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Pyrolysis and Hydrolysis of
Montcey Oil Shale
at Short Residence Times

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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 Engineering and Petroleum-Refining)

Golden, Colorado

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ABSTRACT

Pyrolysis and hydrolysis of Montcey oil shale of the Eastern Paris Basin, France, using supercritical toluene as a solvent was studied at short residence times in a tubing-bomb reaction system which produced very fast heating rates. Utilizing this system, oil yields in excess of 160% Fischer Assay can be obtained for temperatures in the range of 425°C and residence times of 30 minutes. For residence times shorter than 2.5 minutes high organic carbon conversions can be obtained for temperatures greater than 425°C with oil yields in excess of 150% Fischer Assay even with very low hydrogen partial pressure. The presence of gas phase molecular hydrogen enhanced the conversion of organic carbon but did not significantly change the oil selectivity, which remained above 95% for the majority of the runs. An irreversible pseudo first-order model adequately describes the conversion of organic carbon below 475°C and predicts an apparent activation energy of 31.301 kcal/gmole.

T-3115

DEDICATION

To my family and Father Lamer,
for your loving guidance.

TABLE OF CONTENTS

Section	Page
ABSTRACT	iii
LIST OF TABLES.....	viii
LIST OF FIGURES	ix
ACKNOWLEDGEMENTS	x
1. INTRODUCTION	1
2. BACKGROUND AND LITERATURE	3
3. EQUIPMENT	16
3.1 TUBING-BOMB REACTION SYSTEM	16
3.1.1 Gas Feed	16
3.1.2 Heater and Reactor	18
3.1.3 Eccentric Arm Unit	21
3.1.4 Gas Sampling	21
3.1.5 Supporting Equipment	21
3.2 ANALYTICAL EQUIPMENT	23
3.2.1 Carbon Analyzers	23
3.2.2 Gas Chromatograph	24
3.2.3 Ash Furnace	24
4. EXPERIMENTAL PROCEDURES	25
4.1 RUN CONDITIONS	25
4.1.1 Phase One	25
4.1.2 Phase Two	25
4.1.3 Phase Three	25

4.2	MATERIALS	26
4.2.1	Oil Shale	26
4.2.2	Solvent	28
4.2.3	Gases	28
4.3	EXPERIMENTAL RUN PROCEDURE	28
4.3.1	Start-Up	29
4.3.2	Run Preparation	29
4.3.3	Reaction Procedure	30
4.3.4	Shut-Down	31
4.4	ANALYTICAL PROCEDURE	31
4.4.1	Sample Preparation	31
4.4.2	Solid Analysis	31
4.4.3	Gas Analysis	32
5.	DATA ANALYSIS	33
5.1	ORGANIC CARBON CONVERSION	33
5.2	OIL SELECTIVITY	34
5.3	KINETIC MODELING	36
6.	DISCUSSION OF RESULTS	39
6.1	INTRODUCTION	39
6.2	SOURCES OF ERROR	41
6.2.1	Processing Errors	41
6.2.2	Analytical Errors	43
6.3	PHASE ONE	43
6.4	PHASE TWO	48

6.5 PHASE THREE	54
6.6 KINETIC MODELING	57
7. CONCLUSIONS	72
8. RECOMMENDATIONS	74
LITERATURE CITED	75
APPENDIX A - Reaction Time Correction	79
APPENDIX B - Time Correction Program.....	85
APPENDIX C - Data Analysis Program.....	88
APPENDIX D - Experimental Run Summaries.....	93
APPENDIX E - MINITAB Sample Input and Output	142
APPENDIX F - Equipment Construction	144
APPENDIX G - Solvent Stability Tests	146
APPENDIX H - Fischer Assay	148

LIST OF TABLES

Table 1.	Shale Oil Resources of the World Land Areas ...	4
Table 2.	Properties Typical of Gas, Liquid, and SCF's	.14
Table 3.	Typical Analytical Values, Montcey Oil Shale	.27
Table 4.	Phase One Run Summary	45
Table 5.	Phase One Run Summary	46
Table 6.	Phase Two Run Summary	50
Table 7.	Phase Two Run Summary	51
Table 8.	Phase Three Run Summary, Short Time Runs	55
Table 9.	Phase Three Run Summary, Inert Atmosphere	55
Table 10.	Pseudo-Equilibrium Constant "a"	64

LIST OF FIGURES

Figure 1.	PT Diagram, Pure Fluid Supercritical Region	.12
Figure 2.	Schematic of Reaction System17
Figure 3.	Tubing-bomb Reactor20
Figure 4.	Eccentric Arm Assembly22
Figure 5.	Phase One and Two Run Matrix49
Figure 6.	400 Degree Conversion58
Figure 7.	425 Degree Conversion59
Figure 8.	450 Degree Conversion60
Figure 9.	475 Degree Conversion61
Figure 10.	500 Degree Conversion62
Figure 11.	Kinetic Model Prediction63
Figure 12.	Linear Fit of 400°C Data by 1st Order Model	.65
Figure 13.	Linear Fit of 425°C Data by 1st Order Model	.66
Figure 14.	Linear Fit of 450°C Data by 1st Order Model	.67
Figure 15.	Linear Fit of 475°C Data by 1st Order Model	.68
Figure 16.	Linear Fit of 500°C Data by 1st Order Model	.69
Figure 17.	Arrhenius Plot71
Figure 18.	Typical Temperature History82

ACKNOWLEDGEMENTS

The author would like to thank Dr. Robert M. Baldwin for his patience and guidance provided during the experimental and calculation periods of this thesis. The assistance of the laboratory technicians Elizabeth Kostiuk and Karen Torres in performing the product analysis is gratefully acknowledged. In addition, the assistance of Ken Chen in developing the data analysis computer program was greatly appreciated. Finally, The financial support provided by Southern Pacific Petroleum, N.L., Sydney, Australia is gratefully acknowledged.

1. INTRODUCTION

In the foreseeable future the United States will enter an era of transition. Dwindling supplies of natural fuels will have to be replaced by alternative sources of energy. The replacement of liquid fuels, the base of our economic infrastructure, will become a national priority. Because of the immense reserves of oil shale in the United States and world-wide, considerable attention has been given to producing fuels, particularly distillate fuel, from oil shale.

Many techniques for producing oil from oil shale have been studied but only pyrolysis, or retorting, has developed to commercial feasibility. Another technique, thermal solution, is presently being studied as a means of increasing the efficiency of oil shale processing. Higher organic carbon conversions and more desirable liquid products have been obtained using the thermal solution concept with a vehicle that is a hydrogen donor solvent or in the presence of molecular hydrogen. This increase in shale oil yield can be obtained at temperatures significantly lower than those used in retorting, making thermal solution an attractive alternative to present processing schemes.

The purpose of the research described in this paper was to experimentally determine the rate and extent of shale oil

production from the Montcey oil shale of the Eastern Paris Basin, France, as a function of temperature and hydrogen partial pressure. This involved the construction of a new operating system known as the tubing-bomb reaction system. This system allows for the rapid heating of reactants to operating temperatures, facilitating the collection of isothermal data at short residence times. The experimental program consisted of two phases. Phase one consisted of long residence time runs to determine the effects of temperature and hydrogen partial pressure on equilibrium conversion levels, in supercritical toluene. Phase two consisted of short residence time runs to collect data in the region where kinetics controls conversion, with all other conditions the same as in phase one.

2. BACKGROUND AND LITERATURE

Oil from oil shale is considered to be a likely candidate to replace petroleum due to the large known reserves. Total shale oil resources of the world land areas have been estimated at 342×10^{12} barrels of oil equivalent for grades of shale yielding 10 gallons or greater per ton of shale (1). Known resources by continent are presented in Table 1, with unknown reserves probably much greater than known reserves. This makes oil shale one of the most abundant known sources of hydrocarbons in the world.

The use of oil shale as a fuel is not a recent development. It is generally recognized that the first recorded attempt to produce oil from shale was that noted in British Crown Patent No. 330, issued in 1694, for the production of "oyle from a kind of stone" (2,3). The establishment of a oil shale industry first occurred in France in 1838 where oil shale was distilled to make lamp fuel (4). In 1862, production of oil from shale was begun in Scotland and ran continuously for almost one hundred years, being shut down only when all the high grade reserves were depleted. Other countries have had oil shale industries, most notably Estonia and the Manchuria area of China, with China's oil shale industry still in operation (1,2,4).

In the United States, the prospects for an oil shale

Table 1. Shale Oil Resources of the World
Land Areas, Billions of Barrels

Continents	Oil Equivilant in Deposits	
	Range in Grade Gallons/Short Ton	
	10-25	25-100
Africa	80,000	4,000
Asia	110,000	5,500
Australia	20,000	1,000
Europe	26,000	1,400
North America	50,000	3,000
South America	40,000	2,000
<hr/>	<hr/>	<hr/>
Total	325,000	17,000

Known reserves, 1965.

industry have been turned on and off based on the competition encountered from inexpensive petroleum-derived products (2). The petroleum industries recent trends of rising costs and dwindling known reserves has again focused attention on oil shale development.

Compared to petroleum, the organic matter in shale is a low grade source of energy. The largest problem associated with producing synthetic fuels from oil shale has been the difficulty in developing a process which can efficiently and economically convert the oil shale's organic matter into a high grade energy feedstock. Oil shale can be defined as:

"a wide variety of laminated, solidified mixtures of argillaceous sediments and organic matter having the common property of yielding oil upon destructive distillation, yet being but slightly susceptible to the action of common petroleum solvents." (5)

The organic matter in oil shale, commonly known as kerogen, is best described as:

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

Many processes to remove kerogen from the inorganic rock matrix have been attempted with varying levels of success. In situ, modified in situ, biochemical leaching, solvent extraction, thermal solution and pyrolysis are various processes that have been developed, with retorting, a

form of pyrolysis where oil shale is reacted at atmospheric pressure, high temperatures, and slow heating rates, being the only one developed to commercial practicality. A variety of sophisticated retorting processes have been built on a pilot plant scale, most notably the Union Oil, TOSCO II, Chevron and Petrosix retorts (7). The major disadvantage of retorting is that current methods are very inefficient with respect to liberating the kerogen in oil shale and, at best, can remove only about 70% of the kerogen contained in shale. In addition, present retorting techniques utilize high temperatures (about 550°C), long residence times and slow heating rates, which promote cracking and condensation reactions, thereby lowering the oil yield (4).

A variation of the standard retorting process, known as hydrotorting, involves pyrolysis of oil shale in the presence of a molecular hydrogen atmosphere (7). The addition of hydrogen has been shown to produce higher oil yields than conventional retorting. The increase in oil yield is the direct result of the molecular hydrogen acting as a free radical scavenger, inhibiting the cracking reactions which produce excess product gas and coke on the shale (8). Bench-scale investigations by Texaco in the 1960's claimed that oil shale may be almost totally stripped of its organic material to yield distillates ranging from 105 to 115% of

Fischer Assay, a standardized analysis process which gives inexpensive and easily reproducible results.

The solvent extraction process attempts to remove the portion of kerogen that is soluble in common solvents. Various investigators have attempted the extraction of kerogen using a large number of organic solvents, both polar and non-polar, below the boiling point of the solvents. However, the fraction of kerogen that can be removed by this process is only a small portion of the organic content of the shale (7,9,10,11,12).

In the effort to develop a process that efficiently converts kerogen to a fuel feedstock, interest in the thermal solution process has been renewed. Thermal solution combines the unit operations of pyrolysis and solvent extraction, since it involves the heating of oil shale in the presence of a solvent. As constituents of kerogen are released by thermal bond-breaking, they are solubilized and extracted from the inorganic matrix by the solvent. The advantages of thermal solution compared to conventional retorting is that lower operating temperatures may be used, lowering the energy requirements of the process, and a higher conversion of organic carbon to oil may be obtained. These two factors give thermal solution a significant increase in conversion efficiency over that of retorting.

Most research conducted on the thermal solution process has focused on varying the operating conditions and solvent selection to determine their effect on kerogen conversion and oil yield. Gavin and Aydelotte (10) reported that the organic matter in oil shale could be extracted in high yield using several solvents at or near the solvent's boiling points, using a Soxhlet extraction apparatus. The solvents they investigated included carbon tetrachloride, carbon bisulfide, acetone, ether, benzene and chloroform.

In the early 1900's numerous patents were granted in the U.S. for various thermal solution processes. Work done by Ryan, Day and Hampton was similiar in that finely crushed oil shale was extracted in an oil bath, usually mineral oil, at temperatures between 315 and 371°C (13,14,15). This temperature range was well below the temperatures used in retorting and avoided the undesirable cracking and condensation reactions associated with retorting. The patented processes varied significantly only in the processing of the products and spent shale. Hampton actually had five patents over the span of ten years, all of them minor modifications of the same process.

More recent research done by D'yakova (16,17) studied the effects of various solvents on oil shale using the thermal solution process and reported yields of 72 to 96%

conversion of the kerogen in a suite of seven shales reacted at temperatures between 380 and 430°C. The solvents investigated by D'yakova were anthracene oil, tetralin, petroleum fuel oil, diesel fuel, hydrogenated shale tars and shale oil distillate. Thermal solution continued to be studied after World War Two, with an increased emphasis on product yield, kerogen composition and the reaction mechanisms of pyrolysis.

A U.S. patent was granted to Buchan (18) for a thermal solution process which emphasized "the production of high quality liquid fuel fractions from kerogen". Schnackenburg and Prien (5) performed thermal solution experiments using a suite of 11 solvents to gain information on the composition of kerogen. In their study they were careful to avoid the supercritical state of their solvents by choosing a reaction temperature of 200°C. An extension of this work by Thompson and Prien (6) studied the effect of higher temperatures on kerogen extraction. Their results showed a significant increase in conversion when the reaction temperature was increased from 200 to 400°C.

Studies by Jensen et al. and Gavin et al. also investigated the thermal solution process to determine the composition of Green River and other Colorado oil shales (18,19). The Green River oil shale study also investigated the ef-

fects of hydrogenation and reported a significant decrease in gas make and coke formation, adding evidence that hydrogen inhibits these undesirable secondary reactions. Gregoli (20), Patzer (21), and Green (22) have all recently been granted patents for hydrogenation of oil shale in hydrogen donor and non-donor solvents in the presence and absence of gas phase molecular hydrogen.

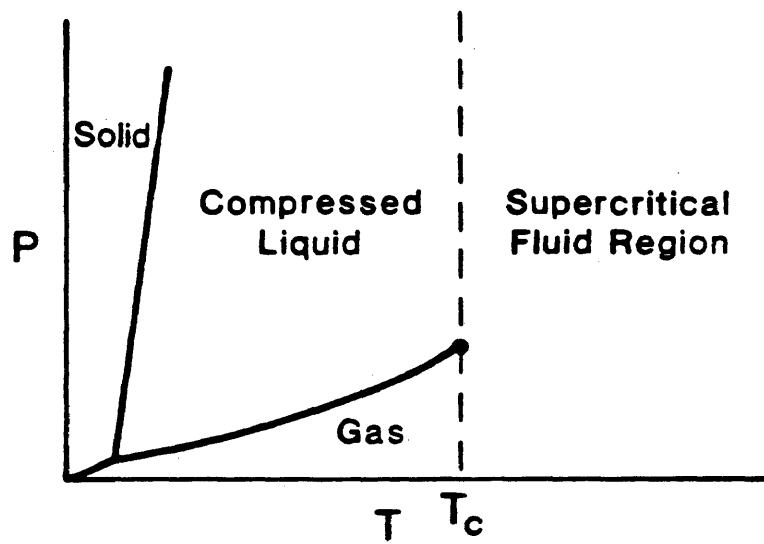
Gregoli's patent was issued for a fluidized bed hydrogenation process in which a shale/solvent slurry was introduced to a fluidized bed. The bed was at supercritical conditions with respect to the fluidizing medium. Using this process, oil yields of 140% of Fischer Assay were obtained.

Pratzer obtained a patent for a process in which finely ground oil shale and an organic solvent were reacted in a one-liter stirred autoclave at temperatures from 385 to 440°C and pressures from 250 to 2,000 psi for times of 20 to 120 minutes.

Green's patent placed emphasis on the use of a hydrogen donor solvent, tetralin, and a molecular hydrogen atmosphere at pressures of 10 to 200 atmospheres. His patent claimed high yields of liquid hydrocarbons boiling between 40-500°C and reduced amounts of hydrocarbon gases when compared to conventional retorting.

The present focus of thermal solution processing has been the studying of the effect of solvents in the supercritical state. The use of supercritical and critical-solvent processes is a fairly new development, being called "chemical engineering's new unit operation" (23,34). Many researchers from a variety of industries have studied supercritical fluid phenomena (25,26,27,28,29). A pure supercritical fluid (SCF) is a fluid that is at a temperature above its vapor-liquid critical point for a pure solvent. Thus it cannot be liquified by increasing the system pressure. Figure 1 illustrates the supercritical region. The interest in SCF phenomena is due to the phase equilibrium and mass transfer behavior exhibited by solvent/solute mixtures at and above the critical point of the solvent. High-molecular-weight solutes having vapor pressures lower than even a micron (0.001 mm Hg) experience "enhanced" solubility near the solvents critical point (24). By careful selection of the solvent, SCF extraction (SCFE or SCE) can be used to effect separations that are sensitive to high temperatures or difficult to perform with more established unit operations. In addition, SCF's retain the desirable characteristics of both a gas and a liquid. The density of a SCF is close to that of a liquid, enhancing the "loading" power of the solvent. The diffusion and viscosity

Figure 1. PT diagram showing the pure fluid supercritical region



characteristics are similar to those of a gas, giving SCF's mass transfer properties superior to that of a liquid phase solvent. Typical values are given in Table 2.

The major difficulty in studying SCF's effects on kerogen extraction is presented by the complexity of the product and interactions between the solvent and the kerogen. As stated by Ely (25):

"Although a substantial amount of process oriented experimental work is still being performed, recent emphasis has been on systematic experimental studies of model systems (as opposed to complex, ill-defined mixtures) and better theoretical understanding of high pressure phase equilibria"

Because of the complex nature of shale oil products, experimental thermal solution work has concentrated on optimization of organic carbon conversion and oil yields. Work by Baldwin (8,30,31), Frank (32), Bennett (33), and Winkler (34) has applied thermal solution to an Australian oil shale, using tetralin and toluene in both molecular hydrogen atmospheres and inert atmospheres. Manley (35) used thermal solution in the pyrolysis and hydrolysis of Kentucky oil shale. Baldwin (8) has found that while the extent of conversion is remarkably insensitive to the nature of the solvent, the presence of a supercritical (dense gas) phase is significant in short residence time reactions, where heating rate and pyrolysis is aided by the characteristics of the supercritical phase.

Table 2.

Properties Typical of Gas, Liquid and Supercritical Fluid

Property	Gas	SCF	Liquid
Density (g/cc)	$(0.6-2.0) \times 10^{-3}$	0.2-0.9	0.6-1.6
Diffusion Coefficient (cc/s)	0.1-0.4	$(0.2-0.7) \times 10^{-3}$	$(0.2-2.0) \times 10^{-5}$
Viscosity (cp)	$(1-3) \times 10^{-2}$	$(1-9) \times 10^{-2}$	0.2-3.0

It can be concluded that hydrolysis by thermal solution is an attractive alternative to conventional retorting. By investigating the effects of thermal solution on a variety of shales, the individual properties of a particular shale will not bias the conclusions reached concerning thermal solution. By experimenting with the Montcey oil shale of the Eastern Paris Basin, France, additional information will be added to the body of knowledge of thermal solution processes.

