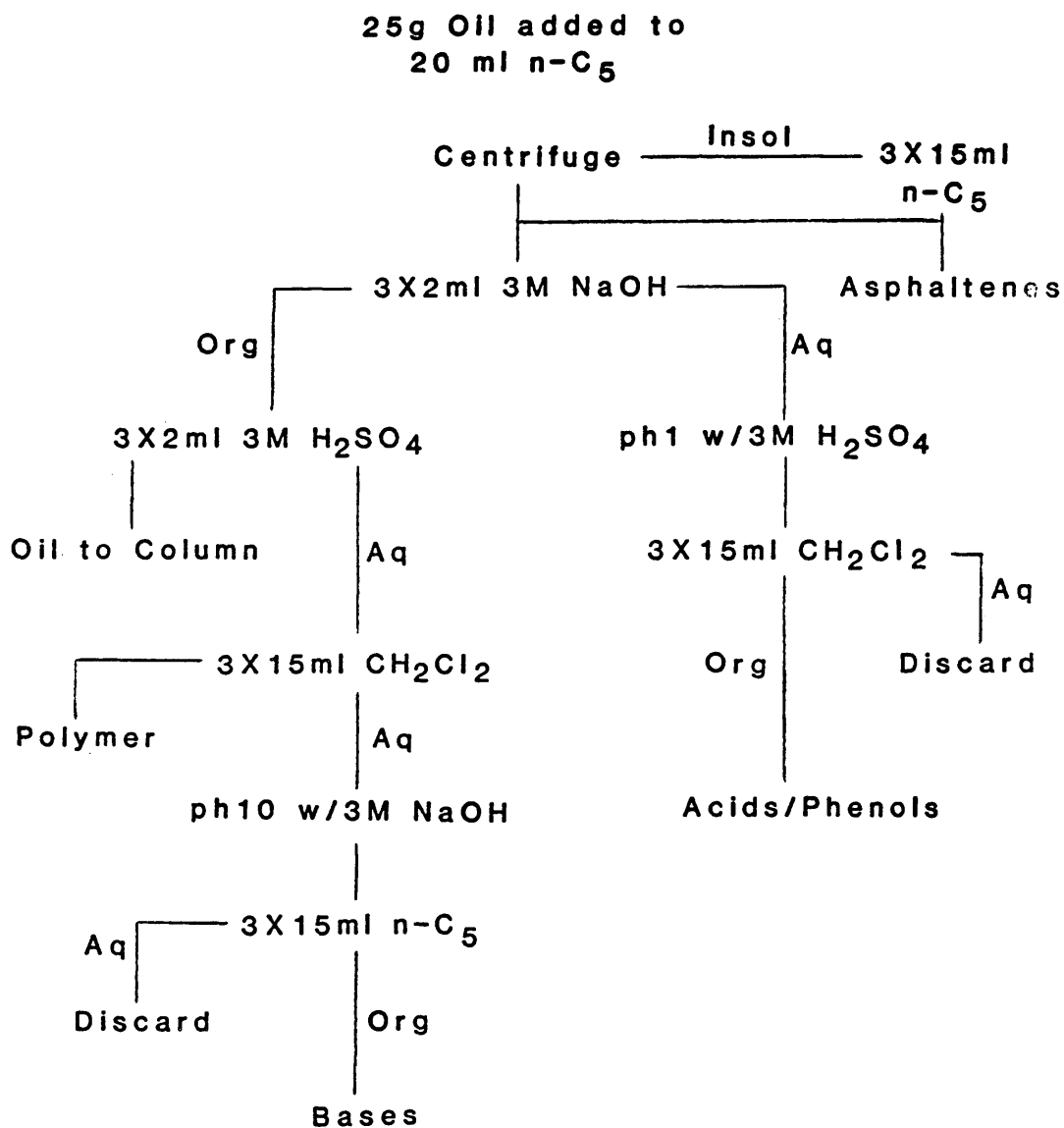
The liquid phase recovered from the bulk of the reaction slurry was decanted from the spent shale after centrifugation. The solvent/oil solution was then rotary evaporated to remove the toluene solvent. The remaining oil was weighed, pipetted to a sample vial and stored under refrigeration prior to chromatographic fractionation.

Reaction gases were collected in 500 ml stainless steel gas cylinders through the sampling valve on the reactor. Prior to collection the cylinders were evacuated by a Welch vacuum pump.

Fractionation of Oil Samples

The characterization of oil samples by open column chromatographic separation has been attempted by many other workers (23,24,25,26,27). The method of Rovere and Crisp (28) was chosen for use in this study. The extraction scheme used to isolate the asphaltenes, acids, bases and polymeric material from the raw oil prior to chromatographic separation is shown in Figure 2. There were two modifications made to the procedure. Use of pure component solutions showed that the void volume of the column was 125

Figure 2
Extraction Scheme



T-3098

ml instead of 95 ml. This probably resulted from differences in column packing particle size and packing technique. This difference in void volume did not affect the proper distribution of the solution components into their respective eluate fractions using the same solvent volumes called for by the reference. The components used in the test solutions and the fractions they appeared in are shown in Table 5. The second modification made in the procedure was to collect an additional 250 ml of methanol after fraction 20. This was done to clear the column of chromophoric material which remained on the column. This additional 250 ml of methanol eluate was labeled fraction 21. The reason for the necessity of additional methanol to elute all of the sample could have resulted from slight differences in adsorbants which resulted in a slower elution rate for the most polar components in the oil. The entire solvent elution sequence for the open column chromatographic separation is shown in Table 6.

The 15 mm I.D. glass chromatography column manufactured by Fischer-Porter Co. was slurry packed in hexane with 58 grams of silica gel, followed by 23 grams of alumina. The silica gel and alumina were prepared following the procedures outlined by Rovere and Crisp. The pre-extracted oil sample weighing approximately 1.5 grams was applied to the top of the packing and collection of the fractions was

Table 5
Pure Component Fractionation

Component	Fraction #	Designation by Rovere (28)
Tridecane	2	alkanes
1-Octene	4	alkenes
Propylbenzene	6	alkyl substituted benzenes
Indan	9	C1-C6 substituted indans C2-C5 substituted tetra- hydronaphthalenes
Pyrene	13,14	highly substituted poly- aromatic hydrocarbons
Undecylcyanide	15	nitriles

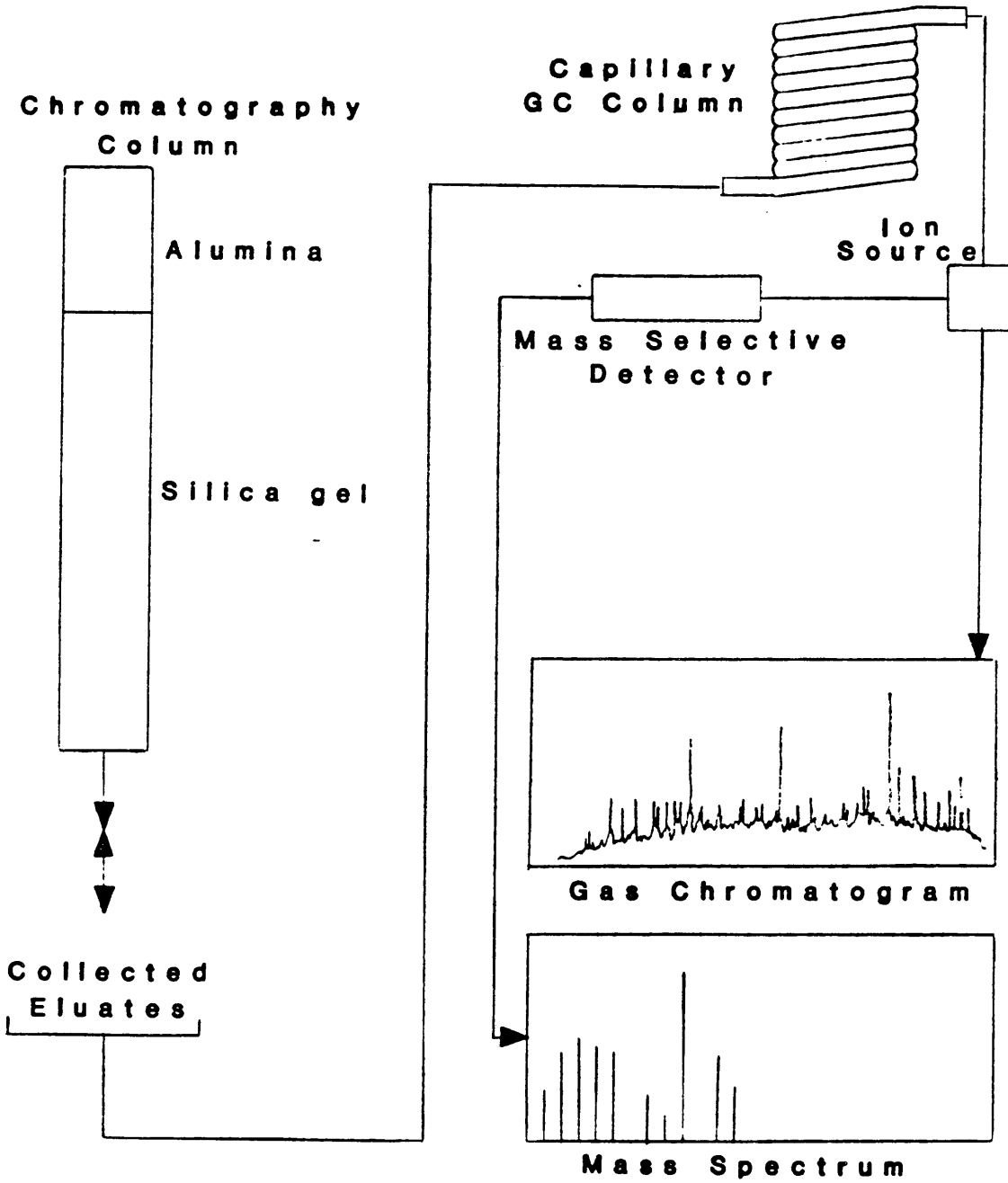
Table 6
Chromatographic Elution Sequence

Fraction	Solvent	Volume (ml)
1	Hexane	125
2	Hexane	35
3	Hexane	10
4	Hexane	35
5	Hexane	40
6	Hexane	100
7	Hexane	85
8	Hexane	50
9	Hexane	50
10	Hexane	100
11	Hexane/Dichloromethane (9:1)	150
12	Hexane/Dichloromethane (9:1)	100
13	Hexane/Dichloromethane (4:1)	150
14	Hexane/Dichloromethane (4:1)	100
15	Dichloromethane	250
16	Dichloromethane/Chloroform (9:1)	250
17	Chloroform/Ether (9:1)	150
18	Chloroform/Ether (9:1)	100
19	Ether	250
20	Methanol	250
21	Methanol	250

T-3098

begun at a rate of 2 ml/min.. The collected eluates were rotary evaporated to remove the solvents and then weighed on a Mettler analytical balance. The samples were then refrigerated until the GC/MS analysis was performed.

Figure 3
Fractionation Scheme



DATA ANALYSIS

Organic Carbon Conversion

The organic carbon conversion data were calculated by performing total and inorganic carbon analyses on the feed shale and the samples collected from the reactor. The organic carbon was calculated from the difference of the total and inorganic results. The organic carbon conversion (OCC) was calculated using the organic carbon data and the following expression.

$$\text{OCC} = \frac{(\% \text{ org. C in feed}) - (\% \text{ org. C in spent shale})}{(\% \text{ org. C in feed})}$$

Oil Selectivity

The oil selectivity was defined as the fraction of the organic carbon converted that resulted in shale oil product. The gas analysis was used to calculate the amount of carbon converted to carbon oxide and hydrocarbon gases. Pure component standard gases were used to generate GC response

T-3098

factors. The total mass of carbon converted to organic carbon products was obtained from the organic carbon analysis. The oil selectivity was then calculated using the following expression.

$$\% \text{ Oil Selectivity} = \frac{(\text{mass of C converted}) - (\text{mass of C in gas})}{(\text{mass of C converted})}$$

Kinetic Modeling

Modeling the conversion of oil shale carbon to gas and oil products was attempted using three different irreversible kinetic expressions for 1st, 2nd and 3/2's orders. The concentration of hydrogen gas was assumed to remain constant and was not included in the rate expression. The mass balance and the accompanying integrated form for each are shown on the following page.

	Mass Balance	Integrated Form
1st Order	$\frac{dX}{dt} = k (a - X)$	$X = a - a e^{-kt}$
2nd Order	$\frac{dX}{dt} = k (a - X)^2$	$X = \frac{kta^2}{kta + 1}$
3/2's Order	$\frac{dX}{dt} = k (a - X)^{3/2}$	$X = a - (0.5 kt + a^{1/2})$

X = Organic Carbon Conversion

t = reaction time

a = pseudo equilibrium conversion

k = rate constant

The pseudo equilibrium conversion was used as a fitting parameter in these models. A linear regression program was used to optimize the R-squared value for all possible values of "a" for each model. The plots for the experimental data and the predicted values for the three models were made on X vs. t axes for each different reaction condition.

GC/MS Peak Identification

The fractions generated by the chromatographic separation of the shale oils were further characterized by GC/MS. The major peaks of selected fractions were identified using the HP 59973 NBS Mass Spectral Library software.

RESULTS AND DISCUSSION

System Constraints and Data Errors

As a result of the manner in which the reactor system was constructed and operated there were several errors inherent in the analysis of the data.

Organic Carbon Conversion

The technique for removing samples from the reactor was such that approximately 0.1 gram of solids were collected per sampling. Removing as small a sample as possible was desirable for two reasons. The first reason was due to the effect removing a sample had on the total system pressure. Approximately 50 to 75 psia was lost upon removing a sample from the reactor. As a result, the pressure dropped continuously in the reactor throughout the course of the run as samples were taken. The second reason that smaller samples were desirable is because there was no method to insure that the sample removed was homogeneous. The result of withdrawing a non-homogeneous sample would be the mole fractions of reaction components changing during the run. Both of these confounding effects were minimized by sampling the smallest amount possible from the reactor

T-3098

contents.

The equation used in this study to calculate organic carbon conversion is not exact. In order to be correct an ash analysis would have to be done on the feed shale and on the sample removed from the reactor. The reason that ash is used in the organic carbon conversion calculation is that it can be safely assumed that ash is unreactive under the reaction conditions and it's mass remains unchanged. As such it serves as a tie-element and forms the basis for the equation shown below.

$$\text{OCC} = \frac{\% \text{ org. C in feed} - \frac{\% \text{ feed ash}}{\% \text{ spent ash}} (\% \text{ org. C in sample})}{\% \text{ org. C in feed}}$$

Unfortunately the ash analysis requires a sample of no less than 1.0 grams. If this large a sample were removed from the reactor the result would be an extremely large system pressure drop. One solution to this dilemma would be to abandon the sampling system and run a separate reaction for each sample. This would allow the entire reactor contents to be removed at the desired sampling time. However this would require approximately four times the number of runs being conducted with associated larger volumes of raw materials being consumed. In addition another error, that of trying to reproduce the same temperature and pressure

T-3098

profile, would be introduced.

