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THERMAL SOLUTION OF STUART
DEPOSIT OIL SHALE
IN A
CONTINUOUS PROCESS UNIT

by
Randal J. Winkler

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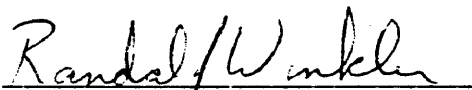
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Golden, Colorado

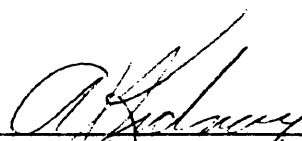
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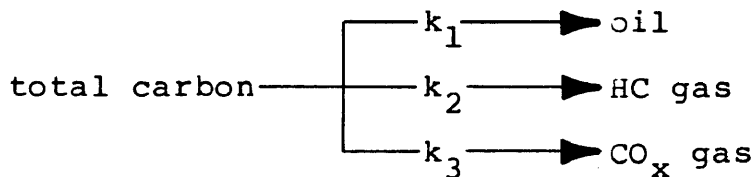
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ABSTRACT

The thermal solution of Stuart Formation (Queensland, Australia) oil shale using tetralin and #2 diesel fuel as solvents was studied in a bench scale continuous stirred tank reactor system (CSTR). An organic carbon conversion of 86.4% was obtained in less than 30 minutes residence time at 425 C using tetralin with a hydrogen gas atmosphere of 1500 psig. It was found that the overall conversion of total carbon to conversion products could be modeled using a first order irreversible expression. In addition, the yield of products was shown to be adequately described by the following mechanism:



Reactions 1, 2 and 3 resulted in activation energies of 31.15, 37.92, and 29.99 Kcal/g-mole respectively. With #2 diesel fuel as a solvent, the effect of hydrogen partial pressure was not apparent at 1500 psig. However, at 850 psig the effect was significant. Regardless of the solvent used, the selectivity for total carbon conversion to oil was high, ranging from 95.4 to 97.8%.

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INTRODUCTION

Throughout the years, the continual demand upon and limited reserves of the world's supply of liquid fuel have demonstrated the need for the development of alternate energy sources. Because of the immense reserves, oil shale has received considerable attention as an alternate energy source, particularly as a source of liquid fuel.

Currently, only one technique, pyrolysis or retorting, has been developed commercially to recover oil from oil shale. A second technique, thermal solution, appears to convert a higher percentage of the organic matter in oil shale to volatile products, but is far less advanced from a commercial standpoint than retorting. This process consists of heating oil shale in the presence of a solvent, with or without a hydrogen gas atmosphere, and extracting the conversion products.

The objective of this study was two-fold. Phase 1 experiments were conducted to investigate the effects of operating temperature and residence time on the conversion of organic carbon to volatile products and the resulting yield structure (oil/gas) during the thermal solution of an Australian oil shale (Stuart A) in a hydrogen donor solvent (tetralin). Phase 2 experiments were conducted to

investigate the effect of total pressure and hydrogen partial pressure on organic carbon conversion and oil selectivity in a limited hydrogen donor solvent (#2 diesel fuel). Both series of experiments were conducted using a bench scale continuous stirred tank reactor system (CSTR).

BACKGROUND

2.1 Oil Shale Resources

Oil shale is a fine-grained sedimentary rock containing a diffused solid organic matter of a complex chemical composition which is not appreciably soluble in conventional petroleum solvents. However, by heating the oil shale to temperatures above 800-900°F in the absence of oxygen, the organic matter is pyrolyzed to combustible liquids, gases, and coke which remains on the inorganic matrix.

The United States Geological Survey (USGS) estimated that the world's total oil shale deposits, with a yield of at least 5 gallons per ton, amount to over 4×10^{15} tons and have a potential shale oil yield of over 2×10^{15} barrels.⁽¹⁾ A breakdown of the distribution of these resources is presented in Table 1.

Australian oil shale was first discovered as blocks in a river bed in the colony of New South Wales by a French scientific expedition in 1902. In 1815, the first recorded discovery of in-situ oil shale was found in the Hartley Valley, just east of the present town of Lithgow, New South Wales.

Since then, major oil shale deposits have been found in Western Australia, New South Wales, Tasmania, and

TABLE 1

Distribution of the World's Oil Shale Resources

<u>Location</u>	<u>Resources</u> <u>10¹² barrels</u>	<u>Per Cent of</u> <u>Total Resources</u>
Asia	700	34.3
Africa	500	24.5
North America	300	14.7
South America	250	12.3
Europe	170	8.3
Australia	120	5.9
Total	<hr/> 2,040	<hr/> 100.00

Queensland, with demonstrated reserves estimated from 2.7×10^8 (3) to 15×10^8 (4) barrels.

The majority of Australian oil shale deposits are found in Queensland, with the largest being that of the Toolebuc Formation. The inferred resources of this deposit are estimated between 2×10^{12} (5) and 3×10^{12} (6) barrels of in-situ oil from oil shale yielding an average of approximately 12 gallons per ton.

In addition to the Toolebuc Formation, oil shale deposits are found in the Durango Basin and the Narrows area. The Narrows is located on the eastern seaboard of Queensland, north-west of Gladstone. Oil shale can be found on both sides of, and under, the narrow channel separating Curtis Island from the mainland of Australia. The oil shale from the Narrows area is a brownish, soft rock containing 16-25% organic matter, up to 16% inherent moisture, and an oil yield averaging 25 gallons per ton. (7)

The two deposits which exist in the Narrows area are the Rundle deposit and the Stuart deposit. The oil shale used in this study was taken from the upper portion of the Kerosine Creek seam in the Stuart A deposit and was provided by Southern Pacific Petroleum N.L.

2.2 Oil Shale Origin

Oil shales were formed by the deposition of organic matter in sedimentary silt and mud at the bottom of shallow lakes and seas, followed by the decay of the organic matter and lithification of the inorganic sediment.⁽⁸⁾

The relative proportions of organic and inorganic matter in oil shales results from the variation in the rates of inorganic sedimentation and organic matter accumulation.

The organic matter consists mainly of decomposed remains of small marine plants such as algae. However, some oil shales, such as the torbanites of Queensland, contain some animal fossil remains.⁽⁹⁾

The oil shales in Queensland range in age from Cambrian to Miocene.⁽¹⁰⁾ The Stuart deposit is believed to have been formed during the Tertiary Age by the deposition of algae in a shallow lake, giving rise to fine grained mudstone with a specific gravity of 1.75.

2.3 Oil Shale Composition

As mentioned previously, oil shales consist of two distinct components: an organic component and an inorganic component. Typical values of the relative proportions of inorganic and organic matter in western U.S. oil shales are presented in Table 2.⁽¹¹⁾

TABLE 2

Mineral Content vs Grade of U.S. Oil Shales⁽¹¹⁾

<u>Fischer Assay (GPT)</u>	<u>Inorganic Matter (Wt. %)</u>	<u>Organic Matter (Wt. %)</u>
10.5	92.2	7.8
26.7	84.0	16.0
36.3	80.1	19.9
57.1	67.0	33.0

2.3.1 Organic

The organic component of oil shale consists primarily of benzene-insoluble kerogen and a relatively small fraction of benzene soluble bitumen. Typical compositions of kerogen, which vary widely with strata within a deposit, are presented in Table 3^(12,13) for several Australian oil shale deposits and the Green River deposit. A range of compositions from various deposits throughout the world is also included.

The exact chemical structure of kerogen, which varies with the geographical location of the oil shales, still remains to be determined. Prien⁽¹⁴⁾ postulated that kerogen is an

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

2.3.2 Inorganic

The inorganic portion of oil shale is comprised of a complex mineral suite which is highly dependent on the deposit location. The host rock is usually a dolomitic marlstone with major constituents consisting of anacime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{XH}_2\text{O}$), quartz (SiO_2), potassium feldspar ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{S}:\text{O}_2$), sodium feldspar ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$),

TABLE 3

Composition of Kerogen

Deposit	C (%)	H (%)	N (%)	S (%)	O (%)
Coorongite, Aus. (13)	77.15	10.75	0.99	0.51	10.60
Hartley Valley, Aus. (13)	84.4	10.05	1.01	0.78	3.8
Marrangaroo, Aus. (13)	84.2	11.93	0.31	1.02	2.54
Newnes, Aus (13)	85.8	10.3	0.86	0.74	2.3
Torbanite, N.S.W., Aus. (13)	85.0	10.0	0.30	0.70	4.0
Tasmanite, Aus. (13)	77.5	9.99	0.59	5.20	6.6
Green River, U.S.A. (12)	80.5	10.3	2.39	1.04	5.75
Range (12)	64.0-88.0	7.15-12.8	0.1-3.05	0.1-8.8	0.75-24.7

dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), and illite.
($\text{K}_2\text{O}_3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$).⁽¹⁵⁾

2.4 Shale Oil Properties

The chemical and physical properties of shale oil are different from those of conventional crudes. Both consist primarily of long-chain hydrocarbon molecules with boiling points that roughly span the same range. However, shale oils tend to have a higher olefin content, higher concentrations of nitrogen and oxygen, and a higher pour point and viscosity.⁽¹⁶⁾ Typical oil properties for two oil shales are compared with the properties of Arabian light crude in Table 4.⁽¹⁷⁾ Although the composition of the hydrocarbons making up shale oil is dependent on the source rock, Table 5 gives values for a typical crude and a western U.S. shale oil.⁽¹⁷⁾

2.5 Oil Shale Retorting

Although oil may be extracted from oil shale by several techniques, only pyrolysis (retorting) has received the attention required to develop commercial processing technology.⁽¹⁸⁾ Retorting involves heating oil shale to temperatures above 800-900°F in the absence of oxygen to allow the organic matter to thermally decompose or

TABLE 4

Shale Oil Properties⁽¹⁷⁾

	Arabian Light Crude	Union (B)	TOSCO 11
Oil Properties			
Gravity (°API)	33.4	21.2	21.1
SG (60°/60°F)	0.858	0.927	0.927
Pour Point (°F)	-30	60	80
Pour Point (°C)	-34	15	27
Viscosity, (cs at 100°F)	6.14	33.5	22
Viscosity, (SUS at 100°F)	47	150	106
Element Analysis			
Carbon, wt %	--	85.3	85.1
Hydrogen, wt %	--	11.15	11.6
Nitrogen, wt %	--	1.77	1.9
Oxygen, wt %	--	1.12	0.8
Sulfur, wt %	1.8	0.61	0.9
Ash, wt %	--	0.03	--
C/H ratio	--	--	7.34
ASTM Distillation			
Initial BP, °F	--	145	200
10% over	200	397	275
20% over	310	--	410
30% over	415	660	500
40% over	515	--	620
50% over	615	797	--
60% over	715	--	775
70% over	825	903	850
80% over	945	--	920
90% over	--	1037	--
End point, °F	1050	1100	--

TABLE 5

Shale Oil Composition⁽¹⁷⁾

<u>Hydrocarbon</u>	<u>Western U.S. Shale Oil (%)</u>	<u>Typical Crude (%)</u>
Alkanes	20	15
Aromatics	20	50
Aromatic resins	25	--
Naphthenes	--	35
Olefins	35	--

pyrolyze. The resultant vapors are condensed to recover a liquid product (shale oil) and a gaseous product. A carbonaceous residue (coke) is also produced which remains on the inorganic matrix.

Retorting is currently being accomplished commercially both in place (in situ) and aboveground.⁽¹⁹⁾

2.5.1 True In Situ (TIS)

In TIS retorting, the deposit is fractured to increase its permeability. The top layer of the retort is ignited by injecting air and burning a supplemental fuel. Heat generation is maintained by the combustion of coke on the spent shale. As the coke is consumed, the combustion zone moves slowly down the retort, pyrolyzing lower layers of oil shale. Shale oil, aided by the downward flow of gases, condenses as it moves away from the combustion zone and is collected in sumps at the bottom of the retort and then pumped to the surface.

The formation of large impermeable blocks and irregular fracturing patterns, resulting in unrecoverable oil, is a major problem associated with TIS retorting which typically results in low oil recoveries.⁽²⁰⁾

2.5.2 Modified In Situ (MIS)

In MIS retorting, which is more efficient than TIS retorting, a portion of the oil shale is mined from the

underground deposit and either discarded or processed in aboveground retorts. The remaining oil shale is blasted to fill the void and retorted in the same manner as a TIS retort.

2.5.3 Aboveground

In aboveground retorting, oil shale is mined, crushed, and then processed in retorting vessels. These retorts may be either directly-heated or indirectly-heated.⁽²¹⁾

Directly-heated retorts utilize heat generated within the retorting vessel to pyrolyze the oil shale. In indirectly-heated retorts, heat is generated outside the retorting vessel and transferred to the oil shale by a heat carrying medium such as hot solids or gases.

2.6 Thermal Solution

Thermal solution, which converts a higher percentage of the organic matter in oil shale to volatile products than conventional retorting, consists of heating the oil shale in the presence of a solvent and extracting the soluble conversion products. A modification of this process is the extraction of the conversion products under a high partial pressure of hydrogen.

The temperatures required for thermal solution of oil

shale are typically lower than those associated with re-torting. Prien⁽²²⁾ suggested a series of stages that occur during the thermal decomposition of kerogen which would explain this temperature variation. According to Prien, under gentle heating kerogen softens to a rubber-like material, showing elastic and swelling properties. Although some carbon dioxide and hydrogen sulfide gases are given off, this "rubberoid" is still relatively insoluble. Upon further heating, the rubberoid cracks to form a viscous, though soluble, bitumen with the liberation of more hydrogen sulfide, carbon dioxide, and water. Additional heating produces a liquid, oily product. Finally, at even higher temperatures, the oil is cracked and vaporized leaving coke residue.

Since the early 1900's, a considerable amount of work describing thermal solution of oil shale has been published. However, a majority of this work was completed utilizing some type of batch apparatus, with a smaller portion pertaining to continuous systems. A major objective of past work has been to investigate the effect of varying operating conditions and solvents on the conversion of organic material and the resulting yield structure (oil/ gas).

Gavin and Aydelotte⁽²³⁾ reported on the extraction of organic matter from oil shales with several solvents at

or near their boiling points using a Soxhlet apparatus. A portion of their results are shown in Table 6. Solvents used in their study included carbon tetrachloride, carbon bisulphide, acetone, ether, benzene, and chloroform.

Several early patents which describe processes for the solvent extraction of oil shale and other shale-like materials at elevated temperatures were granted to Ryan⁽²⁴⁾, Day^(25,26), and Hampton.^(27,28,29)

Ryan⁽²⁴⁾ proposed a process in which finely ground oil shale was digested in an oil bath at 600-700°F. This temperature was considered too low to effect destructive distillation of the kerogen yet high enough to effect conversion of the kerogen to soluble material.

Day^(25,26) also proposed to digest finely ground oil shale in an oil bath at temperatures ranging from 500-700°F. In addition, spent shale was separated from the bath and retorted. The product vapors from the retort were condensed and used to replenish the oil bath.

Hampton^(27,28,29) proposed a process similar to Day's with the exception that steam was mixed with the oil bath vapors to allow the mixture to crack at temperatures above 700°F.