3. EQUIPMENT

3.1 TUBING-BOMB REACTOR SYSTEM

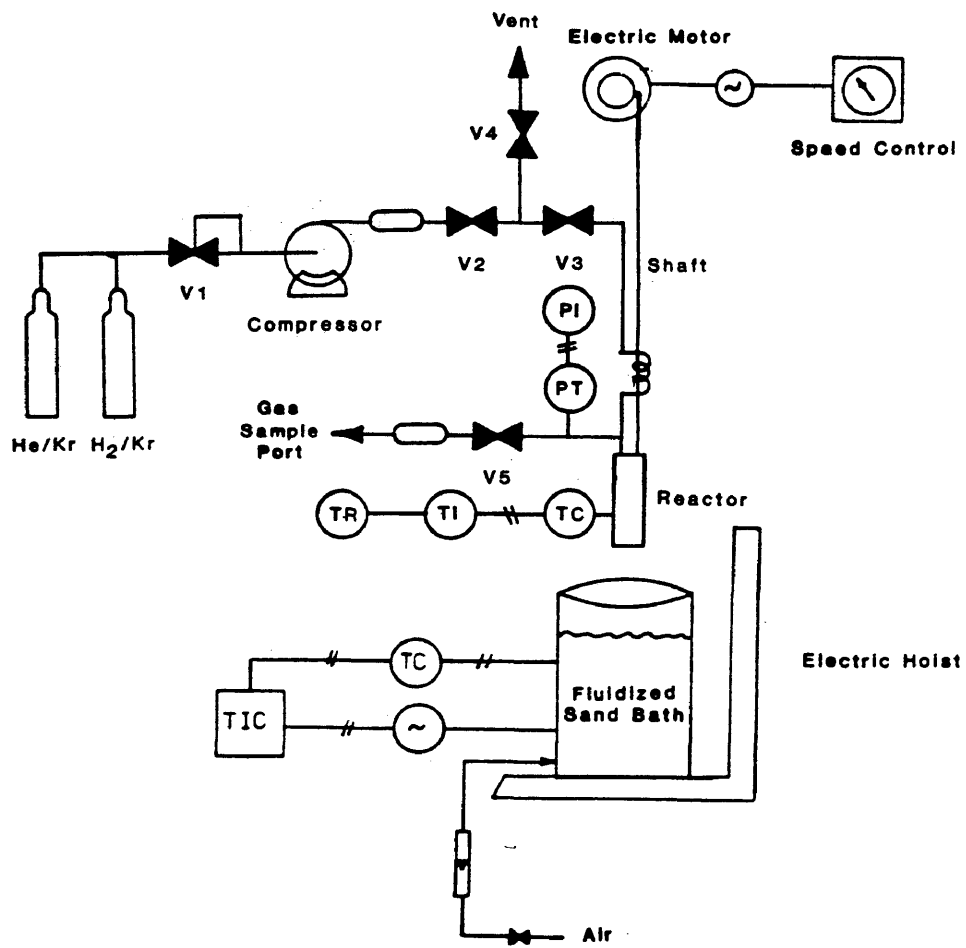
A schematic of the tubing-bomb reactor system is shown in Figure 2. Basically, the system consists of a gas feed system, a gas sampling system, and a small reactor of approximately 20 ml in volume which is attached to an eccentric arm on an electric motor drive. The reactor is immersed in an electrically heated sand bath, where rapid heating of the reactor takes place. The rapid heating rate minimizes nonisothermal data collection at reaction times as short as one minute.

The system was designed, built, and tested to operate in a true batch mode. Operation in a semibatch mode is possible with minor modifications. The construction of the system was assisted by information provided by Cities Service Research and Development Co. of Tulsa, Oklahoma. Dr. John Potts of Cities Service provided diagrams and photographs of the eccentric arm assembly, which proved to be invaluable during the construction phase.

3.1.1 Gas Feed

The gas feed equipment allows the reactor to be charged with various gas environments with a high degree of control over inlet pressure. Gas from industrial compressed gas cylinders (K size) flows through a Hoke dome loaded, self-

Figure 2. Schematic of Reaction System



regulating valve, V1. The tubing throughout the gas feed system is $\frac{1}{4}$ " 316 stainless steel. The gas then flows to the inlet of a Whitey Laboratory Compressor, number 6092. A Mercoid pressure switch automatically shuts down the compressor in the event of an overpressurized compressor discharge. The conditions of this experiment did not require the use of the compressor.

From the compressor discharge the gas flows into a one liter surge tank, then through a Whitey micrometering valve, V2, to either the reactor or to an atmospheric vent. The reactor is isolated from the gas feed system by a Nupro JB series forged body valve, V3, with 1/8 inch Swagelok connections. The system is designed such that vacuum can be drawn on the reactor side of valve V3. This allows the gas feed system to be purged by vacuum. In addition, this prevents reactor product gas from flowing back through valve V3, insuring that the composition of gas charged to the reactor is that of the true feed.

The atmospheric vent valve, V4, is a Whitey NB series bonnet union valve.

3.1.2 Heater and Reactor

The heater and reactor assembly will be described along with the electronic equipment used in their operation.

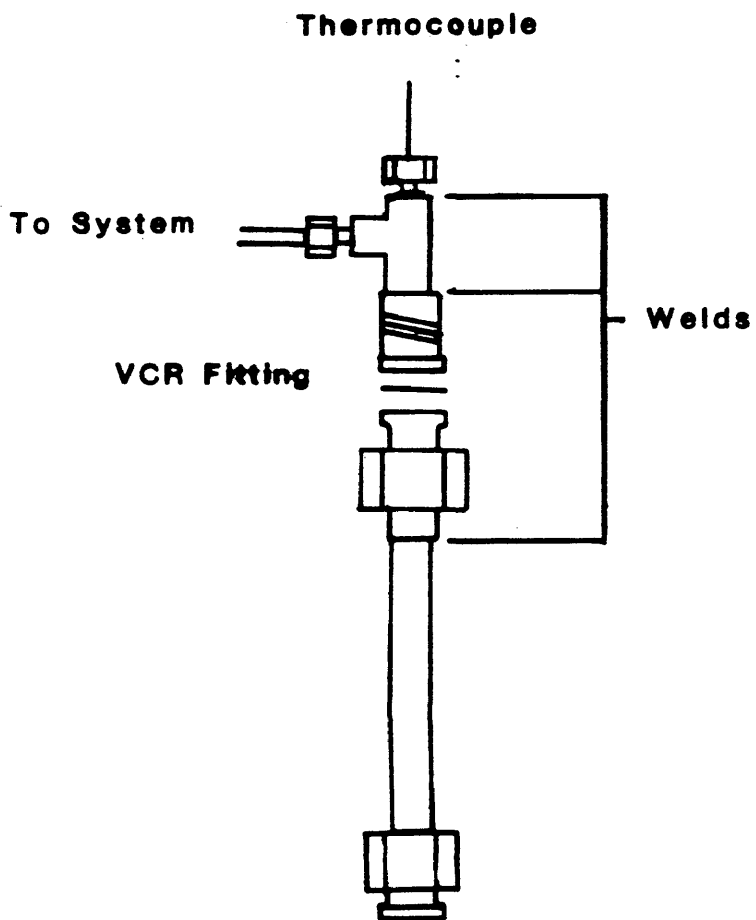
The heater used was a Tecam fluidized bed sand bath,

Model SBL2D. The bath temperature was controlled by a Leeds & Northrup Electromax III temperature controller connected to a Leeds & Northrup zero voltage power pack. The temperature sensor was a K type thermocouple. The dry air supply to the fluidized bed was controlled by a Dwyer rotometer.

A drawing of the reactor is shown in Figure 3. The body of the reactor consists of $\frac{1}{2}$ " OD 316 stainless steel tubing, capped at the bottom by a Swagelok $\frac{1}{2}$ " cap and welded at the top to a Cajon VCR gland-type gasket fitting. The reactor head is a combination of a VCR glanded fitting, a Swagelok male run tee, a K type thermocouple in a 1/16 inch stainless steel sheath, and a 1/8 inch autoclave connector on the gas feed line. Three threaded fittings on the reactor head were removed and the pieces welded together to minimize leaks caused by thermal cycling.

The temperature in the reactor is displayed by a Omega Digital Thermometer, Model 115, and recorded by a Leeds & Northrup Speedomax single pen strip chart recorder. The pressure in the reactor is monitored and displayed by a Heise Transducer and Digital Pressure Indicator, Models 715A and 715, respectively. The pressure transducer is connected to the reactor by 1/16 " 316 stainless steel tubing. A Swagelok tee connects the gas sampling system to this line.

Figure 3. Tubing-bomb Reactor



3.1.3 Eccentric Arm Unit

A drawing of the motor-driven eccentric arm is shown in Figure 4. The agitation provided by the eccentric arm performs two functions. It enhances the heat transfer characteristics of the fluidized bed, thereby shortening the nonisothermal reaction time, and also provides for mixing of the reactor contents. The eccentric arm has a range of one and one-half inches and was run at a speed of approximately 120 RPM during operation of the system. The assembly was fabricated by Mr. Herman Stump of Boulder, Colorado. The materials used are listed in appendix F.

The motor drive unit consists of a Reliance Electric MiniPak Plus D-C drive controller and a $\frac{1}{4}$ HP, type TPR electric motor.

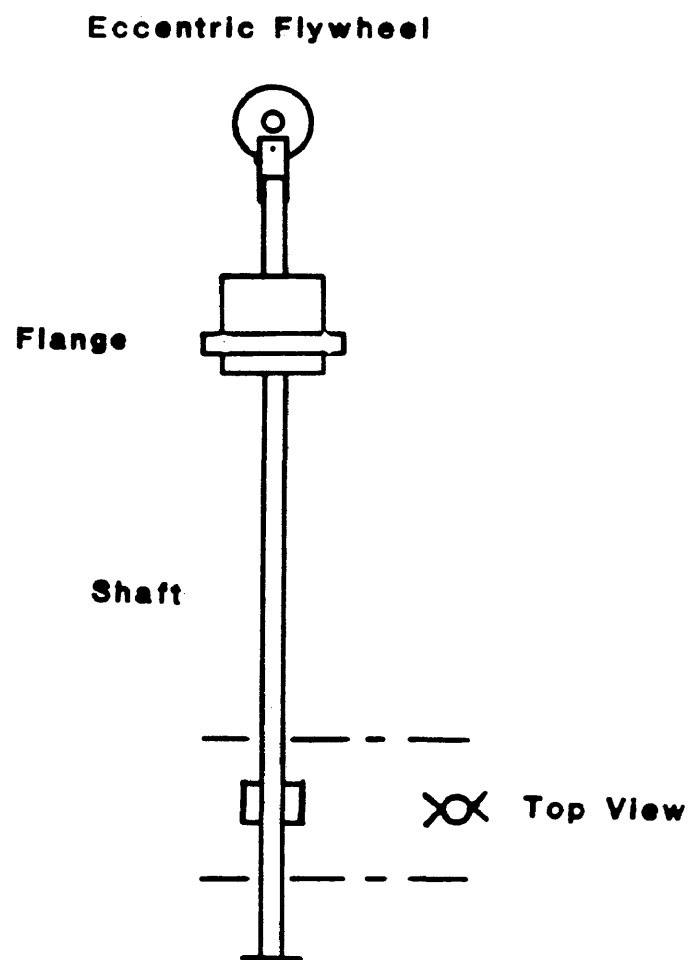
3.1.4 Gas Sampling

The gas sampling system consists of a one liter surge tank with a Swagelok female quick connect sample port. The system is isolated by a Whitey micro-metering valve, valve V5, which allows for the gentle bleeding of reactor pressure. The gas sampling bombs consisted of a Swagelok male quick connect, a Whitey DK series shut-off valve, and a 75 ml Whitey sample cylinder.

3.1.5 Supporting Equipment

This section will describe all supporting equipment

Figure 4. Eccentric Arm Assembly



which is not directly related to the process, but is essential to the operation of the equipment. This will include the physical supporting structure and safety equipment.

The reactor room, located in room 310 of Alderson Hall, measures approximately eight feet by eleven feet. The bulkheads consist of steel/wood/steel sandwiched together. The room has a sliding door of similiar construction. The reactor, gas sampling system, and eccentric arm assembly are supported by a Unistrut frame.

Safety devices for the operating personnel are located nearby. The reactor room is continously vented by a 1200 SCFM exhaust blower, effecting a complete volume change every 35 seconds. A sensing head for a combustibile gas detector is located near the control panel. A thermally activated fire extinguisher is located over the reactor and is good for type "B" and "C" fires. A safety shower, first aid kit, and eye wash station are located in the laboratory. Mine Safety Appliance Co. Sling air respirators are located at both exits of the laboratory.

3.2 ANALYTICAL EQUIPMENT

3.2.1 Carbon Analyzers

A total carbon analyzer and carbon dioxide coulometer, Models 5020 and 5030, respectively, manufactured by Coulometrics Inc., were used for total and inorganic carbon

analysis.

3.2.2 Gas Chromatograph

A Carle Analytical gas chromatograph, Model 111H, with a Hewlett-Packard integrator, Model 3390A, was used for product gas analysis.

3.2.3 Ash Furnace

A Thermolyne furnace, model A1630, was used to perform the ashings of shale samples.

4. EXPERIMENTAL PROCEDURES

4.1 RUN CONDITIONS

4.1.1 Phase One

The objective of the initial series of runs was to investigate the effect of temperature and hydrogen partial pressure on organic carbon conversion and oil selectivity at medium to long residence times. The following set of experimental conditions was used in the run matrix.

Solvent: Toluene

Initial Total Pressure: 800 psig (@ ambient T)

Hydrogen Partial Pressure: 400, 800 psig

Reaction Pressure at Autogenous: 1500 psig

Temperature: 400, 425, 450, 475, 500 °C

Residence Time: 12, 30, 60 minutes

The initial matrix was performed to determine the equilibrium conversion of the Montcey shale.

4.1.2 Phase Two

The second phase of the project consisted of investigating the short residence time effect on organic carbon conversion and oil yield. The residence times selected were 5, 7, and 10 minutes with all other experimental variables being the same as in phase one.

4.1.3 Phase Three

The final set of experimental runs consisted of a

series of runs to determine the organic carbon conversion during the non-isothermal heat up period. This was accomplished by heating the fluidized sand bath to 550 °C, initiating reaction as in the normal procedure, and quenching the reaction as it approached the temperature of interest. This set of runs was made for 400, 425, 450, 475, and 500 °C. In addition a run matrix was performed repeating the short residence time runs of phase two using an inert atmosphere of helium.

4.2 MATERIALS

4.2.1 Oil Shale

The oil shale used in this study was provided by Southern Pacific Petroleum(S.P.P.) N.L. of Sydney, Australia. The source was the marly Toarcian oil shale of the eastern Paris Basin, taken from the Montcey Permit, drill hole MOD-8, Noroy-le-Bourg. Typical analytical values for oil shale from the Montcey area are given in Table 3. The oil shale delivered by S.P.P. consisted of two kilograms collected from each of 30 separate one meter drilling cores. The samples were thoroughly mixed together, finely ground, and delivered wet packed in a 55 gallon drum.

Prior to use the shale was centrifuged to remove gross water, dried at ambient pressure and 100 degrees C for five hours, then vacuum dried at 60 degrees for a minimum of 48

Table 3.

Typical Analytical Values for Oil Shale
from the Montcey Area

<u>Component</u>	<u>Weight Percent</u>
SiO ₂	28
Al ₂ O ₃	10
CaO	22
Fe ₂ O ₃	4
CO ₂	16
MgO	2
Na ₂ O	0.4
K ₂ O	2
P ₂ O ₅	0.3
S	3

Values provided by S.P.P., June 26, 1985.

hours or until the water trap immersed in liquid nitrogen remained ice free. After drying, the shale resembled a hard clay. The shale was then ground in a ball mill and re-screened to a -200 mesh particle size (0.074 millimeter diameter and smaller).

4.2.2 Solvent

The solvent used in this study was toluene. Initially several solvents were considered; toluene, benzene, and acetone. These solvents were charged to the reactor and tested for compositional stability at reaction temperatures and pressures. Both the feed and product solvents were analyzed by gas chromatography and showed no thermal degradation. The results of these tests are given in appendix G.

4.2.3 Gases

The industrial grade gas used throughout this study was supplied by General Air of Denver. All gas cylinders had either an Argon or Krypton tracer. To study the effect of hydrogen partial pressure while maintaining the same overall reactor pressure two compositions were used; hydrogen with tracer and 50 percent hydrogen with tracer and the balance inert. Helium with tracer was also used.

4.3 EXPERIMENTAL RUN PROCEDURE

Experimental runs were made using the following procedure. A single run or multiple runs may be done between the

start-up and shut-down of the system.

4.3.1 Start-up

1. Fluidize the sand bath and set the temperature controller to the desired reaction temperature. Turn on the temperature controller. The bed takes several hours to heat up. Adjust the air flow during heat up to prevent excessive bubbling of the bed.

2. Turn on the pressure indicator, light, flashing red light, and exhaust fan. Check that the pressure transducer is zeroed.

3. Test the bed temperature by probing with a K type thermocouple attached to the digital thermometer. Minor adjustments to the temperature controller may be necessary.

4.3.2 Run Preparation

1. Charge the reactor with 2.00 grams of shale, 4.0 ml of toluene, and two small stainless steel bearings.

2. Seal the reactor with a nickel gasket in the VCR fitting. Attach the reactor to the eccentric arm.

3. Attach the vacuum pump to the gas sample port and evacuate the reactor system.

4. Isolate the gas sampling system by closing valve V5 and open the reactor to the gas feed system with valve V3. Make sure the feed side is not at high pressure.

5. Slowly open the metering valve, V2, and raise the

pressure to 800 psig. Close valves V2 and V3.

6. Check the "make and break" fittings with Snoop for gas leaks. Observe the pressure indicator for decreasing pressure, a sign of leaking.

7. Connect the reactor thermocouple. The digital thermometer should not be on when disconnected from a thermocouple.

4.3.3 Reaction Procedure

1. When the reactor is leak free, check that all the panel controls are on except for the compressor.

2. Turn on the eccentric arm controller. A small pressure drop will be observed as some gas goes into solution.

3. Initiate reaction by raising the fluidized bed to the indicated level.

4. Observe the pressure indicator for signs of leaks.

5. At the end of reaction time, lower the fluidized bed and quench the reactor with cold compressed air. When the reactor temperature is below 350 °C, turn off the temperature recorder and eccentric arm. Once the reactor is below 100 °C, quench with ice water.

6. Bleed gas to the gas sampling system and take a gas sample.

7. Remove the reactor from the eccentric arm and place

the contents in a centrifuge tube. The reactor is cleaned with solvent and a wire bore cleaner. Another run may be made or the system may be shut-down.

4.3.4 Shut-Down

1. Turn off the panel controls except for the flashing light. Leave the bed fluidized while cooling.

2. Vent the gas feed to the atmosphere. Close the gas cylinders.

4.4 ANALYTICAL PROCEDURE

4.4.1 Sample Preparation

The reaction products were collected in a centrifuge tube as a slurry. Additional spent shale was removed from the reactor by a toluene wash to a second centrifuge tube. The sample was then centrifuged and the solvent and shale oil were decanted and saved.

The spent shale was combined in one centrifuge tube and washed twice in toluene, then twice in acetone. The shale was centrifuged after each wash and the liquid discarded.

After the final wash, the spent shale was dried overnight at 100 °C and ambient pressure. The spent shale was then transferred to a labeled sample bottle and stored in a desiccator prior to being analyzed.

4.4.2 Solid Analysis

The spent shale was analyzed for carbon and ash con-

tent. The carbon in oil shale exists as either organic carbon or as inorganic carbon in the form of carbonate. Total carbon and inorganic carbon were determined using the Coulometrics total carbon and carbonate carbon analyzers. The organic carbon content was determined by calculating the difference between total carbon and inorganic carbon.

The ash content of the feed and spent shale samples was determined by a variation of ASTM procedure D3174-82. The samples were weighed in tared crucibles and placed in a cold muffle furnace. The samples were then heated to 800°C and ashed for three hours. The cooled samples were weighed and the fraction of ash calculated by dividing the ashed shale weight by the weight prior to ashing.

4.4.3 Gas Analysis

Gas samples were collected in evacuated 75 ml stainless steel cylinders and analyzed on a Carle gas chromatograph with a Hewlett-Packard integrator for H₂, CO, CO₂, Ar or Kr, H₂S, and hydrocarbons from C₁ through C₅.

5. DATA ANALYSIS

At the completion of each experimental run, the solid and gaseous products of reaction were analyzed. These data provided the information necessary to calculate the conversion of organic carbon and to determine the oil/gas selectivity. For the purpose of this thesis the oil/gas selectivity is defined as the percent of total carbon converted to products that ends up as liquid products. The calculation uses the total carbon as opposed to organic carbon due to the fact that the source of carbon in the product gases may be either organic or inorganic in origin(35). These calculations were performed with the aid of a computer program developed by Ken Chen, based on a computer program originally written by Dr. R.M. Baldwin. The advantage of Chen's program was the ability to save each run summary on a MULTI-PLAN spreadsheet and retain the data for future print out or modification. At the conclusion of the experimental program a kinetic model for the reaction was formulated.