Reactor contents were quickly cooled during the Phase I runs and the ash analysis performed. An ash was also done on the feed shale. These results were used to calculate the organic carbon conversion using the rigorous equation and they were compared to the results obtained using the less exact equation. For the four runs made in Phase I these comparisons showed the difference in organic carbon conversion results to be less than 3%. This analysis showed the ratio of ash in the feed to ash in the spent shale remained fairly constant. This is the expected result since mineral species are by far the predominate constituents of this particular oil shale.

Oil Selectivity

In calculating the oil selectivity, the reaction gases were sampled with a 500 ml cylinder through a valve after the contents had cooled to 25°C. Sampling at reaction temperatures would have resulted in a sample containing large amounts of toluene. This solvent, once condensed would contaminate the cylinder. Sampling at temperature would also have resulted in unacceptable pressure loss in the system. Because of these reasons the oil selectivity was not monitored during the course of the reactions.

System Pressure

When the reactor containing the bulk of the toluene used for the reaction had been heated to 25°C above the desired run temperature, the shale slurry was injected into the hot reactor with high pressure helium. The helium was supplied from a cylinder through a back pressure regulator which was set 600 psia above the reactor pressure prior to injection. The injection of the slurry was monitored by observing the reactor pressure rise. The valve from the high pressure helium source was closed when the reactor pressure had stabilized. After closing the the helium valve the reactor pressure continued to rise as a result of the cold slurry being quickly heated. It was not possible to obtain a consistant final system pressure for separate runs in the reactor. As a consequence, the hydrogen partial pressures differed for runs that started with the same 300 psia cold hydrogen charge.

T-3098

Water Content of the System

The oil shale was dried in an oven at 125°C before being used in the reactor to remove the free water present. Since there are inherent amounts of mineral hydrates contained in the inorganic matter of the shale, the absolute effect of water on the reaction is unknown. It can be assumed that the water contained in the mineral hydrates is released at the higher reaction temperatures and would thus contribute to the effects that additional water exerted.

Reaction Temperature

The electric heater that was mounted externally to the bottom shell of the reactor was not capable of raising the temperature of the contents much above 475°C. Because the contents were heated 25°C above the desired run temperature to accommodate the injection of the cold slurry and equilibrate to the run temperature quickly, the range of temperatures examined in this study was bounded at a maximum of 450°C.

Phase One

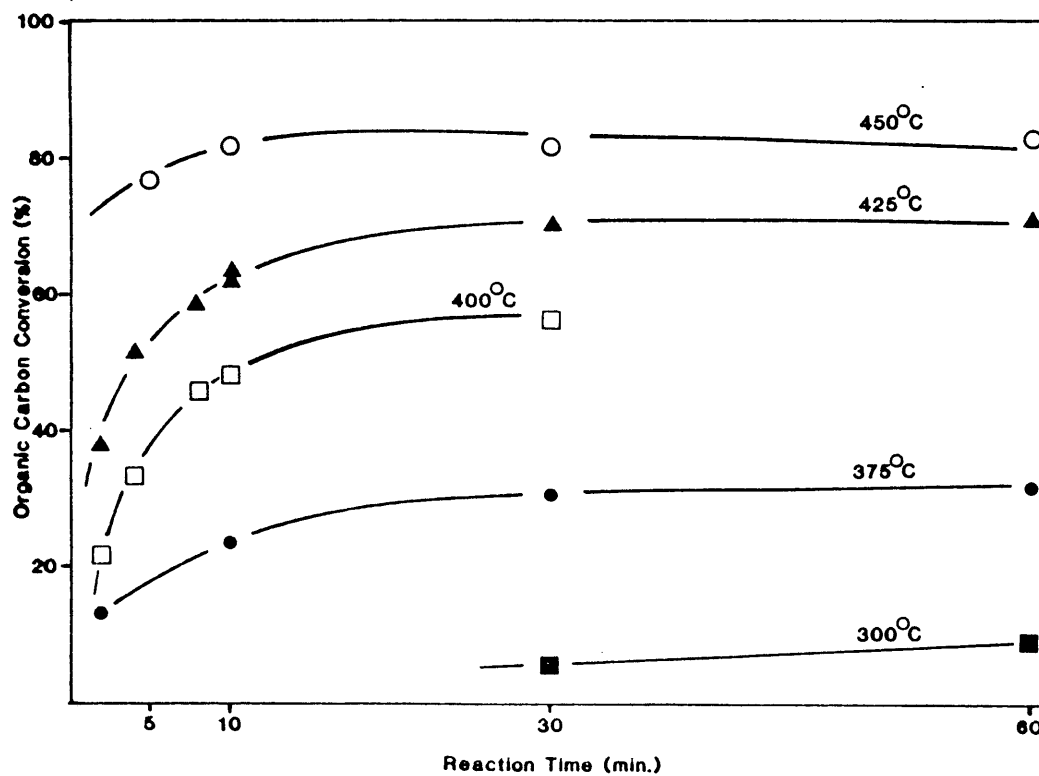
The objectives of the phase one experiments were to observe the effects of temperature and reaction time on the organic carbon conversion and oil selectivity of the Luxembourg oil shale.

The range of temperatures investigated was from 300°C to 450°C. Samples were taken from the reactor at 2 minutes at the earliest and 60 minutes maximum. Conversion isotherms for the five phase one runs are shown in Figure 4. All the phase one runs were made with the standard set of conditions outlined in the experimental design section of this thesis. All of these runs had a cold hydrogen charge of 300 psia.

The results illustrated in Figure 4 show the expected trends in organic carbon conversion as a function of temperature. The conversion increases rapidly with increasing temperatures and asymptotic values for conversion are attained sooner.

Figure 4

Hydrogen Atmosphere Conversion Isotherms



The effect of temperature on the oil selectivity for the same isotherms is shown in Table 7. The 60 minute organic carbon conversions are given along with the oil selectivity for four different temperatures. Only 60 minute points were analyzed for oil selectivity because of system constraints outlined earlier. The oil selectivity decreased with temperature increase but remained well above 90% for all the runs. This is consistent with data collected for a Kentucky oil shale where temperatures above 450°C were investigated in a similar reactor system (29). Results from that study showed a drop in oil selectivity below 90% when the reaction temperature exceeded 460°C.

The increase in conversion with temperature may be a consequence of the increased rate of homolytic reactions taking place. Homolysis of bonds in the kerogen matrix can result in the production of new molecular species which are then solubilized away into the fluid solvent phase. That the oil selectivity decreases as the temperature increases is most likely due to an increased rate of gas forming reactions with high activation energies for which high temperatures are necessary for appreciable quantities of low molecular weight gases to form.

Table 7
Summary of Phase One Results

Reaction Temperature ($^{\circ}$ C)	O.C.C. (%)	Oil Selectivity (%)
300	9.2	96.5
375	30.9	96.2
425	70.8	95.8
450	82.6	93.3

- Organic Carbon Conversions are for 60 min. samples.
- 300 psia initial hydrogen pressure for all runs.

Phase Two

The objectives for the phase two experiments were fourfold. The first objective was to observe the effect of hydrogen partial pressure on organic carbon conversion. The second objective was to observe the effect of adding water to the reaction system both with and without the presence of gas phase molecular hydrogen. Thirdly, the effect of changing the pH of the system was investigated. Lastly, the modeling of the kinetics was attempted for the irreversible conversion of kerogen to gas and oil products.

Using the phase one results it was decided to investigate two intermediate temperatures, 375°C and 425°C. At these temperatures the conversion was substantial enough to expect observations over a range much larger than the error in repeat measurements of organic carbon conversion. In addition, the rate was moderate enough at these temperatures to permit samples to be taken during the period of maximum change in conversion. Both of these criteria are of importance in the testing of a kinetic model.

The sampling times for the 375°C runs were at 5, 10, 30 and 60 minutes. For the 425°C runs the samples were taken at 2, 4, 8 and 10 minutes. These times were selected because

T-3098

the phase one results indicated that a pseudo steady state would be attained by the time the last sample was taken.

Effect of Hydrogen Gas Pressure and Added Water

The data for the phase two results are summarized in Table 8. The amount of water added for the standard reaction conditions was 2.0 ml. The water was added to the injection vessel prior to the injection of the slurry to the reactor. Where a hydrogen atmosphere was not desired, the reactor was charged with 300 psia cold helium. The results for four different reaction conditions at 375°C and 425°C are shown in Figures 5 and 6 respectively.

As was the case in the phase one experiments, the conversion increases with temperature for each set of reaction conditions. For both the 375°C and the 425°C runs the highest conversions were obtained in the system with a hydrogen gas atmosphere and added water present.

It was also observed that the conversions were higher for the helium/water system compared to the helium only system.

Table 8
Summary of Phase Two Results

Reaction Conditions	Reaction Temperature ($^{\circ}\text{C}$)	O.C.C. (%)
Helium	375	35.4
Helium	425	47.4
Hydrogen	375	30.5
Hydrogen	425	70.7
Helium/Water	375	39.0, 36.2
Helium/Water	425	57.1
Hydrogen/Water	375	42.3
Hydrogen/Water	425	77.1
Hydrogen	400	56.4
Hydrogen (200 psia)	400	62.3
Helium/Water (20 ml)	375	15.0

- Conversion results shown are 10 min samples for the 425°C runs and 30 min samples for the 375°C runs.

- unless indicated all runs were with 300 psia initial gas pressure at room temperature.

- unless indicated the amount of water used was 2.0 ml

Figure 5
375°C Isotherms

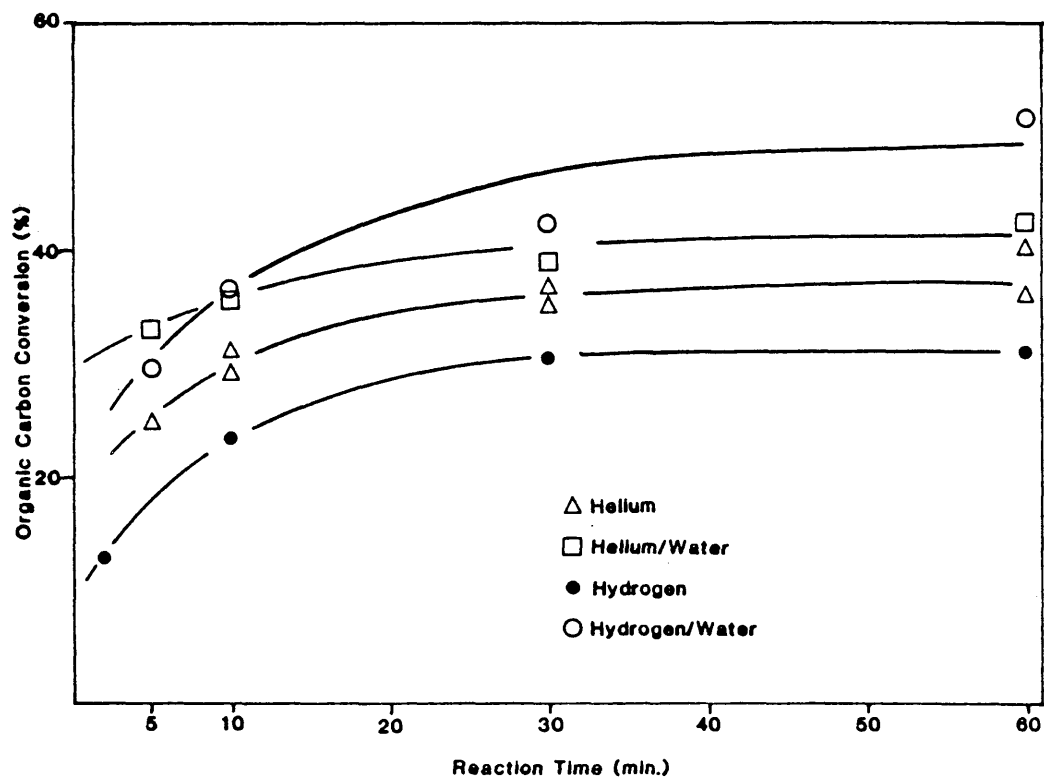
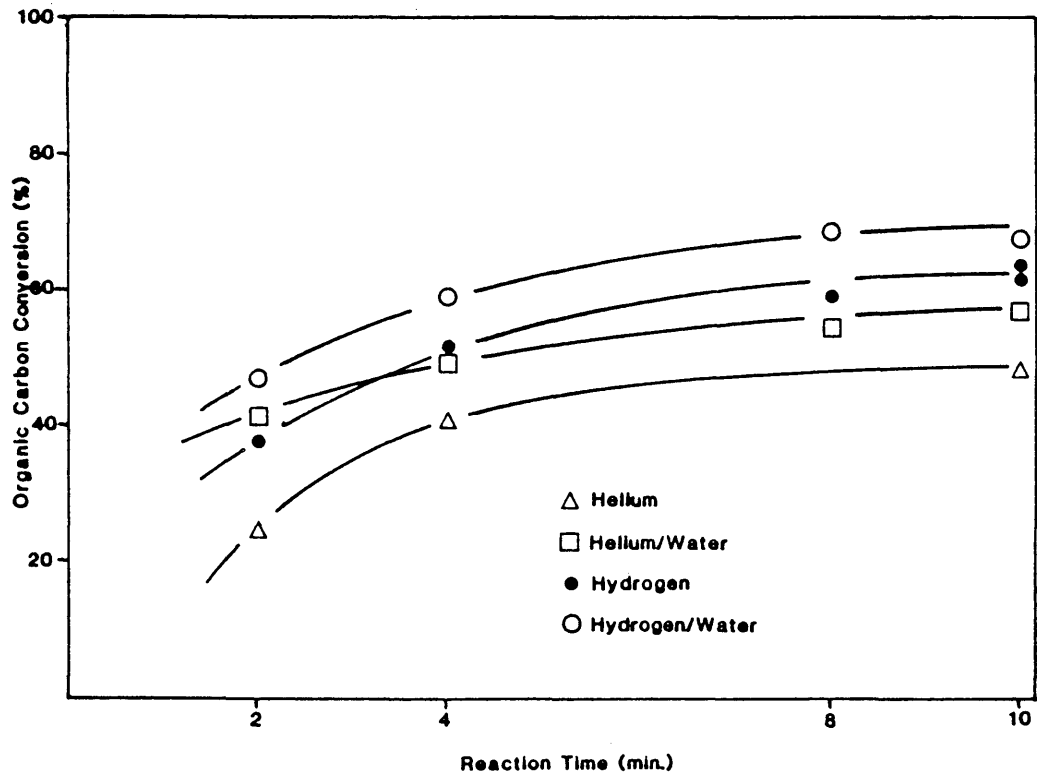


Figure 6
425°C Isotherms



T-3098

A very surprising trend was observed for the system with a hydrogen atmosphere without water added. At 425°C this system showed conversions second in magnitude only to the hydrogen/water system. At 375°C however, the hydrogen only system yielded the lowest conversions of all four.