Dulhunty⁽³⁰⁾ reported on the effectiveness of several solvents used in extracting organic matter from

TABLE 6

Solubilities of Various Oil Shales (13)

Solvent	Utah				Wyoming	
	Kentucky (% Soluble)	Soldier's Summit (% Soluble)	Colorado DeBeque (% Soluble)	Green River (% Soluble)	Colorado DeBeque (% Soluble)	Green River (% Soluble)
Carbon Tetrachloride	0.037	0.740	2.040	1.195		
Carbon Bisulphide	0.015	0.760	1.850	1.270		
Acetone	--	0.530	1.330	1.220		
Ether	--	0.745	--	--		
Benzene	0.060	0.910	2.230	1.370		
Chloroform	0.140	1.050	1.750	1.750		

torbanite. He concluded that aromatic solvents, such as coal tar naphtha, petroleum kerosene, tetralin, quinoline, and torbanite crude oil distillate, were most suitable for thermal extraction of torbanite above 350°C.

D'yakova^(31,32) studied the effect of various solvents on the thermal solution of oil shale for various temperatures and reaction times. Solvents used in his studies included anthracene oil, tetralin, primary shale tars, their hydrogenation products, and distillates. Powdered shale and solvent in mixtures of 30-70 parts solvent and 70-30 parts shale were reacted in a batch reactor for 5-60 minutes at temperatures from 300-430°C and at pressures of 20-40 atm. D'yakova concluded that at the optimum temperatures (380-430°C), 75-95 per cent of the organic matter was extracted in 5-15 minutes.

Jensen⁽³³⁾ conducted an extensive study of the thermal solution of Green River oil shale in batch, semi-continuous, and continuous reactors. The batch reactor was operated at temperatures ranging from 700-950°F, and the continuous unit was operated at temperatures ranging from 750-850°F. Solvents used in this study included petroleum kerosene, quinoline, anthracene oil, and shale-derived gas oil. Jensen also studied thermal extraction with direct hydrogenation using a batch autoclave at total

pressures as high as 4,300 p.s.i.

More recently, Patzer⁽³⁴⁾ 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 385-440°C and pressures from 250-2,000 p.s.i. for 20-120 minutes.

A patent was granted to Greene⁽³⁵⁾ for a process in which finely ground oil shale and tetralin were reacted in the presence of hydrogen at pressures from 10-200 atmospheres and temperatures from 300-650°C. According to Greene, selective extraction and hydrogenation of the kerogen occurs such that high yields of liquid hydrocarbons boiling between 40-500°C are obtained and hydrocarbon gas yields are reduced compared to conventional retorting.

Using a batch autoclave, Baldwin and Frank⁽³⁶⁾ investigated the effect of operating variables on organic carbon conversion and the resulting yield structure (oil/gas) during the thermal solution of an Australian oil shale (Stuart A). Reaction temperatures of 375, 400 and 425°C, and residence times of 10 and 60 minutes were employed at pressures ranging from 1000 to 1500 p.s.i. Results showed that at 425°C and 60 minutes, an organic carbon conversion of 92% was obtained. Increasing the

reaction temperature resulted in increased organic carbon conversion and decreased the selectivity for oil formation.

2.7 Conclusions

Several advantages have been associated with the thermal solution process as compared with conventional retorting. Perhaps the most significant is the higher conversion of organic matter with consequently shorter retention times at relatively lower reaction temperatures. Using an aromatic solvent such as tetralin, high conversion rates can be obtained in less than 30 minutes retention time at temperatures from 380-430°C. However, there are also disadvantages to the thermal solution process, such as the necessity for fine grinding of the shale, the difficulty of separating the solvent and product oil from the spent shale, and the cracking, polymerization and condensation of some solvents.

EQUIPMENT

3.1 Continuous Process Unit

A schematic of the continuous process unit is shown in Figure 1. The unit was originally designed, built, and tested by Barker⁽³⁷⁾ to be used for coal hydrogenation studies. The unit is capable of operating in either a tubular-flow reactor mode or a continuous stirred-tank reactor mode. The latter was used throughout this study.

The maximum feed throughput of the unit in this study was approximately 4.7 liters per hour of slurry with a solvent to shale weight ratio of 4/1.

For the purpose of equipment description, the unit can be broken down into the following sub-systems:

- gas feed
- slurry feed
- preheater and reactor
- liquid sampling
- gas sampling and cleanup

3.1.1 Gas Feed

The gas feed equipment, shown in Figure 3, supplies a regulated flow of gas to the preheaters and reactor. Gas from industrial compressed gas cylinders (K size) flows through a Hoke regulator to the suction of a motor-driven Aminco diaphragm compressor, Model 46-13411. By

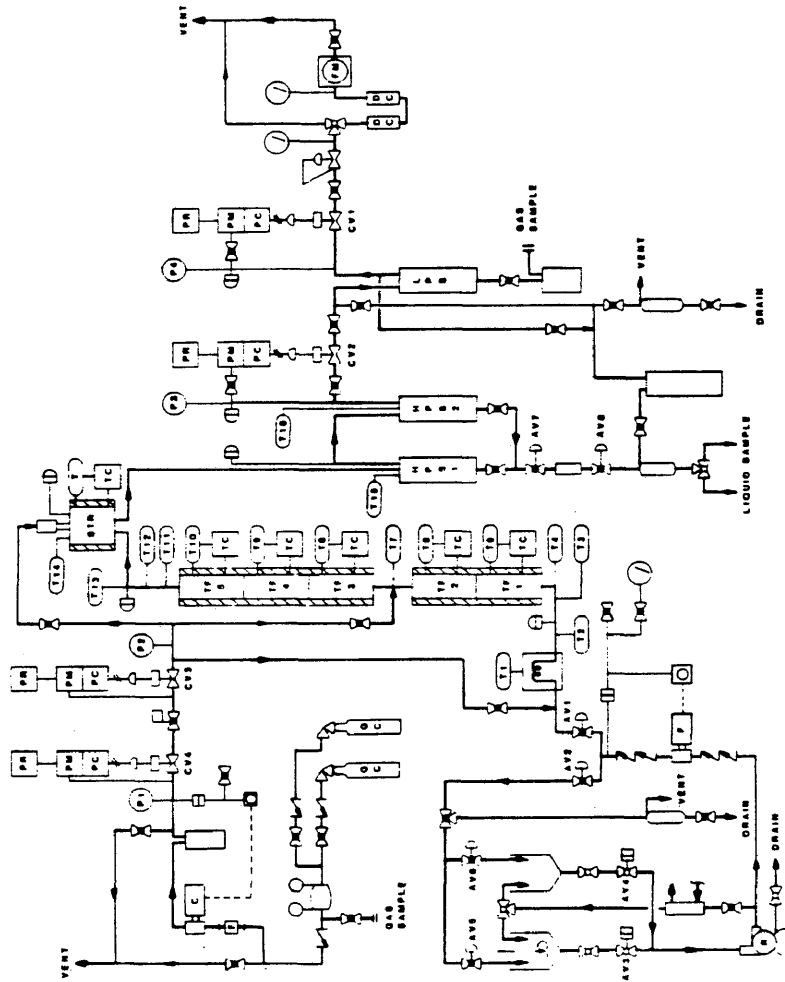


Figure 1 - Continuous Process Unit

	BALL VALVE	AV	AIR VALVE
	REGULATING/SHUTOFF VALVE	CV	CONTROL VALVE
	CHECK VALVE	DC	DESSICANT COLUMN
	METERING VALVE	FM	FLOW METER
	SELF CONTAINED CONTROL VALVE	GC	GAS CYLINDER
	PISTON OPERATOR	HPS	HIGH PRESSURE SEPARATOR
	DIAPHRAM OPERATOR	LPS	LOW PRESSURE SEPARATOR
	DIAPHRAM OPERATOR WITH POSITIONER	P	PRESSURE GAUGE
	RUPTURE DISC	PC	PRESSURE CONTROLLER
	PRESSURE SWITCH	PM	PRESSURE MONITOR
	FILTER	PR	PRESSURE RECORDER
	PRESSURE GAUGE	STR	STIRRED TANK REACTOR
	ISOLATION DIAPHRAM	TC	TEMPERATURE CONTROLLER
	THERMOCOUPLE	TF	TUBE FLOW HEATER
	GAS REGULATOR		

Figure 2 - Abbreviations and Notations

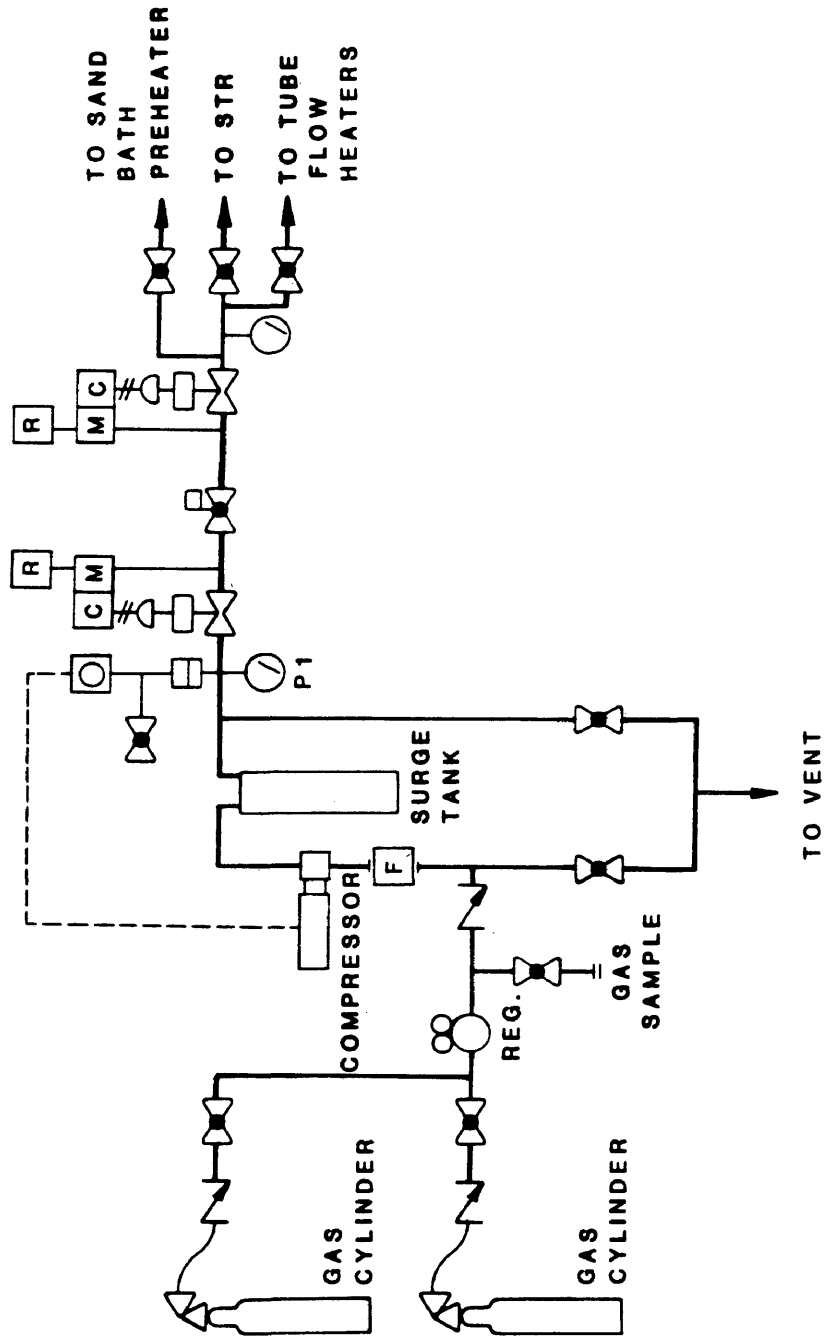


Figure 3 - Gas Feed

regulating the inlet pressure to the compressor, the gas flow rate is controlled. The compressor calibration curve for an operating pressure of 1500 psig is shown in Figure 4.

From the compressor discharge, gas flows into a two liter surge tank which serves to dampen oscillations. The gas then flows through a forward pressure regulator, a metering valve, and finally a backward pressure regulator. The regulators and metering valve serve to maintain the pressure of the compressor discharge in addition to further dampening oscillations.

A Mercoid pressure switch automatically shuts down the compressor in the event of an over-pressurized compressor discharge.

3.1.2 Slurry Feed

The slurry feed equipment, shown in Figure 5, supplies either solvent or solvent/shale slurry to the preheaters and reactor at operating pressure. Feed flows by gravity from either the slurry feed tank or the solvent feed tank to the suction of the recycle pump. The recycle pump used in this study was a Moyno single screw rotary pump, Type "L3". A mixer is provided in the slurry feed tank to prevent shale from settling out of the slurry.