5.1 ORGANIC CARBON CONVERSION

The organic carbon conversion (OCC) was calculated in the following manner. Before and after reaction the shale was analyzed for total carbon and inorganic carbon content. The weight percent of organic carbon was calculated by difference. Performing a mass balance on the organic carbon

in the reactor gives the following relationship:

$$OC(\text{shale feed}) = OC(\text{shale spent}) + OC(\text{gas}) + OC(\text{liquid})$$

where OC = mass of organic carbon

From this relationship the fraction of organic carbon converted (OCC) follows as:

$$OCC = \frac{OC(\text{shale feed}) - OC(\text{shale spent})}{OC(\text{shale feed})}$$

The mass of organic carbon is then calculated as the mass of shale times the weight fraction of organic carbon. Due to the problems inherent in determining the mass of spent shale quantitatively, the mass of the spent shale was calculated by an ash balance. Based on the assumption that the ash content of the shale is non-reactive, the following relationship can be used.

$$\text{mass of spent shale} = \text{mass of feed shale} \frac{(\% \text{ ash feed})}{(\% \text{ ash spent})}$$

Substituting this into the organic carbon conversion expression yields:

$$OCC = \frac{(\% \text{ OC feed}) - \frac{(\% \text{ ash feed})}{(\% \text{ ash spent})} \times (\% \text{ OC spent})}{\% \text{ OC feed}}$$

5.2 OIL SELECTIVITY

The oil selectivity was calculated as the percent of

total carbon converted that was converted to C5+ "liquid" products. This was determined to be the amount of total carbon converted minus the carbon in the product gas. To calculate the carbon content of the product carbon, the following procedure was used. The ideal gas law was used to calculate the number of moles of krypton, the tracer gas, in the initial reactor charge based on the known feed gas composition, reactor volume, initial pressure and initial temperature. Since the moles of inert krypton remains constant, the product gas moles can be determined by the 'tracer-tie' procedure. The product gas was analyzed by gas chromatography and the relative areas determined. The identifiable peaks of the gas chromatographs were hydrogen, hydrogen sulfide, hydrocarbon gases through C4, carbon monoxide, carbon dioxide, nitrogen, oxygen, and krypton. The following calculations were then performed.

$$\text{Tracer Adjustment} = \text{TA} = \frac{\text{moles Kr in feed}}{\text{Kr area} \quad \text{Kr RF}}$$

where: RF= response factor from calibration gas
Area= gas chromatogram peak area

Moles of carbon can then be calculated as:

$$\text{gmoles carbon} = \text{TA} \quad (\text{area } C_i) \quad (\text{RF } C_i) \quad (B_i)$$

where: RF C_i =response factor, species i
 B_i =gmoles of carbon/gmoles of component i

With the gmoles of carbon calculated, the mass of carbon was found by multiplying the gmoles by the molecular weight of carbon. The mass of carbon converted was calculated as follows:

$$\begin{aligned} \text{mass of C converted} &= (\text{mass of feed}) (\% \text{ total C feed}) \\ &\quad - (\text{mass of spent}) (\% \text{ total C spent}) \end{aligned}$$

The oil selectivity was then expressed as follows:

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

5.3 KINETIC MODELING

At the completion of the experimental program the data collected were used to generate a kinetic model relating temperature and time to organic carbon conversion. The conversion is defined as the amount of organic carbon converted to solvent soluble products and gas. In selecting an appropriate model, it has been shown by several researchers that the kinetics of oil shale pyrolysis can be adequately modeled by various irreversible models (8,35,36, 37,38,39). To model the experimental data, three kinetic models were tested. The three models tested were as follows:

	<u>Rate Expression</u>	<u>Integrated Form</u>
1st order in X	$\frac{dX}{dt} = k(a-X)$	$X = a - a \exp(-kt)$
3/2's order in X	$\frac{dX}{dt} = k(a-X)^{3/2}$	$X = a - \left(\frac{1}{2}kt + a^{-\frac{1}{2}} \right)^{-2}$
2nd order in X	$\frac{dX}{dt} = k(a-X)^2$	$X = \frac{kta^2}{kta + 1}$

where X=fractional organic carbon conversion(OCC)
t=reaction time
a=pseudo equilibrium OCC at infinite time
k=rate constant(Arrhenius expression)

The various models were tested by applying them to the low temperature (400°C and 425°C) data. This was done due to the fact that at high temperatures the organic carbon conversion occurred at such a fast rate that a good conversion versus time profile was not obtained. At the lower temperatures the conversion proceeds at a rate which provides excellent conversion time histories.

By linearizing the integrated forms of the kinetic models, a linear regression program may be used to test the adequacy of each model in fitting the experimental data. The following linearized forms were used, with k being the unknown.

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

$$\text{3/2's order:} \quad 2 \left[\frac{1}{a-X} - a^{-\frac{1}{2}} \right] = kt$$

$$\text{2nd order:} \quad \frac{1}{a-X} - \frac{1}{a} = kt$$

Because the kinetic expressions are only valid for isothermal reaction, a time adjustment had to be made for the finite period required for heatup. The procedure for the time adjustment is explained in appendix A and resulted in the calculation of an equivalent time of isothermal reaction equal to the nonisothermal reaction time.

With the reaction times adjusted, the linearized models were tested using the statistical library package MINITAB, a computer program developed at Pennsylvania State University. MINITAB provided information on the fit of the various models as well as giving the rate constants for various temperatures. A sample of the input and output of MINITAB is presented in appendix E.

To complete the kinetic modeling an Arrhenius plot was generated to determine values for the apparent frequency factor (k_0) and the apparent activation energy (E_a).

6. DISCUSSION OF RESULTS

6.1 INTRODUCTION

The results of the experimental program are summarized in the following sections along with an analysis of error in the program. Detailed results for all the experimental runs are summarized in Appendix C. During the course of the experimental work, a total of 96 runs were completed. For various reasons 13 of these runs were not used in the analysis. The justification for excluding the results of these runs are as follows.

Nine of the excluded runs occurred during the first one third of the program and can be attributed to operator inexperience. Since the reaction system used for this program was new, no previous experience was available on the operating characteristics of the system. One problem encountered by the operator was improper heater adjustment, which led to temperature overshoot, undershoot, or temperature fluctuations around the reaction temperature. Another problem was reactor pressure leaks caused by the thermal cycling of the reactor. Runs 3,4, and 22 were excluded for temperature overshoot greater than 5°C. Run 5 experienced severe pressure drops during reaction. Runs 2,26, and 49 were excluded because the chemical analysis gave results far out of the range expected by comparison to other data

points. Runs 16-20 were excluded because of reaction with a feed gas which had no tracer component. Finally, run 81 was excluded because the spent shale sample was not analyzed for carbon and ash content.

During the course of the experimental work three major changes were made to the system. First, after run 19 the reactor configuration was changed, with the reactor head fitting being changed from a Swagelok to a VCR connection. Each VCR fitting gave good pressure seals for over 30 runs, where the Swagelok fitting usually failed after approximately three runs.

Second, after run 45 the gas sampling system was modified by the addition of a surge tank. This change allowed for the gas sample to be taken at or near atmospheric pressure and eliminated the possibility of product gas remaining in solution with the oil and solvent, a distinct possibility at the previous sampling pressure of 130 psig.

Finally, the tracer in the feed gas was changed from argon to krypton after run 80. The reason for this change was to check for and eliminate errors in the gas analysis. The gas chromatograph was unable to separate the peaks for argon and oxygen, thus small air leaks resulted in uncertainties in the calculation of oil selectivity. Because an accurate tracer peak was required for the gas

analysis, the substitution of krypton eliminated this problem, as the krypton peak eluted by itself and an accurate area for the tracer in the product gas was always obtained.

6.2 SOURCES OF ERROR

6.2.1 Processing Errors

The processing variables of temperature, pressure, and reaction time accounted for most of the experimental errors experienced. The temperature of the reactor during the initial runs would cycle above and below the desired temperature several times during a long residence time run. Runs experiencing temperature fluctuations greater than 5°C over the desired temperature were eliminated from further data analysis. Runs during the latter portion of the program experienced more stable temperature profiles, with the temperature controlled to within $\pm 2^{\circ}\text{C}$ of the desired temperature due to adjustments made to the temperature controller by the operator.

The reactor's autogenous pressure during reaction also varied. Before the reactor modification after run 19, small pressure leaks were present during approximately half of the runs. When a leak was observed by falling reactor pressure, the reaction was terminated at the shortest run time possible. If the pressure dropped over 100 psi the reaction was quenched, the reactants discarded, and the run was done

again at the same operating conditions. With the autogenous pressure in the range of 1800-2100 psi, it was assumed that pressure drops of less than 100 psi would still yield valid results.

The error in reaction time can be divided into two sources. First, the actual isothermal reaction time had to be adjusted due to the presence of the nonisothermal heatup time. As discussed in Appendix A, this was done with zero order kinetics based on the assumption that temperature dominated the conversion during this time. The error in this adjustment can be attributed to the fact that in reality the conversion is affected by concentration and that an estimate of the apparent activation energy was used which was not equal to the experimentally calculated apparent activation energy.

The second source of reaction time error occurred during the reaction quench. The temperature dropped from reaction temperature to 350°C, the temperature at which reaction can be assumed to stop, in approximately 10-15 seconds. This quench time was assumed to be instantaneous and no time adjustment was made. For the medium and long residence time runs this is an excellent assumption but is less valid for short residence times (5 minutes and shorter).

6.2.2 Analytical Errors

The error in the analysis can generally be taken to be small as two to three repetitions were done on each carbon analysis and ashing. However several data points that appeared to be out-of-range were reanalyzed and the apparent organic carbon conversion changed by as much as 25%. While not every out-of-range data point responded to this reanalysis, the repetition of the analysis saved the effort of duplicating the experimental runs of several data points.

With an understanding of the sources of error, the results of the experimental program are presented as follows. The initial runs, phase one, were intended to study a broad range of time and temperatures to determine the region of interest and the organic carbon conversion at long residence times. Efforts were then concentrated during the second phase on short residence times. The experimental program was concluded with a study of very short residence time runs and also a matrix of runs in an inert atmosphere to determine the role of molecular hydrogen in organic carbon conversion.

6.3 PHASE ONE

The objective of the initial experimental runs was to determine the effect of temperature and hydrogen partial pressure on organic carbon conversion and oil/gas selectivi-

ty at medium to long residence times. The results of these runs are summarized in Tables 4 and 5. Several conclusions can be drawn from this series of experiments.

Comparing the organic carbon conversion for the longest residence times at the various temperatures, the temperature range of interest was established to be between 400° and 500°C. The one run made at 350°C (run 1, Table 3.) showed that at this temperature the kerogen in the Montcey oil shale produced no measurable quantities of solvent-soluble liquid products or product gas. Because of the absence of measurable reaction at 350°C, this temperature was eliminated from further study.

The temperature range of 400-500°C was chosen for further study at shorter residence times since the organic carbon conversions at these temperatures were close to or had reached a maximum at extended reaction times. This provided no meaningful rate information though other characteristics of the Montcey oil shale could be observed.

The temperatures which gave the largest organic carbon conversions were 400° and 425°C. At both these temperatures the organic carbon conversion maximized at approximately 64 to 65% at reaction times of 30 to 60 minutes. At temperatures above 425°C the conversion decreased with increasing time. For reaction at 500°C and high hydrogen partial pres-

Table 4. Phase One Run Summary*

<u>Run Number</u>	<u>Temp.(°C)</u>	<u>Time(min)</u>	<u>OCC</u>	<u>%OY</u>	<u>%FA</u>
1	350	10	0.0	-	-
24	400	60	63.83	99.4	159.8
25		30	62.71	99.4	157.0
12	425	60	60.62	97.9	149.5
27		60	65.27	98.0	161.1
6		30	60.56	98.4	150.1
8		10.5	62.95	99.3	157.5
21	450	60	56.33	94.5	134.1
14		60	57.07	94.9	136.4
7		30	62.94	96.9	153.6
13		10.5	59.74	98.6	148.4
15	475	60	53.67	92.1	124.5
23		60	55.19	89.3	124.2
11		30	53.51	91.5	123.3
9		10.5	58.84	97.2	144.1
10		10.5	58.84	97.2	144.1
28	500	60	53.12	69.6	93.1
29		30	61.65	85.0	132.0
30		10.5	51.41	91.4	118.4

OCC= organic carbon conversion

%OY= percent oil selectivity

%FA= percent of carbon to oil as compared to Fischer Assay

* Initial gas composition was 95% Hydrogen, 5% Argon

Table 5. Phase One Run Summary*

<u>Run Number</u>	<u>Temp.(°C)</u>	<u>Time(min)</u>	<u>OCC</u>	<u>%OY</u>	<u>%FA</u>
31	400	10	42.84	98.9	106.7
32		60	57.10	98.7	142.0
33		30	58.58	99.0	146.1
34	425	60	60.69	97.9	149.7
35		30	58.81	98.7	146.2
36		10.5	56.19	99.3	140.6
37	450	60	55.22	94.7	131.7
38		30	54.57	97.0	133.3
39		10.5	57.72	98.3	142.9
46		10.5	62.79	-	-
47		10.5	59.72	96.1	144.6
40	475	60	50.32	90.0	114.1
41		30	50.98	94.3	121.1
42		10.5	53.34	97.0	130.3
43	500	60	45.31	80.0	91.3
44		30	47.11	87.1	103.4
45		10.5	52.10	95.2	124.9

* Initial gas composition was 50% Hydrogen, 5% Argon, 45% Helium.

sure, the organic carbon conversion decreased from 52.1 percent at 10.5 minutes to 45.3 percent at 60 minutes. At 450°C the organic carbon conversion changes from an average of 60.1 percent at 10.5 minutes to 55.2 percent at 60 minutes. This observation agrees with the premise that at higher temperatures undesirable condensation reactions occur which deposit coke on the inorganic matrix while producing gaseous products. While the accuracy of the the gas analysis with the argon tracer is questionable, the percent oil/gas selectivity shows the highest gas make to be at 500°C and 60 minutes for both values of hydrogen partial pressure, once again showing the negative effect of cracking on conversion of kerogen to oil.

In terms of the effect of hydrogen partial pressure the data shows the benefits of the use of thermal solution with a hydrogen atmosphere. The organic carbon conversion for all temperatures was consistently higher for the initial hydrogen partial pressure of 800 psig when compared to the 400 psig conversion levels and was particularly noticeable at long residence times. At 400°C and 60 minutes the increase in initial hydrogen pressure increased the conversion from 57.1 to 63.8 percent. The largest effect was observed at 500°C and 60 minutes with the conversion increasing from 45.3 to 53.1 percent with increased hydrogen partial pres-

sure. The hydrogen partial pressure level did not appear to have as great an effect on the oil/gas selectivity, with the selectivity values remaining high for both pressures. The effect of the presence of hydrogen was studied in more detail in the final stage of the program and is discussed later.

Overall the results of these preliminary experiments gave justification and direction for further study. The organic carbon conversion and oil/gas selectivity gave apparent oil yields in excess of Fischer Assay for all but the 500°C and 60 minute runs. At lower temperatures the oil yield was consistently over 130% of Fischer Assay and as high as 161% at 425°C, 60 minutes, and high hydrogen partial pressure.

6.4 PHASE TWO

The principle objective of the phase two experiments was to extend the phase one experimental matrix into the short residence time region. The complete matrix for phase one and phase two is shown in Figure 5. A summary of the results for runs done with 800 psig and 400 psig hydrogen partial pressure is presented in Tables 6 and 7, respectively. These run summaries give further insight into the characteristics of the Montcey oil shale.

Studying the results of the 400°C runs, it can be

Figure 5. Phase One and Two Run Matrix

		Time, Minutes					
		5	7	10	12	30	60
Temperature, °C	400	H	H	H	H	H	H
		L	L	L	L	L	L
	425	H	H	H	H	H	H
		L	L	L	L	L	L
	450	H	H	H	H	H	H
	L	L	L	L	L	L	
475	H	H	H	H	H	H	
	L	L	L	L	L	L	
500	H	H	H	H	H	H	
	L	L	L	L	L	L	
		Phase Two			Phase One		

H Equals 95% Hydrogen In Feed Gas

L Equals 50% Hydrogen In Feed Gas

Table 6. Phase Two Run Summary*

<u>Run Number</u>	<u>Temp.(°C)</u>	<u>Time(min)</u>	<u>OCC</u>	<u>%OY</u>	<u>%FA</u>
60	400	10	53.89	99.3	134.8
61		8	49.15	99.3	122.9
62		5	39.92	99.3	99.8
63		3	26.30	87.8	58.2
68	425	3.5	54.94	99.3	137.4
67		5.5	61.80	93.8	146.0
55		5.5	56.08	98.3	138.9
56		8.5	61.16	98.2	151.3
54		10.5	64.74	97.7	159.3
70	450	3.5	66.20	88.7	147.9
69		5.5	65.05	97.8	160.2
57		5.5	63.76	--	--
58		5.5	64.75	95.3	155.4
59		8.5	61.82	91.2	142.0
50		8.5	62.82	92.3	146.1
51		8.5	61.61	92.6	143.7
72	475	3.5	62.60	--	--
53		5.5	60.01	92.4	139.7
52		8.5	58.10	88.0	128.8
64	500	3.5	58.45	93.2	137.2
65		5.5	55.77	96.6	135.7
66		8.5	56.12	79.8	112.8

* Initial gas composition was 95% Hydrogen, 5% Argon.

Table 7. Phase Two Run Summary*

<u>Run Number</u>	<u>Temp. (°C)</u>	<u>Time (min)</u>	<u>OCC</u>	<u>%OY</u>	<u>%FA</u>
79	400	8	39.73	98.9	99.0
80		3	20.22	99.2	50.5
73	475	8.5	56.98	92.3	132.5
74		5.5	61.62	95.3	147.9
75		3.5	63.08	97.5	154.9
76	500	8.5	55.73	87.7	123.1
77		5.5	56.40	88.2	125.3
78		3.5	57.53	90.98	131.8

* Initial gas composition was 50% Hydrogen, 5% Argon, and 45% Helium

concluded that the reaction times selected give an excellent profile for the organic carbon conversion versus time. For the hydrogen partial pressure of 800 psig the organic carbon conversions of 26.30, 39.92, 49.15, and 53.89 for the adjusted times of 3, 5, 8, and 10, respectively, represents conversions well below the maximum conversion level achieved at long residence time. The oil/gas selectivity for the 400°C runs was uniformly high (over 98%) and shows that the gas forming pyrolysis reactions have reasonably high activation energies, thus requiring higher temperatures in order to proceed.

Studying the results of the 425°C runs, it is obvious that the conversion is close to completion for the shortest residence time, though kinetics is still controlling conversion as the organic carbon conversion increases from 54.9 percent at 3.5 minutes to 61.2 percent at 8.5 minutes. The oil/gas selectivity remained high, greater than 98% except for one run, indicating that the gas formation reactions are still not very rapid.

For the temperatures of 450°, 475°, and 500°C the highest conversions again occur at the shortest residence times. This indicates that the conversion proceeds at a rate for which organic carbon conversion is essentially complete before 3.5 minutes. For longer reaction times the

organic carbon conversion decreases with time. This trend, along with the increase in gas make, indicates that cracking and condensation reactions are taking place. A difference must be made between the two types of reactions as cracking reactions do not always produce coke as condensation reactions do. Cracking reactions, thermal decomposition reactions which produce gaseous products from the thermal cleaving of high molecular weight components, do not necessarily produce coke on the shale. The cracking reactions most probably proceed by a free radical mechanism which results in high molecular weight free radicals that may react with another free radical or molecular hydrogen to produce a liquid compound, or with other high molecular weight free radicals on the surface of the shale to form "fixed" carbon or coke.

While the high temperature runs had lower oil/gas selectivity values, the level of organic carbon conversion at the short residence times was within the same range as that obtained at the lower temperatures and longer residence times. Because of this high organic carbon conversion there was justification for additional runs at very short residence times. In addition, the final experimental phase included runs with a completely inert atmosphere in order to determine the true role of hydrogen.

6.5 PHASE THREE

The final phase of the experimental program consisted of two series of runs. First, very short residence time runs were performed by quenching the reactor as soon as the reaction temperature was reached. By performing these runs with the fluidized sand bath at approximately 500° or 520°C, the heatup period was held to a minimum. Because of the elevated temperature of the sand bath the time adjustment computer program was modified in terms of the step change in temperature to accurately calculate the time adjustments. The final runs consisted of a brief reaction matrix program of runs in an inert atmosphere. These hydrogen-free runs were made to determine the role of molecular hydrogen in the reaction. The composition of the feed gas varied during this portion of the program. The composition of the feed gas is presented in every run summary in Appendix C.