A possible reason to explain these unexpected results is the existence of a "capping" phenomena where atomic hydrogen is present to react with a free radical species formed in the kerogen matrix. This "capping" rate would be faster than some additional reaction rate resulting in the formation of a molecule free of the kerogen matrix. Although there were four individual points to support the existence of this phenomena, two additional runs were made at an intermediate temperature of 400°C. With a 300 psia cold hydrogen charge, the conversion was 56.4%, between the 375°C and 425°C results. Lowering the hydrogen pressure to 200 psia, resulting in a lower hydrogen partial pressure, gave an organic carbon conversion of 62.3%.

These data combined with the other two conversion isotherms indicate that at some point between 400°C and 425°C the curves for helium and hydrogen intersect resulting in a "crossover point" where hydrogen presence begins to have a positive effect on the organic carbon conversion. It may be that as temperatures rise above this crossover point, the rate of bond breakage in the kerogen

T-3098

accelerates faster than the rate of free radical capping of activated species still attached to the matrix. Activated species, radicals or alkenes which become independent of the shale, may then be transformed into stable molecules through reaction with hydrogen in the fluid phase. The result would be a greater rate of production of gas and oil. Solubilized away from the kerogen in a helium atmosphere, activated species may be more liable to condense or polymerize, resulting in nonproductive coking on the particle surface.

In order to observe the effect of adding more water to the system, an experiment at 375°C was run with 20 ml of water added instead of the standard 2.0 ml. The result shown in Table 8 was a dramatic reduction in organic carbon conversion. With 20 ml of water the conversion was 15.0% at 30 minutes compared to 39.0% with 2.0 ml water added and 35.4% with no water added. These data indicate the possible existence of a crossover effect for water somewhere between 2.0 and 20 ml added for this system.

T-3098

Effect of pH Change

Five runs were made to investigate the effect on conversion of using 37% HCl in the system instead of distilled water. The acid was introduced to the system in the identical manner that the water was introduced. Runs were made at 300, 375 and 425°C; the results are summarized in Table 9. These data show that at 375°C there was no significant change in conversion compared to the water runs for either a helium or hydrogen atmosphere. At 425°C the runs with a helium atmosphere showed conversion results similar for water and HCl, 57.1% and 55.4%. With a hydrogen atmosphere the 425°C data show higher conversions with water compared to HCl, 77.1% compared to 68.2%.

An additional experiment was performed to see if pretreating the shale with HCl and then reacting it under the standard set of conditions would result in enhanced conversions. 25 grams of shale was slurried with 250 ml of 37% HCl at room temperature for 24 hours. It was felt that in this manner it may be possible to demineralize the shale which would result in a shale with a kerogen matrix more exposed to chemical attack. The pretreated shale was filtered from the acid solution and washed to neutrality with distilled water. After drying in an oven and resizing the mass of solids had been reduced 28.7% to 17.83 grams.

Table 9
Results of Hydrochloric Acid Experiments

Reaction Gas	Temperature	Time (min.)	O.C.C.(%)	
			H ₂ O	HCl
He	300°C	30	N/A	14.9
He	375°C	30	39.0, 36.2	37.8
He	425°C	10	57.1	55.4
H ₂	375°C	30	42.3	39.0
H ₂	425°C	10	77.1	67.4

T-3098

The acidic supernate derived from the acid treatment was a very dark green liquor indicating the presence of metallic chlorides. The demineralized shale was then reacted in the system at 375°C with a 300 psia cold hydrogen charge. The result at 30 minutes reaction time was a 28.7% conversion compared to 30.5% for untreated shale under the same conditions.

Kinetic Modeling

The linearized forms of the three irreversible models for the conversion of organic carbon to oil and gaseous products were used to predict values for conversion.

An IMSL linear correlation program, RLONE, was used to calculate the R-squared values for each model. The program which was written to access RLONE evaluated the data for all values of "a", the pseudo steady state equilibrium conversion, between 0.000 and 1.000 in 0.001 increments. In this manner the value of "a" served as a fitting parameter in the kinetic analysis. The value of "a" was set by the regression with the highest R-squared value. The highest values for R-squared that were obtained in this way are shown in Table 10.

Table 10
Results of Kinetic Modeling

Reaction Condition	Temperature (°C)	R-Squared Value		
		1st	3/2's	2nd
Helium	375	.249	.836	.965
Helium	425	.957	.882	.976
Hydrogen	375	.923	.981	.994
Hydrogen	400	.988	.999	.997
Hydrogen	425	.890	.939	.995
Helium/Water	375	.923	.957	.927
Helium/Water	425	.970	.993	.993
Hydrogen/Water	375	.966	.981	.955
Hydrogen/Water	425	.943	.999	.990

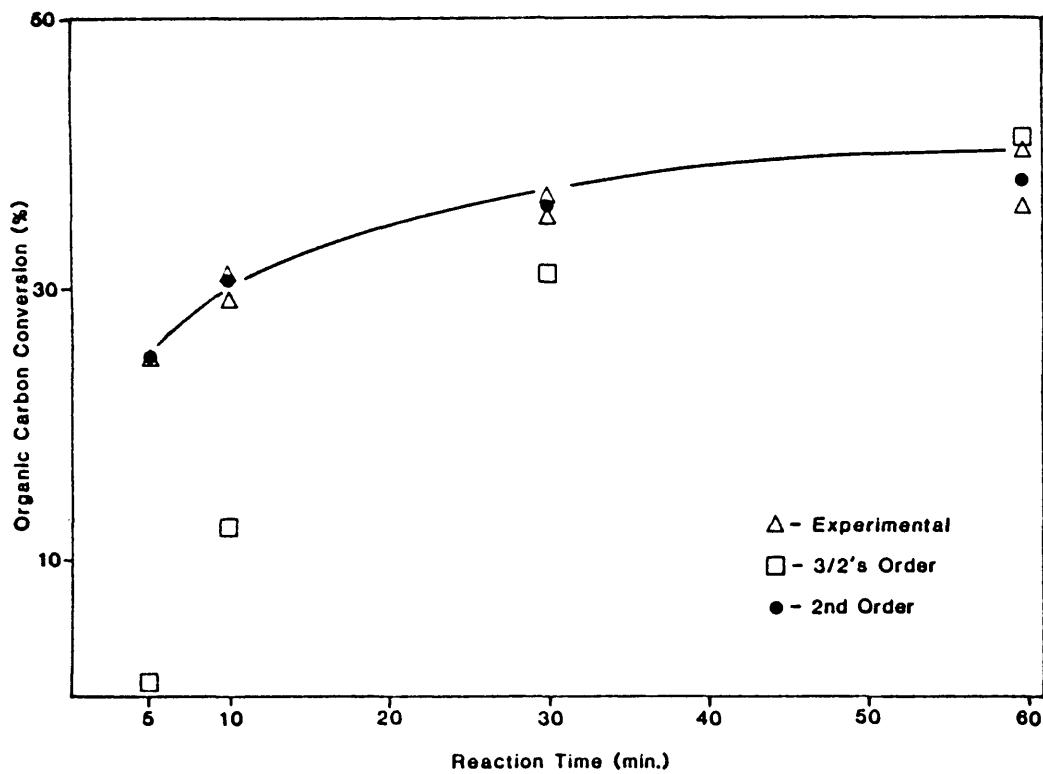
T-3098

The Table 10 data show that the 1st order model failed to give the best correlation in all nine cases, and was lowest for seven of the nine.

Plots of the predicted values for the 2nd order and 3/2's order models with the experimental data were made and are presented in Figures 7-15.

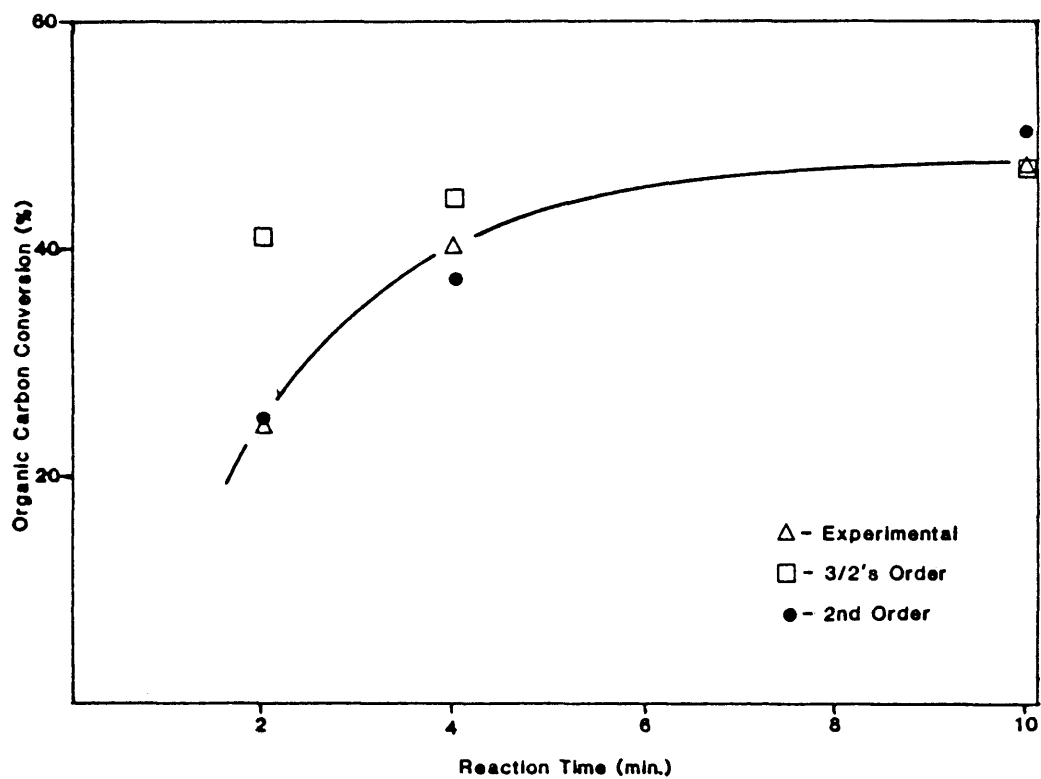
Examination of the plots along with the R-squared values indicate that the second order model adequately described the kinetics for the cases when water was not added to the system. In the cases where water was added the results are not clear. The R-squared results did not concur with the data fit of the predicted values for those systems. A possible explanation for this discrepancy is that the best model is of an order intermediate between 3/2's and 2nd. Alternatively, it is possible that the R-squared coefficient is not a good predictor of linearity for these systems.

Figure 7
Helium - 375°C



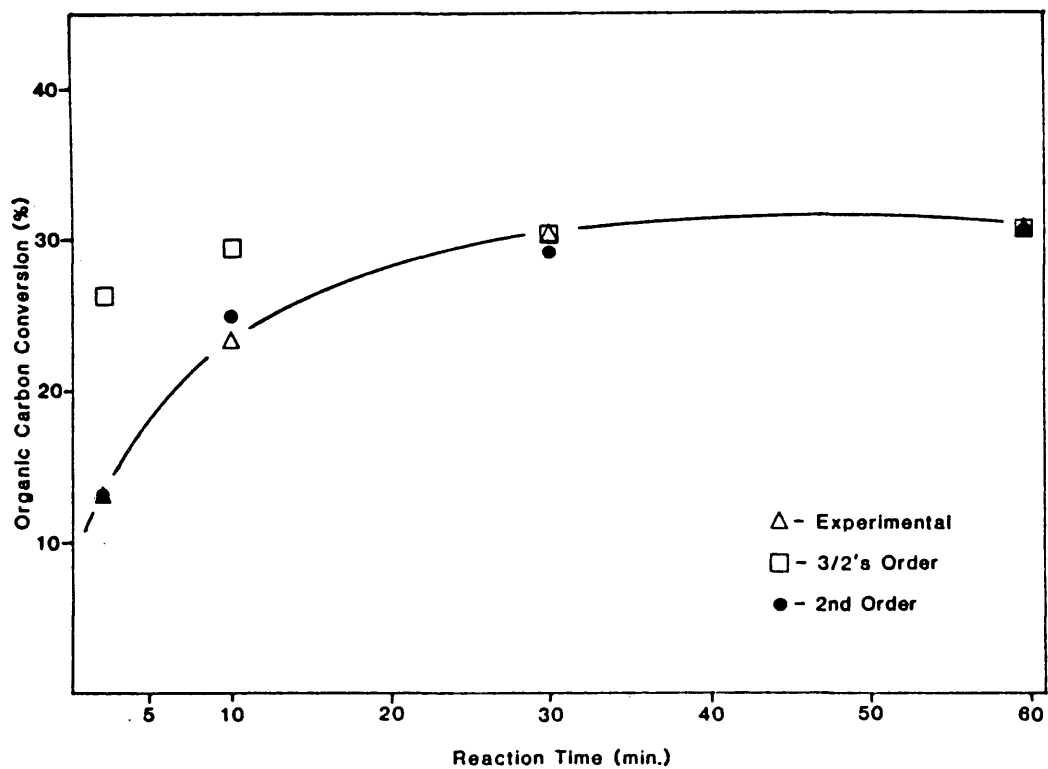
Conversion Isotherm for Helium System - 375°C