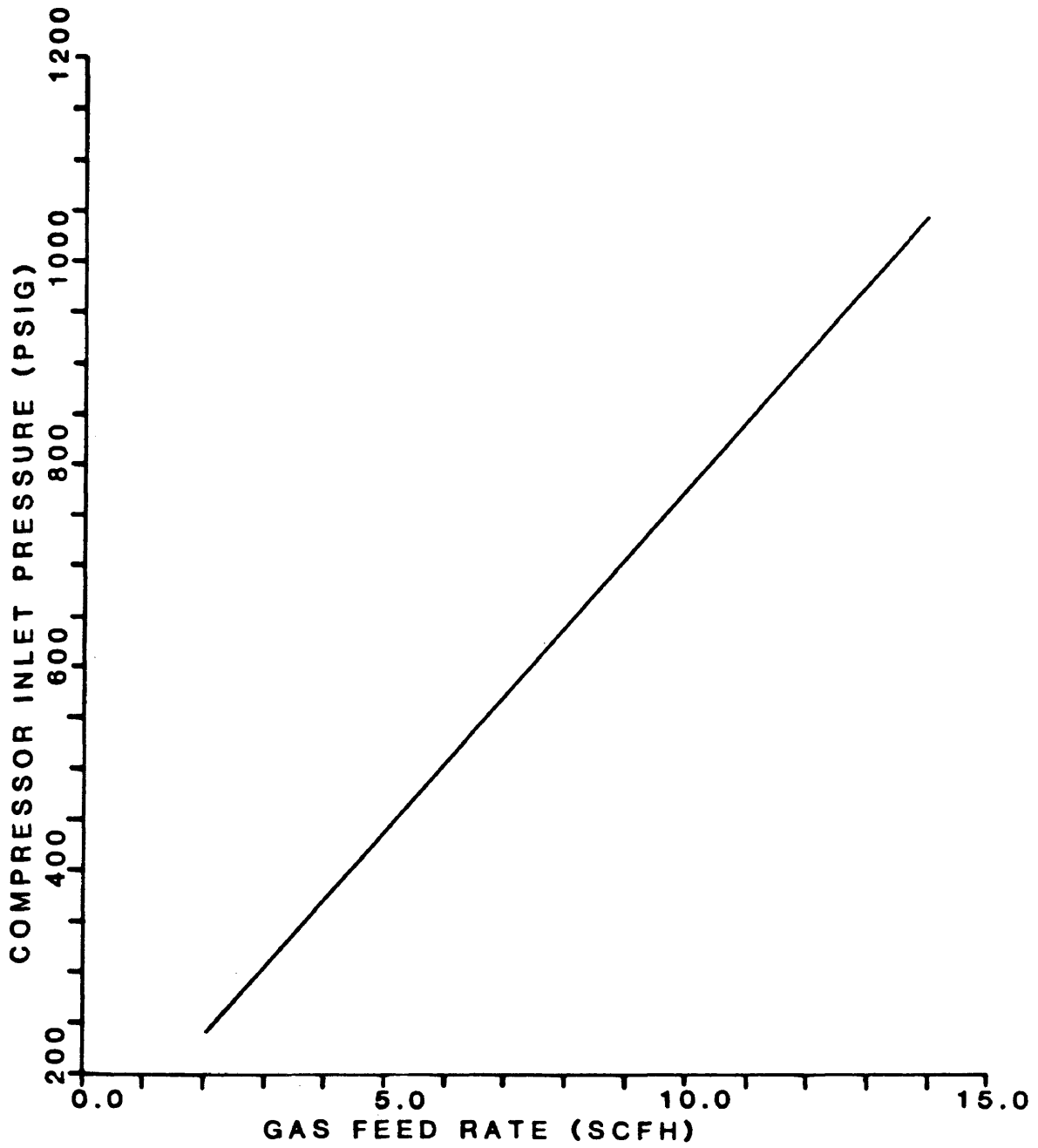


Figure 4 - Compressor Calibration Curve

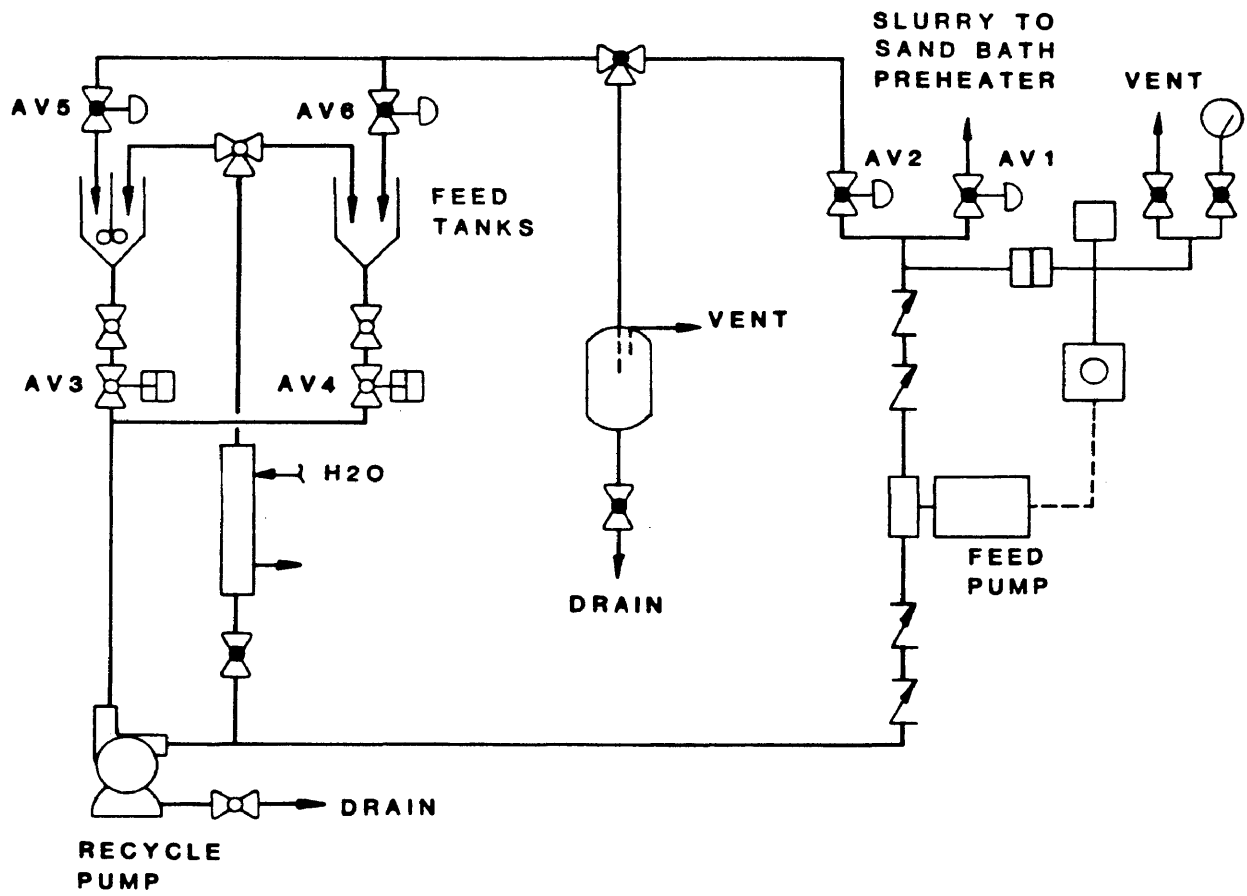


Figure 5 - Slurry Feed

From the recycle pump, feed is pumped either to the inlet of the feed pump or through a regulating valve, cooling coil, and back to the feed tank. The regulating valve can be used to vary the pressure at the suction of the feed pump.

Two feed pumps were used in this study. The first was a Milton Roy, Model "C", metering pump and the second was a Bran and Lubbe, Type "N-P31", metering pump. Calibration curves for these two pumps are given in Figures 6 and 7.

Feed from the feed pump is pumped either to the preheater and reactor system or back to the feed tank. A blowdown system is provided to relieve line pressure between the feed pump and valves 1 and 2 upon an emergency shut down.

A Mercoid pressure switch automatically shuts the feed pump off in the event of an over pressurized feed pump discharge.

Valves 1, 2, 5 and 6 are high pressure rated, pneumatic valves manufactured by Autoclave Engineers. Valves 3 and 4 are pneumatic ball valves manufactured by Whitey.

3.1.3 Preheater and Reactor

A schematic of the preheater and reactor equipment is shown in Figure 8. Slurry is pumped from the slurry feed

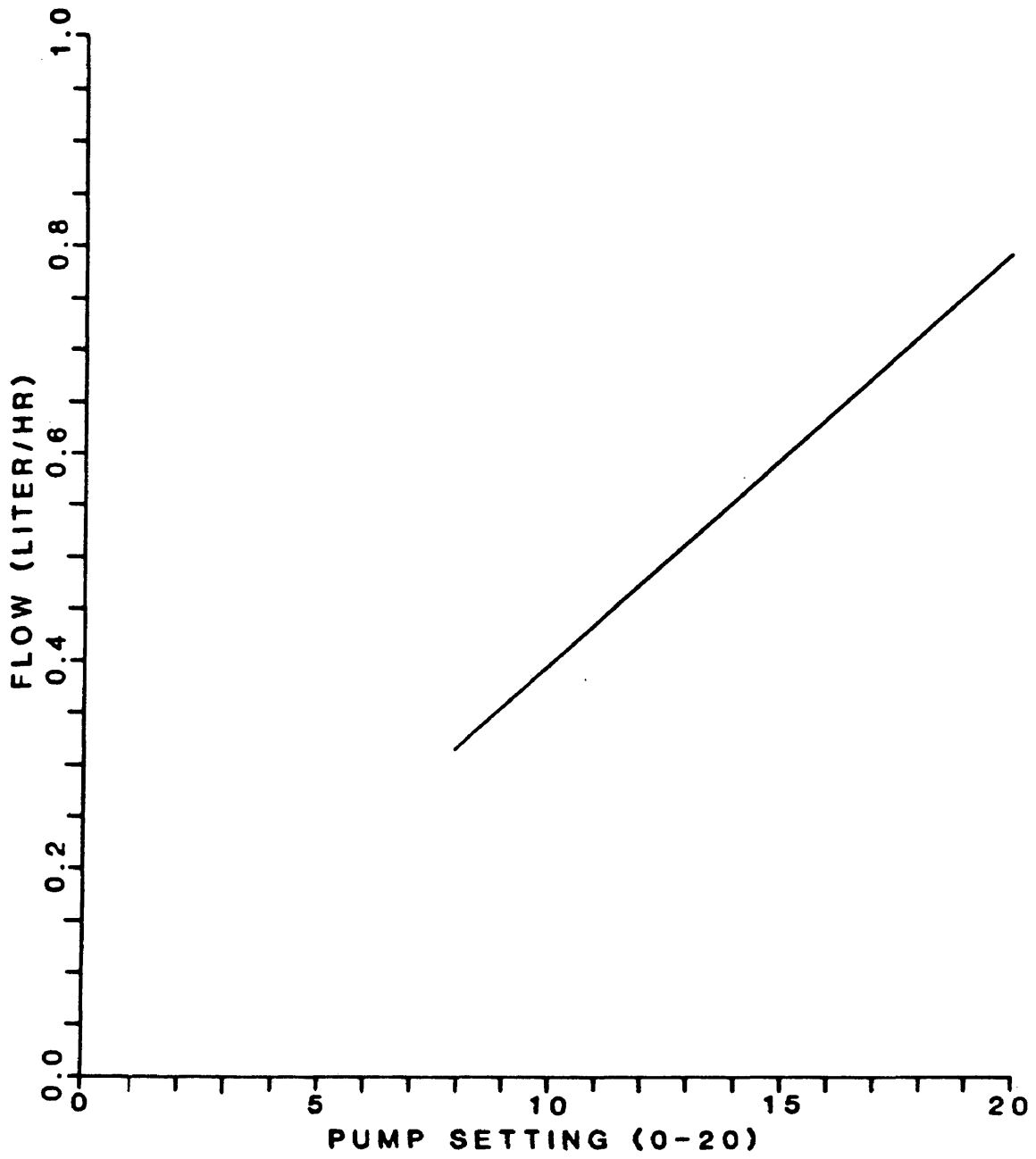


Figure 7 - Bran & Lubbe Feed Pump Calibration Curve

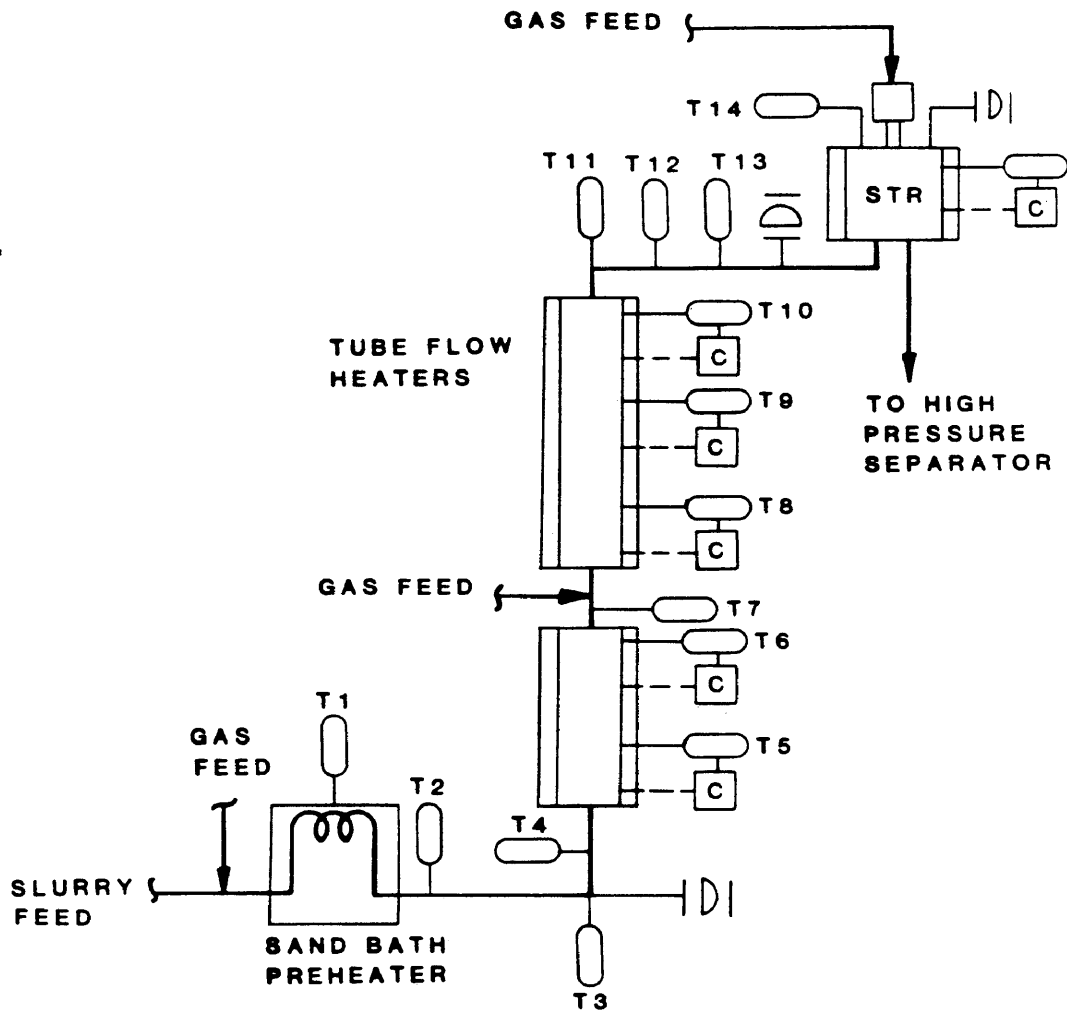


Figure 8 - Preheater and Reactor

pump, through the fluidized sand bath heater, tubular heaters, and finally to the continuous stirred-tank reactor (CSTR). Gas is introduced either at the inlet to the sand bath heater, between the two tubular heaters or in the CSTR. During this study, gas entered the system at the inlet to the sand bath heater.

The fluidized sand bath heater, Tecem Model SBL-1, consists of a 20-foot, 0.250 inch O.D., 316 stainless steel coil in a fluidized sand bath.

The tubular heaters are vertical, upflow, tubular heaters consisting of two and three zones respectively. These heaters are 0.375 inch O.D., 316 stainless steel tubing encased within aluminum sheathes and Thermoline electrical resistance furnaces. Athena, Model 2121-P-0, proportional controllers are used to maintain fixed wall temperatures within the tubular heaters.

The CSTR is a one-liter Magnedrive autoclave reactor manufactured by Autoclave Engineers. A dip tube within the reactor, which serves as the exit for liquid and gaseous products, maintains a volume in the reactor of 800 ml.

The CSTR stirring assembly is operated at 1500 rpm to ensure uniform concentrations and to minimize mass transfer effects. The rotation speed is monitored via a

magnetic detection ring and tachometer.

The CSTR heater is a jacket type heater manufactured by Autoclave Engineers. The heater is controlled by a Honeywell, Model R7355C-1025-1, controller and 120V SCR and has a maximum operating temperature of 1200°F.

"J" type thermocouples monitor the fluid and wall temperatures at the locations indicated on Figures 1 and 8.

3.1.4 Liquid Sampling

The liquid sampling equipment, shown in Figure 9, consists of two high pressure liquid-gas separators, a control valve, two automatic valves, a sample collection tube, and an atmospheric liquid-gas separator.

The high pressure separators are two-liter vessels manufactured by Autoclave Engineers. Operating pressure in the separators is maintained by a Research Control valve (air to close), controlled by an Acco Bristol, Model OB5645C, controller.

Valves 7 and 8 are automatically controlled by a signal timer and relay to allow continuous periodic sampling of the liquid products. The frequency of the sampling cycle is adjustable to allow for various pumping rates. Valves 7 and 8 are both high pressure rated, air operated valves manufactured by Autoclave Engineers.