The very short residence time runs are summarized in Table 8. This shows that for 425°C the experimental procedure produced an excellent data point for use in kinetic modeling. For 450°C the two runs produced organic carbon conversions well below the level of the previous shortest residence time, 42.16 and 44.01 percent compared to 54.9 percent organic carbon conversion at 3.5 minutes. However for the difference in the time values, .41 and .88 minutes,

Table 8. Phase Three Run Summary*

<u>Run Number</u>	<u>Temp.(°C)</u>	<u>Time(min)</u>	<u>OCC</u>	<u>%OY</u>	<u>%FA</u>
87	425	.07	12.94	93.2	30.4
86	450	.41	42.16	--	--
82		.88	44.01	94.7	105.0
83	475	.81	46.36	--	--
84	500	1.70	58.25	94.7	138.9
85		.455	59.28	93.9	140.2

* Initial gas composition for each run is presented in appendix C.

Table 9. Phase Three Run Summary*

<u>Run Number</u>	<u>Temp(°C)</u>	<u>Time(min)</u>	<u>OCC</u>	<u>%OY</u>	<u>%FA</u>
91	425	2.5	44.45	99.1	111.0
93		5.5	59.69	91.6	137.7
92		8.5	61.73	97.0	150.8
88	450	2.5	61.48	99.3	153.8
89		5.5	62.94	87.1	138.1
90		8.5	57.83	88.8	129.4
96	475	2.5	60.68	98.7	150.9
94		5.5	56.51	97.5	138.8
95		8.5	58.35	96.8	142.3

* Initial gas composition was 99% Helium, 1% Krypton.

a greater difference in the two organic carbon conversion values should be expected, raising questions as to the validity of one of the data points.

For the 500°C runs the largest organic carbon conversion was given again by the shortest residence time. It can be concluded that at 500°C the organic carbon conversion is essentially instantaneous with the onset of condensation reactions occurring immediately.

The final run series for thermal solution with no hydrogen in the gas atmosphere, presented in Table 9, gave evidence that the Montcey oil shale is relatively unreactive to wide changes in initial hydrogen partial pressure under the conditions of the experiment. The importance of this observation is that, based on the observed conversion levels for the various initial hydrogen pressure levels, a high pressure hydrogen atmosphere is not necessary to effect high organic carbon conversions. This is attributed to the condition of very fast heatup experienced by the reactants. Previous investigations on the effect of hydrogen during pyrolysis have concluded that high hydrogen pressure is needed based on conditions where the reactants experienced long heatup periods. With the very fast heating rates used in the present program, high hydrogen pressure was not required. The organic carbon conversions presented in Table

9 varied by less than five percentage points from the values given in Table 6 for reaction with 800 psig partial hydrogen pressure.

To help visualize the effect of hydrogen on the conversion, Figures 6,7,8,9, and 10 show organic carbon conversion versus time for the isotherms studied. The effect of hydrogen may be more noticeable in inhibiting condensation reactions at high temperatures and long residence times but that is not an area of interest.

6.6 KINETIC MODELING

Three psuedo-irreversible kinetic models, first, 3/2's, and second order in organic carbon remaining were tested using the organic carbon conversion data for the 800 psig hydrogen partial pressure runs. By applying MINITAB to the linear forms of the models and using the data from the residence times where large changes in organic carbon conversion occurred it was determined that the first-order irreversible kinetic model provided the best fit of the data. The residual sum of squares of the 3/2's and second order models was one to two orders of magnitude greater than that of the first order model. A plot of the three models' prediction of organic carbon conversion versus time at 425°C is presented in Figure 11. From this figure it can be clearly seen that the first-order model best fits the data.

Figure 6. 400 Degree Conversion

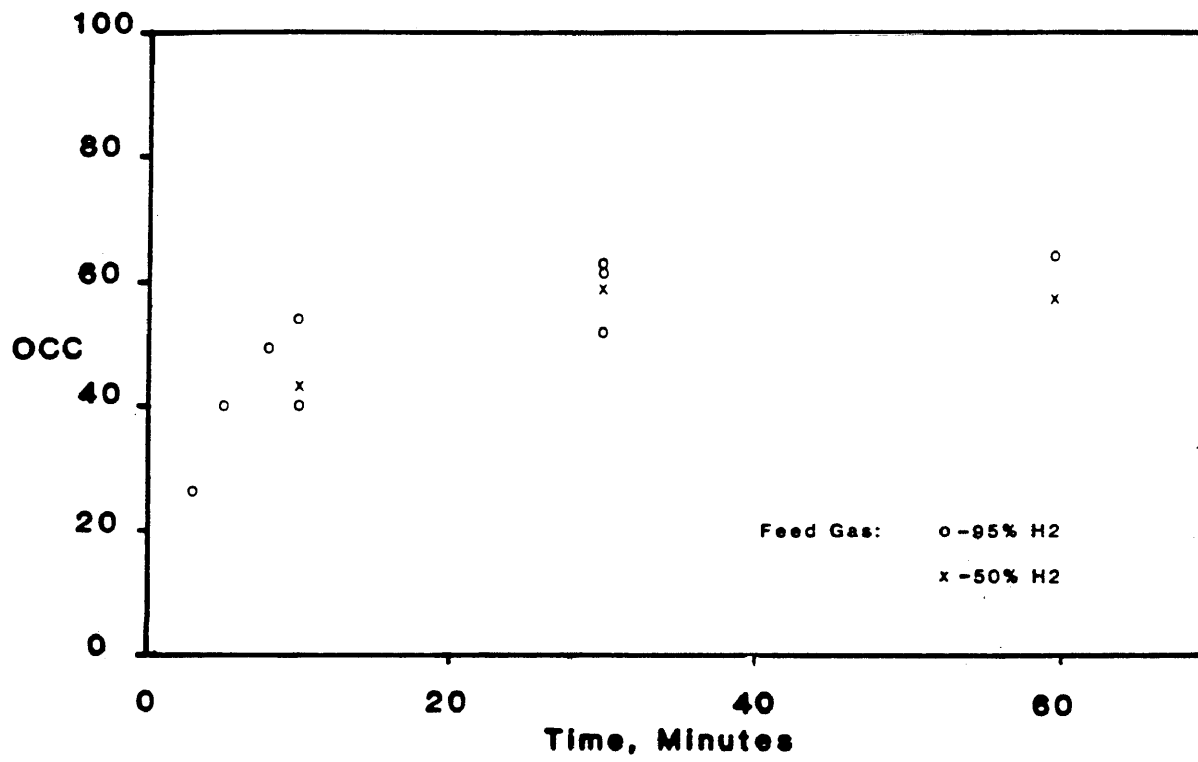


Figure 7. 425 Degree Conversion

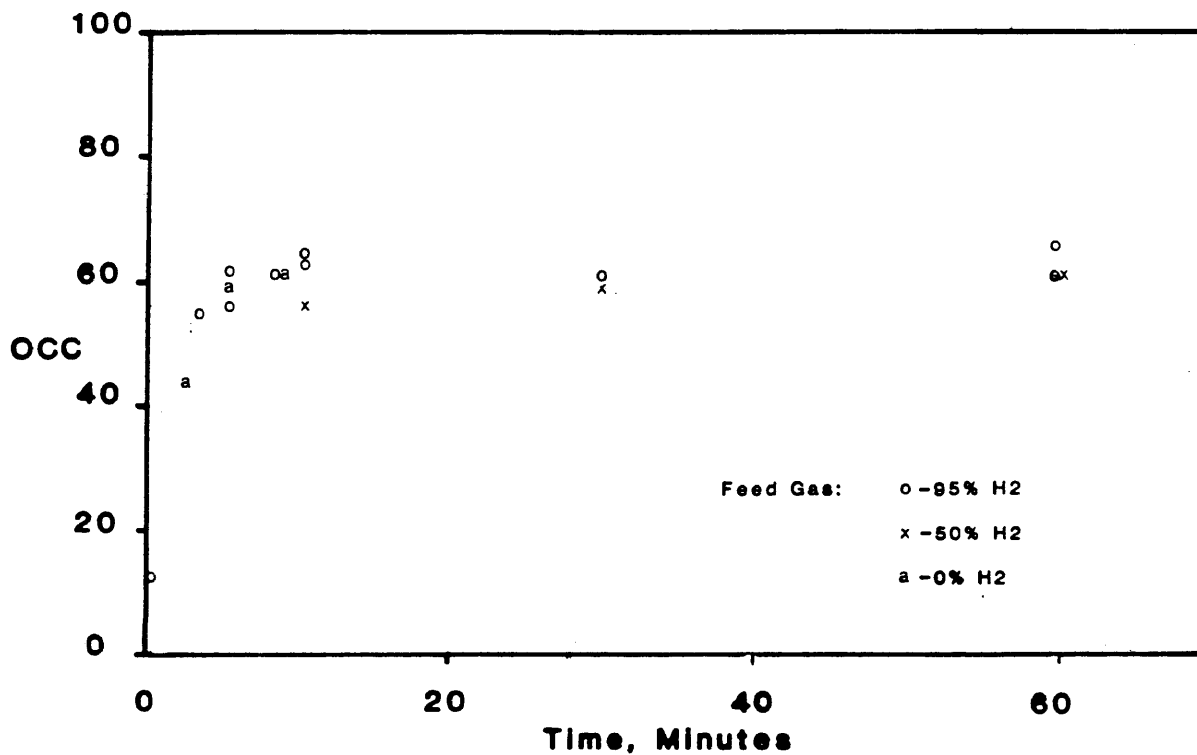


Figure 8. 450 Degree Conversion

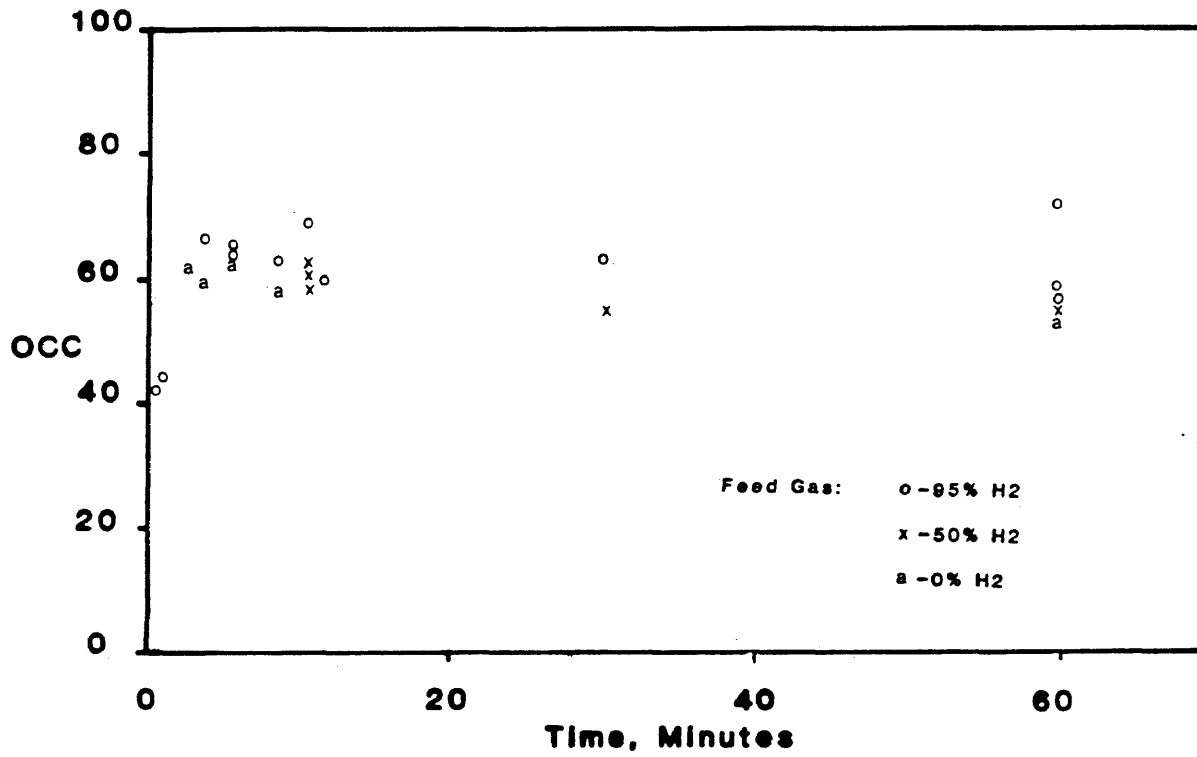


Figure 9. 475 Degree Conversion

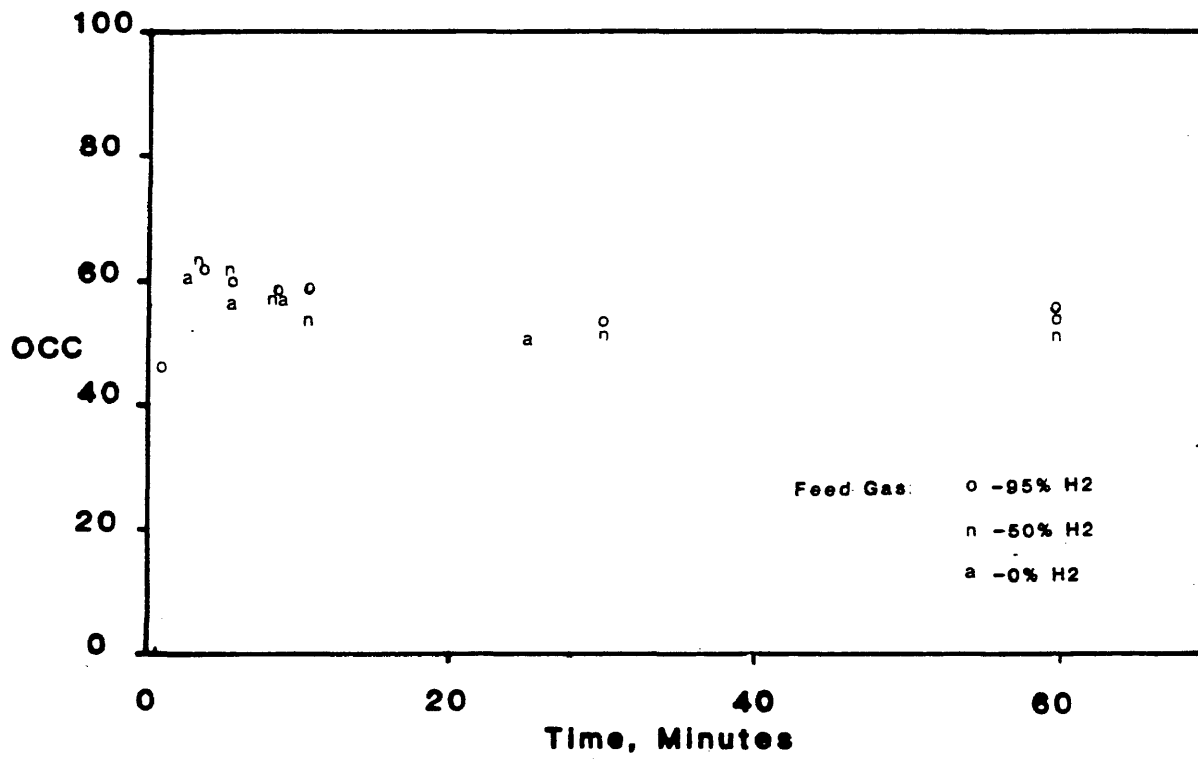


Figure 10. 500 Degree Conversion

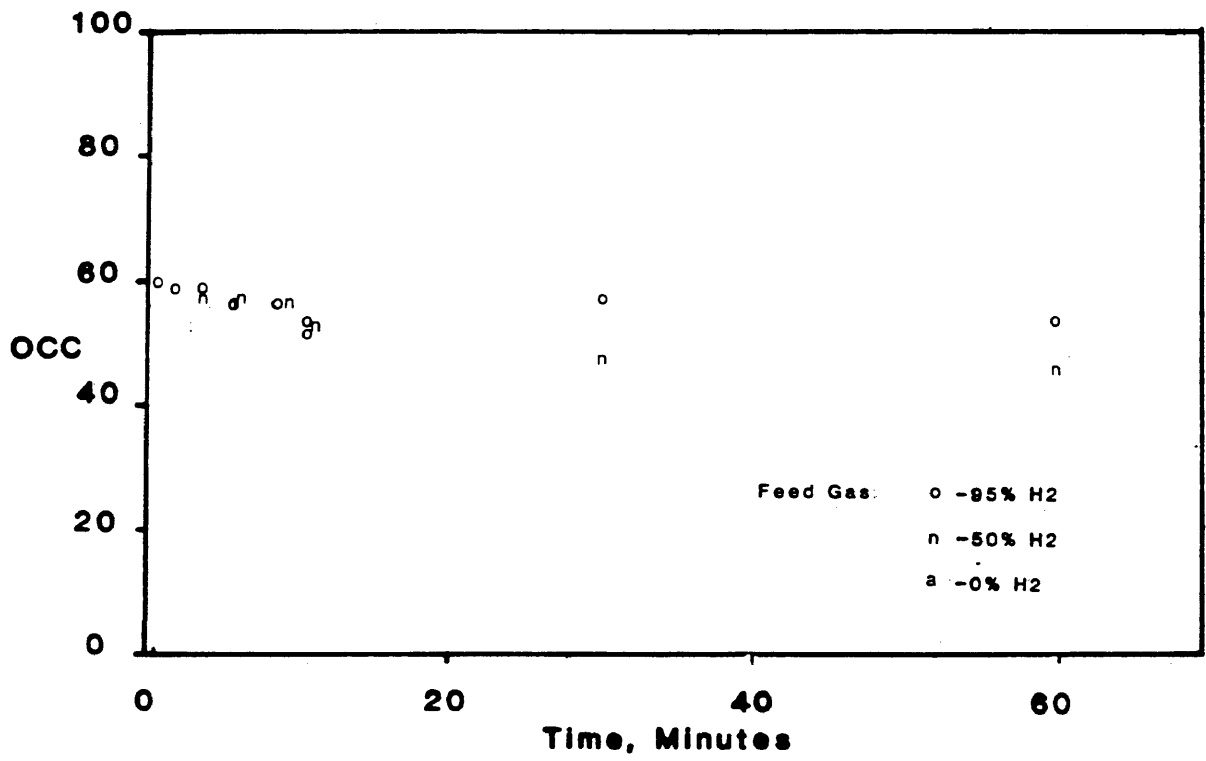
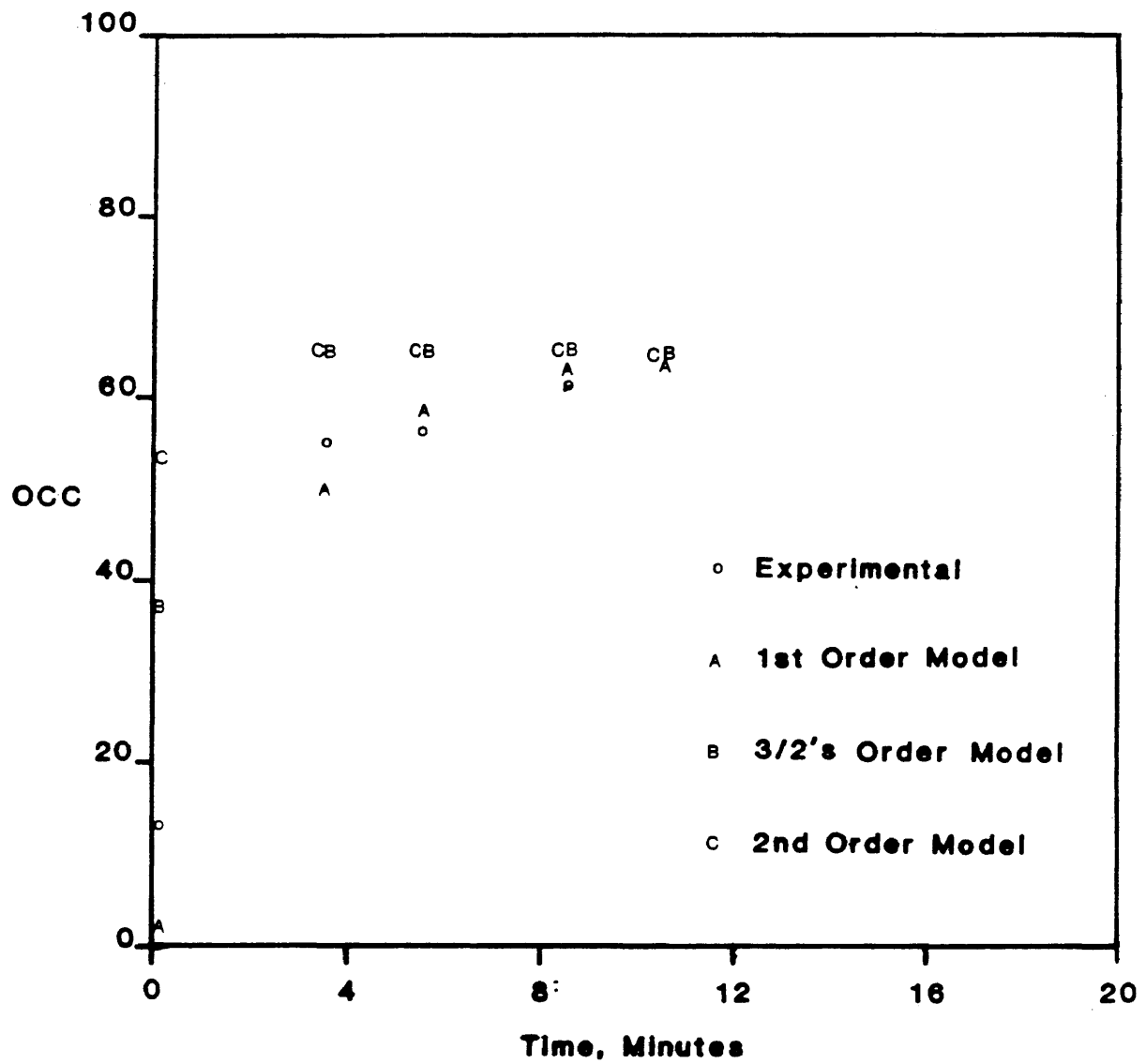


Figure 11. Kinetic Model Prediction



As a result the 3/2's and second order models were eliminated from further consideration. Plots were made to confirm the adequacy of the model for the temperatures investigated and are presented along with associated r^2 values in Figures 12, 13, 14, 15, and 16. These figures confirm the adequacy of the first-order model.