Figure 8
Helium - 425°C



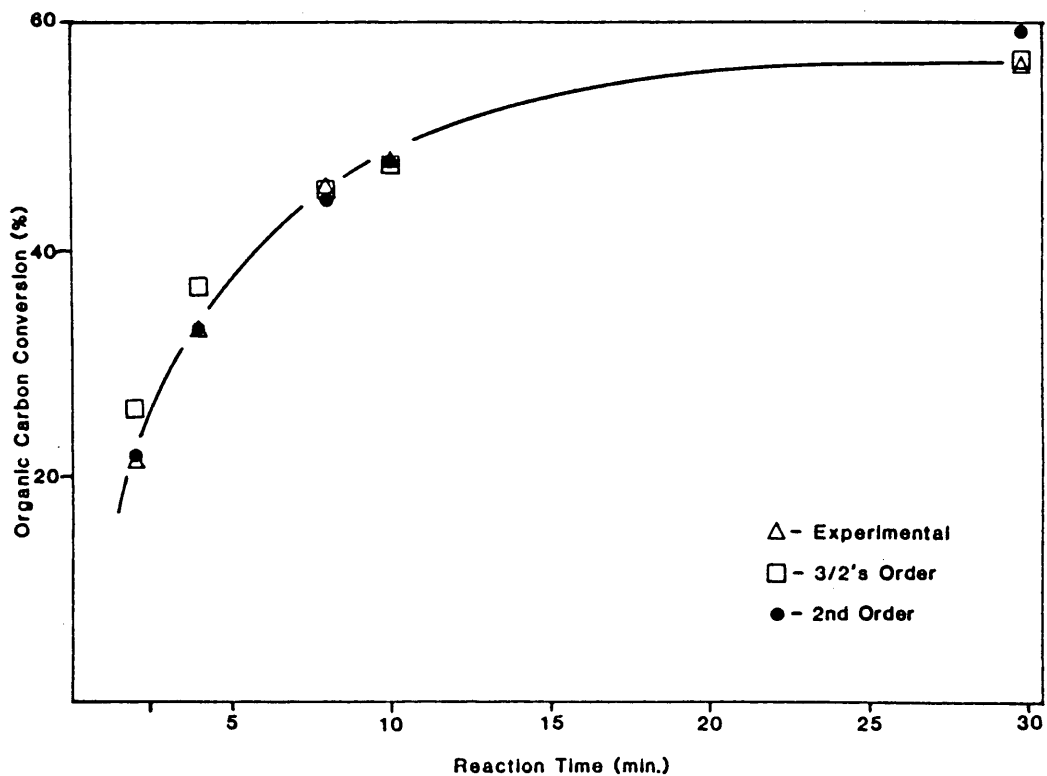
Conversion Isotherm for Helium System - 425°C

Figure 9
Hydrogen - 375°C



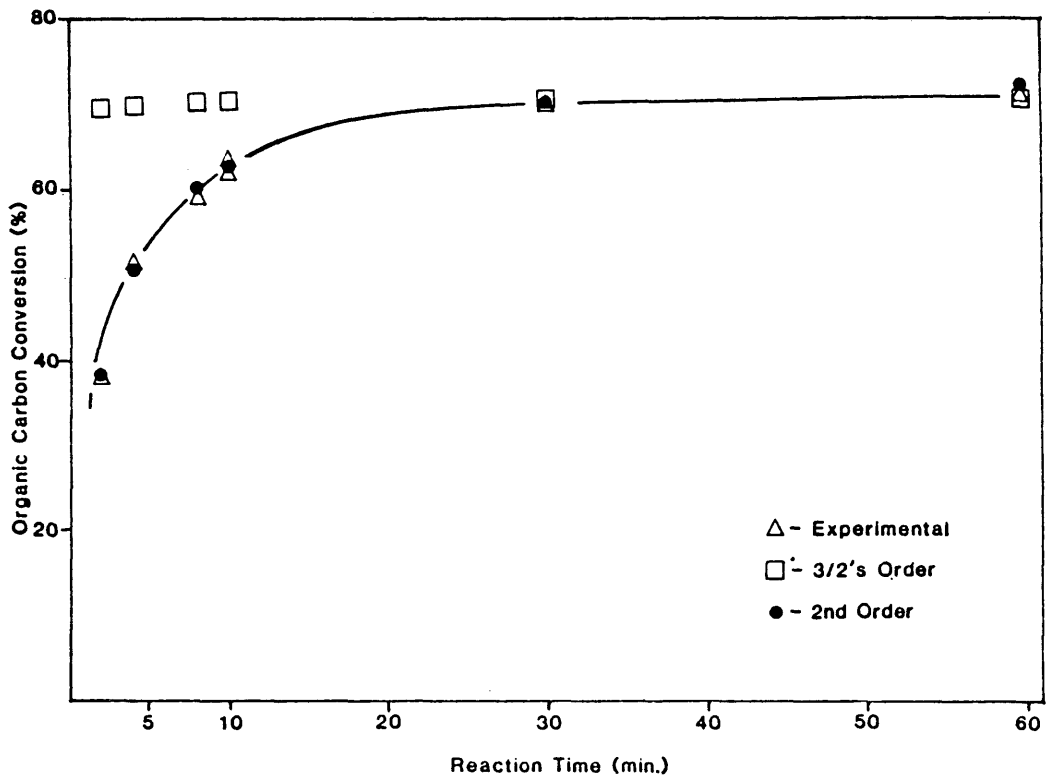
Conversion Isotherm for Hydrogen System - 375°C

Figure 10
Hydrogen - 400°C



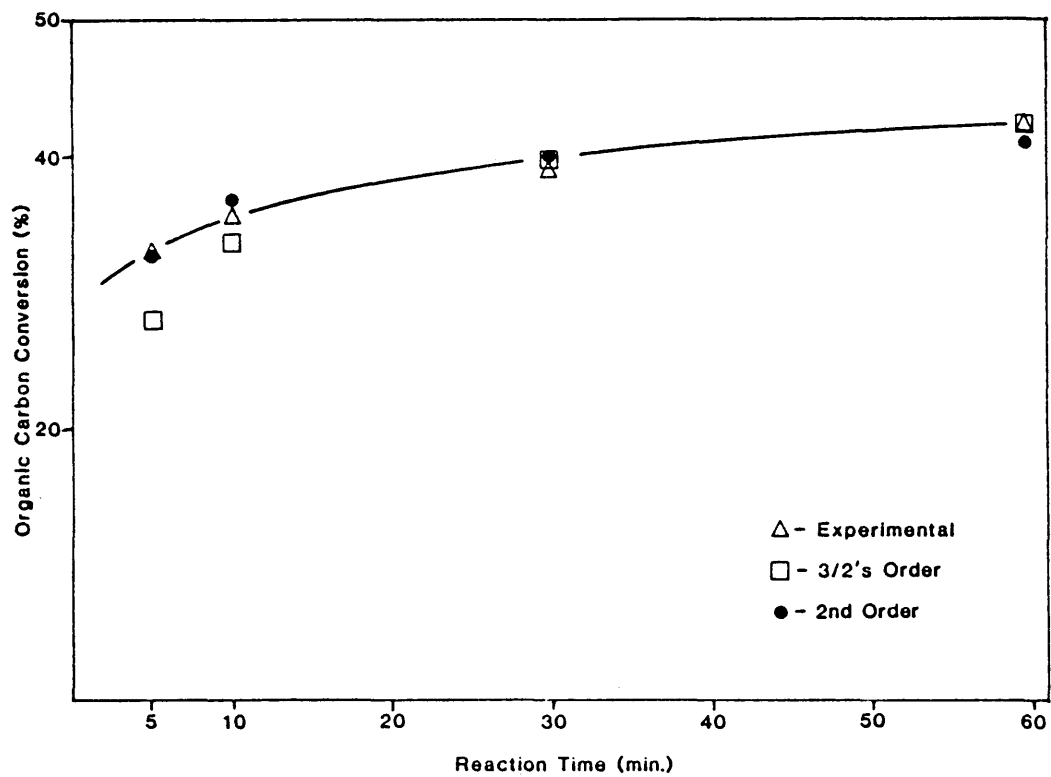
Conversion Isotherms for Hydrogen System - 400°C

Figure 11
Hydrogen - 425°C



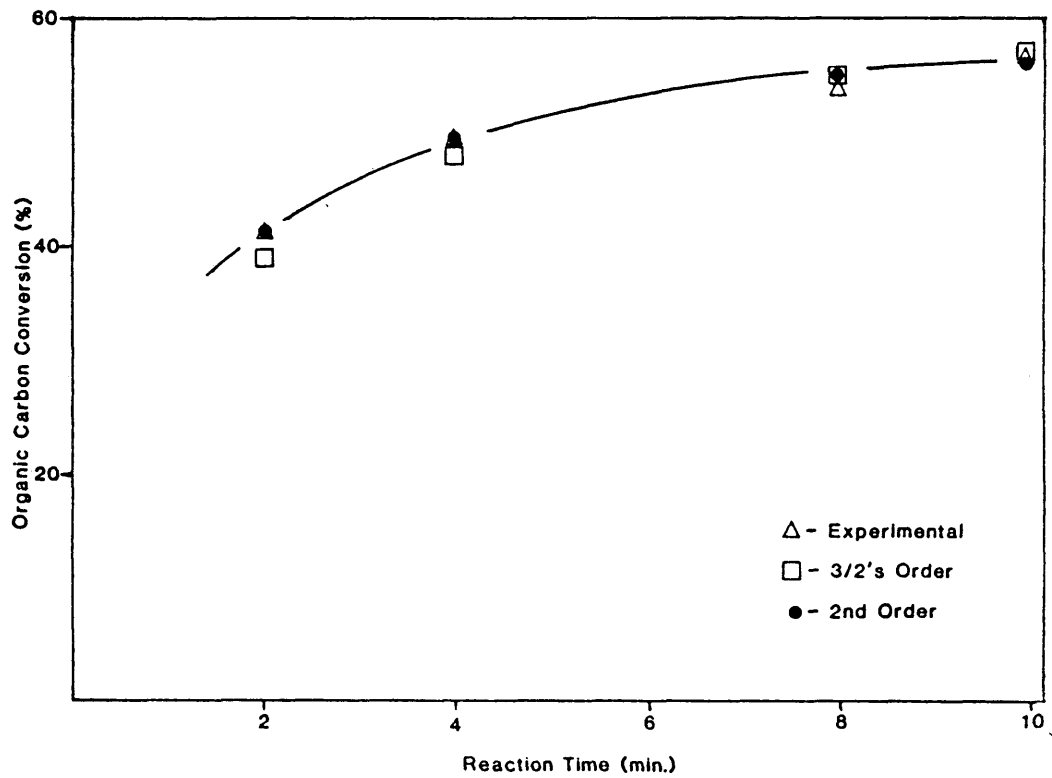
Conversion Isotherm for Hydrogen System - 425°C

Figure 12
Helium/Water - 375°C



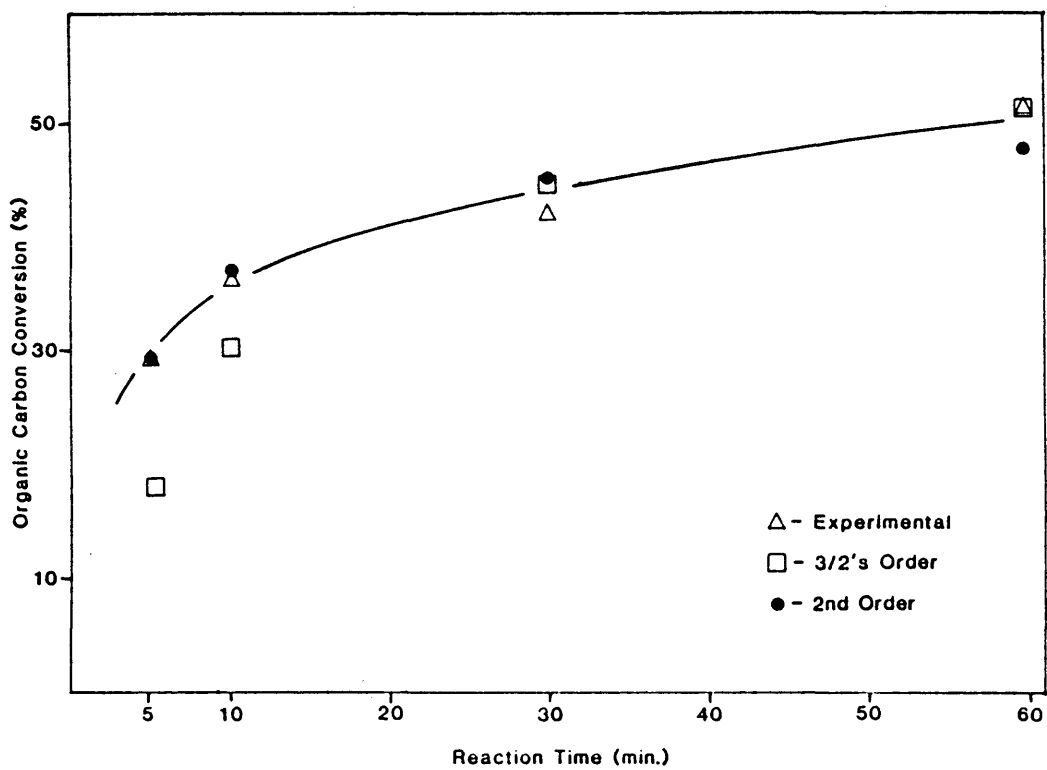
Conversion Isotherm for Helium/Water System - 375°C

Figure 13
Helium/Water - 425°C



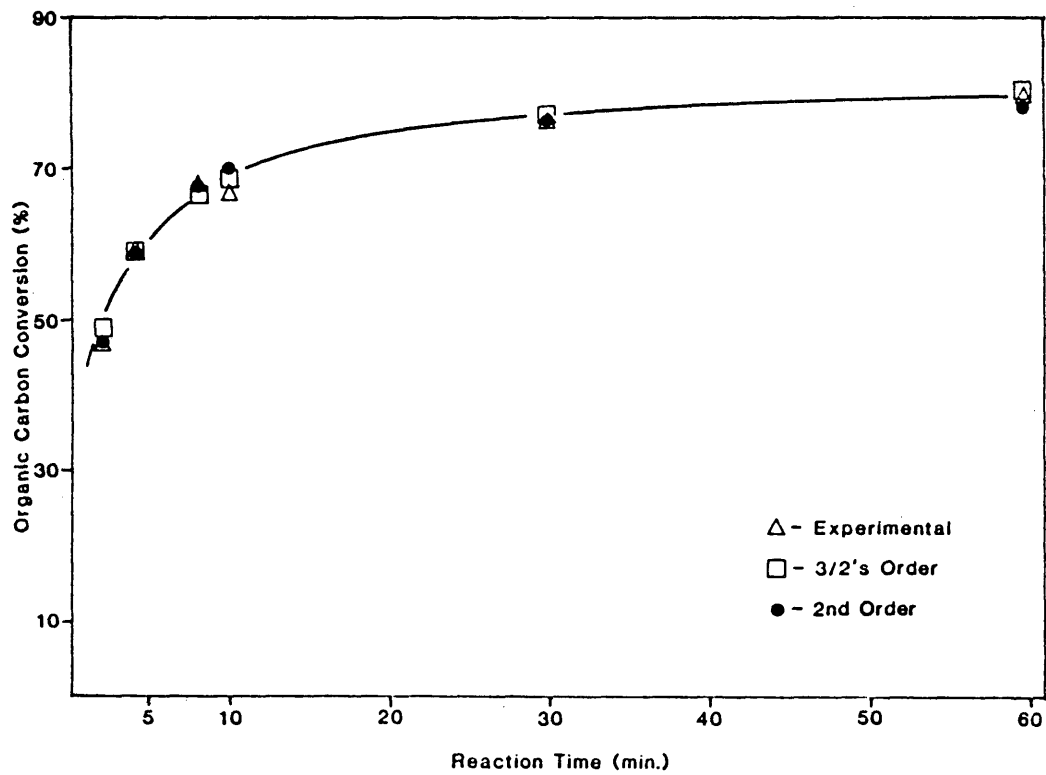
Conversion Isotherm for Helium/Water System - 425°C

Figure 14
Hydrogen/Water - 375°C



Conversion Isotherm for Hydrogen/Water System - 375°C

Figure 15
Hydrogen/Water - 425°C



Conversion Isotherm for Hydrogen/Water System - 425°C

Phase Three

Fractionation of Oils

Four oils that were generated in the batch reactor system, one for each reaction condition that was modeled in Phase Two, along with a Fischer Assay oil were fractionated by the scheme shown in Figure 2. The results of the fractionation are shown in Table 11. Mass recoveries ranged from 95.3% to 102.4% .