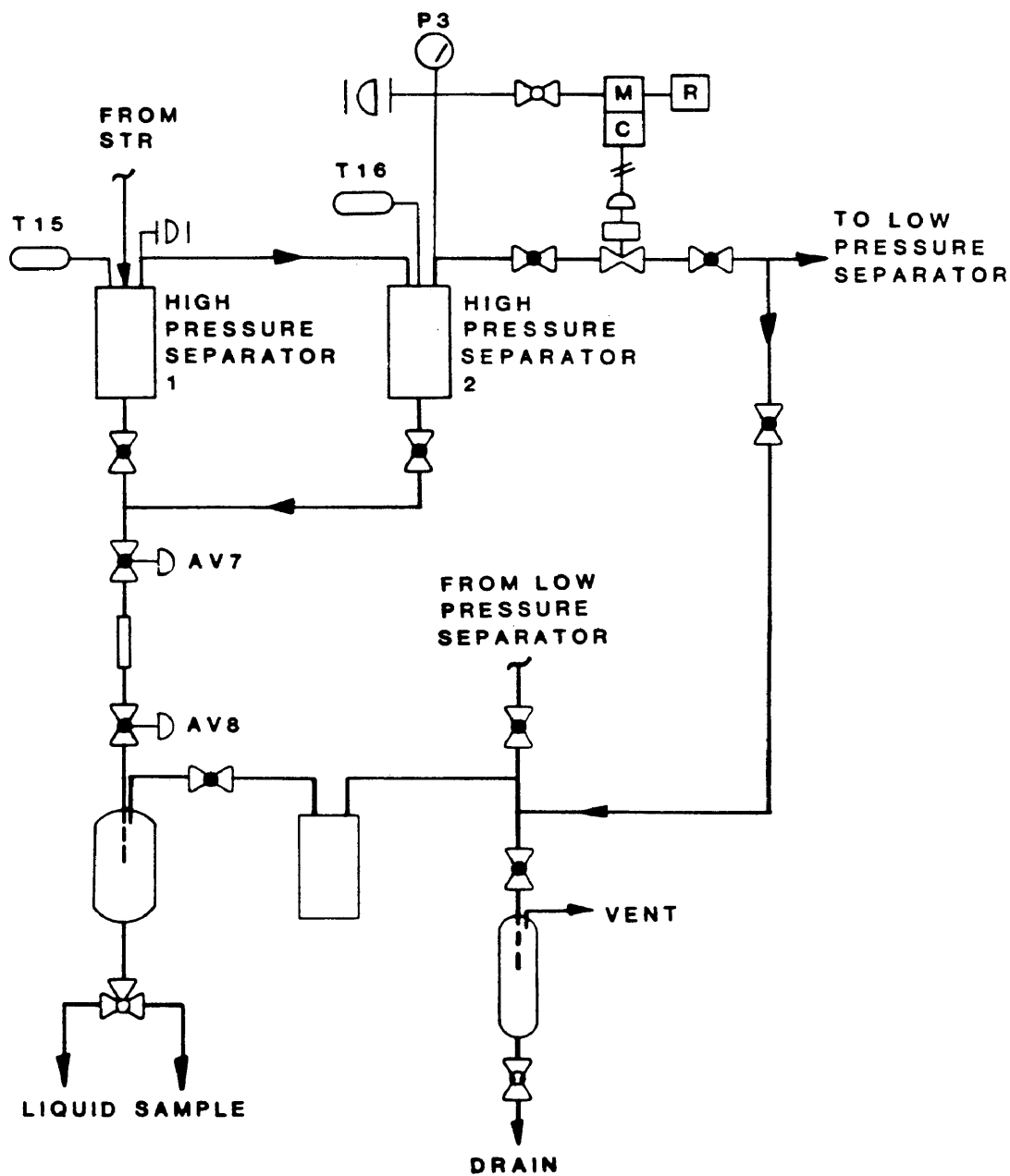


Figure 9 - Liquid Sampling

3.1.5 Gas Sampling and Cleanup

The gas sampling and cleanup equipment, shown in Figure 10, consists of a two-liter Autoclave Engineers low pressure separator, a 500-ml sample cylinder, a Research Control (air to close) valve, a self-contained back-pressure valve, a dessicant column, and a dry gas meter, Rockwell Model D75-S.

Pressure in the low pressure separator is maintained by the Research Control valve at approximately 40 psig. The Research Control valve is controlled by an Acco Bristol, Model OBJ645C, controller.

The sample cylinder is evacuated and then charged with product gases from the low pressure separator, which can then be transferred to a smaller sample cylinder for analysis. Product gases which are not sampled pass through a dessicant column to remove any moisture, through the dry gas meter, and finally are vented to the atmosphere.

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.

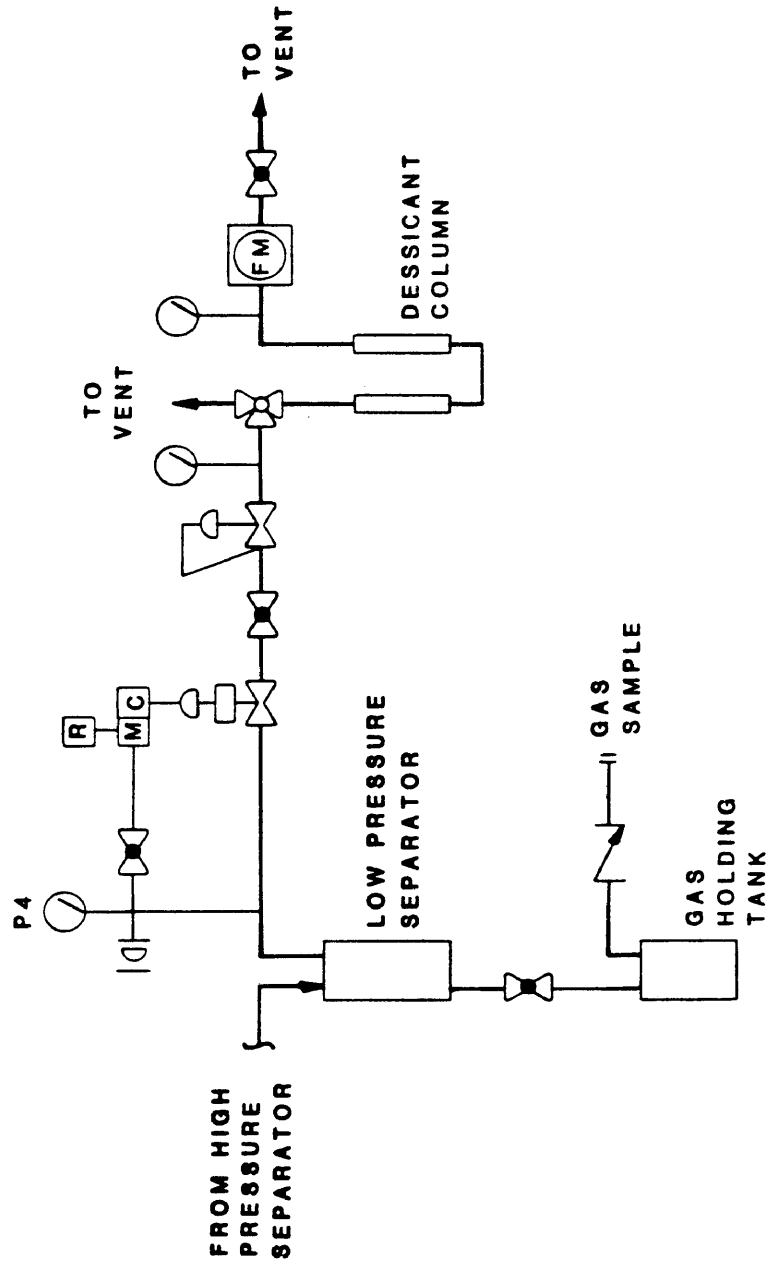


Figure 10 - Gas Sampling and Cleanup

3.2.2 Gas Chromatograph

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

EXPERIMENTAL

4.1 Run Conditions

4.1.1 Phase One

The objectives of the first series of runs were to validate existing batch reactor data and investigate the effect of residence time and temperature on organic carbon conversion, and oil selectivity. The following set of experimental conditions was employed as the run matrix for Phase 1.

Solvent: Tetralin

Solvent-to-Shale Ratio: 4/1 by weight

Total System Pressure: 1500 psig (nominal)

Hydrogen Treatment Rate: 10,000 SCF/ton shale

Temperature: 355, 390, 425 C

Residence Time: 10, 15, 30, 60 minutes (nominal)

4.1.2 Phase Two

The second series of runs was designed to investigate the effect of total pressure and hydrogen partial pressure on organic carbon conversion and oil selectivity in a solvent with limited hydrogen donating potential, closely approximating operation in a true recycle solvent. To accomplish this objective, the following set of experimental conditions was employed.

Solvent: No. 2 Diesel Fuel
Solvent-to-Shale Ratio: 6.5/1 by weight
Total System Pressure: 850, 1500 psig (nominal)
Hydrogen Gas Composition: 50, 95 %
Hydrogen Treatment Rate: 10,000 SCF/ton shale
Temperature: 390 C
Residence Time: 15 minutes (nominal)

4.2 Materials

4.2.1 Oil Shale

The oil shale used in this study was provided by Southern Pacific Petroleum N.L. of Sydney, Australia. The shale was taken from the upper portion of the Kerosine Creek seam in the Stuart A deposit near Gladstone, Queensland, Australia. The ultimate and proximate analyses of the shale are given in Tables 7 and 8.

Seven barrels of shale were prepared for use by the Colorado School of Mines Research Institute (CSMRI). The shale was first wet ground in a ball mill and then wet screened to a -200 +300 mesh fraction.

After drying on a steam plate, the shale resembled a hard clay-like substance. The shale was then processed through a 'powderizer' and stored in plastic bags in 55 gallon drums. The 'powderizer' is a proprietary process

Table 7

Stuart A Oil Shale Proximate Analysis

	<u>As Received</u>	<u>Dry Basis</u>
% Moisture	2.22	--
% Ash	65.29	66.77
% Volatile	29.94	30.62
% Fixed Carbon	2.55	2.61
	<u>100.00</u>	<u>100.00</u>
Btu/lb	4364	4463
% Sulfur	2.16	2.21
MAF Btu/lb	13431	
% MAF Volatile	92.15	
% MAF Fixed Carbon	7.85	
Lbs. Sulfur/Mill. Btu	9.90	

Table 8

Stuart A Oil Shale Ultimate Analysis

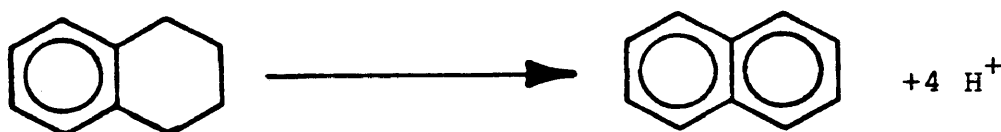
	<u>As Received</u>	<u>Dry Basis</u>
% Moisture	2.22	--
% Carbon	22.05	22.55
% Hydrogen	2.99	3.06
% Nitrogen	0.88	0.99
% Chlorine	0.03	0.03
% Sulfur	2.16	2.21
% Ash	65.29	66.77
% Oxygen	4.38	4.48
	<u>100.00</u>	<u>100.00</u>
Moist Mm free Btu/lb	15040	
% Dry Mm free Volatile	91.46	
% Dry Mm free Fixed Carbon	8.54	
Lbs. Sulfur/Mill. Btu	4.95	

developed at CSMRI. Prior to use, the shale was re-screened to a -200 mesh particle size.

4.2.2 Solvents

Two solvents were used in this study, 1,2,3,4 - tetrahydronaphthalene (tetralin), and No. 2 diesel fuel.

Tetralin is a hydrogen rich solvent that has been widely used in coal liquefaction studies as a hydrogen donor. Tetralin serves as a hydrogen donor via the following reaction:



The tetralin used in this study was 98% pure and supplied by Union Carbide.

The No. 2 diesel fuel was obtained from a local service station and consisted of 76% saturates, 17% olefins, and 7% aromatics with a boiling range between roughly 350 to 650°F as determined by FIA analysis at Hauser Laboratories in Boulder, Colorado.

4.2.3 Gases

The industrial grade gas used throughout this study was supplied by General Air of Denver.

4.3 Experimental Run Procedure

An experimental run proceeds as follows:

1. Start the compressor and set the inlet pressure to the compressor for the desired gas feed rate.
2. Set the feed pump for the correct slurry flow rate.
3. Fill the slurry tank with solvent and start the slurry tank stirrer. Turn the cooling water on.
4. Recycle solvent (valves 2, 3 and 5 open) to purge the system of all air. Close valves 2 and 5 and open valve 1 to the system. Start the feed pump.
5. Turn on the timer and relay controlling valves 7 and 8 and allow gas feed to enter the system at the inlet to the fluidized bath preheater to begin pressurizing the system.
6. Set and turn on the heaters.
7. Turn on the run timer, pressure recorders, and temperature recorder.
8. When the temperature and pressure of the system approaches reaction conditions, purge solvent from the feed tank and add slurry.
9. Periodically take a reading of the feed tank scale to obtain an accurate feed pumping rate.
10. After the stirred tank reactor reaches a steady temperature profile for 5 space times, take a sample.

11. Empty the gas holding pot by vacuum. Open the valve between the low pressure separator and the holding pot until the pressure equalizes at 40 psig. Transfer the gas sample to a gas sample cylinder.

12. Periodically check gas cylinders and replace when necessary. Replenish slurry when needed.

13. Shut down proceeds by turning off all heaters and shutting down the gas feed. Purge slurry from the feed tank and add solvent.

14. Increase the feed pump setting to 100%.

15. Allow the system to cool to less than 200°C. At that time, depressurize the system and open valves 7 and 8.

16. Allow the system to cool to ambient.

17. Give the system a thorough inspection and take care of any necessary servicing at this time. Replace the balls in the feed pump check valves after each run, and rebuild valves 7 and 8 if necessary.

4.4 Analytical Procedure

4.4.1 Sample Preparation

The sample was first collected in a 500 ml Erlenmeyer flask and then transferred to four centrifuge tubes. The

samples were then subjected to the sample preparation scheme shown in Figure 11.

The acetone wash consisted of three separate washes. The centrifuge tubes were sonicated and centrifuged after each wash. The liquid was decanted and collected in a 1000 ml flask.

After the final wash, the liquid was rotovaped at 60°C to separate the acetone from the solvent and shale oil. The remaining solid, spent shale, was allowed to dry at ambient temperature for 24 hours.

The dried spent shale was soxhlet extracted with a 50/50 per cent by volume mixture of benzene and methanol. After the soxhlet was finished, the liquid was again rotovaped at 70°C to separate the benzene/methanol mixture from the solvent and shale oil. The spent shale was dried in an oven at 100°C for 24 hours.