Before determination of k , the rate constant, could be made the pseudo-equilibrium constant "a" had to be determined. An attempt was made to let MINITAB optimize the linear fit with "a" being used as a fitting parameter but the analysis of the residual sum of squares produced a minimum as "a" approached 1.0. Since this disagreed with the observed data, the value of "a" was determined directly from the experimental data and the chosen values are presented below.

Table 10. Pseudo-Equilibrium Constant "a"

<u>Temperature (°C)</u>	<u>Value of "a"</u>
400	.65
425	.66
450	.67
475	.63
500	.60

With the above values of the pseudo-equilibrium constant, MINITAB was used to generate values for the rate constant. The next step in the development of a suitable

Figure 12. Linear Fit of 400 C Organic Carbon Conversion
Data by 1st Order Model

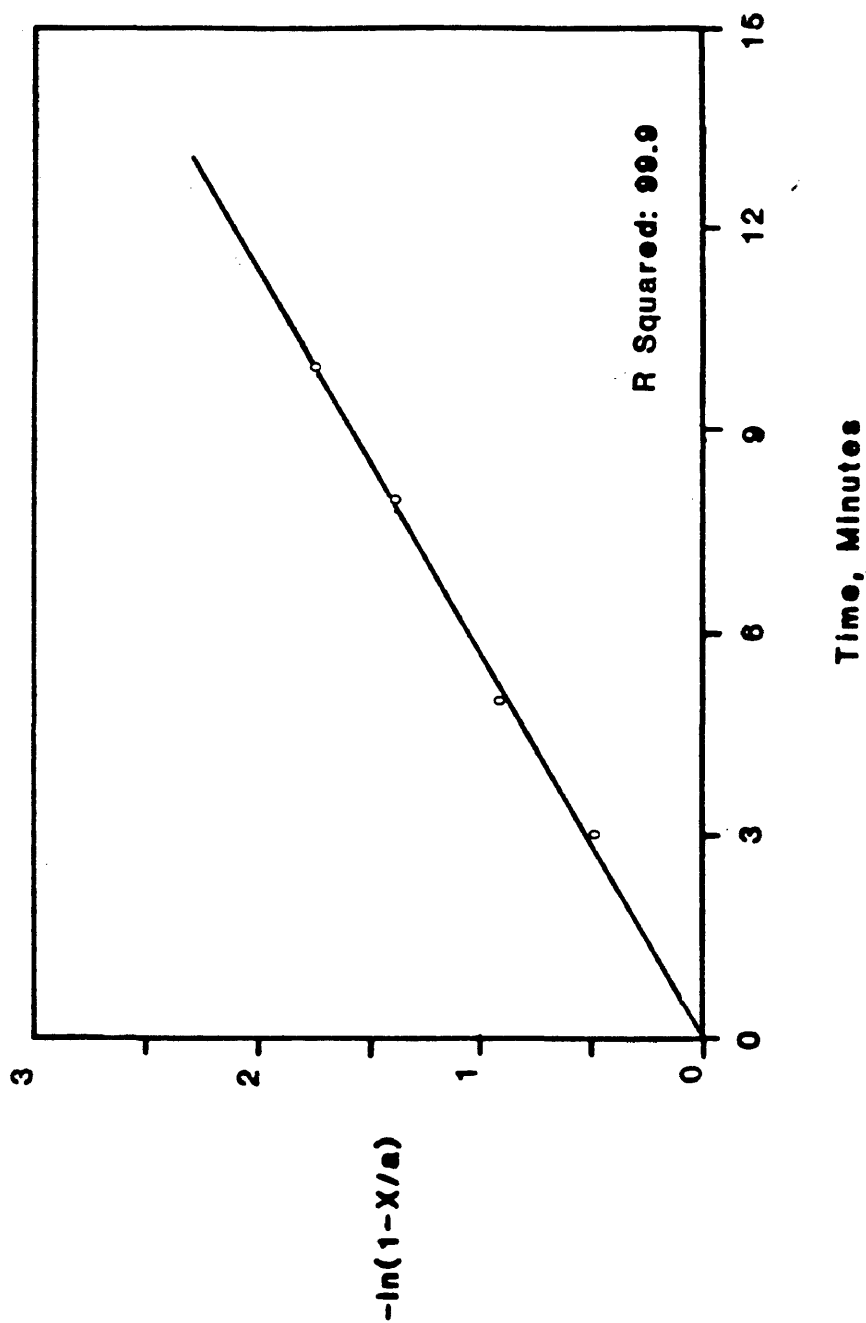


Figure 13. Linear Fit of 425 C Organic Carbon Conversion
Data by 1st Order Model

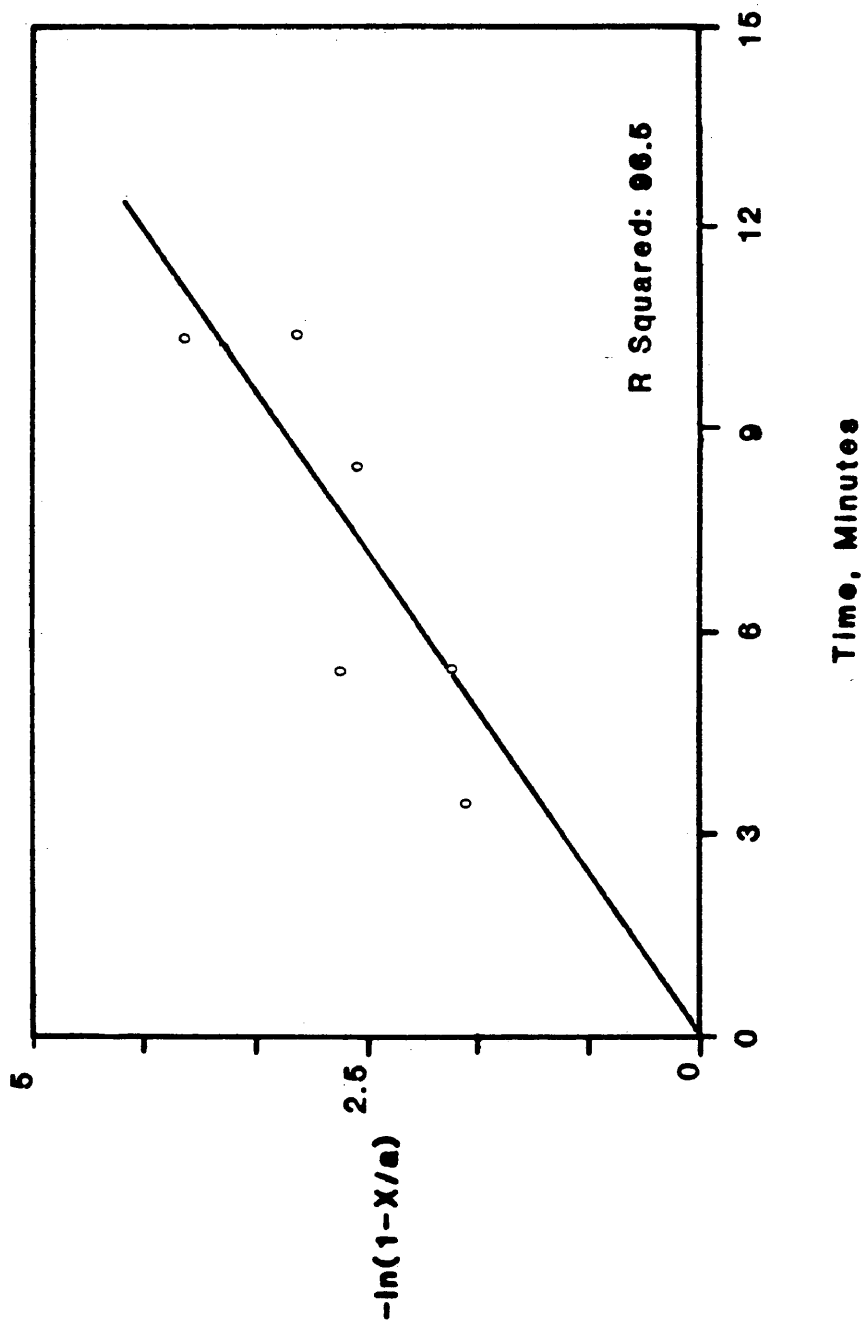
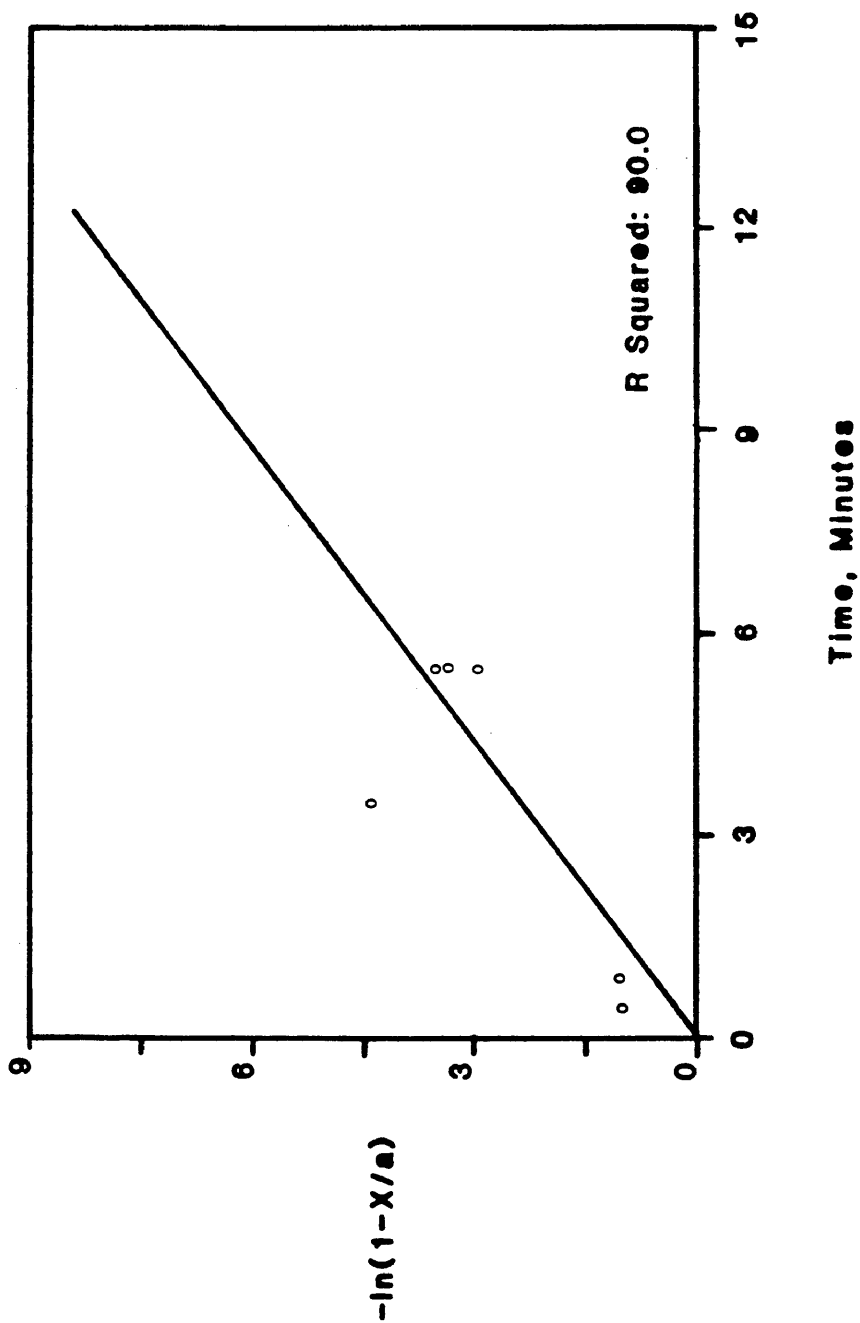


Figure 14. Linear Fit of 450 C Organic Carbon Conversion
Data by 1st Order Model



**Figure 16. Linear Fit of 475 C Organic Carbon Conversion
Data by 1st Order Model**

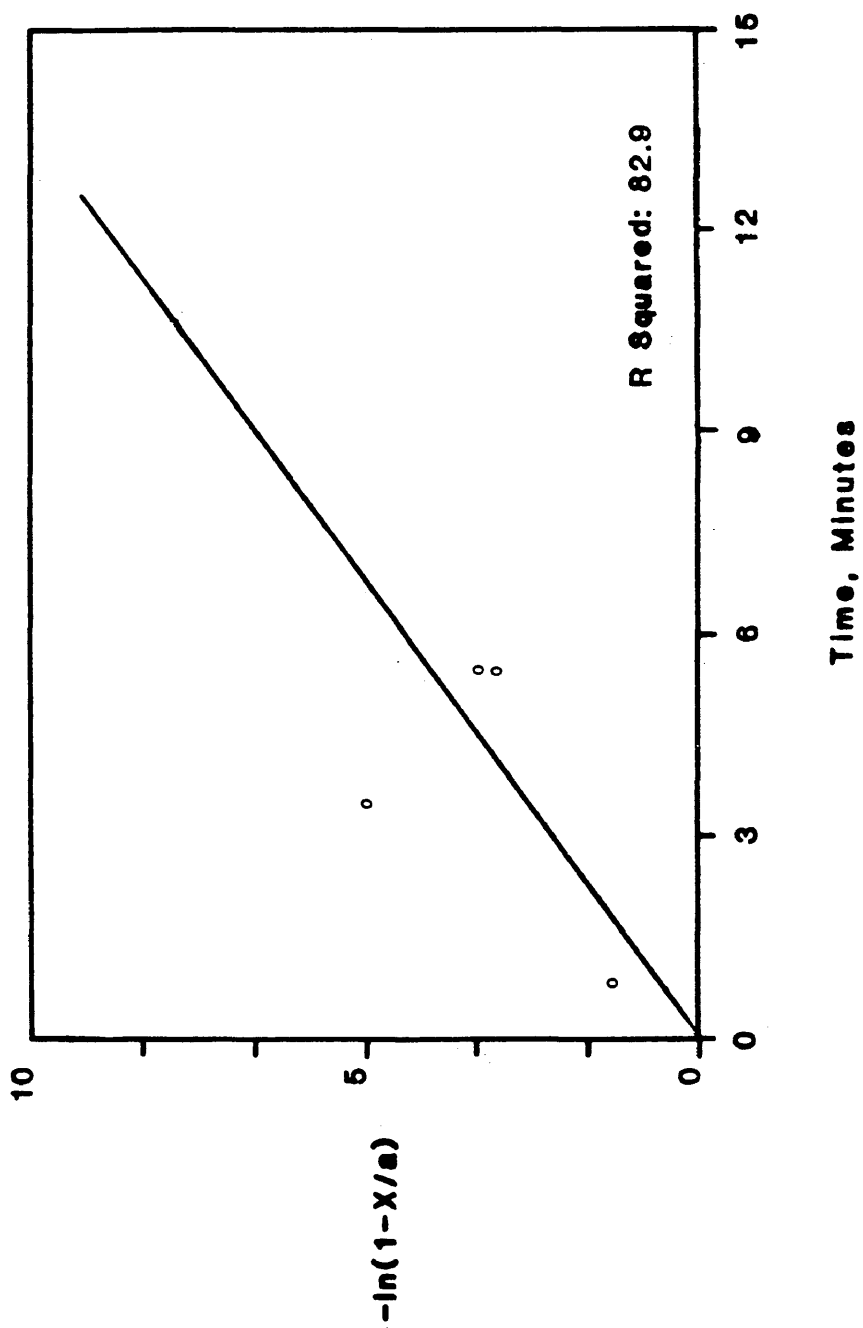
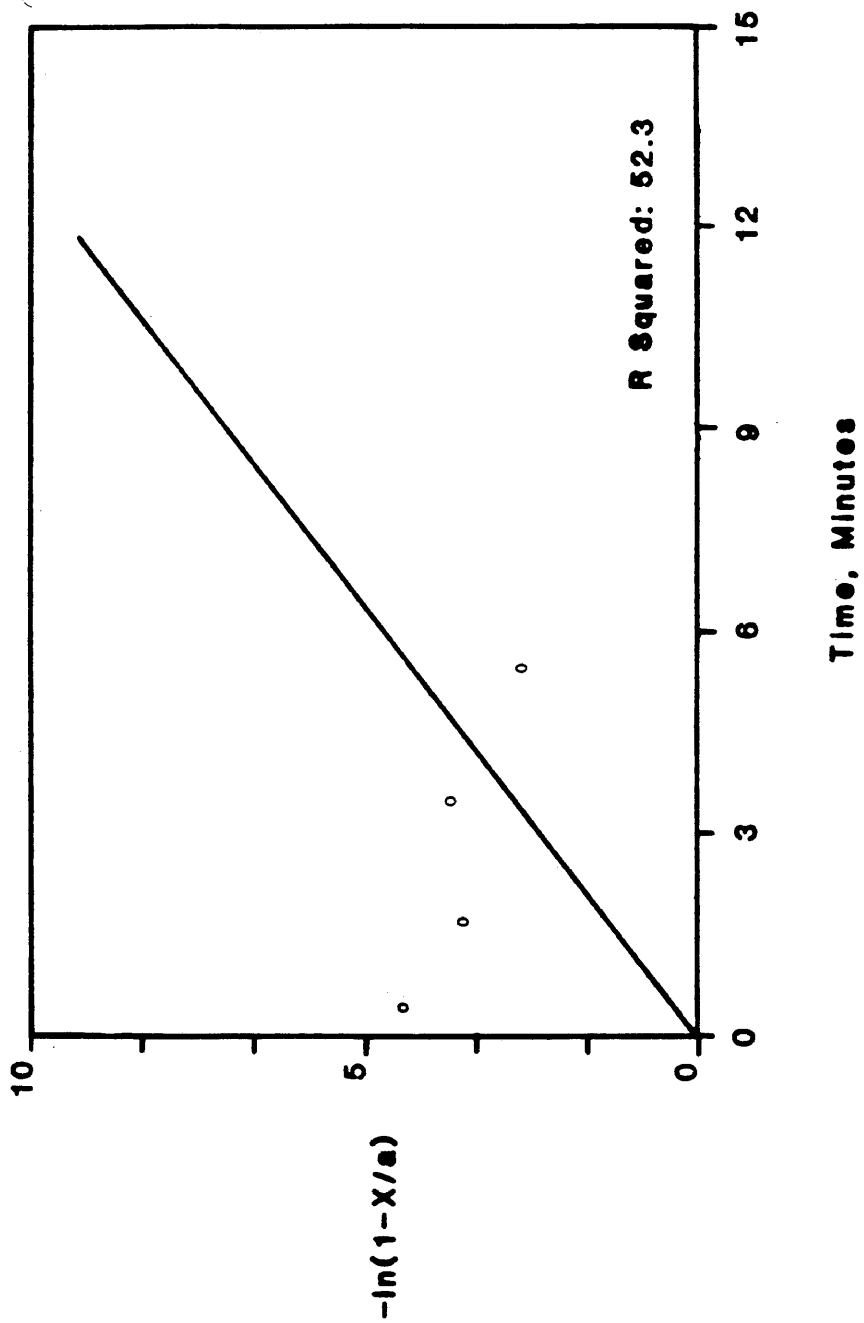