The percentage of alkanes, Fraction 2, was nearly constant for the oils generated in the reactor. The Fischer Assay oil yielded more than twice the amount of material in Fraction 2 than the other oils.

The total amount of aromatics generated, Fractions 6-13, was also greatest for the Fischer Assay oil.

Polymeric materials, Fractions 17-21, were similar in abundance for the helium only oil and the Fischer Assay sample. Polymer production was highest for the oils generated in the presence of water or molecular hydrogen or both.

Table 11
Phase Three Fractionation Results

Fraction	Weight %				
	Run Condition				
	He	H ₂	H ₂ /H ₂ O	He/H ₂ O	Fischer Assay
1	0.1	0.3	<0.1	<0.1	<0.1
2	4.3	4.2	4.4	3.2	9.1
3	0.4	0.8	1.2	0.5	2.3
4	1.2	2.3	2.2	2.0	2.7
5	0.4	0.8	1.2	0.5	0.9
6	3.2	5.4	1.6	2.7	5.4
7	1.6	2.4	2.9	1.1	3.4
8	1.6	0.8	0.7	2.5	1.0
9	2.3	0.5	0.5	0.9	1.4
10	3.6	1.0	0.2	2.2	5.7
11	0.4	0.2	0.9	0.7	0.5
12	0.5	0.1	<0.1	0.2	0.3
13	0.3	0.2	0.2	0.2	0.5
14	0.3	0.2	0.1	0.1	0.3
15	0.8	0.2	0.4	0.5	0.8
16	3.0	1.8	1.1	1.5	2.6
17	22.3	10.7	14.1	17.2	11.9

Table 11 (cont.)

Fraction	Weight %				
	Run Condition				Fischer Assay
	He	H ₂	H ₂ /H ₂ O	He/H ₂ O	
18	8.3	4.8	5.9	9.0	4.7
19	4.0	7.6	6.1	4.0	6.6
20	7.0	15.2	18.8	11.5	23.8
21	7.9	22.5	27.8	20.6	6.5
Asphaltenes	20.5	11.9	4.0	19.8	1.9
Acids	0.8	1.0	0.8	0.9	1.8
Bases	1.4	1.1	1.0	0.7	2.2
Total %	96.2	95.5	95.3	102.4	96.3

T-3098

Nitrile production, Fraction 15, was less than 1.0% for all five samples.

Asphaltene content was highest for the helium run, 20.5%, and lowest for the Fischer Assay oil, 1.9%.

The amounts of acidic and basic materials recovered was similar for all five oils.

Table 12 compares the organic carbon conversion and the amount of heavy polymers recovered from the fractionation. There was a clear reduction in mass in Fractions 18 and 19 for all of the oils. In addition, Fractions 16 and 17 banded out separately for all the samples indicating that they were fundamentally different fractions. Fractions 20 and 21 were a continuous smear of dark black material which failed to separate into bands on the column. These fractions were not soluble in hexane in all proportions and for this reason along with their elution pattern are assumed to consist largely of preasphaltenic material. The data in Table 12 combine the asphaltenes with the Fraction 20 and 21 into an individual group defined as heavy polymeric material. The combined masses for these fractions were normalized with percent recovery used as a base and compared to the organic carbon conversions from the Phase Two data.

Table 12
Comparison of Heavy Polymers vs. Carbon Conversion

Reaction Condition	Heavy Polymer Recovered	O.C.C.	Ratio
Helium	36.8 %	47.4 %	.776
Hydrogen	51.9 %	70.7 %	.734
Hydrogen/Water	53.1 %	77.1 %	.689
Helium/Water	50.7 %	57.1 %	.888
Fischer Assay	33.5 %	45.2 %	.741

- Heavy polymer was combined mass percentages of Fractions 20, 21 and asphaltenes. Percentages of heavy polymer were normalized using the total mass recoveries as a basis.

- Organic Carbon Conversions are 425°C, 10 minute results.

T-3098

The results shown in Table 12 illustrate a trend of increased production of heavy polymers with increasing conversion. The final column in Table 12 is the ratio of heavy polymers recovered to organic carbon conversion, a parameter which could be used to determine the process which is most efficient in producing valuable feedstocks in high yields. The two oils that gave the highest conversions also gave the lowest ratios, the hydrogen and hydrogen/water systems. The hydrogen/water system showed both the highest conversion and the lowest ratio. Hydrogen consumption and heat load data would be necessary to discriminate between these two systems in terms of overall process efficiency.

GC/MS Analysis

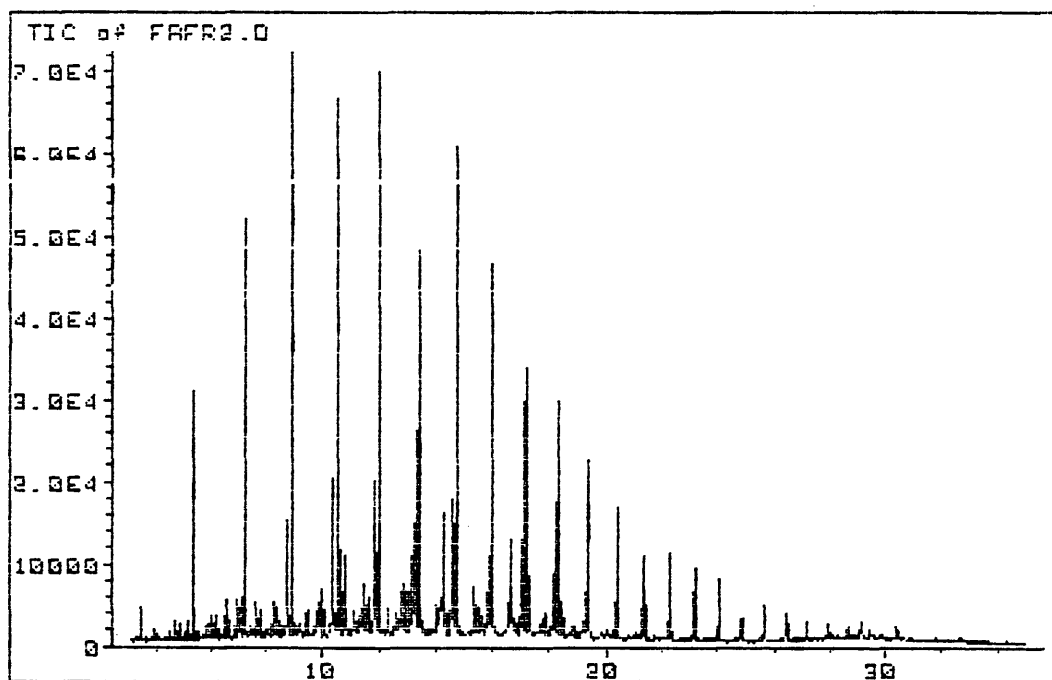
Some of the fractions from the open column chromatographic separation were analyzed by GC/MS.

T-3098

Total Ion Chromatograms for the alkanes, Fraction 2 are presented for all five oils as Figures 16-20. The most prominent peaks which appear as a series starting near the 7 minute point on the time axis are the linear straight chained alkanes. The peak at 8.9 minutes is dodecane. The most abundant alkanes are of lower molecular weight in the Fischer Assay sample compared to the oils from the reactor system.