4.4.2 Solid Analysis

4.4.2.1 Carbon

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

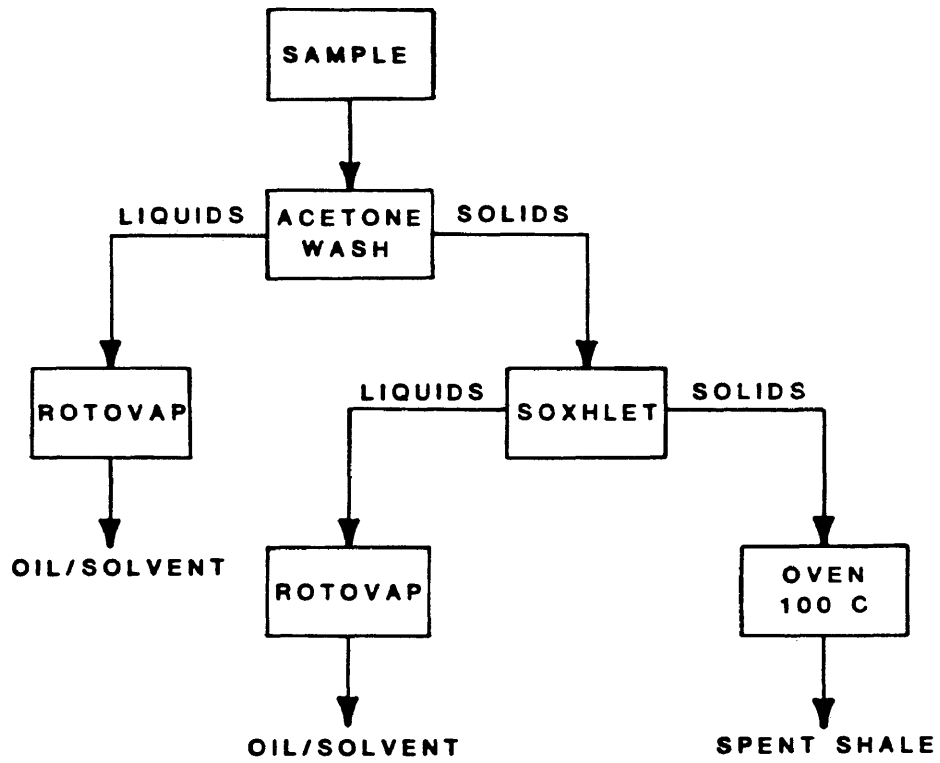


Figure 11 - Sample Preparation

4.4.2.2 Ash

The spent shale and feed samples were dried at 100°C and ambient pressure for a minimum of 18 hours. Weighed samples were then placed in a cold muffle furnace, heated to 750°C, and ashed for 3 hours in accordance with ASTM procedure D3174. The ash contents of the samples were calculated in accordance with ASTM procedure D3180.

4.4.3 Gas Analysis

Gas samples were collected in evacuated 500 ml stainless steel cylinders and analyzed on a Carle gas chromatograph with Hewlett-Packard integrator for hydrogen, carbon monoxide, carbon dioxide, argon, hydrogen sulfide, and various hydrocarbons.

DATA ANALYSIS

5.1 Introduction

Data analysis involved the reduction of experimental results to determine organic carbon conversion and the yield selectivity (oil/gas). The data reduction was accomplished with a computer program. A listing of the program has been included in Appendix A.

5.2 Carbon Conversion

The carbon conversion (CC) is the fraction of total/organic carbon extracted from oil shale which is converted to either oil or gas. Carbon conversion has been calculated using the following equation.

$$\%CC = \frac{\%C_f - \%C_{SS} (\%Ash_f / \%Ash_{SS})}{\%C_f} \times 100$$

where:

- $\% Ash_f$ = per cent ash in feed shale
- $\% Ash_{SS}$ = per cent ash in spent shale
- $\% C_f$ = per cent organic/total carbon in feed shale
- $\% C_{SS}$ = per cent organic/total carbon in spend shale
- $\% CC$ = per cent organic/total carbon conversion

It is possible to use ash as a 'tie element' for calculating CC since ash remains relatively unchanged during the thermal solution process. (38)

5.3 Total Carbon Conversion to Oil

The total carbon conversion to oil is a measure of the selectivity of a process. High selectivities indicate greater oil production and lower gas production, while low selectivities indicate the opposite: lower oil production and greater gas production. The following equation was used to calculate the yield selectivity.

$$\% \text{ SELEC} = \frac{\text{TC}_f - \text{TC}_g - \text{TC}_{ss}}{\text{TC}_f - \text{TC}_{ss}} \times 100$$

where: TC_f = Total carbon in feed shale (gm/min)
 TC_g = Total carbon converted to gas (gm/min)
 TC_{ss} = Total carbon in spent shale (gm/min)

Using an argon tracer, it was possible to calculate the molar flow rate of the product gas. Once this was known, it was possible to calculate the molar and mass flow rates of each individual species in the product gas.

5.4 Kinetic Modeling

The analysis of a continuous stirred tank reactor (CSTR) results in a series of algebraic equations with one or more independent variables. One method of solution of these equations in order to compute rate constants from

experimental data is to apply linear regression using the method of least squares, or multiple linear regression in the event of more than one independent variable.

For a sample of n observations, assuming a linear relationship with one independent variable, the regression line may be estimated by

$$y_x = bx$$

where

y_x = estimated dependent variable

x = independent variable

b = proportionality constant.

Each pair of observations will satisfy the relation

$$y_i = bx_i + e_i$$

where

y_i = observed dependent variable

x_i = observed independent variable

b = proportionality constant

e_i = the error or residual between
estimated and observed dependent
variables.

This series of equations may also be represented by the following series of vectors.

$$Y = bX + E$$

where

Y = the vector of observed dependent
variables

X = the vector of independent variables

b = proportionality constant

E = vector of errors.

The parameter b is estimated such that the sum of the squares of the residuals is a minimum. This minimization procedure is called the method of least squares.

In the case of a CSTR analysis, the parameter to be estimated is the rate constant. The material balance for a CSTR is

$$QC_0 - QC + rV = 0$$

where

Q = volumetric flow rate (liter/hr)

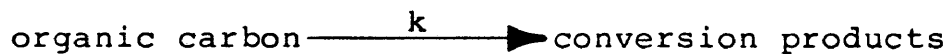
C = mass concentration in reactor
(grams/liter)

C_0 = mass concentration in feed
(grams/liter)

V = volume of reactor (liter)

r = rate of reaction (grams/liter-hr).

For the simple mechanism of



where the reaction is assumed to be first order with respect to organic carbon remaining, the rate of reaction is given by

$$r = -k C$$

or

$$r = -kC_0(1-x)$$

where

$$C = C_0(1-x), \text{ organic carbon}$$

x = organic carbon fractional
conversion.

Substituting this expression into the CSTR material balance yields the following equation in terms of fractional conversion:

$$x/(1-x) = kT$$

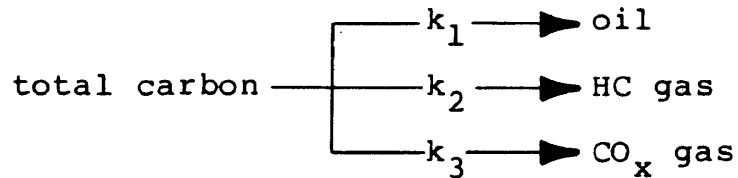
where $T = V/Q$, residence time.

Substituting the residence times, T , and respective fractional organic carbon conversions, x , into this equation yields a series of equations for each temperature. The program MINITAB from Pennsylvania State University can then be used to evaluate the rate constants from the resulting vectors of dependent and independent variables by linear regression using the method of least squares. At present, this program is in the library of computer programs available at Colorado School of Mines. A sample of the input and output for the MINITAB program has been included in Appendix B.

The formulation for the mechanism



is similar to the preceding mechanism. However, for the mechanism



a material balance for each product must be evaluated, resulting in three separate series of equations.

First consider a material balance on oil. Assuming the reaction to be first order with respect to total carbon remaining, the rate of reaction is given by

$$r = -k_1 C$$

or

$$r = -k_1 C_0 (1-x)$$

where

$$C = C_0 (1-x), \text{ total carbon}$$

$$x = \text{total carbon fraction conversion.}$$

Substituting this expression into the CSTR material balance for oil yields the following equation in terms of fractional conversion:

$$S_1 x / (1-x) = k_1 T$$

where

$$T = V/Q, \text{ resident time}$$

$$\text{Oil}_{in} = 0$$

$$\text{Oil}_{out} = S_1 Q C_0 x$$

$$S_1 = \text{selectivity for oil production.}$$

Similar equations may be derived for the total carbon to HC gas and CO_x gas reactions. Each series of equations must be solved separately by linear regression to evaluate the rate constants k_1 , k_2 , and k_3 .

RESULTS

6.1 Phase One

The first series of runs was intended to investigate the effect of temperature and residence time on the organic carbon conversion and oil yield selectivity during the thermal solution of Stuart A oil shale. Reactivity isotherms at 355, 390, and 425 C were calculated for residence times ranging from 10 to 60 minutes in a hydrogen gas atmosphere at a total pressure of 1500 psig. Results of the Phase 1 study are summarized in Tables 9 and 10 and illustrated in Figure 12. The residence times (space times) quoted in the tables are the actual residence times, corrected for hydrogen gas hold up. Complete run summary sheets are included in Appendix C.

All Phase 1 runs were made using tetralin as the solvent and whenever possible, a hydrogen gas treatment rate of approximately 10,000 SCF/ton of shale. However, for each sampling cycle, a minimum gas feed rate was required to maintain the system pressure at 1500 psig. This resulted in hydrogen gas treatment rates greater ranging from 11,400 to 43,400 SCF/ton, depending on the residence time.

The organic carbon conversions obtained in this study compare closely with the data obtained by Frank⁽³⁹⁾ who

Table 9

Phase 1 Carbon Conversion and Product Yield

<u>Sample</u>	<u>Temperature</u> <u>(°C)</u>	<u>Residence</u> <u>Time</u> <u>(Min)</u>	<u>TCC</u> <u>(%)</u>	<u>OCC</u> <u>(%)</u>	<u>Oil</u> <u>Select-</u> <u>ivity</u> <u>(Wt %)</u>	<u>HC Gas</u> <u>Select-</u> <u>ivity</u> <u>(Wt %)</u>	<u>CO_x Gas</u> <u>Select-</u> <u>ivity</u> <u>(Wt %)</u>
CR2-1	355	9.04	19.91	20.10	--	--	--
CR2-2	355	9.04	19.36	19.49	--	--	--
CR3-1	355	12.39	22.09	22.09	--	--	--
CR7-1	355	19.96	22.57	22.62	97.8	0.2	2.0
CR5-1	355	58.33	30.16	30.44	95.9	0.9	3.2
CR1-1	390	8.48	32.55	32.48	--	--	--
CR1-2	390	8.48	36.60	36.83	--	--	--
CR1-3	390	8.48	35.73	35.85	--	--	--
CR3-2	390	12.62	40.59	40.97	--	--	--
CR4-2	390	13.35	48.54	49.25	--	--	--
CR7-2	390	28.44	64.24	65.81	97.8	0.3	1.9
CR6-1	390	55.56	66.30	67.00	96.9	0.7	2.4
CR1-4	425	8.28	62.35	63.30	--	--	--
CR1-5	425	8.28	64.51	65.60	--	--	--
CR1-6	425	8.28	62.32	63.30	--	--	--
CR4-1	425	13.46	70.91	70.91	95.7	1.2	3.1
CR8-1	425	28.22	86.35	86.35	96.3	1.3	2.4

TABLE 10
Phase 1 Product Gas Composition
Hydrogen and Argon Free Basis

Sample	Temperature (°C)	Residence Time (Min)	Hydrogen Gas Feed Rate (SCF/ton)	Gas Produc- tion Rate (SCF/Ton)	CH ₄ (Vol %)	C ₂ (Vol %)	C ₃ (Vol %)	C ₄ (Vol %)	CO (Vol %)	CO ₂ (Vol %)
CR2-1	355	9.04	12,200	57 *	4.26	--	--	--	10.64	85.10
CR2-2	355	9.04	12,200	83 *	4.41	--	--	--	13.24	82.35
CR3-1	355	12.39	14,200	55 *	5.21	1.04	--	--	10.42	83.33
CR7-1	355	19.96	22,400	59	5.76	--	.82	--	15.23	78.19
CR5-1	355	58.33	42,400	149	6.37	6.37	1.28	--	12.74	73.24
CR3-2	390	12.62	14,600	172 *	5.92	1.69	1.70	.17	12.69	77.83
CR4-2	390	13.35	14,200	167 *	7.14	1.78	1.78	.09	15.17	74.04
CR7-2	390	28.44	32,100	150	8.33	--	2.42	--	20.83	68.42
CR6-1	390	55.56	40,700	232	10.10	3.24	2.85	--	22.67	61.14
CR4-1	425	13.46	15,200	278	9.86	4.31	3.69	.80	14.17	67.16
CR8-1	425	28.22	43,400	330	12.77	5.81	4.35	.44	28.30	48.33

* Based on the feed gas flow rate

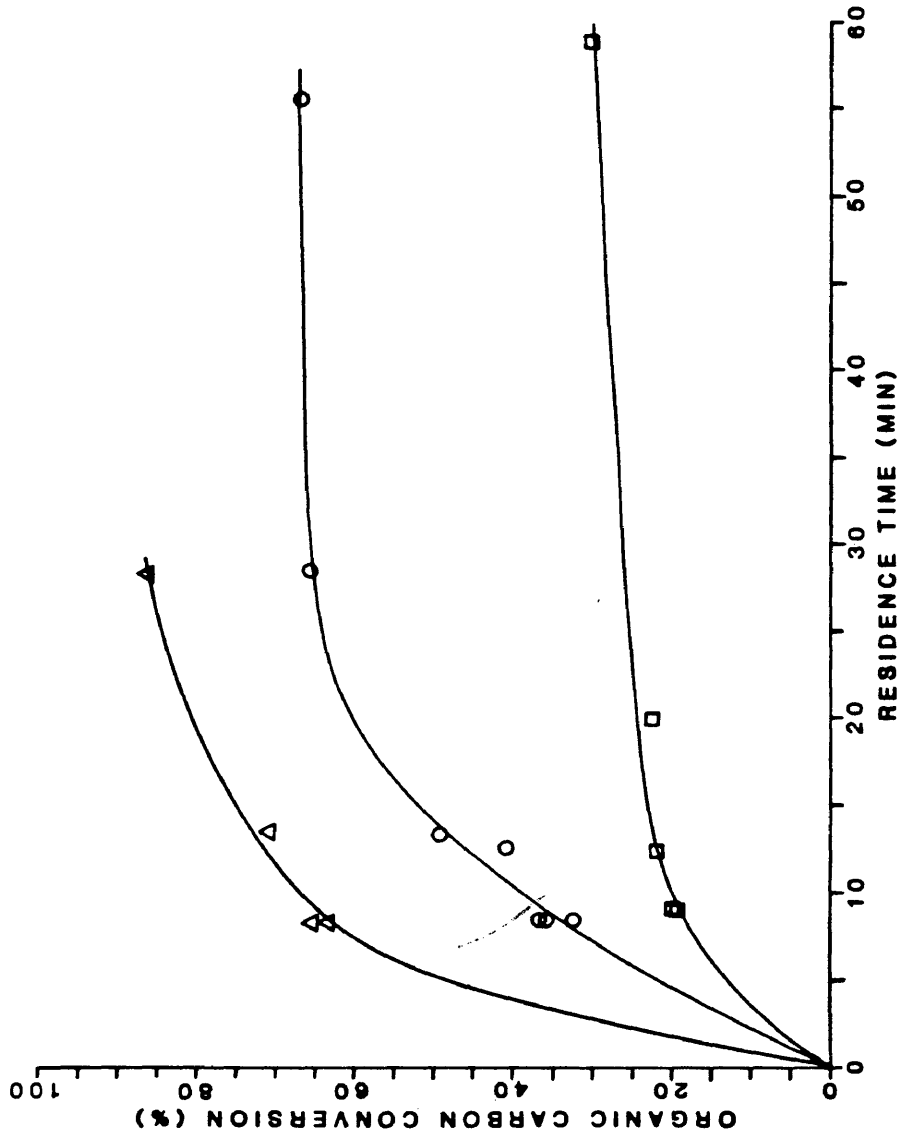


Figure 12 - Phase 1 Reaction Isotherms

performed a series of experiments on thermal solution of Stuart A oil shale in tetralin, using a batch reactor with a gas-driven sample injection system. At 425°C, the following comparison can be made with the data of Frank:

Table 11

OCC Comparison at 425 C and 10 Minutes Residence Time

<u>System</u>	<u>Residence Time (min)</u>	<u>% OCC</u>
CPU	8.3	64.1 <u>+1.3</u>
Batch ⁽³⁹⁾	10.00	68.2
CPU	13.5	70.9

Several attempts were made to collect data at 425°C, 60 minutes residence time in the CSTR. None, however, were successful. During the first attempt, the plunger packing for the Bran and Lubbe pump failed after 2 1/2 hours of service. The grafoil packing typically lasted 5 to 6 hours when pumping slurry at 1500 psig. Two additional attempts were terminated after the tubing between the CSTR and valve AV7 became plugged due to the combination of the low flow rate and high temperature. However, the data obtained at 390°C seems to indicate that the

extent of equilibrium conversion was essentially reached within 30 minutes residence time. A comparison of the data obtained by Frank at 425°C, 60 minutes residence time seems to indicate a similar trend as shown in Table 12.