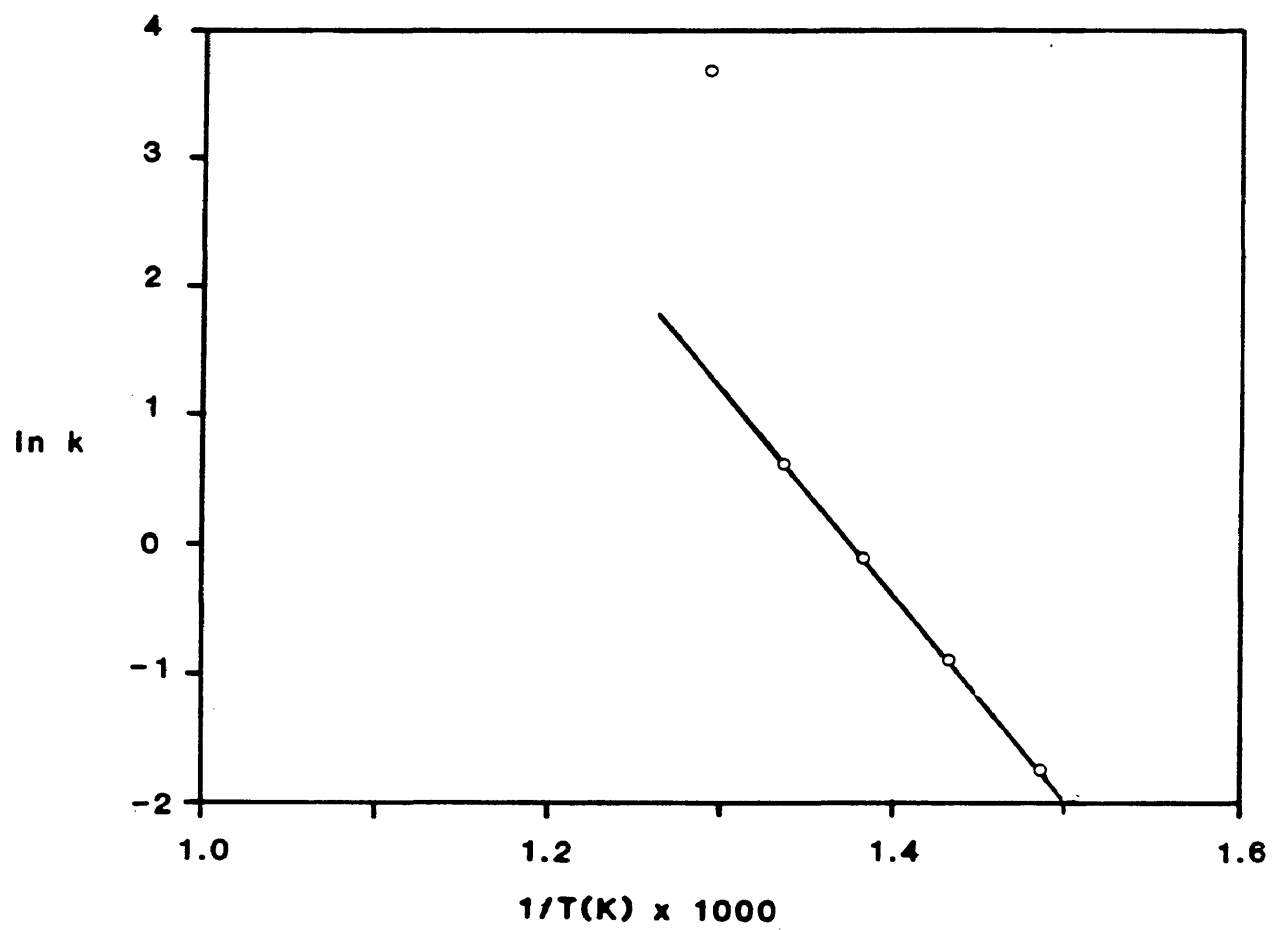
Figure 16. Linear Fit of 500 C Organic Carbon Conversion
Data by 1st Order Model



kinetic model was the preparation of an Arrhenius plot. The MINITAB generated k values were used in plotting $\ln k$ versus $1/\text{temp}$. A good fit of this model to the calculated rate constants will produce a straight line, which is what is shown in Figure 17 for all but the 500°C temperature runs. This indicates that for 500°C the first-order irreversible model does not adequately describe the reactions which are occurring.

Using the k values for 400°, 425°, and 450°C and regressing in MINITAB the apparent frequency factor was found to be $2.6097 \pm .0004 \times 10^9$ and the apparent activation energy was found to be 31.301 kcal/gmole. The activation energy value is in very good agreement with the value obtained by Winkler(34) for the hydrolysis of Stuart oil shale, 31.07 kcal/gmole.

Figure 17. Arrhenius Plot



7. CONCLUSIONS

The conclusions presented here pertain exclusively to the experimental system and Montcey oil shale employed for this research.

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

2. Utilizing this process, oil yields in excess of 160% Fischer Assay can be obtained for temperatures in the range of 425°C and residence times of 30 minutes.

3. For residence times shorter than 2.5 minutes high organic carbon conversions can be obtained for temperatures greater than 425°C with oil yields in excess of 150% Fischer Assay even with very low hydrogen partial pressure.

4. The presence of gas phase molecular hydrogen enhances the conversion of organic carbon but did not produce a significant change in oil selectivity. The oil selectivity was in excess of 95% for the majority of runs. At short residence times, gas phase molecular hydrogen has a negligible effect on organic carbon conversion.

5. At temperatures in excess of 450°C the oil selectivity decreased dramatically at long residence times.

6. An irreversible pseudo first-order model adequately describes the conversion of organic carbon and predicts an

apparent activation energy of 31.301 kcal/gmole.

RECOMMENDATIONS

The following are presented as recommendations for future work in the hydrolysis of Montcey oil shale and utilization of the tubing-bomb reaction system.

1. To further characterize the Montcey oil shale a detailed characterization of the shale oil fractions should be performed. A quantitative analysis of the components present in the product oil might also provide information regarding the reaction mechanism.

2. Modification of the tubing-bomb reaction to increase the accuracy of the very short residence time runs. The addition of a computer for temperature control and monitoring of reaction conditions would increase the accuracy of the nonisothermal reaction correction.

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APPENDIX A
REACTION TIME CORRECTION

Nonisothermal Correction

Due to the fact that the reactor did not reach reaction temperature instantaneously, a correction must be made for the nonisothermal heatup period which exists before reaction temperature is reached. The extent of reaction during this heatup period can be accounted for in the following manner.

The rate of reaction is a function of temperature and concentration and can be expressed as:

$$\text{rate of reaction} = f(T)f(C) = kf(C) \quad (1)$$

with

$$f(T) = k = A \exp(-E/RT) \quad (2)$$

where

- f(C) = function of concentration
- f(T) = function of temperature (Arrhenius expression)
- A = frequency factor
- E = activation energy
- R = gas constant, 1.987 cal/gmol
- T = reaction temperature, Kelvin

During the rapid heating rates experienced by the reactor, it may be assumed that the temperature function controls the rate of reaction and the rate for a batch reactor can be expressed as:

$$\text{rate of reaction} = dX/dt = f(T) = A \exp(-E/RT) \quad (3)$$

For an isothermal zero-order reaction, the extent of reac-

tion is easily calculated by separation and integration.

$$X = A \exp(-E/RT)t \quad (4)$$

where $X=0$ at $t=0$. For nonisothermal reaction, the integration of the right hand side (RHS) is complicated by the time dependency of the temperature.

A typical temperature history of the reactor during heatup is shown in Figure 18. It can be seen that the reactor temperature qualitatively follows the behavior of a first order system responding to a step impulse, with a small deviation at approximately 350°C . This deviation can be attributed to endothermic pyrolysis reactions occurring within the kerogen macrostructure. The temperature profile is not significantly changed from that of an ideal first order system, and can thus be expressed as:

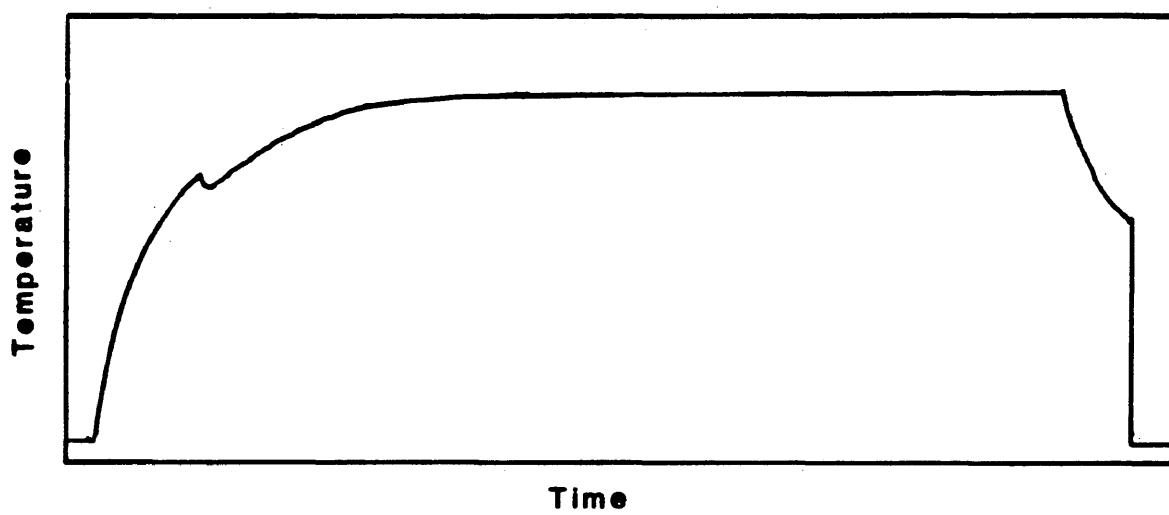
$$T = T_0 + \Delta T(1 - \exp(-t/\tau)) \quad (5)$$

where T_0 = steady state temperature at $t < 0$
 ΔT = step change in the surrounding temperature
 τ = time constant of the reactor, determined experimentally.

Substituting equation (5) into (3), separating variables, equating with the RHS of (4) and simplifying gives:

$$\exp(-E/RT(\text{iso}))t = \exp(-E/R(T_0 + \Delta T(1 - \exp(-t/\tau)))) \quad (6)$$

Figure 18. Typical Temperature History



The RHS of equation (6) can be numerically integrated with an estimate of E, the activation energy. Equation (6) can then be solved for t, the time of isothermal reaction equivalent to the nonisothermal time for equal conversion.

The numerical method used to integrate equation (6) was the composite Simpson's Rule. By repeated application of this formula, greater accuracy may be obtained than that of a single application.

The first step was to determine the time constant of the reactor. Several temperature histories for each reaction temperature were studied. From equation (5) it can be shown that:

$$\begin{aligned}\tau &= .632\Delta T \\ 2\tau &= .865\Delta T \\ 3\tau &= .950\Delta T\end{aligned}$$

From the temperature histories, it was determined that the time constant was 40 seconds for reaction at 400°C and 30 seconds for all other temperatures. The variation in the time constant can be attributed to the endothermic reactions occurring at 350°C. The temperature deviation is sufficiently close to 400°C that for this temperature the lag in heating was significant and had to be accounted for in the time constant.

The next step involved averaging the initial tempera-

tures of the last 46 runs to determine a average for use in the numerical integration. The average initial temperature was 28.5°C.

The computer program used to perform the composite Simpson's rule integration is presented in Appendix B. By varying the size of the integrating interval, it was found that five intervals per reaction minute gave the same results as smaller composite intervals, however 20 intervals per reaction minute was used as a precaution. By changing the values of the independant variables, it was determined that the results were fairly insensitive to the range of the initial temperature but varied significantly with changes in the activation energy. A value of 30.0 kcal/gmol was used.

For the phase three runs, where the fluidized bed temperature was much greater than the final reaction temperature, the program was modified by increasing the size of temperature step change.

APPENDIX B
TIME CORRECTION PROGRAM

Temperature Adjustment Program

```

[15:00:20]
00005 C
00010 C PROGRAM TO CALCULATE THE EQUIVILANT ISOTHERMAL TIME WHICH
00015 C PRODUCES THE SAME CONVERSION AS THE NONISOTHERMAL HEATUP
00020 C PERIOD.
00025 C
00030 C LIST OF VARIABLES
00035 C
00040 C TEMP=REACTION TEMPERATURE
00045 C TBASE=INITIAL TEMPERATURE
00050 C TEMPK=UPPER INTEGRATION LIMIT, 5 DEGREES KELVIN BELOW TEMP
00055 C TAU=TIME CONSTANT OF REACTOR
00060 C DELT=STEP CHANGE IN TEMPERATURE
00065 C SPAN=INTERVAL WHICH SIMPSONS RULE IS APPLIED
00070 C SUM=SUMMATION OF INTEGRATION
00075 C Y=NONISOTHERMAL REACTION TIME
00080 C ICOUNT=COUNTER TO HELP PRINT OUT TIME SS=350
00085 C SS=REACTOR TEMPERATURE
00090 C EQT=EQUIVILANT TIME OF ISOTHERMAL REACTION.
00095 C
00100 C PROGRAM TIME
00200 10 TYPE*, 'INPUT REACTION TEMPERATURE'
00300 READ(4,*) TEMP
00500 TBASE=28.5
00600 TEMPK=TEMP+268
00700 TAU=.5
00800 IF(TEMP.EQ.400.) TAU=2./3.
00900 20 TYPE*, 'INPUT ESTIMATE OF ACTIVATION ENERGY IN CAL/GMOL'
01000 READ(4,*) E
01100 DELT=TEMP-TBASE
01400 C
01500 C THE INTEGRATION IS PERFORMED UNTIL T REACHES WITHIN 5 DEGREES
01600 C OF REACTION T OR A MAXIMUM OF 7 MINUTES ELAPSES
01700 C
01900 SPAN=.05
02000 SMID=SPAN/2.
02100 Y=0.0
02200 SUM=0.0
02300 ICOUNT=1
02400 DO 40 L=1,7
02500 DO 35 K=1,20
02600 TIME=Y+SPAN
02700 TIMEH=Y+SMID
02800 DO 30 M=1,3
02900 PHI=Y
03000 IF(M.EQ.2) PHI=TIMEH
03100 IF(M.EQ.3) PHI=TIME
03200 SS=DELT*(1.-EXP(-PHI/TAU))+273+TBASE
03300 IF(SS.GE.TEMPK) GO TO 80
03400 ST=EXP(-E/(SS*1.987))
03500 IF(M.EQ.1) F1=ST
03600 IF(M.EQ.2) F2=ST
03700 IF(M.EQ.3) F3=ST
03800 30 CONTINUE

```

```
03900      SUM=SUM+(SMID/3.)*(F1+4*F2+F3)
04000      Y=TIME
04100      IF(SS.GE.623.AND.ICOUNT.EQ.1) TYPE*, 'TIME EQUALS ',Y,
04200      A' FOR 350 DEGREES, CONVERSION EQUALS',SUM
04300      IF(SS.GE.623) ICOUNT=2
04400      35 CONTINUE
04500      40 CONTINUE
04600      TYPE*, 'THE INTEGRATION WAS NOT COMPLETED IN 7 MINUTES'
04650      TYPE*, 'TEMPERATURE EQUALS ',SS
04675      TYPE*, 'TIME EQUALS ',Y
04680      TYPE*, 'TEMP=',TEMP, ' TBASE=',TBASE, ' SPAN=',SPAN
04700      GO TO 700
04800      80 TYPE*, 'THE NONISOTHERMAL TIME WAS ',Y, ' MINUTES'
04900      C
05000      C CALCULATE ISOTHERMAL EQUIVILANT TIME
05100      C
05200      XK=EXP(-E/(1.987*(TEMP+273.)))
05300      EQT=SUM/XK
05400      TYPE*, 'THE EQUIVILANT TIME IS ',EQT, ' MINUTES'
05500      TYPE*, 'IS ANOTHER RUN DESIRED? 1=YES, 2=NO'
05600      READ(4,*) J
05700      IF(J.EQ.1) GO TO 10
05800      700 STOP
05900      END
```

APPENDIX C
DATA ANALYSIS PROGRAM

"SAMPLE ID *****"	"FRA-95"		
"Date of Calibration Data:"	"7-22-85"		
"H2 RF (4 comp) R(1):"	19.231		
"H2 RF (2 comp) R(2):"	19.34		
"Kr RF R(3):"	1.4639		
"C3H8 RF R(4):"	1.4557		
"C3H6 RF R(5):"	1.5841		
"i-C4 RF R(6):"	1.3725		
"H2S RF R(7):"	2.6545		
"n-C4 RF R(8):"	1.4766		
"CO2 RF R(9):"	2.1162		
"C2H4 RF R(10):"	1.956		
"C2H6 RF R(11):"	1.8017		
"CH4 RF R(12):"	2.6395		
"CO RF R(13):"	3.6484		
"RUN DATE *****"	"7-27-85"		
"H2 MOL FRAC in Feed Gas MF(1):"	0		
"Kr MOL FRAC in Feed Gas MF(2):"	0.00506		
"NAPHTHALENE MOL FRAC IN MF(3):"	0		
"NAPHTHALENE MOL FRAC OUT MF(4):"	0		
"INITIAL PRESSURE (psig) PI:"	803	"-----"	(PSIG+12)/14.696
"INITIAL TEMPERATURE (C) TI:"	32	"-----"	DEGC+273.15
"Grams of Solvent (gm) SOLWT:"	3.47		
"Grams of Shale (gm) SHLWT:"	2		
"Reactor Head-space (liter):"	0.01205		
"*****"	"*****"	"*****"	
"Sample ID -----"	"FRA-95"		
"Run Date -----"	"7-27-85"		
"Date of Calibration Data -----"	"7-22-85"		
"Pressure (psig) -----"	803		
"Temperature (C) -----"	475		
"gm of H consumed, total:"	D2		
"gm of H consumed, gas phase:"	HG		
"gm of H consumed, oil phase "	HG-6C		
"gm of C in COx gases -----"	CC		
"gm of C in total gases -----"	CG		
"Oil Yield -----"	OY		
"Organic C conversion % -----"	PO		

"TOT MOL GAS (TMS):"	ATM#RHS/G.08205/DEG K
"KR MOL IN (AM):"	TMS#MF2
"H2 MOL IN (HM):"	TMS#MF1
"H2 MOL OUT (NH):"	KRM#(AREA1/AREAC)* RF1/RF3
"WT OF H2 CONSUMED,OIL PHASE (D2):"	2*(HM-NH)
"TOT H2 CONSUMED ,WT (GC):"	D2+H2
"H2 FROM TETRALIN, WT (N2):"	2*2*(SOLWT/132)*(MF 4-MF3)
"TOT C MOL (ML):"	SUMC#KRM/(RF3#AREAC)
"TOT C gm (CB):"	12.01115#ML
"TOT H MOL (MH):"	SUMH#KRM/(RF3#AREAC)
"TOT H gm (HG):"	1.0079#MH
"TOT CO2 C (CC):"	12.01115*(COM:0-00 6)
"SS OUT WT (SD):"	SHLWT*(WF3/WF4)
"Coil+gas WT (CN):"	(SHLWT*WF1)-(SD*WF2)

"COMPOUND"	"# OF C"	"# OF H"	"EC AREA"	"RESP FAC"	"SUNC"	"SUMH"	"MOLES"
"C3H8"	3	8	AREA4	RF4	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"C3H6"	3	6	AREA5	RF5	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"I-C4H10"	4	10	AREA6	RF6	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"H2S"	0	2	AREA7	RF7	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"C4H10"	4	10	AREA8	RF8	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"CO2"	1	0	AREA9	RF9	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"C2H4"	2	4	AREA10	RF10	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"C2H6"	2	6	AREA11	RF11	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"CH4"	1	4	AREA12	RF12	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
"CO"	1	0	AREA13	RF13	RC[-4]*RC[-2]*RC[-1]	RC[-4]*RC[-3]*RC[-2]	KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
			AREA1	RF1			KRN*(RC[-3]*RC[-4]) /(AREA2*RF3)
					SUM(R53:62C11)	SUM(R53:62C12)	SUM(R53:63C13)+KRN