Figure 16

Fischer Assay TIC - Fraction 2

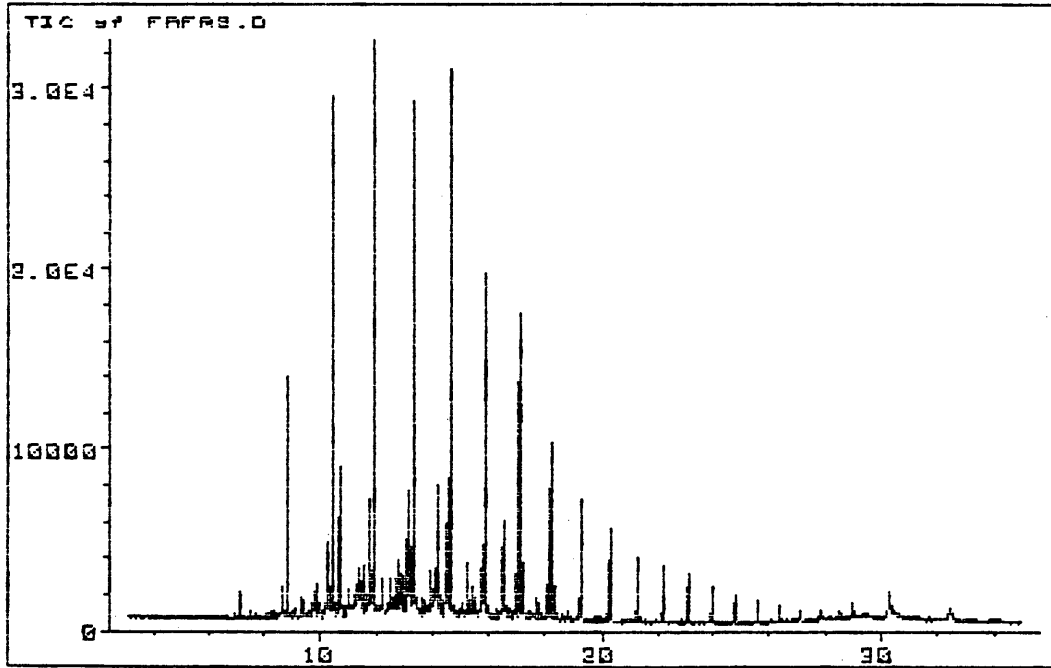


Total Ion Chromatogram

Fischer Assay Sample - Fraction 2

Figure 17

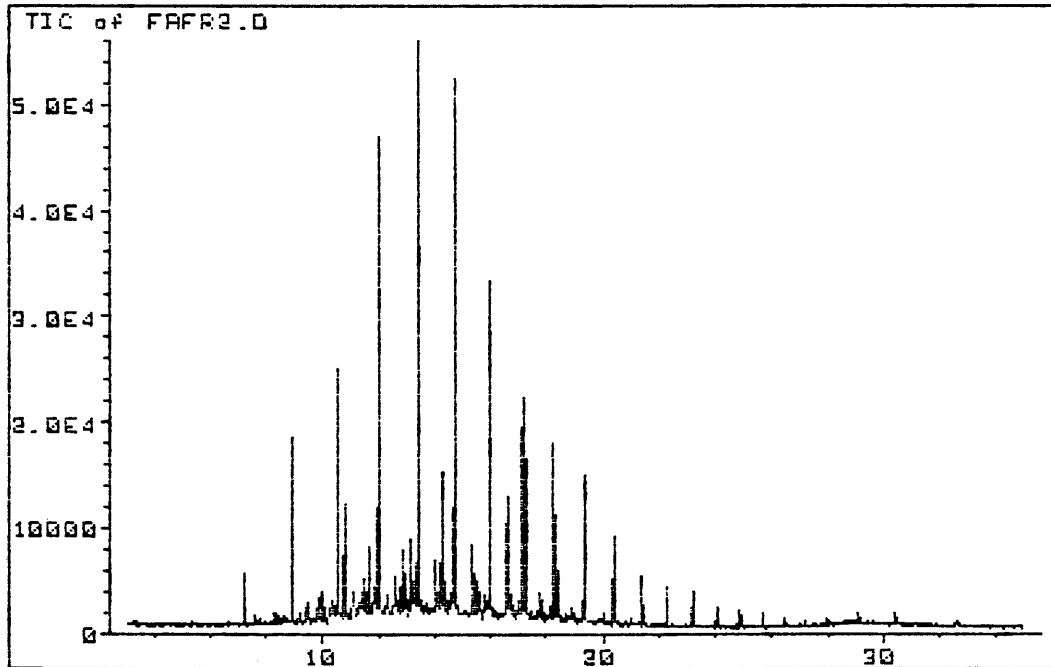
Helium TIC - Fraction 2



Total Ion Chromatogram
Helium System - Fraction 2

Figure 18

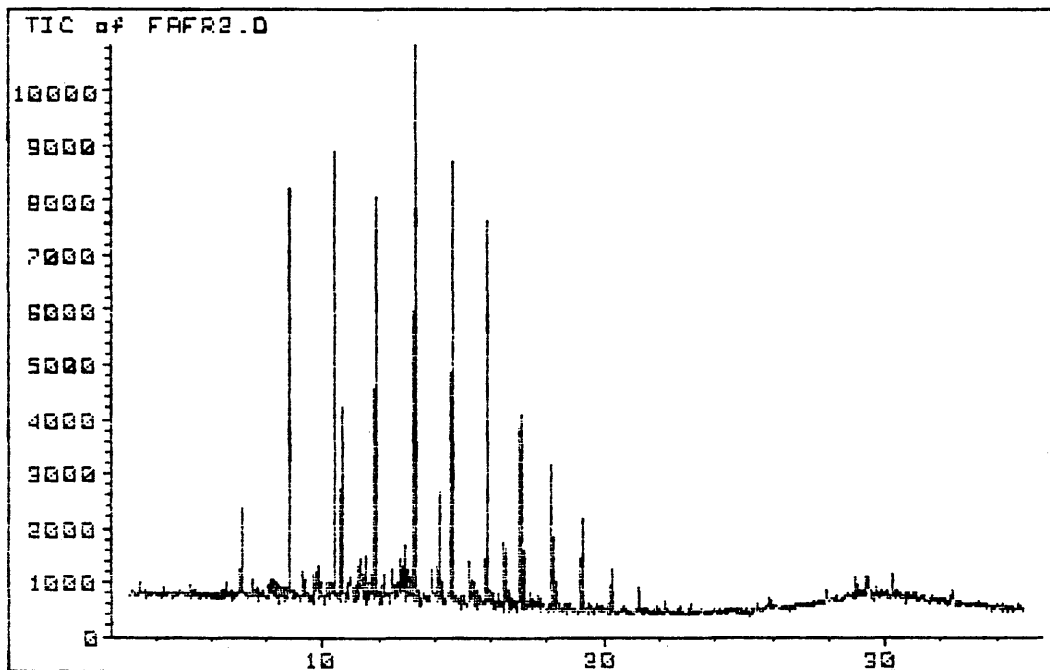
Hydrogen TIC - Fraction 2



Total Ion Chromatogram
Hydrogen System - Fraction 2

Figure 19

Helium/Water TIC - Fraction 2

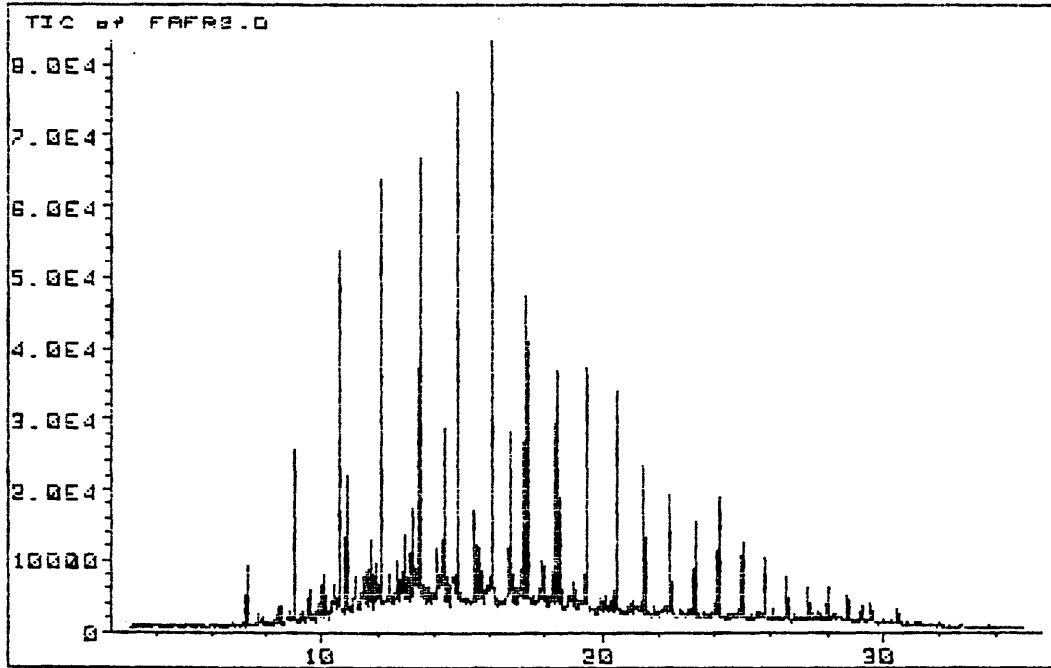


Total Ion Chromatogram

Helium/Water System - Fraction 2

Figure 20

Hydrogen/Water TIC - Fraction 2



Total Ion Chromatogram

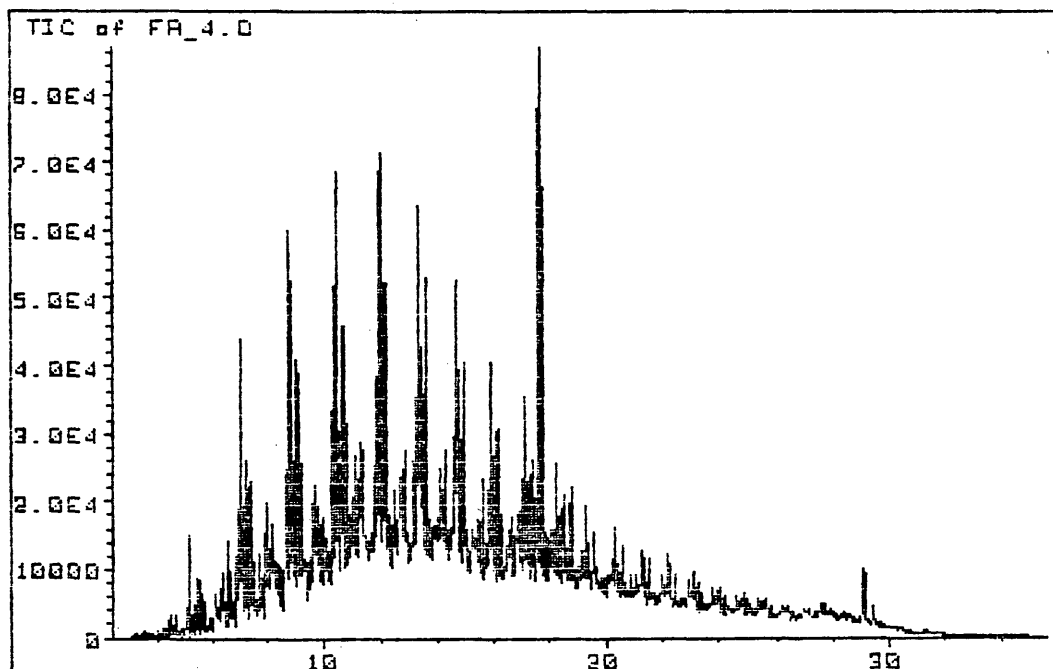
Hydrogen/Water System - Fraction 2

T-3098

The alkene chromatograms, Fraction 4, are shown in Figures 21-25. A similar pattern of molecular series is present, complicated with numerous side peaks and other minor components. At 17.6 minutes a major peak was found in four of the five oils. This peak was identified as 2,4,6,10 - tetramethyl - hexadecene. This compound may be a stable terpene derivative produced from the degradation of biopolymers present in the kerogen of the parent shale. The oil from the helium/water system did not have this component as a major peak in the Fraction 4 TIC.