Table 12
OCC Comparison at 425°C and 60 vs. 30 Minutes
Residence Time

<u>System</u>	<u>Residence Time (min)</u>	<u>% OCC</u>
CPU	28.2	86.4
Batch ⁽³⁹⁾	60.0	87.2

Data on the selectivity of the reaction for oil formation was collected for selected samples as listed in Table 9. In each case, the selectivity for oil formation was between 95 and 98%. These runs were made with an argon tracer in the hydrogen feed gas, permitting quantification of the rate of production of hydrocarbon gases (C₅-).

The product gas production rates and compositions on a hydrogen and argon free basis for various samples are listed in Table 10. The production rates have been estimated based on the feed gas flow rates for samples in

which an argon tracer was not used. This appears to be a good approximation, since the gas production rates are such a small per cent of the total gas flow rate.

Several trends are illustrated from Table 10. An increase in reaction temperature results in an increase in the production of product gas. As temperature or residence time increases, the volume or molar per cent of hydrocarbons and carbon monoxide in the product gas increases while the per cent of carbon dioxide decreases. The increase in hydrocarbons is expected due to the cracking that occurs at higher temperatures. Since the reaction is carried out under a hydrogen atmosphere, these hydrocarbons are usually saturated. It is not fully understood, however, why an increase in temperature results in higher CO concentrations and lower concentrations of CO₂.

A secondary objective of the Phase 1 runs was to investigate the reproducibility and approach to steady state operation that could be expected from the unit. These results are tabulated in Table 13. Sampling for Run CR1 was started at 5.0 space times, after a constant temperature was attained in the reactor, and a sample was withdrawn every 1.0 space time until 3 samples had been accumulated. The first sample of Run CR2 was taken at 5.0 space times and the second was taken at 10.0 space times after a constant

Table 13

Reproducibility

<u>Sample</u>	<u>Temp (°C)</u>	<u>Space Time (min)</u>	<u>OCC (%)</u>
CR1 - 1,2,3	390	8.5	35.1 ± 2.3
CR1 - 4,5,6	425	8.3	64.1 ± 1.3
CR2 - 1,2	355	9.0	19.8 ± 0.4
CR9 - 4,5,6	390	8.6	33.2 ± 0.2

temperature was obtained. The small deviations in the conversion data indicate that samples were taken after the reactor had reached steady state operation. Samples 4, 5 and 6 of Run CR9 had approximately the same reaction conditions as samples 1, 2 and 3 of Run CR1. Sampling for Run CR9 was started at 5.0 space times, after a constant temperature was obtained, and samples were withdrawn continuously until 3 samples had been taken. The results of these runs indicate that excellent reproducibility of the conversion data can be obtained from the continuous unit.

6.2 Phase Two

The second series of runs was intended to investigate the effect of total pressure and hydrogen partial pressure on organic carbon conversion and oil selectivity in a limited hydrogen donor solvent (#2 diesel fuel). Phase 2 runs were made at 390°C and approximately 12 minutes residence time with hydrogen gas feed rates ranging from 10,000 to 21,000 SCF/ton. The feed gases for the two runs consisted of 95/5 and 50/50 per cent by volume mixtures of hydrogen and argon. Samples were taken at total pressures of 850 and 1500 psig for each feed gas mixture. The results of the Phase 2 study are summarized in Tables 14 and 15.

Table 14

Phase 2 Carbon Conversion and Product Yield

<u>Sample</u>	<u>Total Pressure (psig)</u>	<u>Hydrogen Partial Pressure (psig)</u>	<u>TCC (%)</u>	<u>OCC (%)</u>	<u>Oil Selectivity (Wt %)</u>	<u>HC Gas Selectivity (Wt %)</u>	<u>CO_x Gas Selectivity (Wt %)</u>
CR11-1	1500	1500	50.2	50.9	97.3	0.8	1.9
CR12-2	1500	750	49.7	50.5	96.5	1.6	3.0
CR11-2	850	850	47.2	47.7	95.4	1.0	2.5
CR12-1	850	425	32.5	32.6	95.6	1.4	3.0

TABLE 15

Phase 2 Product Gas Composition
Hydrogen and Argon Free Basis

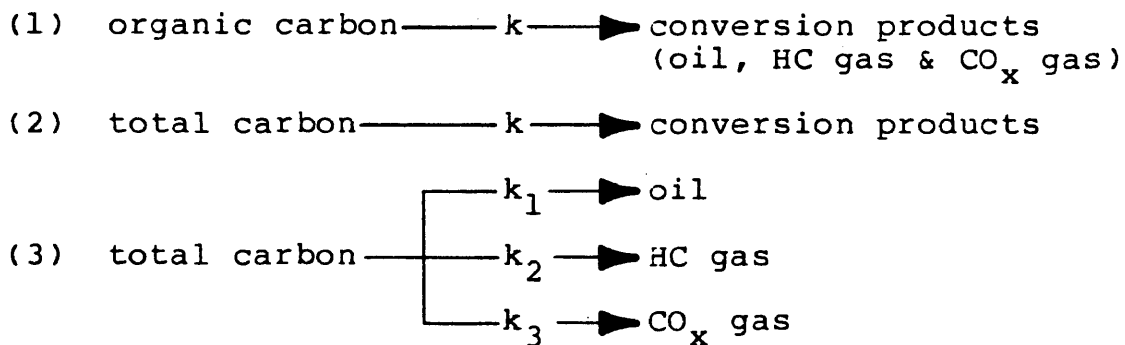
Sample	Total Pressure (PSIG)	Hydrogen Partial Pressure (PSIG)	Hydrogen Gas Feed Rate (SCF/ton)	Gas Production Rate (SCF/ton)	CH ₄ (Vol %)	C ₂ (Vol %)	C ₃ (Vol %)	C ₄ (Vol %)	CO (Vol %)	CO ₂ (Vol %)
CR11-1	1500	1500	21,000	149	10.99	3.82	3.18	1.43	15.45	65.13
CR12-2	1500	750	10,400	234	10.43	4.25	4.06	3.14	11.27	66.85
CR11-2	850	850	20,000	180	10.94	3.25	3.49	.84	16.35	65.14
CR12-1	850	425	10,600	153	11.22	4.07	3.79	1.40	16.27	63.25

As may be seen, the rate and extent of conversion is not only temperature dependent, as demonstrated in Phase 1, but also dependent on total pressure and hydrogen partial pressure. At the higher total pressure, 1500 psig, a reduction in hydrogen partial pressure from 1500 to 850 psig appears to have little effect on organic carbon conversion (50.2% vs. 49.7%). At the lower pressure, 850 psig, the effect is much more apparent, 47.2% vs. 32.5%, at hydrogen partial pressures of 850 and 425 psig respectively.

The yield structure from both the Phase 1 and 2 runs illustrate one of the major advantages of thermal solution versus standard high-temperature retorting: an extremely high selectivity for oil formation.

6.3 Kinetic Analysis

In an attempt to model the observed kinetics of the thermal extraction of oil shale, the following mechanisms were investigated.



By assuming the reaction of organic carbon to conversion products to be first order irreversible with respect to organic carbon remaining, the continuous stirred tank reactor material balance for the first mechanism becomes

$$x/(1-x) = kT$$

where x = organic carbon conversion

T = residence time (hr).

A plot of $x/(1-x)$ versus T for the data at 425°C is presented in Figure 13. The slope of this plot, k , is evaluated by linear regression using the computer library program MINITAB. Values for the rate constants at 390 and 355°C are obtained in a similar manner.

Table 16

Rate Constants - Organic Carbon to Conversion Products

<u>T</u> °C	<u>k</u> (hr ⁻¹)
355	.5683 ± .1501
390	2.7380 ± .3425
425	12.9664 ± .4743

From the Arrhenius Plot of the rate constant versus inverse temperature, shown in Figure 14, an apparent activation energy of 31.07 Kcal/g-mole is obtained as compared

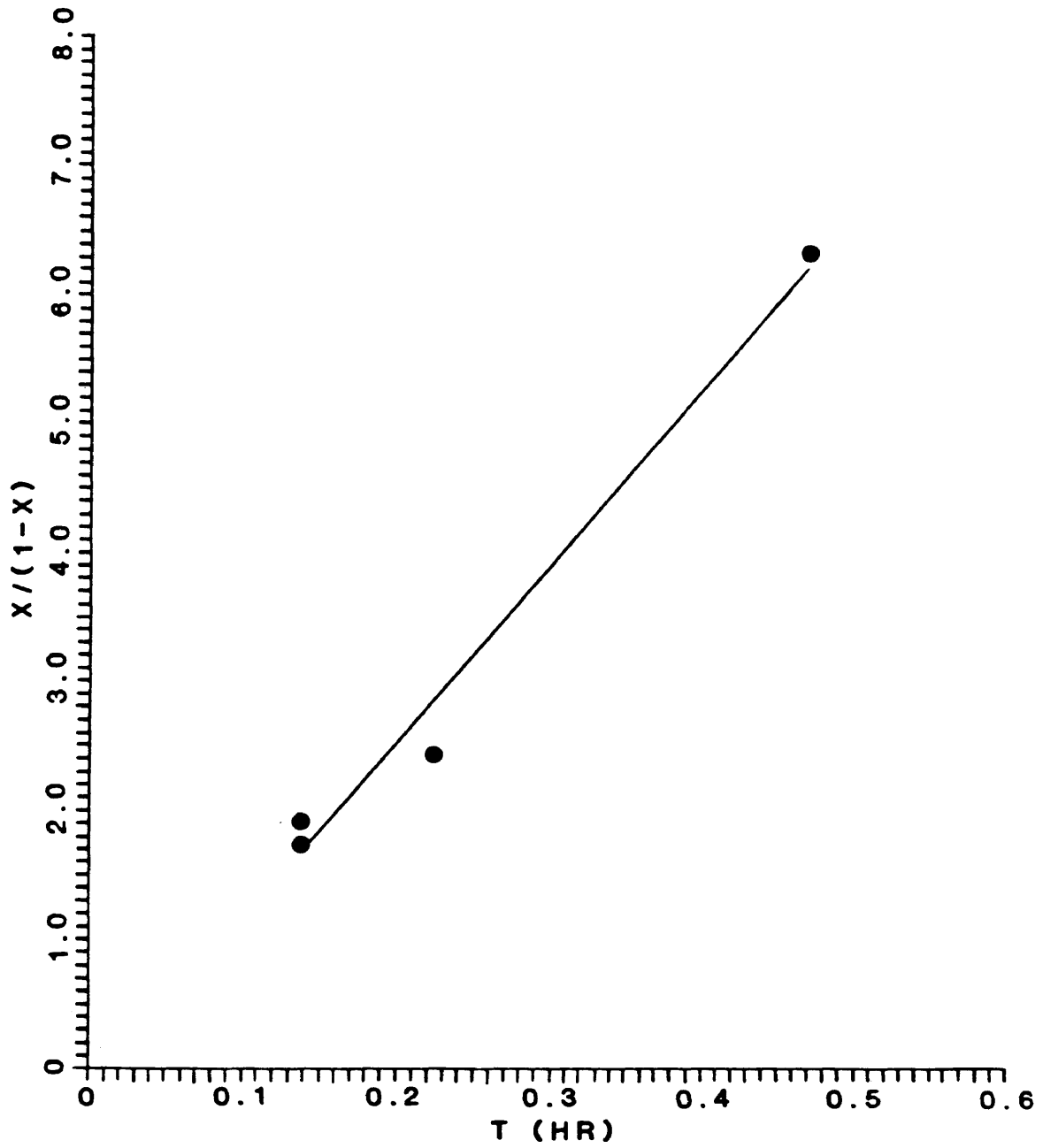


Figure 13 - $x(1-x)$ vs T at 425°C
Organic Carbon to Conversion Products

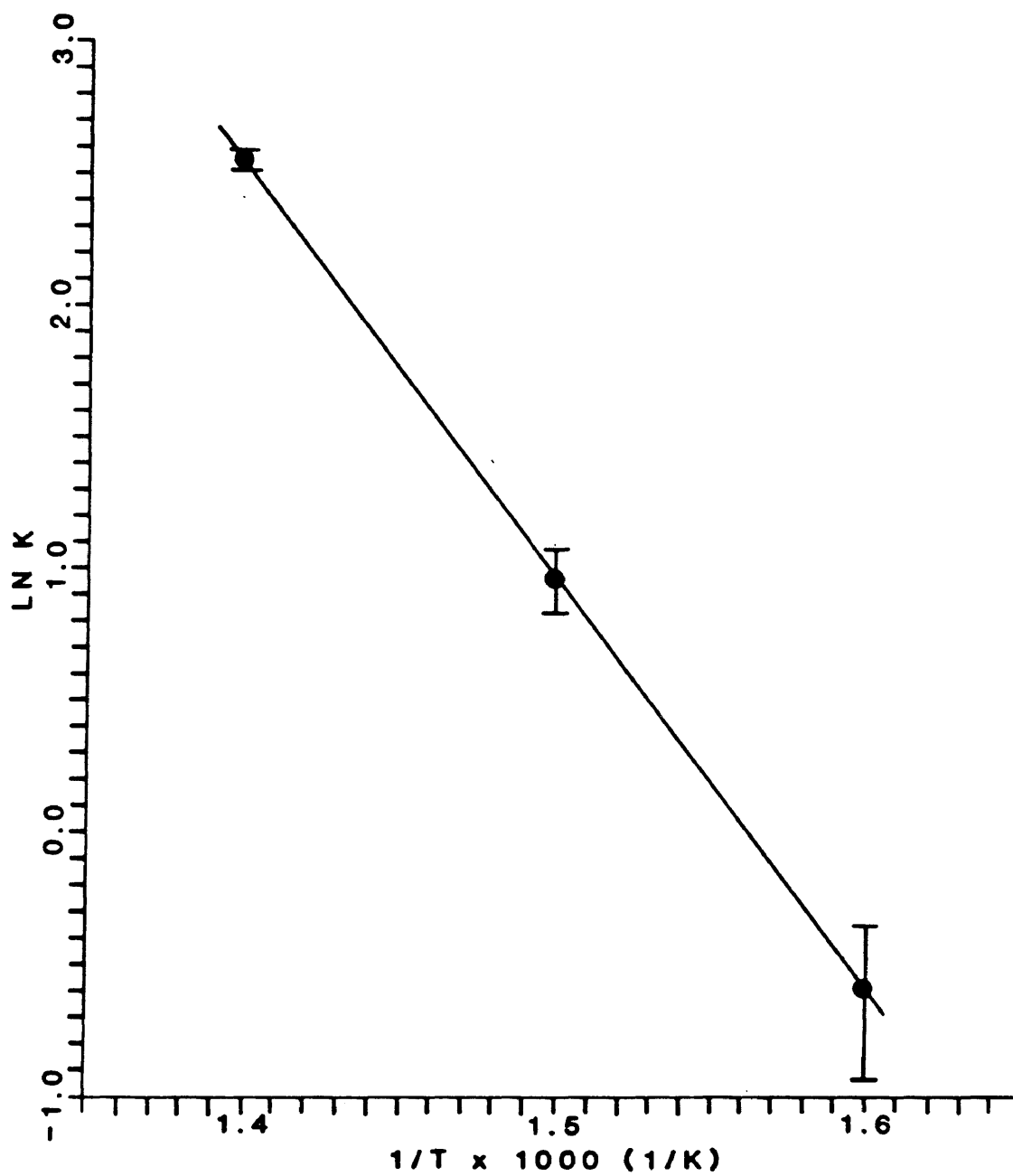


Figure 14 - Arrhenius Plot
Organic Carbon to Conversion Products

to an activation energy of 13.8 Kcal/g-mole obtained by Frank.