APPENDIX D
EXPERIMENTAL RUN SUMMARIES

SAMPLE NUMBER : FRA01

Run_Conditions_:

Initial T (°C):	19	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	350
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
76.94	8.61	5.04	3.57

Calculated Yields :

Organic Carbon Conversion (%):	---
Oil/ Gas Selectivity (%):	65.4
Oil Yield, Percent Fischer Assay (%):	---

SAMPLE NUMBER : FRA06

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	425
Shale (grams):	1.98	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.74	7.53	4.77	2.76

Calculated Yields :

Organic Carbon Conversion (%):	51.6
Oil/ Gas Selectivity (%) :	98.4
Oil Yield, Percent Fischer Assay (%):	127.9

SAMPLE NUMBER : FRA07

Run_Conditions_:

Initial T (°C):	34	Hydrogen in Feed Gas (%):	95
Initial P (psig):	804	Reaction Temperature (°C):	450
Shale (grams):	2.10	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.55	7.69	5.10	2.59

Calculated Yields :

Organic Carbon Conversion (%):	61.2
Oil/ Gas Selectivity (%):	96.9
Oil Yield, Percent Fischer Assay (%):	149.4

SAMPLE NUMBER : FRA09

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	475
Shale (grams):	2.01	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
87.32	6.13	4.89	3.24

Calculated Yields :

Organic Carbon Conversion (%):	58.3
Oil/ Gas Selectivity (%) :	97.5
Oil Yield, Percent Fischer Assay (%):	143.2

SAMPLE NUMBER : FRA10

Run Conditions:

Initial T (°C):	29	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	475
Shale (grams):	2.02	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale Analysis:

% Ash	% Total C	% Inorg. C	% Org. C
86.83	8.08	4.90	3.18

Calculated Yields :

Organic Carbon Conversion (%):	58.8
Oil/ Gas Selectivity (%):	97.2
Oil Yield, Percent Fischer Assay (%):	144.0

SAMPLE NUMBER : FRA11

Run Conditions:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	475
Shale (grams):	1.97	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale Analysis:

% Ash	% Total C	% Inorg. C	% Org. C
77.20	8.13	4.89	3.24

Calculated Yields :

Organic Carbon Conversion (%):	53.5
Oil/ Gas Selectivity (%) :	91.5
Oil Yield, Percent Fischer Assay (%):	123.5

SAMPLE NUMBER : FRA12

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	425
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.72	7.66	4.93	2.73

Calculated Yields :

Organic Carbon Conversion (%):	60.6
Oil/ Gas Selectivity (%):	97.9
Oil Yield, Percent Fischer Assay (%):	149.4

SAMPLE NUMBER : FRA13

Run_Conditions_:

Initial T (°C):	22	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.10	7.69	4.93	2.76

Calculated Yields :

Organic Carbon Conversion (%):	59.7
Oil/ Gas Selectivity (%) :	98.6
Oil Yield, Percent Fischer Assay (%):	148.3

SAMPLE NUMBER : FRA14

Run_Conditions_:

Initial T (°C):	31	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.59	7.84	4.88	2.96

Calculated Yields :

Organic Carbon Conversion (%):	57.1
Oil/ Gas Selectivity (%):	94.9
Oil Yield, Percent Fischer Assay (%):	136.5

SAMPLE NUMBER : FRA15

Run_Conditions_:

Initial T (°C):	35	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	475
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.95	8.23	4.51	3.72

Calculated Yields :

Organic Carbon Conversion (%):	53.7
Oil/ Gas Selectivity (%) :	92.1
Oil Yield, Percent Fischer Assay (%):	124.6

SAMPLE NUMBER : FRA16

Run_Conditions_:

Initial T (°C):	21	Hydrogen in Feed Gas (%):	0
Initial P (psig):	799	Reaction Temperature (°C):	450
Shale (grams):	2.04	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.22	7.72	4.89	2.83

)

Calculated Yields :

Organic Carbon Conversion (%):	59.3
Oil/ Gas Selectivity (%):	100.0
Oil Yield, Percent Fischer Assay (%):	149.4

SAMPLE NUMBER : FRA17

Run_Conditions_:

Initial T (°C):	28	Hydrogen in Feed Gas (%):	0
Initial P (psig):	802	Reaction Temperature (°C):	475
Shale (grams):	2.00	Nominal Residence Time (min):	25.0
Solvent (grams):	3.46	Actual Residence Time (min):	23.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.45	8.27	4.88	3.39

Calculated Yields :

Organic Carbon Conversion (%):	50.8
Oil/ Gas Selectivity (%) :	100.0
Oil Yield, Percent Fischer Assay (%):	128.0

SAMPLE NUMBER : FRA18

Run_Conditions_:

Initial T (°C):	22	Hydrogen in Feed Gas (%):	0
Initial P (psig):	802	Reaction Temperature (°C):	465
Shale (grams):	2.03	Nominal Residence Time (min):	25.0
Solvent (grams):	3.46	Actual Residence Time (min):	----

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.92	8.13	4.86	3.27

Calculated Yields :

Organic Carbon Conversion (%):	52.8
Oil/ Gas Selectivity (%):	100.0
Oil Yield, Percent Fischer Assay (%):	133.0

SAMPLE NUMBER : FRA19

Run_Conditions_:

Initial T (°C):	22	Hydrogen in Feed Gas (%):	0
Initial P (psig):	804	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	25.0
Solvent (grams):	3.46	Actual Residence Time (min):	----

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.11	8.06	4.76	3.88

Calculated Yields :

Organic Carbon Conversion (%):	44.2
Oil/ Gas Selectivity (%) :	100.0
Oil Yield, Percent Fischer Assay (%):	111.3

SAMPLE NUMBER : FRA20

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	0
Initial P (psig):	804	Reaction Temperature (°C):	450
Shale (grams):	2.02	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	----

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.62	8.26	4.99	3.27

Calculated Yields :

Organic Carbon Conversion (%):	52.6
Oil/ Gas Selectivity (%):	100.0
Oil Yield, Percent Fischer Assay (%):	132.5

SAMPLE NUMBER : FRA21

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	802	Reaction Temperature (°C):	450
Shale (grams):	1.99	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	----

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.47	7.92	4.77	4.15

Calculated Yields :

Organic Carbon Conversion (%):	39.8
Oil/ Gas Selectivity (%) :	94.5
Oil Yield, Percent Fischer Assay (%):	94.7

SAMPLE NUMBER : FRA22

Run_Conditions_:

Initial T (°C):	24	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	480
Shale (grams):	2.01	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	----

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.71	8.28	4.93	3.35

Calculated Yields :

Organic Carbon Conversion (%):	51.5
Oil/ Gas Selectivity (%):	75.7
Oil Yield, Percent Fischer Assay (%):	98.2

SAMPLE NUMBER : FRA23

Run_Conditions_:

Initial T (°C):	32	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	475
Shale (grams):	2.01	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	----

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.00	8.12	5.01	3.11

Calculated Yields :

Organic Carbon Conversion (%):	55.2
Oil/ Gas Selectivity (%) :	89.3
Oil Yield, Percent Fischer Assay (%):	124.2

SAMPLE NUMBER : FRA24

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	400
Shale (grams):	1.93	Nominal Residence Time (min):	60
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.62	7.42	4.89	2.53

Calculated Yields :

Organic Carbon Conversion (%):	63.8
Oil/ Gas Selectivity (%):	99.4
Oil Yield, Percent Fischer Assay (%):	159.7

SAMPLE NUMBER : FRA25

Run_Conditions_:

Initial T (°C):	28	Hydrogen in Feed Gas (%):	95
Initial P (psig):	802	Reaction Temperature (°C):	400
Shale (grams):	1.99	Nominal Residence Time (min):	30
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.05	7.65	4.95	2.70

Calculated Yields :

Organic Carbon Conversion (%):	61.1
Oil/ Gas Selectivity (%) :	99.4
Oil Yield, Percent Fischer Assay (%):	153.0

SAMPLE NUMBER : FRA27

Run_Conditions_:

Initial T (°C):	31	Hydrogen in Feed Gas (%):	95
Initial P (psig):	803	Reaction Temperature (°C):	425
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.31	7.58	5.16	2.42

Calculated Yields :

Organic Carbon Conversion (%):	65.3
Oil/ Gas Selectivity (%):	98.0
Oil Yield, Percent Fischer Assay (%):	161.2

SAMPLE NUMBER : FRA28

Run_Conditions_:

Initial T (°C):	29	Hydrogen in Feed Gas (%):	95
Initial P (psig):	798	Reaction Temperature (°C):	500
Shale (grams):	1.99	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.16	8.51	5.25	3.26

Calculated Yields :

Organic Carbon Conversion (%):	53.1
Oil/ Gas Selectivity (%) :	69.6
Oil Yield, Percent Fischer Assay (%):	93.1

SAMPLE NUMBER : FRA29

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	500
Shale (grams):	2.00	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.96	8.42	5.44	2.98

Calculated Yields :

Organic Carbon Conversion (%):	57.0
Oil/ Gas Selectivity (%):	85.0
Oil Yield, Percent Fischer Assay (%):	122.0

SAMPLE NUMBER : FRA30

Run_Conditions_:

Initial T (°C):	22	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	500
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.94	8.20	4.83	3.37

Calculated Yields :

Organic Carbon Conversion (%):	51.4
Oil/ Gas Selectivity (%) :	91.4
Oil Yield, Percent Fischer Assay (%):	118.3

SAMPLE NUMBER : FRA31

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	802	Reaction Temperature (°C):	400
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.0

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
76.49	8.78	4.89	3.98

Calculated Yields :

Organic Carbon Conversion (%):	42.8
Oil/ Gas Selectivity (%):	
Oil Yield, Percent Fischer Assay (%):	xx

SAMPLE NUMBER : FRA32

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	400
Shale (grams):	2.02	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.8	7.75	4.78	2.97

Calculated Yields :

Organic Carbon Conversion (%):	57.1
Oil/ Gas Selectivity (%) :	98.9
Oil Yield, Percent Fischer Assay (%):	142.2

SAMPLE NUMBER : FRA33

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	400
Shale (grams):	2.00	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.33	7.96	5.11	2.85

Calculated Yields :

Organic Carbon Conversion (%):	58.6
Oil/ Gas Selectivity (%):	99.0
Oil Yield, Percent Fischer Assay (%):	146.1

SAMPLE NUMBER : FRA34

Run_Conditions_:

Initial T (°C):	32	Hydrogen in Feed Gas (%):	95
Initial P (psig):	809	Reaction Temperature (°C):	425
Shale (grams):	2.01	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.77	7.95	5.23	2.72

Calculated Yields :

Organic Carbon Conversion (%):	60.7
Oil/ Gas Selectivity (%) :	97.8
Oil Yield, Percent Fischer Assay (%):	149.5

SAMPLE NUMBER : FRA35

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	425
Shale (grams):	2.00	Nominal Residence Time (min):	30
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.77	7.92	5.07	2.85

Calculated Yields :

Organic Carbon Conversion (%):	58.8
Oil/ Gas Selectivity (%):	98.7
Oil Yield, Percent Fischer Assay (%):	146.2

SAMPLE NUMBER : FRA36

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	802	Reaction Temperature (°C):	425
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.48	7.82	4.80	3.02

Calculated Yields :

Organic Carbon Conversion (%):	56.2
Oil/ Gas Selectivity (%) :	99.3
Oil Yield, Percent Fischer Assay (%):	140.6

SAMPLE NUMBER : FRA37

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	95
Initial P (psig):	807	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.55	8.21	5.12	3.09

Calculated Yields :

Organic Carbon Conversion (%):	55.2
Oil/ Gas Selectivity (%):	94.7
Oil Yield, Percent Fischer Assay (%):	131.7

SAMPLE NUMBER : FRA38

Run_Conditions_:

Initial T (°C):	29	Hydrogen in Feed Gas (%):	95
Initial P (psig):	797	Reaction Temperature (°C):	450
Shale (grams):	1.99	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.92	8.13	4.98	3.15

Calculated Yields :

Organic Carbon Conversion (%):	54.6
Oil/ Gas Selectivity (%) :	97.0
Oil Yield, Percent Fischer Assay (%):	133.4

SAMPLE NUMBER : FRA39

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	95
Initial P (psig):	805	Reaction Temperature (°C):	450
Shale (grams):	2.01	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
76.55	7.77	4.89	2.88

Calculated Yields :

Organic Carbon Conversion (%):	----
Oil/ Gas Selectivity (%):	98.3
Oil Yield, Percent Fischer Assay (%):	----

SAMPLE NUMBER : FRA40

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	475
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.59	8.41	4.98	3.43

Calculated Yields :

Organic Carbon Conversion (%):	50.3
Oil/ Gas Selectivity (%) :	90.0
Oil Yield, Percent Fischer Assay (%):	114.0

SAMPLE NUMBER : FRA41

Run_Conditions_:

Initial T (°C):	31	Hydrogen in Feed Gas (%):	95
Initial P (psig):	798	Reaction Temperature (°C):	475
Shale (grams):	2.01	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.49	8.34	4.96	3.38

Calculated Yields :

Organic Carbon Conversion (%):	51.0
Oil/ Gas Selectivity (%):	94.3
Oil Yield, Percent Fischer Assay (%):	121.1

SAMPLE NUMBER : FRA42

Run_Conditions_:

Initial T (°C):	16	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	475
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.8	8.33	5.1	3.32

Calculated Yields :

Organic Carbon Conversion (%):	53.3
Oil/ Gas Selectivity (%) :	97.0
Oil Yield, Percent Fischer Assay (%):	130.2

SAMPLE NUMBER : FRA43

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	500
Shale (grams):	2.00	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.47	8.78	5.01	3.77

Calculated Yields :

Organic Carbon Conversion (%):	45.3
Oil/ Gas Selectivity (%):	80.0
Oil Yield, Percent Fischer Assay (%):	91.3

SAMPLE NUMBER : FRA44

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	500
Shale (grams):	1.99	Nominal Residence Time (min):	30.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.14	8.67	5.04	3.63

Calculated Yields :

Organic Carbon Conversion (%):	47.1
Oil/ Gas Selectivity (%) :	87.1
Oil Yield, Percent Fischer Assay (%):	103.3

SAMPLE NUMBER : FRA45

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	803	Reaction Temperature (°C):	500
Shale (grams):	1.99	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.42	8.29	4.99	3.27

Calculated Yields :

Organic Carbon Conversion (%):	52.1
Oil/ Gas Selectivity (%):	95.2
Oil Yield, Percent Fischer Assay (%):	124.9

SAMPLE NUMBER : FRA46

Run_Conditions_:

Initial T (°C):	28	Hydrogen in Feed Gas (%):	95
Initial P (psig):	803	Reaction Temperature (°C):	450
Shale (grams):	2.01	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.92	7.75	5.17	2.58

Calculated Yields :

Organic Carbon Conversion (%):	62.8
Oil/ Gas Selectivity (%) :	67.0
Oil Yield, Percent Fischer Assay (%):	106.0

SAMPLE NUMBER : FRA47

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.85	7.84	5.05	2.79

Calculated Yields :

Organic Carbon Conversion (%):	55.2
Oil/ Gas Selectivity (%):	96.1
Oil Yield, Percent Fischer Assay (%):	133.6

SAMPLE NUMBER : FRA48

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	95
Initial P (psig):	805	Reaction Temperature (°C):	450
Shale (grams):	2.01	Nominal Residence Time (min):	60.0
Solvent (grams):	3.46	Actual Residence Time (min):	---

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.03	7.91	5.05	2.86

Calculated Yields :

Organic Carbon Conversion (%):	58.8
Oil/ Gas Selectivity (%) :	86.9
Oil Yield, Percent Fischer Assay (%):	128.7

SAMPLE NUMBER : FRA50

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.9	7.64	5.06	2.58

Calculated Yields :

Organic Carbon Conversion (%):	63.2
Oil/ Gas Selectivity (%):	92.3
Oil Yield, Percent Fischer Assay (%):	146.9

SAMPLE NUMBER : FRA51

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.46	7.75	5.00	2.75

Calculated Yields :

Organic Carbon Conversion (%):	60.6
Oil/ Gas Selectivity (%) :	92.6
Oil Yield, Percent Fischer Assay (%):	141.3

SAMPLE NUMBER : FRA52

Run_Conditions_:

Initial T (°C):	20	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	475
Shale (grams):	2.03	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.86	7.97	5.04	2.93

Calculated Yields :

Organic Carbon Conversion (%):	58.2
Oil/ Gas Selectivity (%):	88.0
Oil Yield, Percent Fischer Assay (%):	129.7

SAMPLE NUMBER : FRA53

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	95
Initial P (psig):	803	Reaction Temperature (°C):	475
Shale (grams):	2.00	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.41	7.82	4.96	2.86

Calculated Yields :

Organic Carbon Conversion (%):	59.0
Oil/ Gas Selectivity (%) :	92.4
Oil Yield, Percent Fischer Assay (%):	137.3

SAMPLE NUMBER : FRA54

Run_Conditions_:

Initial T (°C):	28	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	425
Shale (grams):	2.01	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.42	7.49	5.02	2.47

Calculated Yields :

Organic Carbon Conversion (%):	64.6
Oil/ Gas Selectivity (%):	97.7
Oil Yield, Percent Fischer Assay (%):	159.0

SAMPLE NUMBER : FRA55

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	95
Initial P (psig):	795	Reaction Temperature (°C):	425
Shale (grams):	2.01	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.79	8.07	4.42	3.65

Calculated Yields :

Organic Carbon Conversion (%):	47.3
Oil/ Gas Selectivity (%) :	98.3
Oil Yield, Percent Fischer Assay (%):	117.1

SAMPLE NUMBER : FRA56

Run_Conditions_:

Initial T (°C):	30	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	425
Shale (grams):	2.00	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.12	7.73	4.96	2.77

Calculated Yields :

Organic Carbon Conversion (%):	60.1
Oil/ Gas Selectivity (%):	98.2
Oil Yield, Percent Fischer Assay (%):	148.7

SAMPLE NUMBER : FRA57

Run_Conditions_:

Initial T (°C):	Hydrogen in Feed Gas K(%):
Initial P (psig):	Reaction Temperature (°C):
Shale (grams):	Nominal Residence Time (min):
Solvent (grams):	Actual Residence Time (min):

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C

Calculated Yields :

Organic Carbon Conversion (%):	
Oil/ Gas Selectivity (%) :	
Oil Yield, Percent Fischer Assay (%):	xx

SAMPLE NUMBER : FRA58

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
80.03	7.54	5.02	2.52

Calculated Yields :

Organic Carbon Conversion (%):	64.6
Oil/ Gas Selectivity (%):	95.3
Oil Yield, Percent Fischer Assay (%):	155.1

SAMPLE NUMBER : FRA59

Run_Conditions_:

Initial T (°C):	28	Hydrogen in Feed Gas (%):	95
Initial P (psig):	802	Reaction Temperature (°C):	450
Shale (grams):	2.01	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.88	7.71	4.91	2.80

Calculated Yields :

Organic Carbon Conversion (%):	54.6
Oil/ Gas Selectivity (%) :	91.2
Oil Yield, Percent Fischer Assay (%):	125.4

SAMPLE NUMBER : FRA60

Run_Conditions_:

Initial T (°C):	21	Hydrogen in Feed Gas (%):	95
Initial P (psig):	802	Reaction Temperature (°C):	400
Shale (grams):	2.00	Nominal Residence Time (min):	12.0
Solvent (grams):	3.46	Actual Residence Time (min):	10.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.26	8.2	4.22	3.98

Calculated Yields :

Organic Carbon Conversion (%):	42.1
Oil/ Gas Selectivity (%):	99.3
Oil Yield, Percent Fischer Assay (%):	105.3

SAMPLE NUMBER : FRA61

Run_Conditions_:

Initial T (°C):	26	Hydrogen in Feed Gas (%):	95
Initial P (psig):	799	Reaction Temperature (°C):	400
Shale (grams):	2.00	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
76.69	8.50	4.37	4.13

Calculated Yields :

Organic Carbon Conversion (%):	39.5
Oil/ Gas Selectivity (%) :	99.3
Oil Yield, Percent Fischer Assay (%):	98.8

SAMPLE NUMBER : FRA63

Run_Conditions_:

Initial T (°C):	25	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	400
Shale (grams):	2.01	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
75.33	9.97	5.12	5.12

Calculated Yields :

Organic Carbon Conversion (%):	23.6
Oil/ Gas Selectivity (%):	87.8
Oil Yield, Percent Fischer Assay (%):	52.2