Figure 21

Fischer Assay TIC - Fraction 4

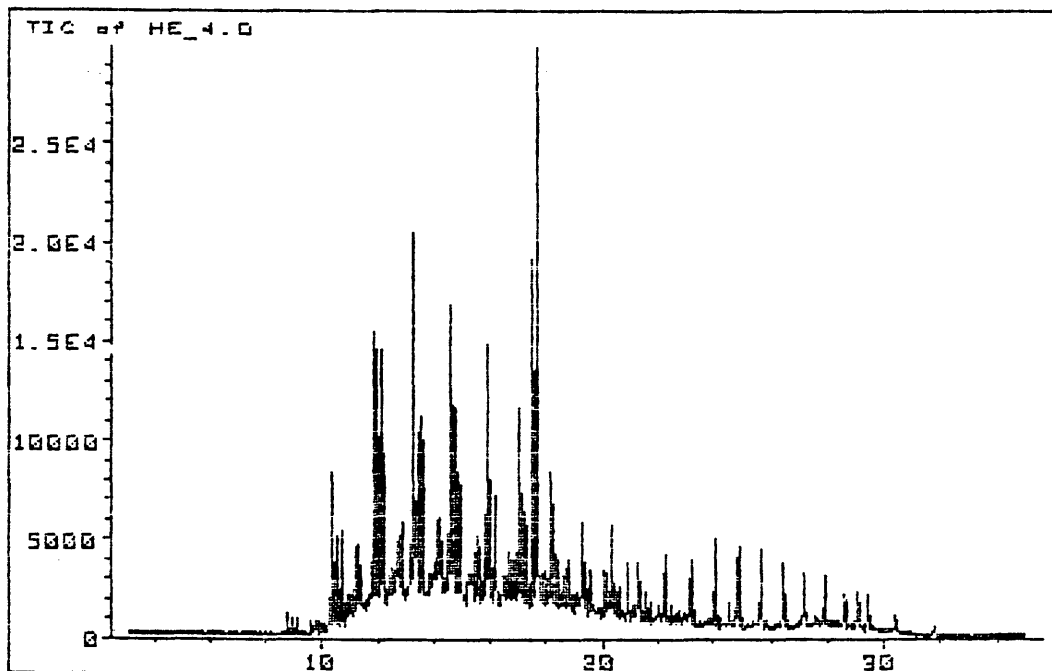


Total Ion Chromatogram

Fischer Assay Sample - Fraction 4

Figure 22

Helium TIC - Fraction 4

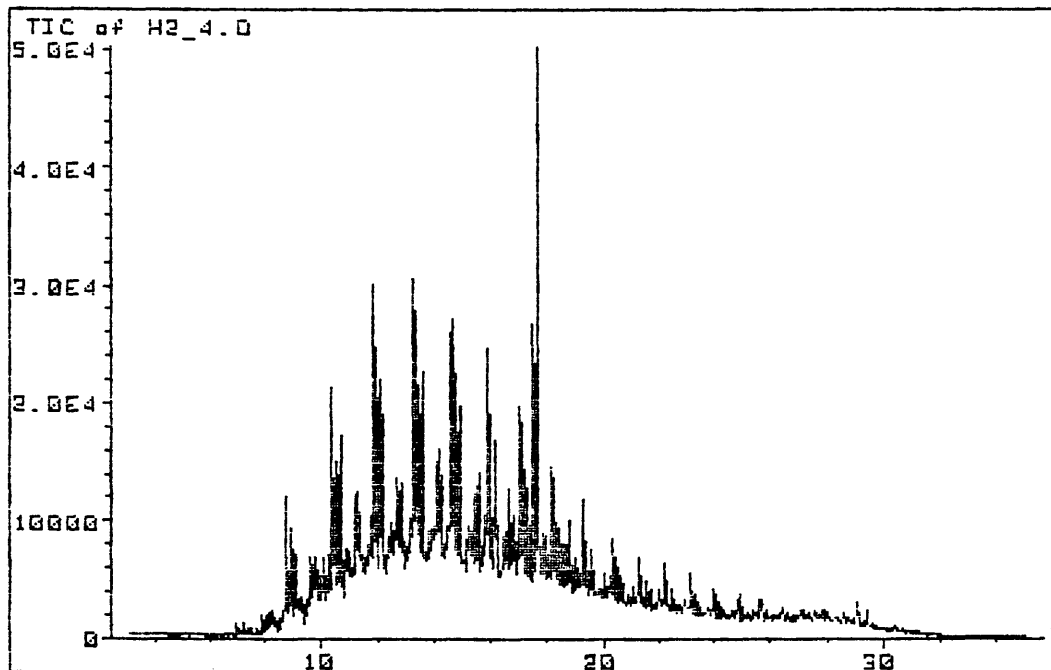


Total Ion Chromatogram

Helium System - Fraction 4

Figure 23

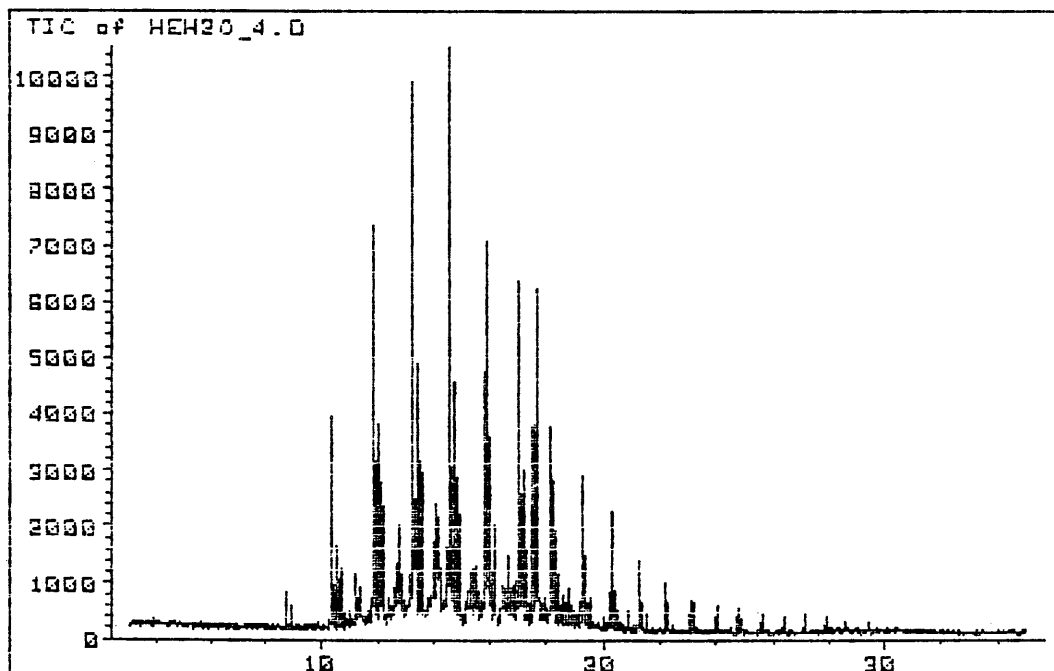
Hydrogen TIC - Fraction 4



Total Ion Chromatogram
Hydrogen System - Fraction 4

Figure 24

Helium/Water TIC - Fraction 4

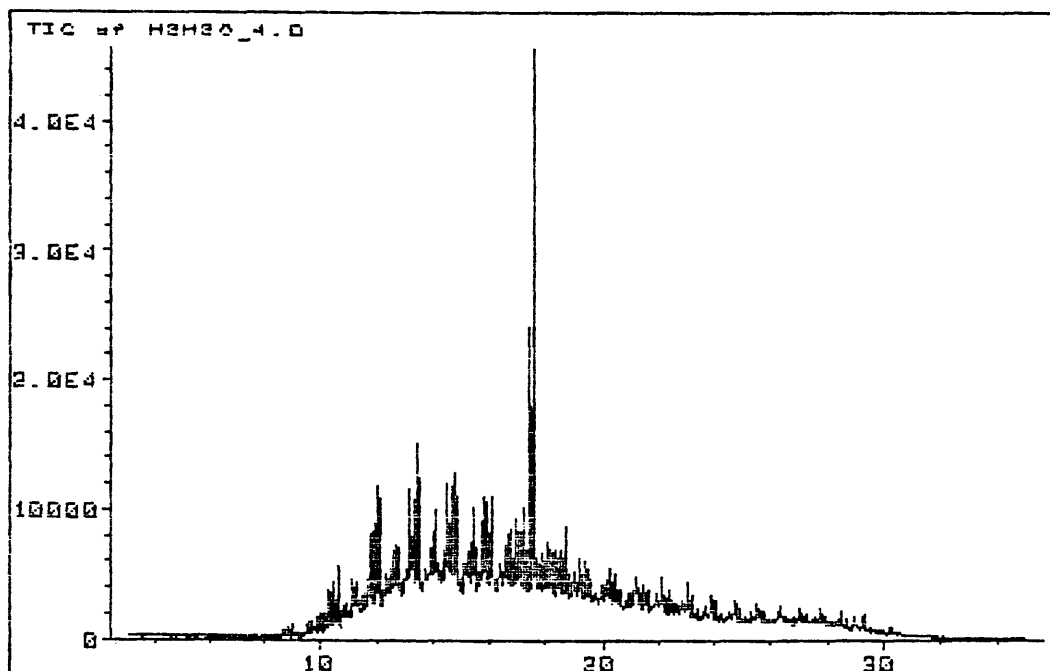


Total Ion Chromatogram

Helium/Water System - Fraction 4

Figure 25

Hydrogen/Water TIC - Fraction 4



Total Ion Chromatogram

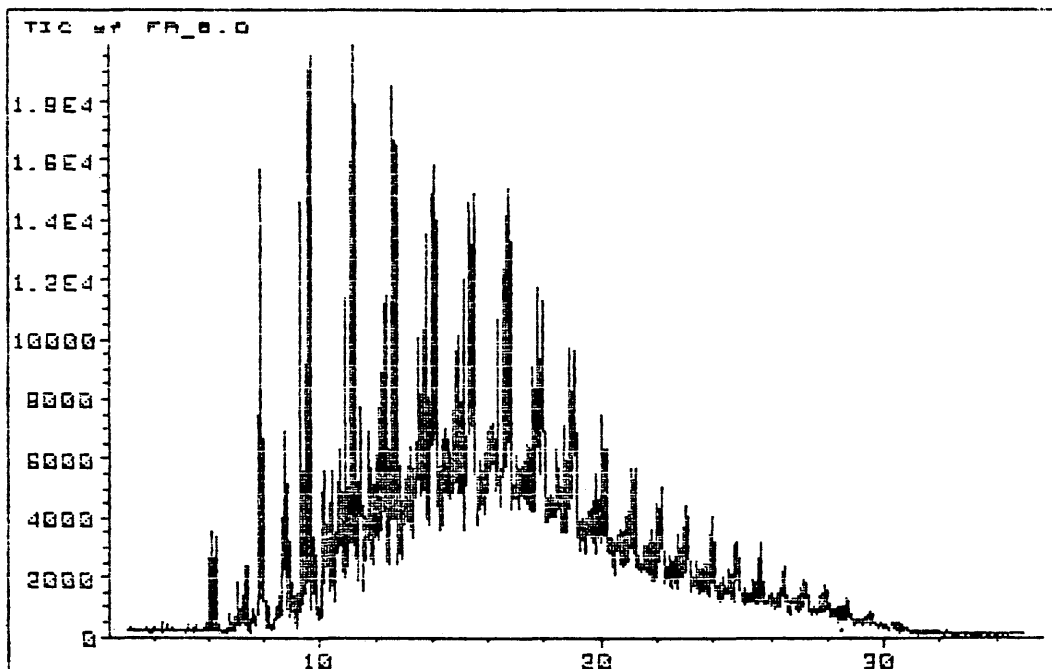
Hydrogen/Water System - Fraction 4

T-3098

The Fraction 6 TIC's, Figures 26-30, also showed the typical pattern of molecular series for methylene indexed chains similar to the Fraction 2 chromatograms. The peak at 14.1 minutes was identified as n-octyl benzene. As was the case for the Fraction 2 comparisons, the Fischer Assay TIC is shifted towards lower molecular weight compared to the other oils.

Figure 26

Fischer Assay TIC - Fraction 6

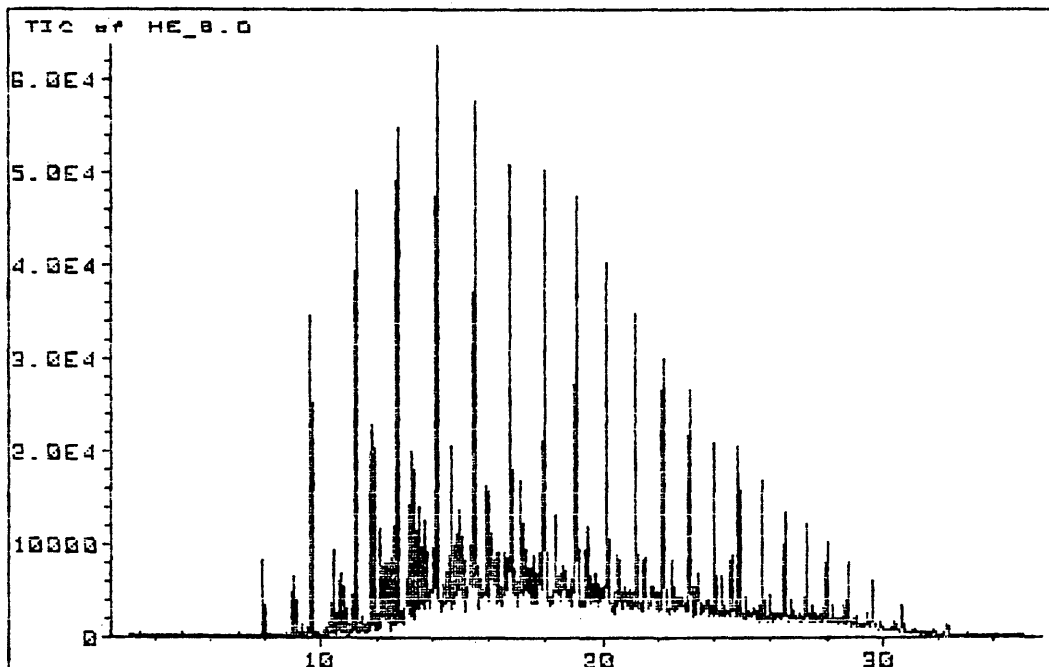


Total Ion Chromatogram

Fischer Assay Sample - Fraction 6

Figure 27

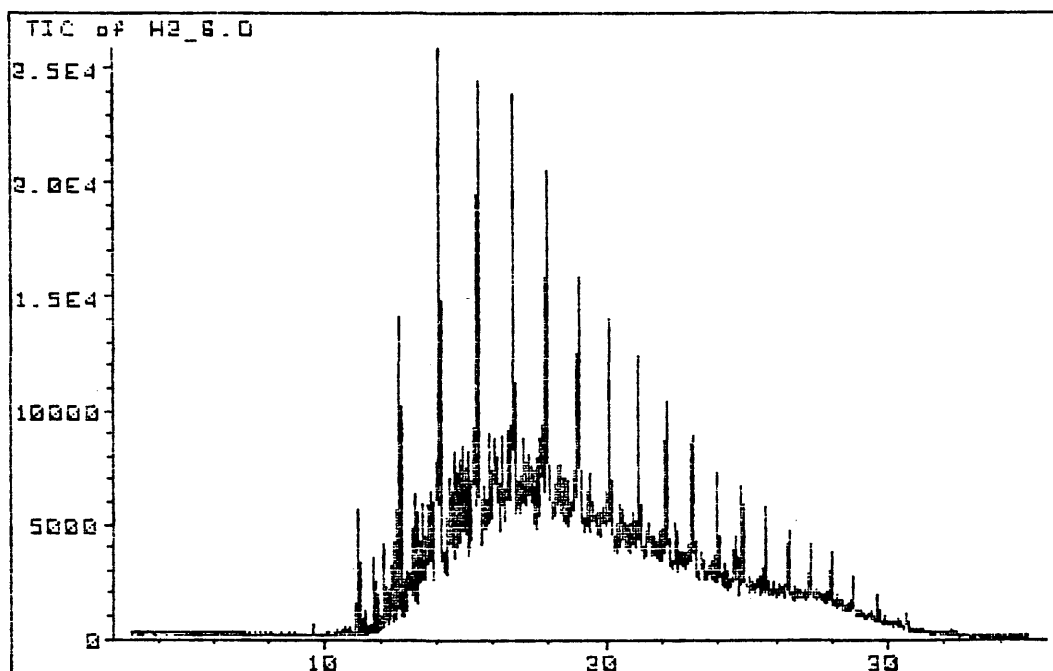
Helium TIC - Fraction 6



Total Ion Chromatogram
Helium System - Fraction 6

Figure 28

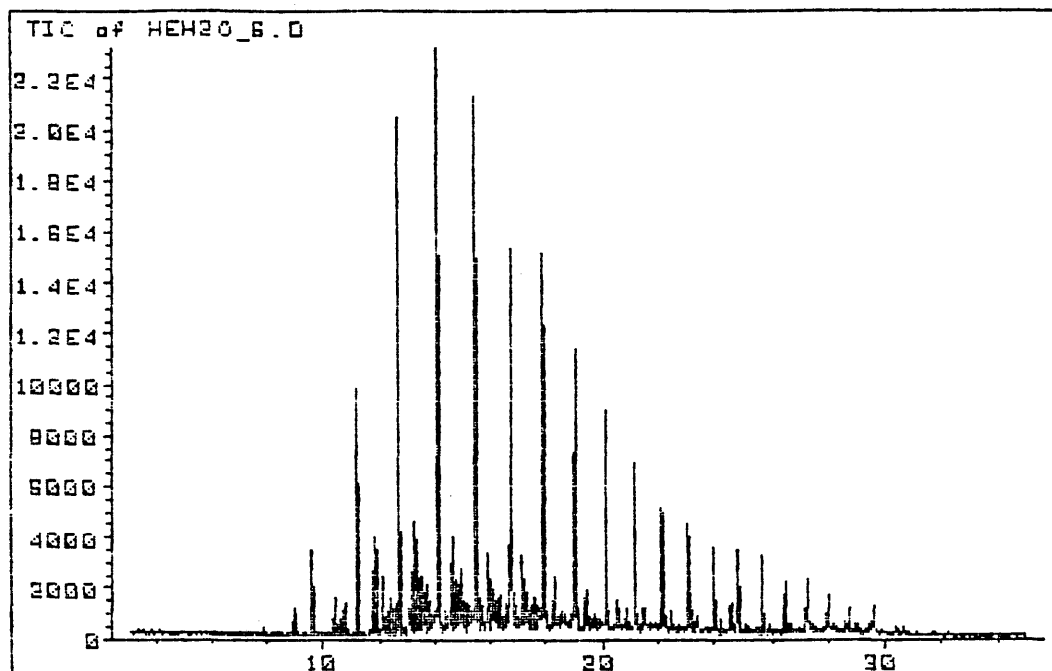
Hydrogen TIC - Fraction 6



Total Ion Chromatogram
Hydrogen System - Fraction 6

Figure 29

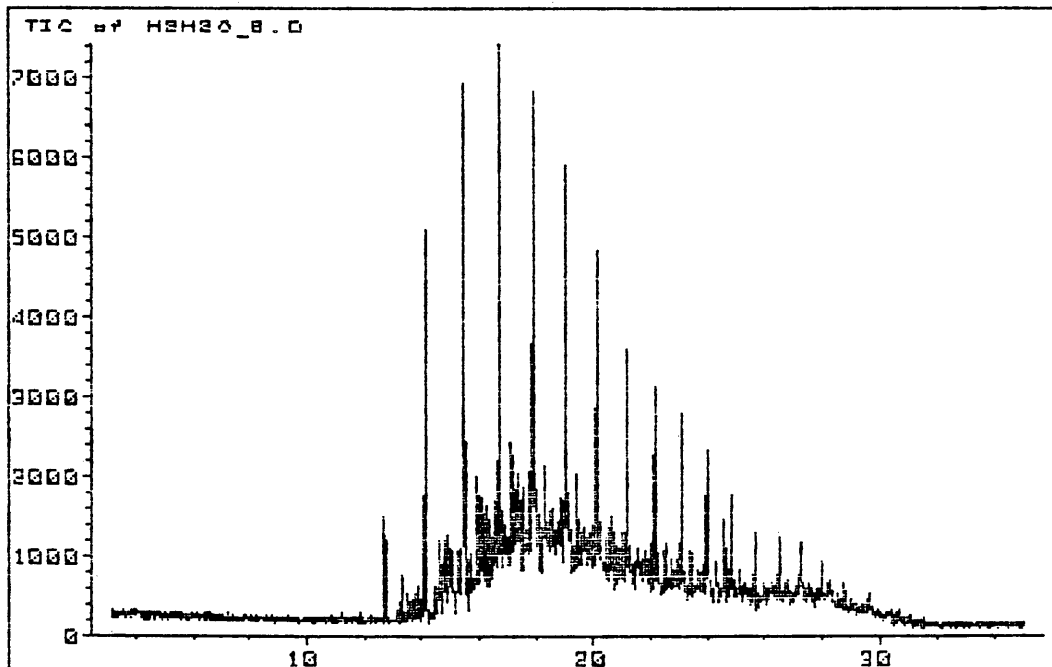
Helium/Water TIC - Fraction 6



Total Ion Chromatogram
Helium/Water System - Fraction 6

Figure 30

Hydrogen/Water TIC - Fraction 6



Total Ion Chromatogram

Hydrogen/Water System - Fraction 6

CONCLUSIONS

1. High organic carbon conversions can be obtained using a thermal solution process which employs supercritical toluene.
2. The highest conversion and the lowest ratio of heavy polymer to conversion was achieved for the system with a hydrogen atmosphere and small amounts of water added.
3. The presence of molecular hydrogen enhanced conversion at high reaction temperatures but was not effective at lower temperatures.
4. The reactions without water added to the system can be adequately modeled with a second order irreversible rate expression. The results for the reactions with small amounts of water added were not clear in discriminating between models.
5. A chromatographic separation technique was successfully used to classify five oils into 24 separate fractions.

6. Some of the fractions derived from open column chromatographic separation were examined by GC/MS. The oils produced by the thermal solution process in the batch reactor system for four different reaction conditions appear very similar.

RECOMMENDATIONS

1. Perform a three dimensional matrix of experiments to study the effect of reaction temperature, hydrogen partial pressure and amount of water in the system. A construction of this surface would yield optimum operating conditions.
2. Perform hydrogen consumption and heat load analysis. These data would permit the study of preliminary process economics.
3. Use deuterium oxide and deuterium gas tracers to determine the fate of hydrogen in the system.
4. Develop a more sophisticated kinetic model and test it by performing a detailed mass balance for all reaction products.