Similarly, by assuming the reaction of total carbon to conversion products to be first-order, irreversible with respect to total carbon remaining, the CSTR material balance for the second mechanism becomes

$$x/(1-x) = kT$$

where x = organic carbon conversion

T = residence time (hr).

Again, using the library program MINITAB to solve for k by linear regression, the following values are obtained.

Table 17

Rate Constants - Total Carbon to Conversion Products

<u>T</u> (°C)	<u>k</u> (hr ⁻¹)
355	.5625 ± .1498
390	2.6341 ± .3191
425	12.8702 ± .4836

From the Arrhenius plot of these rate constants, shown in Figure 15, an apparent activation energy of 31.10 Kcal/g-mole is obtained.

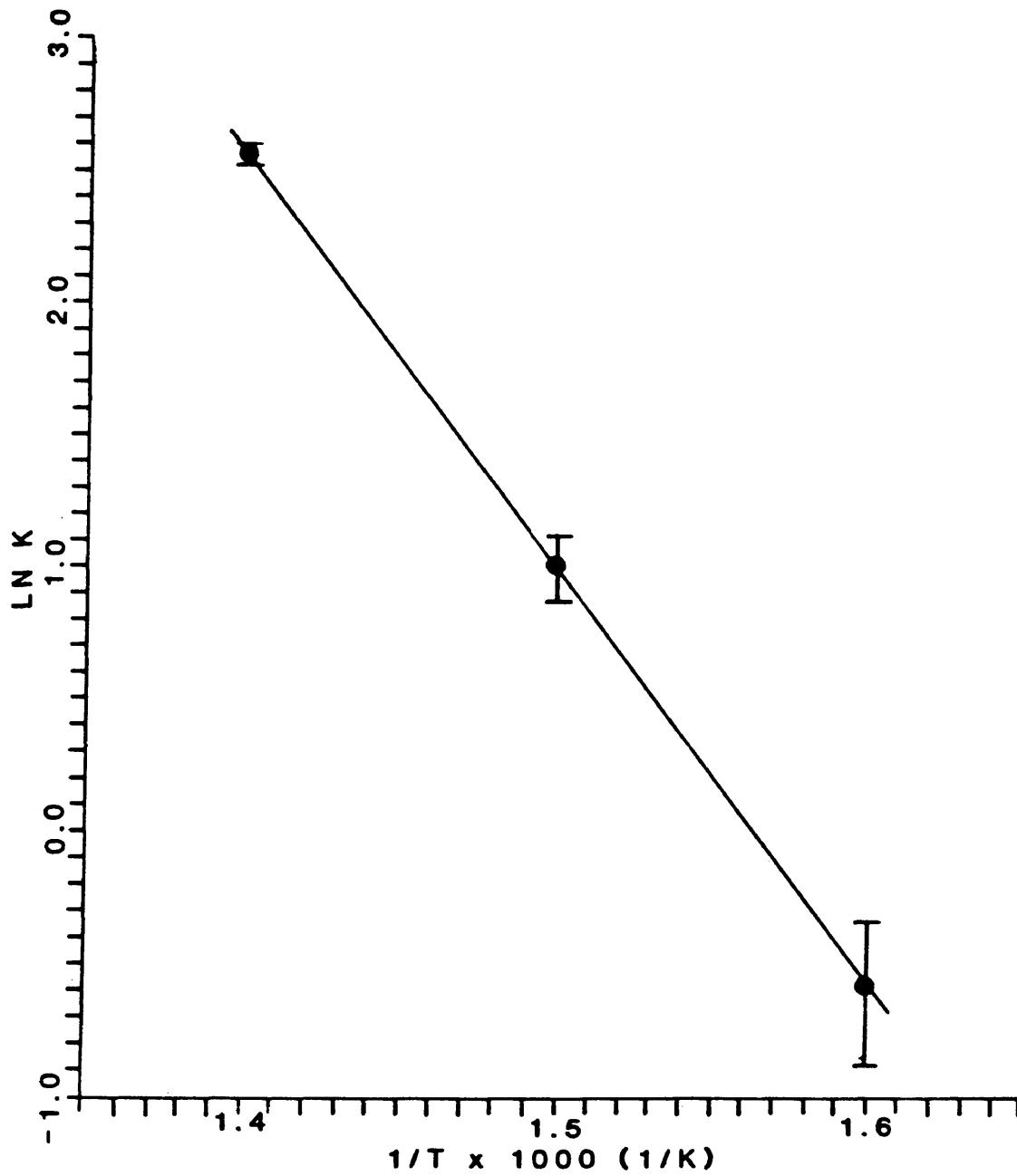


Figure 15 - Arrhenius Plot
Total Carbon to Conversion Products

For the third mechanism all three reactions, total carbon to oil, total carbon to HC gas, and total carbon to CO_x gas, are assumed to be first-order, irreversible with respect total carbon remaining. Using the material balance for the CSTR and the rate equations for the various products, the following set of equations was developed.

$$(1) \quad S_1 x/(1-x) = k_1 T$$

$$(2) \quad S_2 x/(1-x) = k_2 T$$

$$(3) \quad S_3 x/(1-x) = k_3 T$$

where

- x = total carbon conversion
- T = residence time (hr)
- S_1 = selectivity to oil formation
- S_2 = selectivity to HC gas formation
- S_3 = selectivity to CO_x gas formation.

Using MINITAB, the values shown in Table 18 for k_1 , k_2 , and k_3 are obtained. From the Arrhenius plots of these rate constants, Figures 16, 17, and 18, activation energies of 31.15, 37.92, and 29.99 Kcal/g-mole are obtained for the reactions total carbon to oil, total carbon to HC gas, and total carbon to CO_x gas. The overall activation energy obtained from the summed reaction constants is 31.18 Kcal/g-mole.

Table 18
 Rate Constants - Total Carbon to Oil, HC Gas,
 and CO_x Gas

<u>T</u> (°C)	<u>k₁</u> (hr ⁻¹)	<u>k₂</u> (hr ⁻¹)	<u>k₃</u> (hr ⁻¹)	<u>k's</u> (hr ⁻¹)
355	.5429 _{±.1476}	.0036 _{±.0003}	.0159 _{±.0029}	.5624 _{±.1508}
390	2.5002 _{±.4261}	.0146 _{±.0013}	.0593 _{±.0090}	2.5741 _{±.4364}
425	12.4801 _{±.5727}	.1636 _{±.0136}	.3254 _{±.0032}	12.9691 _{±.5895}