SAMPLE NUMBER : FRA64

Run_Conditions_:

Initial T (°C):	38	Hydrogen in Feed Gas (%):	95
Initial P (psig):	795	Reaction Temperature (°C):	500
Shale (grams):	2.01	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.17	7.92	3.04	3.88

Calculated Yields :

Organic Carbon Conversion (%):	56.3
Oil/ Gas Selectivity (%):	93.2
Oil Yield, Percent Fischer Assay (%):	132.2

SAMPLE NUMBER : FRA65

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	95
Initial P (psig):	803	Reaction Temperature (°C):	500
Shale (grams):	2.02	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.00	8.10	4.95	3.15

Calculated Yields :

Organic Carbon Conversion (%):	54.6
Oil/ Gas Selectivity (%):	96.6
Oil Yield, Percent Fischer Assay (%):	132.9

SAMPLE NUMBER : FRA66

Run_Conditions_:

Initial T (°C):	34	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	500
Shale (grams):	2.01	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.12	8.08	4.82	3.26

Calculated Yields :

Organic Carbon Conversion (%):	53.1
Oil/ Gas Selectivity (%) :	79.8
Oil Yield, Percent Fischer Assay (%):	106.7

SAMPLE NUMBER : FRA67

Run_Conditions_:

Initial T (°C):	22	Hydrogen in Feed Gas (%):	95
Initial P (psig):	798	Reaction Temperature (°C):	425
Shale (grams):	2.01	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.97	7.68	4.60	3.08

Calculated Yields :

Organic Carbon Conversion (%):	55.6
Oil/ Gas Selectivity (%):	93.8
Oil Yield, Percent Fischer Assay (%):	131.4

SAMPLE NUMBER : FRA68

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	95
Initial P (psig):	800	Reaction Temperature (°C):	425
Shale (grams):	2.02	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.32	8.13	4.18	3.95

Calculated Yields :

Organic Carbon Conversion (%):	42.6
Oil/ Gas Selectivity (%) :	99.3
Oil Yield, Percent Fischer Assay (%):	106.6

SAMPLE NUMBER : FRA69

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	95
Initial P (psig):	805	Reaction Temperature (°C):	450
Shale (grams):	2.00	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
79.11	7.49	5.04	2.45

Calculated Yields :

Organic Carbon Conversion (%):	65.1
Oil/ Gas Selectivity (%):	97.8
Oil Yield, Percent Fischer Assay (%):	160.4

SAMPLE NUMBER : FRA70

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	450
Shale (grams):	2.01	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
79.14	7.41	4.94	2.47

Calculated Yields :

Organic Carbon Conversion (%):	66.2
Oil/ Gas Selectivity (%) :	88.7
Oil Yield, Percent Fischer Assay (%):	147.9

SAMPLE NUMBER : FRA71

Run_Conditions_:

Initial T (°C):	22	Hydrogen in Feed Gas (%):	95
Initial P (psig):	801	Reaction Temperature (°C):	475
Shale (grams):	2.01	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.82	7.78	4.89	2.89

Calculated Yields :

Organic Carbon Conversion (%):	60.8
Oil/ Gas Selectivity (%):	94.4
Oil Yield, Percent Fischer Assay (%):	144.6

SAMPLE NUMBER : FRA72

Run_Conditions_:

Initial T (°C):	29	Hydrogen in Feed Gas (%):	95
Initial P (psig):	803	Reaction Temperature (°C):	475
Shale (grams):	2.00	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
79.04	7.66	4.98	2.68

Calculated Yields :

Organic Carbon Conversion (%):	62.6
Oil/ Gas Selectivity (%) :	96.8
Oil Yield, Percent Fischer Assay (%):	152.6

SAMPLE NUMBER : FRA73

Run Conditions:

Initial T (°C):	31	Hydrogen in Feed Gas (%):	50
Initial P (psig):	802	Reaction Temperature (°C):	475
Shale (grams):	2.02	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.5

Shale Analysis:

% Ash	% Total C	% Inorg. C	% Org. C
77.59	8.00	4.95	3.05

Calculated Yields :

Organic Carbon Conversion (%):	57.0
Oil/ Gas Selectivity (%):	92.3
Oil Yield, Percent Fischer Assay (%):	132.1

SAMPLE NUMBER : FRA74

Run Conditions:

Initial T (°C):	28	Hydrogen in Feed Gas (%):	50
Initial P (psig):	802	Reaction Temperature (°C):	475
Shale (grams):	2.02	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale Analysis:

% Ash	% Total C	% Inorg. C	% Org. C
79.07	7.73	4.93	2.80

Calculated Yields :

Organic Carbon Conversion (%):	61.6
Oil/ Gas Selectivity (%) :	95.3
Oil Yield, Percent Fischer Assay (%):	147.9

SAMPLE NUMBER : FRA75

Run_Conditions_:

Initial T (°C):	29	Hydrogen in Feed Gas (%):	50
Initial P (psig):	797	Reaction Temperature (°C):	475
Shale (grams):	2.02	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.53	7.61	4.91	2.70

Calculated Yields :

Organic Carbon Conversion (%):	63.1
Oil/ Gas Selectivity (%):	97.5
Oil Yield, Percent Fischer Assay (%):	155.0

SAMPLE NUMBER : FRA76

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	50
Initial P (psig):	802	Reaction Temperature (°C):	500
Shale (grams):	2.00	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.0

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.17	8.07	4.81	3.26

Calculated Yields :

Organic Carbon Conversion (%):	55.7
Oil/ Gas Selectivity (%) :	87.7
Oil Yield, Percent Fischer Assay (%):	123.2

SAMPLE NUMBER : FRA77

Run_Conditions_:

Initial T (°C):	33	Hydrogen in Feed Gas (%):	50
Initial P (psig):	800	Reaction Temperature (°C):	500
Shale (grams):	2.00	Nominal Residence Time (min):	7.0
Solvent (grams):	3.46	Actual Residence Time (min):	5.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.62	8.08	4.94	3.14

Calculated Yields :

Organic Carbon Conversion (%):	56.4
Oil/ Gas Selectivity (%):	88.2
Oil Yield, Percent Fischer Assay (%):	125.3

SAMPLE NUMBER : FRA78

Run_Conditions_:

Initial T (°C):	29	Hydrogen in Feed Gas (%):	50
Initial P (psig):	802	Reaction Temperature (°C):	500
Shale (grams):	2.01	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.5

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.53	7.96	5.00	2.96

Calculated Yields :

Organic Carbon Conversion (%):	57.5
Oil/ Gas Selectivity (%) :	91.0
Oil Yield, Percent Fischer Assay (%):	131.8

SAMPLE NUMBER : FRA79

Run_Conditions_:

Initial T (°C):	27	Hydrogen in Feed Gas (%):	50
Initial P (psig):	800	Reaction Temperature (°C):	400
Shale (grams):	2.00	Nominal Residence Time (min):	10.0
Solvent (grams):	3.46	Actual Residence Time (min):	8.0

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.20	8.43	4.29	4.14

Calculated Yields :

Organic Carbon Conversion (%):	38.8
Oil/ Gas Selectivity (%):	98.9
Oil Yield, Percent Fischer Assay (%):	96.7

SAMPLE NUMBER : FRAB0

Run_Conditions_:

Initial T (°C):	23	Hydrogen in Feed Gas (%):	50
Initial P (psig):	804	Reaction Temperature (°C):	400
Shale (grams):	2.01	Nominal Residence Time (min):	5.0
Solvent (grams):	3.46	Actual Residence Time (min):	3.0

Shale_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.20	9.69	4.21	5.48

Calculated Yields :

Organic Carbon Conversion (%):	19.0
Oil/ Gas Selectivity (%) :	99.2
Oil Yield, Percent Fischer Assay (%):	47.5

SAMPLE NUMBER : FRAB2

Run_Conditions_:

Initial T (°C):	39
Initial P (psig):	805
Shale (grams):	2.00
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	95
Reaction Temperature (°C):	450
Nominal Residence Time (min):	1.67
Actual Residence Time (min):	0.88

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
76.28	8.50	4.70	3.80

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	92.8566	i-C4H10	0
CH4	0.5557	CO	0.0939
C2H4	0	CO2	0.4812
C2H6	0.0308	Ar/Kr	5.9709
C3H6	0		
C3H8	0.0109		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	44.0
Oil/ Gas Selectivity (%):	94.7
Oil Yield, Percent Fischer Assay (%):	105.0

SAMPLE NUMBER : FRA85

Run_Conditions_:

Initial T (°C):	41
Initial P (psig):	797
Shale (grams):	2.06
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	500
Nominal Residence Time (min):	1.6
Actual Residence Time (min):	0.45

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.00	7.75	4.96	2.79

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	91.2074	i-C4H10	0
CH4	0.8969	CO	0
C2H4	0	CO2	0.5717
C2H6	0	Ar/Kr	6.9427
C3H6	0.0199		
C3H8	0.0731		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	59.3
Oil/ Gas Selectivity (%):	93.9
Oil Yield, Percent Fischer Assay (%):	140.3

SAMPLE NUMBER : FRAB7

Run Conditions :

Initial T (°C):	35
Initial P (psig):	804
Shale (grams):	2.02
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	95
Reaction Temperature (°C):	425
Nominal Residence Time (min):	0.75
Actual Residence Time (min):	0.07

Chemical Analysis :

% Ash	% Total C	% Inorg. C	% Org. C
74.23	10.55	4.80	5.75

Product Gas Analysis :

Component	Mole %	Component	Mole %
H2	93.646	i-C4H10	0
CH4	0	CO	0
C2H4	0	CO2	0.4028
C2H6	0	Ar/Kr	5.7326
C3H6	0		
C3H8	0		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	12.9
Oil/ Gas Selectivity (%):	93.2
Oil Yield, Fercent Fischer Assay (%):	30.3

SAMPLE NUMBER : FRA88

Run_Conditions_:

Initial T (°C):	31
Initial P (psig):	803
Shale (grams):	1.99
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	450
Nominal Residence Time (min):	4.0
Actual Residence Time (min):	2.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.02	7.57	4.93	2.604

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	5.2406	CO	0
C2H4	0	CO2	20.8299
C2H6	0	Ar/Kr	73.9296
C3H6	0		
C3H8	0		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	61.5
Oil/ Gas Selectivity (%):	99.3
Oil Yield, Percent Fischer Assay (%):	153.4

SAMPLE NUMBER : FRA89

Run_Conditions_:

Initial T (°C):	32
Initial P (psig):	805
Shale (grams):	2.00
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	450
Nominal Residence Time (min):	7.0
Actual Residence Time (min):	5.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.34	7.54	4.99	2.55

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	8.6859	CO	0
C2H4	0	CO2	26.5979
C2H6	25.9758	Ar/Kr	20.9568
C3H6	0		
C3H8	16.1637		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	62.9
Oil/ Gas Selectivity (%):	87.1
Oil Yield, Percent Fischer Assay (%):	138.0

SAMPLE NUMBER : FRA90

Run_Conditions_:

Initial T (°C):	33
Initial P (psig):	802
Shale (grams):	2.01
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	450
Nominal Residence Time (min):	10.0
Actual Residence Time (min):	8.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.28	7.88	4.98	2.90

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	26.6549	CO	0
C2H4	0	CO2	20.9498
C2H6	2.5872	Ar/Kr	23.4511
C3H6	0		
C3H8	23.2581		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	57.8
Oil/ Gas Selectivity (%):	88.8
Oil Yield, Percent Fischer Assay (%):	129.3

SAMPLE NUMBER : FRA91

Run_Conditions_:

Initial T (°C):	30
Initial P (psig):	803
Shale (grams):	2.02
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	425
Nominal Residence Time (min):	4.0
Actual Residence Time (min):	2.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
76.27	8.71	4.94	3.77

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	0	CO	0
C2H4	0	CO2	14.6028
C2H6	5.3480	Ar/Kr	80.0493
C3H6	0		
C3H8	0		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	44.4
Oil/ Gas Selectivity (%):	99.1
Oil Yield, Percent Fischer Assay (%):	110.8

SAMPLE NUMBER : FRA92

Run_Conditions_:

Initial T (°C):	34
Initial P (psig):	803
Shale (grams):	2.00
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	425
Nominal Residence Time (min):	10.0
Actual Residence Time (min):	8.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.52	7.58	4.94	2.69

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	2.4987	CO	0
C2H4	0	CO2	4.4553
C2H6	11.0674	Ar/Kr	60.3235
C3H6	0		
C3H8	20.6544		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	61.7
Oil/ Gas Selectivity (%):	97.0
Oil Yield, Percent Fischer Assay (%):	150.8

SAMPLE NUMBER : FRA93

Run_Conditions_:

Initial T (°C):	31
Initial P (psig):	802
Shale (grams):	2.00
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	425
Nominal Residence Time (min):	7.0
Actual Residence Time (min):	5.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.79	7.73	4.94	2.79

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	13.1159	CO	0
C2H4	0	CO2	13.2330
C2H6	3.3122	Ar/Kr	33.2137
C3H6	0		
C3H8	33.8583		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	59.7
Oil/ Gas Selectivity (%):	91.6
Oil Yield, Percent Fischer Assay (%):	137.7

SAMPLE NUMBER : FRA94

Run_Conditions_:

Initial T (°C):	32
Initial P (psig):	803
Shale (grams):	2.02
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	475
Nominal Residence Time (min):	7.0
Actual Residence Time (min):	5.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.27	8.01	5.02	2.99

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	12.3246	CO	0
C2H4	0	CO2	9.1178
C2H6	2.1301	Ar/Kr	59.3336
C3H6	0		
C3H8	13.6506		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	56.5
Oil/ Gas Selectivity (%):	97.5
Oil Yield, Percent Fischer Assay (%):	138.8

SAMPLE NUMBER : FRA95

Run_Conditions_:

Initial T (°C):	32
Initial P (psig):	803
Shale (grams):	2.00
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	475
Nominal Residence Time (min):	10.0
Actual Residence Time (min):	8.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
78.25	7.98	5.08	2.90

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	15.9791	CO	0
C2H4	0	CO2	12.9073
C2H6	2.6068	Ar/Kr	51.9315
C3H6	0		
C3H8	13.8908		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	58.3
Oil/ Gas Selectivity (%):	96.8
Oil Yield, Percent Fischer Assay (%):	142.2

SAMPLE NUMBER : FRA96

Run_Conditions_:

Initial T (°C):	32
Initial P (psig):	802
Shale (grams):	2.02
Solvent (grams):	3.47
Hydrogen in Feed Gas (%):	0
Reaction Temperature (°C):	475
Nominal Residence Time (min):	4.0
Actual Residence Time (min):	2.5

Chemical_Analysis_:

% Ash	% Total C	% Inorg. C	% Org. C
77.74	7.77	5.05	2.72

Product_Gas_Analysis_:

Component	Mole %	Component	Mole %
H2	0	i-C4H10	0
CH4	15.1924	CO	0
C2H4	0	CO2	14.8886
C2H6	4.7743	Ar/Kr	61.2509
C3H6	0		
C3H8	0		
n-C4H10	0		

Calculated Yields :

Organic Carbon Conversion (%):	60.7
Oil/ Gas Selectivity (%):	98.7
Oil Yield, Percent Fischer Assay (%):	150.9

APPENDIX E
MINITAB SAMPLE INPUT AND OUTPUT

MINITAB Sample Input and Output, Arrhenius Plot

.R LBY:MINITAB
[23:03:29]

AASE 81.1 *** COPYRIGHT - PENN STATE UNIV. 1981
SEPT. 4, 1985 *** Colorado School of Mines * DECsystem-1091

STORAGE AVAILABLE 19800

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

-- READ C1 C2

-- -1.7243, -.00148588

-- -.8861, -.00143267

-- -.1057, -.00138313

-- BRIEF

-- REGRESS Y INTO C1 ON 1 PREDICTOR IN C2

THE REGRESSION EQUATION IS

Y = 21.7 +15753. X1

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	21.6825	0.0001	214477.14
X1	C2	15752.8	0.1	223528.41

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS

S = 0.000005121

WITH (3- 2) = 1 DEGREES OF FREEDOM

R-SQUARED =100.0 PERCENT

R-SQUARED =100.0 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	1.310490	1.310490
RESIDUAL	1	0.000000	0.000000
TOTAL	2	1.310490	

APPENDIX F
EQUIPMENT CONSTRUCTION

ECCENTRIC ARM MATERIALS

The eccentric arm was fabricated by Mr. Herman Stump of Boulder, Colorado. The materials used in the construction consist of the following.

- Flange: Body-cold rolled steel
Oil seals-National oil seal, .75x1.123x.25
Ball Bushings-Thompson #A-122026
- Shaft: Lower Shaft-316 stainless steel, 3/4" dia.
Brackets-1/8" thick 316 stainless steel plate
Upper Shaft-drill rod, 3/4" dia.
Shaft Connector-drill rod, 3/4" dia.
- Flywheel: Body-colded roll steel, 2" dia. by 1/2" thick
Connecting Pins-drill rod, 1/4" dia.
- Connecting Rod
Body-cold rolled steel, 3"x1.25"x.5"
ball Bearings-Fafnir, #51KDD7

APPENDIX G
SOLVENT STABILITY TESTS

Solvent Stability Tests, Tubing-bomb Reactor

The feed components were subjected to a temperature of 450°C for a residence time of 10 minutes.

FEED	PURITY OF PRODUCT, VOLUME %
Toluene Feed	99.8
Toluene/H ₂	99.2
Toluene/He	99.6
Toluene/H ₂ /Spent Shale	98.6
Benzene Feed	99.9
Benzene/H ₂	99.9
Benzene/He	99.9
Decalin Feed	98.8
Decalin/H ₂	97.4
Decalin/He	98.6

APPENDIX H
FISCHER ASSAY

DATE : 8/2/84

SAMPLE NUMBER BALDWIN
 SAMPLE DESCRIPTION FRENCH OIL SHALE
 TERMINAL TEMP 932 DEG. F
 FISHER ASSAY NO. FB2682

FISCHER ASSAY YIELDS	AS ANALYZED	NORMALIZED	
OIL (LB/TON)	69.4	69.5	
(GAL/TON)	8.8	8.9	
API GRAVITY	18.9	18.9	
GAS (LB/TON)	36.7	36.7	
(SCF/TON)	588.7	589.5	
WATER (LB/TON)	40.8	40.9	
(GAL/TON)	4.9	4.9	
SS (LB/TON)	1850.3	1852.9	
TOTAL (LB/TON)	1997.2	2000.0	
VARIANCE (PC)	- .1		
GAS (NORMALIZED)	(LB/TON)		(LB/100 LB) (FA OIL)
H2	1.01		1.46
CO	.84		1.21
CO2	9.06		13.04
H2S	16.28		23.43
C1	2.81		4.04
C2	1.67		2.40
C2-	.44		.64
C3	1.07		1.54
C3-	1.07		1.54
I-C4	0.00		0.00
N-C4	.63		.90
C4-	1.01		1.46
C5	.11		.16
C6+	.72		1.04
YIELDS (NORMALIZED)	LB/TON	SCF/TON	LB/100 LB F A OIL
C3 & LIGHTER	34.2	574.8	49.4
SCRUBBED C3&LIGHTER [LESS CO2 & H2S]	8.9	315.8	12.8
C4 & HEAVIER	71.9		103.7
TOTAL HYDROCARBONS INCL. H2 & CO, LB/TON	80.9		116.5
C4 & HEAVIER (GAL/TON)		9.3	
API GRAVITY		21.7	

GAS ANALYSIS

SAMPLE NUMBER	BALDWIN
SAMPLE DESCRIPTION	FRENCH OIL SHALE
FISCHER ASSAY NO.	PB2682

COMPONENT MOLE PERCENT

H2	32.59
CO	1.93
CO2	13.24
H2S	30.69
C1	11.28
C2	3.56
C2-	1.01
C3	1.56
C3-	1.63
I-C4	0.00
N-C4	.69
C4-	1.16
C5	.10
C6+	.54
SUM	100.00

AVERAGE MOLE WT	23.61
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LBS C IN GAS/TON SHALE	10.52
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WT. PERCENT TOTAL CARBON	28.66
WT. PERCENT SULFUR	41.71

BTU VALUE OF GAS (CALC.)	GROSS	NET
C3 & LIGHTER* (BTU/SCF)	592.55	536.49
SCRUBBED C3 & LIGHTER (BTU/SCF)	712.49	638.79
WHOLE GAS* (BTU/SCF)	665.45	604.56
SCRUBBED WHOLE GAS (BTU/SCF)	837.13	755.63

*[INCL. H2S & CO2]