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T-3098

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APPENDIX A

REACTOR RUNS DATA

T-3098

Run: # 1

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 300°C

Sample Time (min.)	Organic Carbon Conversion (%)
10	-
30	5.6
60	9.2

T-3098

Run: # 2

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
10	20.4
30	30.5
60	30.9

Run: # 3

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
10	63.7
30	70.7
60	70.8

Run: # 4

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 450°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	76.8
10	82.0
30.	81.8
60	82.6

Run: # 5

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 300°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	10.6
10	-
30	14.9
60	-

T-3098

Run: # 6

Solvent: 5 ml Toluene / .15 g HCl

Shale Charge: .5 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
30	46.7

* Run in tubing bomb reactor system

Run: # 7

Solvent: 300 ml Toluene

Shale Charge: 17.83 g - 25.0 g Raw shale demineralized with HCl
prior to reaction.

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

Sample Time (min.)

Organic Carbon Conversion (%)

30

28.7

T-3098

100

Run: # 8

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	24.6
4	40.3
8	-
10	47.4

Run: # 9

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	38.4
4	51.9
8	55.3
10	55.4

..PGNO102

Run: # 10

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	24.8
10	29.3
30	36.8
60	40.7

Run: # 11

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	25.1
10	31.3
30	35.4
60	36.0

Run: # 12

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	33.1
10	35.7
30	39.0
60	42.3

Run: # 13

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	29.6
10	36.6
30	42.3
60	51.7

Run: # 14

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	13.2
10	23.5
30	39.0
60	47.2

Run: # 15

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	18.4
10	25.4
30	37.8
60	45.6

Run: # 16

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	38.0
4	51.8
8	59.3
10	62.2

Run: # 17

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	41.4
4	49.4
8	54.0
10	57.1

Run: # 18

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	-
10	27.6
30	36.2
60	46.9

Run: # 19

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	47.0
4	58.9
8	68.4
10	67.0

Run: # 20

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	49.6
4	57.5
8	66.5
10	67.4

Run: # 21

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
5	-
10	23.6

Run: # 22

Solvent: 300 ml Toluene / 20 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
30	15.0

Run: # 23

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 400°C

Sample Time (min.)

Organic Carbon Conversion (%)

30

56.4

Run: # 24

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 400°C

Sample Time (min.)

Organic Carbon Conversion (%)

30

60.9

T-3098

117

Run: # 25

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 200 psi H₂

Reaction Temperature: 400°C

Sample Time (min.)

Organic Carbon Conversion (%)

30

62.3

T-3098

Run: # 26

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
30	81.4
60	81.4

T-3098

Run: # 27

Solvent: 300 ml Toluene / 2 ml HCl

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 450°C

Sample Time (min.)	Organic Carbon Conversion (%)
10	77.9
30	79.1

Run: # 28

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 425°C

Sample Time (min.)	Organic Carbon Conversion (%)
30	77.1
60	80.1

T-3098

Run: # 29

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 450°C

Sample Time (min.)	Organic Carbon Conversion (%)
10	81.0
30	84.2

Run: # 30

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	13.2
4	14.6
8	15.4
10	23.5

Run: # 31

Solvent: 300 ml Toluene

Shale Charge: 25 g

Gas Charge: 300 psi H₂

Reaction Temperature: 400°C

Sample Time (min.)	Organic Carbon Conversion (%)
2	21.6
4	33.2
8	45.2
10	48.0

T-3098

Run: # 32

Solvent: 300 ml Toluene

Shale Charge: 75 g

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

* 30 min. reaction time . Resulting oil submitted for
characterization

T-3098

Run: # 33

Solvent: 300 ml Toluene

Shale Charge: 75 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

* 30 min. reaction time . Resulting oil submitted for
characterization

T-3098

Run: # 34

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 75 g

Gas Charge: 300 psi H₂

Reaction Temperature: 375°C

* 30 min. reaction time . Resulting oil submitted for
characterization

T-3098

Run: # 35

Solvent: 300 ml Toluene / 2 ml H₂O

Shale Charge: 75 g

Gas Charge: 300 psi He

Reaction Temperature: 375°C

* 30 min. reaction time . Resulting oil submitted for
characterization

APPENDIX B

COLUMN CHROMATOGRAPHY DATA

Helium
Shale Oil Fractionation

Run Condition: Helium

Mass of Oil to Column: .8490g

Fraction	Gross(g)	Tare(g)	Net(g)
#1	7.6437	7.6420	.0017
#2	7.6901	7.6426	.0475
#3	7.6469	7.6422	.0047
#4	7.6551	7.6418	.0133
#5	7.6467	7.6425	.0042
#6	7.6765	7.6411	.0354
#7	7.6596	7.6422	.0174
#8	7.6598	7.6418	.0180
#9	7.6670	7.6420	.0250
#10	7.6810	7.6413	.0397
#11	7.6459	7.6411	.0048
#12	7.6470	7.6420	.0050
#13	7.6456	7.6419	.0037
#14	7.6440	7.6410	.0030
#15	7.6497	7.6408	.0089
#16	7.6737	7.6404	.0333
#17	7.8630	7.6071	.2559

T-3098

Fraction	Gross(g)	Tare(g)	Net(g)
#18	7.7450	7.6424	.1026
#19	7.6853	7.6418	.0435
Asphaltenes	22.9429	22.4618	.4810
Acids	12.8489	12.8295	.0194
Bases	13.1478	13.1148	.0330

Fischer Assay
Shale Oil Fractionation

Run Condition: Fischer Assay

Mass of Oil to Column: 1.3742g

Fraction	Gross(g)	Tare(g)	Net(g)
#1			<.0001
#2	7.7402	7.6080	.1322
#3	7.6423	7.6082	.0341
#4	7.6474	7.6074	.0400
#5	7.6210	7.6076	.0134
#6	7.6873	7.6082	.0791
#7	7.6568	7.6078	.049
#8	7.6586	7.6446	.0141
#9	7.6275	7.6074	.0201
#10	7.7280	7.6450	.083
#11	7.6529	7.6452	.0077
#12	7.6126	7.6080	.0047
#13	7.6149	7.6079	.0070
#14	7.6495	7.6450	.0045
#15	7.6200	7.6088	.0112
#16	7.6837	7.6454	.0383
#17	7.8188	7.6448	.1740

T-3098

Fraction	Gross(g)	Tare(g)	Net(g)
#18	7.6751	7.6064	.0687
#19	7.7380	7.6419	.0961
Asphaltenes	19.2144	19.1749	.0395
Acids	13.1265	13.0891	.0374
Bases	13.0992	13.0543	.0449

Helium / H₂O
Shale Oil Fractionation

Run Condition: Helium / H₂O

Mass of Oil to Column: .9090g

Fraction	Gross(g)	Tare(g)	Net(g)
#1	7.0144	7.0139	.0005
#2	7.0504	7.0139	.0365
#3	7.0191	7.0138	.0053
#4	7.1216	7.0986	.0230
#5	7.1030	7.0986	.0044
#6	7.1290	7.0982	.0308
#7	7.0432	7.0145	.0287
#8	7.1109	7.0987	.0122
#9	7.1088	7.1001	.0098
#10	7.1249	7.0990	.0259
#11	7.0227	7.0147	.0080
#12	7.0166	7.0141	.0025
#13	7.1024	7.1000	.0024
#14	7.0172	7.0156	.0016
#15	7.0208	7.0148	.0060
#16	7.1162	7.0991	.0171
#17	7.2152	7.0167	.1985

T-3098

Fraction	Gross(g)	Tare(g)	Net(g)
#18	7.2033	7.0998	.1035
#19	7.0615	7.0155	.0460
Asphaltenes	18.4496	18.0195	.4301
Acids	13.1943	13.1753	.0190
Bases	13.0031	12.9880	.0151

Hydrogen / H₂O
Shale Oil Fractionation

Run Condition: Hydrogen / H₂O

Mass of Oil to Column: 1.0489g

Fraction	Gross(g)	Tare(g)	Net(g)
#1	7.5373	7.5362	.0011
#2	7.6211	7.5722	.0489
#3	7.5490	7.5356	.0134
#4	7.5595	7.5351	.0244
#5	7.5778	7.5733	.0045
#6	7.5909	7.5729	.0180
#7	7.5676	7.5349	.0327
#8	7.5803	7.5725	.0078
#9	7.5419	7.5359	.0060
#10	7.5821	7.5722	.0099
#11	7.5749	7.5727	.0022
#12	7.5368	7.5360	.0008
#13 & 14	7.5385	7.5348	.0037
#15	7.5384	7.5342	.0042
#16	7.5850	7.5725	.0125
#17	.6916	.5350	.1569
#18	.6376	.5723	.0653

T-3098

Fraction	Gross(g)	Tare(g)	Net(g)
#19	.6477	.5800	.0677
Asphaltenes	19.2578	19.1489	.1089
Acids	13.0013	12.9806	.0207
Bases	12.9341	12.9057	.0284

Hydrogen
Shale Oil Fractionation

Run Condition: Hydrogen

Mass of Oil to Column: 1.6303g

Fraction	Gross(g)	Tare(g)	Net(g)
#1	7.3458	7.3402	.0056
#2	7.5472	7.4677	.0795
#3	7.5827	7.5677	.0150
#4	7.0275	6.9832	.0443
#5	7.3511	7.3457	.0054
#6	7.5747	7.4718	.1029
#7	7.6158	7.5705	.0453
#8	7.9995	6.9847	.0148
#9	7.4810	7.4710	.0100
#10	7.3650	7.3460	.0190
#11	6.9883	6.9845	.0038
#12	7.5723	7.5696	.0027
#13	7.3498	7.3447	.0042
#14	7.4737	7.4707	.0030
#15	7.5734	7.5688	.0046
#16	7.0174	6.9840	.0334
#17	7.6763	7.4735	.2028

T-3098

Fraction	Gross(g)	Tare(g)	Net(g)
#18	7.4351	7.3447	.0904
#19	7.1283	6.9835	.1448
Asphaltenes	22.8600	22.5295	.3305
Acids	13.0655	13.0371	.0284
Bases	13.1932	13.1633	.0299

APPENDIX C

REACTOR CONTROL PROGRAM

T-3098

Computer listing of program used for reactor
temperature control

```

10 DEF FN V(X) = (44 - PEEK (1146)) * ( PEEK (1274) * 256
+ PEEK (1402))
12 HOUR = 1532:MIN = 1660:SEC = 1788
14 CLK = 50177: CALL CLK + 7
16 P = 100
17 I = 5
18 INPUT " RUN TEMPERATURE";TSET
20 DEF FN DEC(X) = PEEK (HOUR) / 24 + PEEK (MIN) / 1440 +
PEEK (SEC) / 86400
30 START = FN DEC(X)
40 CALL CLK + 7
45 POKE 49314,N + 1:V(N) = FN V(X)
50 INJECT = FN DEC(X)
60 TT = INJECT - START
65 HOME : VTAB 15
67 IF TT * 1440 > = 0.5 THEN GOTO 200
70 PRINT INT ((5 - TT * 1440) * P) / P, "MINUTES TO
INJECTION"
72 FOR K = 1 TO 500: NEXT K
90 GOTO 40
200 TX = 159 - TSET / 3.3
205 CALL CLK + 7:START = FN DEC(X)
207 PRINT ""
210 HGR : HCOLOR= 3: HPLOT 0,0 TO 279,0 TO 279,159 TO 0,159
TO 0,0
220 FOR N = 0 TO 260 STEP 10: HPLOT N,TX TO N + 1,TX: NEXT N
230 FOR N = 0 TO 158 STEP 32
240 FOR M = 0 TO 278 STEP 4
250 HPLOT M,N TO M + 2,N: NEXT M: NEXT N
260 K = 11.81:G = .806: HOME
270 VTAB 24
280 DHTR = 40:FULL = 0:H2O = 0: POKE 51000,0:HTR = 0: POKE
49400,0
285 POKE 49314,0
290 FOR N = 0 TO 3
300 FOR W = 1 TO 15: CALL 49664: NEXT W
310 POKE 49314,N + 1:V(N) = FN V(X)
320 NEXT N
330 C = (V(3) - V(0)) / K - 273
340 FOR N = 1 TO 3
350 IN F = 3 THEN GOTO 285
360 V = (V(N) - V(0)) * G: GOSUB 1100
370 P = 10
375 F = 100
380 TEMP = INT (T * P + .5) / P
390 IF N = 1 THEN GOTO 420
400 IF N = 2 THEN GOTO 1000

```

T-3098

```
410 NEXT N
420 PRINT "REACTOR TEMP",TEMP
430 Q = Q + 1:TP = 159 - (T-/ 3.3)
440 IF Q > 258 THEN GOTO 200
450 HPLOT Q,TP
481 IF INT (TT * 1440 * F) / F < I THEN GOTO 486
482 PRINT ""
483 IF I = 5 THEN I = 10: GOTO 490
484 IF I = 10 THEN I = 30: GOTO 490
485 IF I = 30 THEN I = 60
486 CALL CLK + 7:ELAPSE = FN DEC(X)
487 TT = ELAPSE - START
490 OF TT > = .0416667 THEN GOTO 800
500 IF TEMP > TSET + 1 THEN GOTO 600
510 IF H2O = 0 THEN GOTO 530
520 H2O = 0:POKE 51000,0
530 APR = TSET - TEMP
540 IF APR > 6.3 THEN GOTO 700
550 IF TEMP < TSET THEN GOTO 900
560 IF HTR = 0 THEN GOTO 580
570 HTR = 0: POKE 49400,0
580 GOTO 400
600 IF HTR = 0 THEN GOTO 630
610 HTR = 0: POKE 49400,0
630 IF H2O = 0 THEN H2O = 1: POKE 51000,0
640 GOTO 400
700 IF FULL = 1 THEN GOTO 730
720 FULL = 1: POKE 49400,63
725 PER = 63
730 GOTO 400
800 IF HTR = 0 THEN GOTO 280
810 HTR = 0: POKE 49400,0
820 IF H2O = 1 THEN GOTO 840
830 H2O = 1: POKE 51000,1
840 IF TEMP < 100 THEN GOTO 1080
850 GOTO 400
900 PER = APR * 10
910 IF DHTR = PER THEN GOTO 930
920 DHTR = PER: POKE 49400, INT (PER)
930 GOTO 400
1000 PRINT "HEATER TEMP",TEMP
1010 PRINT INT (PER), INT (TT * 1440 * F) / F
1020 GOTO 410
1080 END
1100 IF V < 326 THEN T = C + V / 4.07: RETURN
1110 OF V < 654 THEN T = C + 80 + (V - 326) / 4.11: RETURN
1120 IF V < 1137 THEN T = T + C + 160 + (V - 654) / 4.02:
RETURN
1130 IF V <1935 THEN T = T + C + 280 + (V - 1137) / 4.2:
RETURN
```


T-3098

1140 IF V < 2932 THEN T = T + C + 470 + (V - 1935) / 4.26:
RETURN

1150 IF V < 3614 THEN T = T + C + 704 + (V - 2932) / 4.11:
RETURN