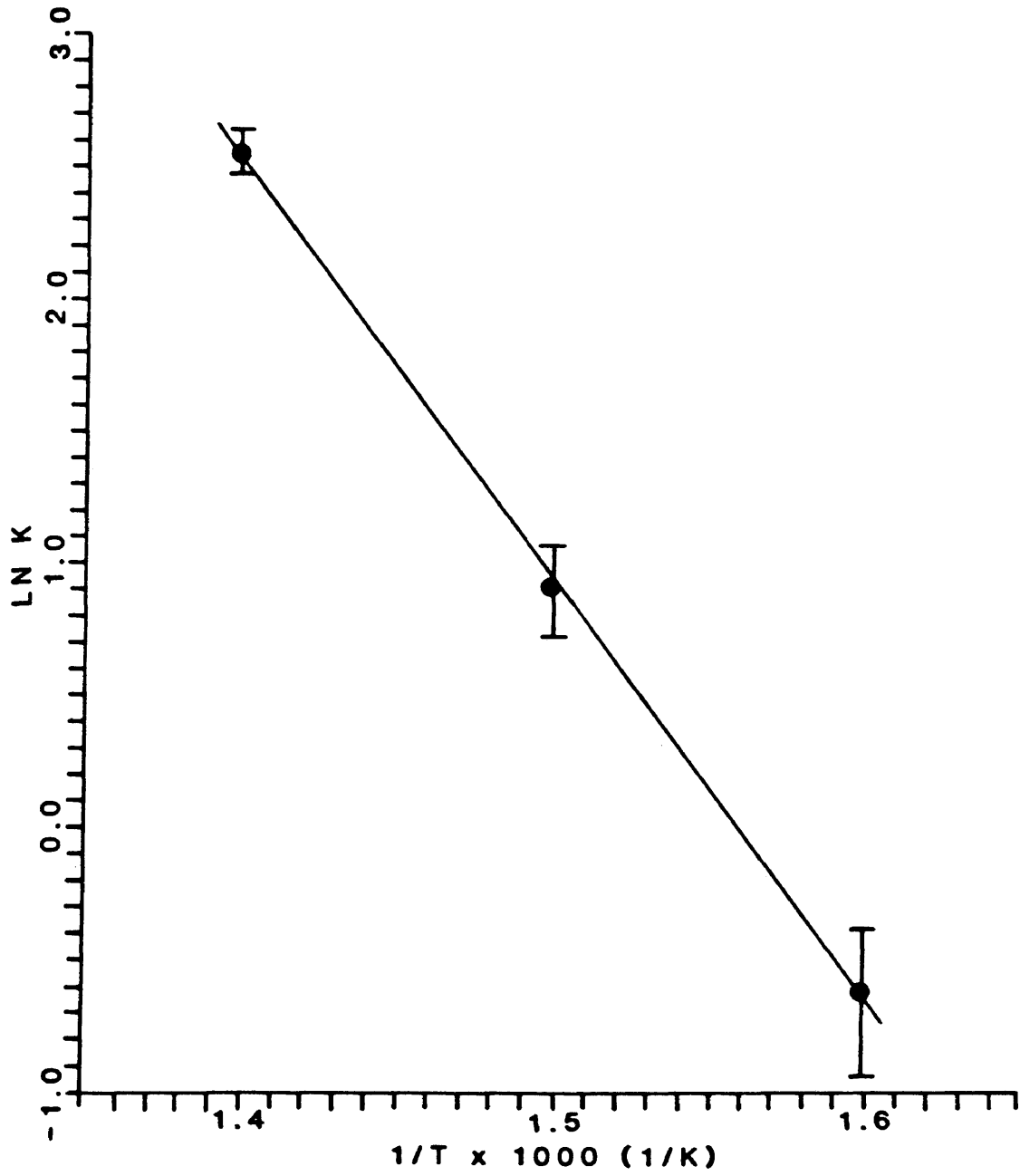


Figure 16 - Arrhenius Plot Total Carbon to Oil

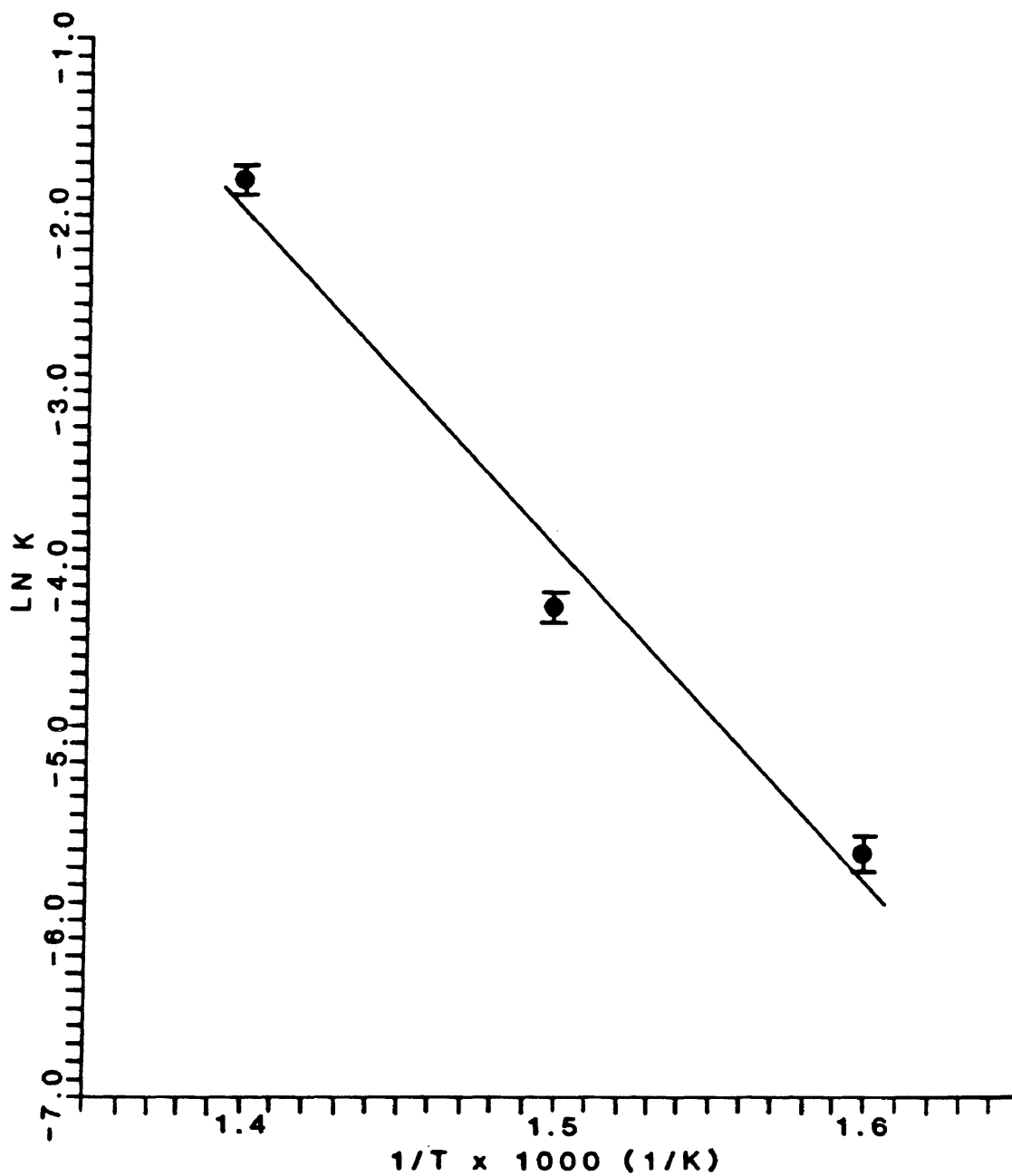


Figure 17 - Arrhenius Plot Total Carbon to HC Gas

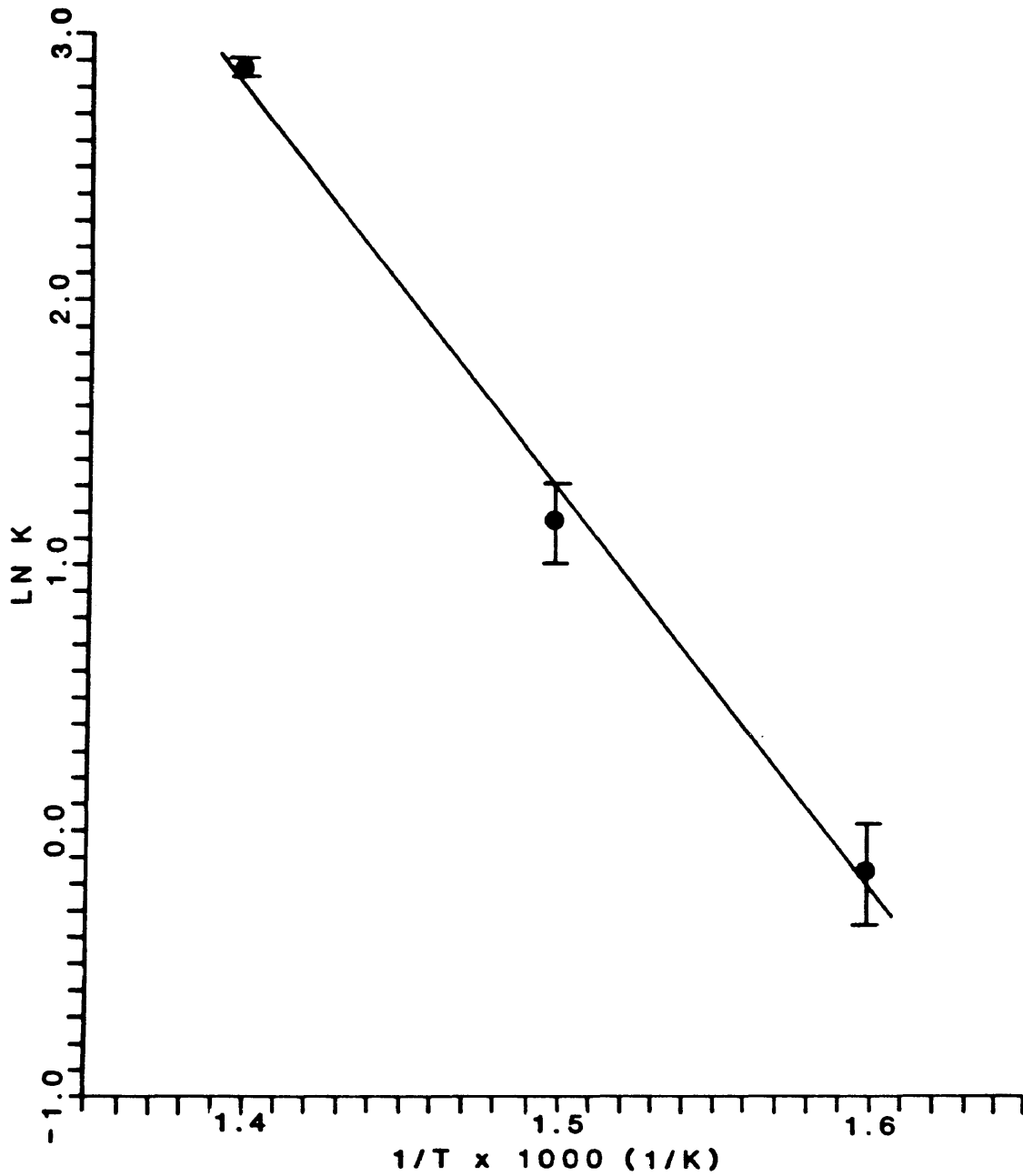


Figure 18 - Arrhenius Plot Total Carbon to CO_x Gas

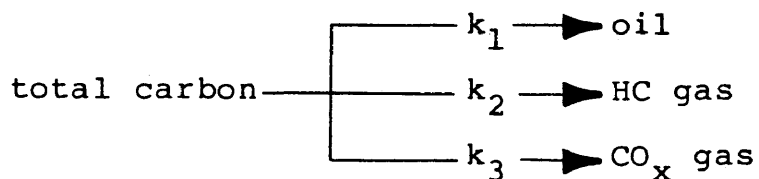
CONCLUSIONS

The conclusions which follow apply strictly to the experimental system employed in this study. The system considered was a 800 ml (liquid volume) continuous stirred tank reactor system (CSTR).

(1) Using tetralin as a solvent, organic carbon conversions of 65.8 and 86.4% were obtained in less than 30 minutes residence at temperatures of 390 and 425°C respectively under a hydrogen atmosphere of 1500 psig.

(2) The CSTR data has been modeled successfully as a first-order, irreversible reaction for the conversion of total carbon to oil, HC gas, and CO_x gas. The overall activation energy of this reaction was 31.1 Kcal/g-mole.

(3) The data on product distribution were modeled successfully with the following mechanism:



where all reactions were assumed to be first order and irreversible. Activation energies of 31.2, 37.9, and 30.0 Kcal/g-mole were found for the reactions total carbon to oil, HC gas, and CO_x gas respectively.

(4) No correlation was found between the activation energy obtained by Frank and those obtained in this study.

(5) Using #2 diesel fuel as a solvent, the effect of hydrogen partial pressure was not apparent at 1500 psig. At a lower pressure, 850 psig, the effect of hydrogen partial pressure was significant.

(6) Gas make in both system, tetralin and #2 diesel fuel, yielded primarily CO, CO₂ and C₁ through C₄ paraffin hydrocarbon gases.

(7) In both systems, the selectivity for carbon conversion to oil was high, ranging 95.4 to 97.8%.

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APPENDIX A
DATA ANALYSIS PROGRAM

```

C
C.....DATA ANALYSIS
C
C.....PROGRAMED BY RANDAL J. WINKLER
C
C
C.....DEFINITIONS.....
C
C   ASHF   = ASH IN FEED SHALE (WT. %)
C   ASHF   = ASH IN SPENT SHALE (WT. %)
C   AR     = ARGON IN PRODUCT GAS (MOLE %)
C   ARF    = ARGON IN FEED GAS (MOLE %)
C   CF     = CARBON FEED RATE (GM/MIN)
C   CG     = CARBON IN PRODUCT GAS (GM/MIN)
C   CSS    = CARBON IN SPENT SHALE (GM/MIN)
C   CO     = CARBON MONOXIDE IN PRODUCT GAS (MOLE %)
C   CO2    = CARBON DIOXIDE IN PRODUCT GAS (MOLE %)
C   CH4    = METHANE IN PRODUCT GAS (MOLE %)
C   C2H4   = ETHENE IN PRODUCT GAS (MOLE %)
C   C2H6   = ETHANE IN PRODUCT GAS (MOLE %)
C   C3H6   = PROPENE IN PRODUCT GAS (MOLE %)
C   C3H8   = PROPANE IN PRODUCT GAS (MOLE %)
C   C4H8N  = N-BUTENE IN PRODUCT GAS (MOLE %)
C   C4H8I  = I-BUTENE IN PRODUCT GAS (MOLE %)
C   C4H10N = N-BUTANE IN PRODUCT GAS (MOLE %)
C   C4H10I = I-BUTANE IN PRODUCT GAS (MOLE %)
C   DEN    = SLURRY DENSITY (GM/ML)
C   FRAC   = FRACTION OF SHALE IN SLURRY
C   GASF   = GAS FEED RATE (SCFH)
C   GASFM  = GAS FEED RATE (MOLE/MIN)
C   GASP   = GAS PRODUCT RATE (SCFH)
C   GASPM  = GAS PRODUCT RATE (MOLE/MIN)
C   H2     = HYDROGEN IN PRODUCT GAS (MOLE %)
C   H2F    = HYDROGEN IN FEED GAS (MOLE %)
C   HI     = HYDROGEN IN FEED GAS (MOLE/MIN)
C   HO     = HYDROGEN IN PRODUCT GAS (MOLE/MIN)
C   HS     = HYDROGEN CONSUMED FROM SOLVENT (MOLE/MIN)
C   HT     = TOTAL HYDROGEN CONSUMED (SCFH)
C   HTO    = TOTAL HYDROGEN CONSUMED (SCF/BBL OF OIL)
C   HTS    = TOTAL HYDROGEN CONSUMED (SCF/TON OF SHALE)
C   MW     = MOLECULAR WEIGHT OF SOLVENT
C   NAFF   = NAPHTHALENE IN FEED (MOLE %)
C   NAFF   = NAPHTHALENE IN PRODUCT (MOLE %)
C   OCC    = ORGANIC CARBON CONVERSION (%)
C   OCF    = ORGANIC CARBON IN FEED SHALE (%)
C   OCF    = ORGANIC CARBON IN SPENT SHALE (%)
C   OIL    = OIL PRODUCTION (ML/MIN)
C   SELECT = CARBON TO OIL SELECTIVITY
C   SHALE  = NO. OF PARTS OF SHALE IN SLURRY
C   SHARAT = SHALE FEED RATE (GM/MIN)

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```

C      SLURAT = SLURRY FEED RATE (ML/MIN)
C      SOLM   = SOLVENT FEED RATE (MOL/MIN)
C      SOLV   = NO. OF PARTS OF SOLVENT IN SLURRY
C      TCS    = TOTAL CARBON IN SHALE (%)
C      TCSS   = TOTAL CARBON IN SPENT SHALE (%)
C
C          INTEGER RUNID,SAMPL
C          REAL  NAPP,NAPP,MW
C
C      1      CONTINUE
C
C      .....ENTER DATA
C
C          WRITE(4,100)
C          READ(4,400) RUNID,SAMPL
C          WRITE(4,105)
C          READ(4,405) IDEC
C          WRITE(4,90)
C          READ(4,505) TEMP
C          WRITE(4,120)
C          READ(4,505) SLURAT
C          WRITE(4,130)
C          READ(4,505) DEN
C          WRITE(4,125)
C          READ(4,500) SOLV,SHALE
C          WRITE(4,140)
C          READ(4,505) GASF
C          WRITE(4,205)
C          READ(4,500) H2F,H2
C          WRITE(4,95)
C          READ(4,505) P
C          WRITE(4,110)
C          READ(4,500) ASHF,ASHP
C          WRITE(4,115)
C          READ(4,500) OCF,OCF
C
C          IF(IDEC.EQ.1) GO TO 10
C
C          WRITE(4,135)
C          READ(4,500) TCS,TCSS
C          WRITE(4,145)
C          READ(4,500) ARF,AR
C          WRITE(4,150)
C          READ(4,505) CH4
C          WRITE(4,155)
C          READ(4,505) C2H4
C          WRITE(4,164)
C          READ(4,505) C2H6
C          WRITE(4,160)
C          READ(4,505) C3H6
C          WRITE(4,165)

```

```

      READ(4,505) C3H8
      WRITE(4,170)
      READ(4,505) C4H8N
      WRITE(4,175)
      READ(4,505) C4H8I
      WRITE(4,180)
      READ(4,505) C4H10N
      WRITE(4,185)
      READ(4,505) C4H10I
      WRITE(4,190)
      READ(4,505) CO
      WRITE(4,195)
      READ(4,505) CO2
C
      IF(IDEQ.EQ.2) GO TO 10
C
      WRITE(4,200)
      READ(4,500) NAF,F,NAFF
      WRITE(4,205)
      READ(4,500) H2F,H2
      WRITE(4,210)
      READ(4,505) MW
C
10    CONTINUE
C
C.....CALCULATE RESIDENCE TIME
C
      VOL = 800.0
      T = TEMP + 273.
      DVOL = (GASF/60.)*(T/298.)*(14.7/P)*(1000000./35.3147)
      VOL = VOL - DVOL
      RES = VOL/(SLURAT)
C
C.....CALCULATE HYDROGEN FEED RATE (SCF/TON)
C
      FRAC = SHALE/(SHALE+SOLU)
      GFR = (GASF*H2F/(SLURAT*IDEN*FRAC))*(454*2000/6000)
C
C.....CALCULATE ORGANIC CARBON CONVERSION (%)
C
      OCC = (OCF-(OCF*(ASHF/ASHF)))/OCF*100.
C
C.....CALCULATE CARBON TO OIL SELECTIVITY
C
C      (1) CALCULATE FRACTION OF SHALE IN SLURRY
C
      FRAC = SHALE/(SHALE + SOLU)
      IF(IDEQ.EQ.1) GO TO 20
C
C      (2) CALCULATE SHALE FEED RATE (GM/MIN)

```

```

C
C      SHARAT = SLURAT*DEN*FRAC
C
C      (3)  CALCULATE SPENT SHALE RATE (GM/MIN)
C
C      SSRAT = SHARAT*ASHF/ASHF
C
C      (4)  CALCULATE CARBON FEED RATE (GM/MIN)
C
C      CF = SHARATE*TCS/100.
C
C      (5)  CALCULATE CARBON IN SPENT SHALE (GM/MIN)
C
C      CSS = SSRAT*TCSS/100.
C
C      (6)  CALCULATE GAS FEED RATE (MOLE/MIN)
C
C      GASFM = GASF/(359.*60)
C
C      (7)  CALCULATE GAS PRODUCT RATE (SCFH)
C
C      GASPF = GASF*ARF/AR
C
C      (8)  CALCULATE GAS PRODUCT RATE (MOLE/MIN)
C
C      GASPM = GASPF/(359.*60.)
C
C      (9)  CALCULATE CARBON IN PRODUCT GAS (GM/MIN)
C
C      CG = GASPM*((CH4*12.) + (C2H4*24.) + (C2H6*24.)
1          + (C3H6*36.) + (C3H8*36.)
2          + (C4H8N*48.) + (C4H8I*48.)
3          + (C4H10N*48.) + (C4H10I*48.)
4          + (CO*12.) + (CO2*12.))/100.
C
C      (10) CALCULATE CARBON TO OIL SELECTIVITY
C
C      SELECT = 100.* ((CF-CSS)/453.6-CG)/((CF-CSS)/453.6)
C
C      IF(IDEQ.EQ.2) GO TO 20
C
C.....CALCULATE HYDROGEN CONSUMPTION
C
C      (1)  CALCULATE H2 IN FEED GAS (MOLE/MIN)
C
C      HI = GASFM*H2F/100.
C
C      (2)  CALCULATE H2 IN PRODUCT GAS (MOLE/MIN)
C
C      HO = GASPM*H2/100.

```

```
C
C      (3)  CALCULATE SOLVENT FEED RATE (MOLE/MIN)
C
C      SOLM = (1.-FRAC)*(SLURAT*DEN/MW)
C
C      (4)  CALCULATE H2 CONSUMED FROM SOLVENT (MOLE/MIN)
C
C      HS = 2.*SOLM*((NAFF-NAFF)/100.)
C
C      (5)  CALCULATE TOTAL H2 CONSUMED (SCFH)
C
C      HT = (HS + (HO-HI))*359.*60
C
C      (6)  CALCULATE TOTAL H2 CONSUMED (SCF/TON OF SHALE)
C
C      HTS = (HT*453.5923*2000.)/(SHARAT*60.)
C
C      (7)  CALCULATE OIL PRODUCTION (ML/MIN)
C
C      OIL = (CF-CG-CSS)/.8/.9
C
C      (8)  CALCULATE TOTAL H2 CONSUMED (SCF/BBL OF OIL)
C
C      HTD = (HT*1000.*42)/(OIL*.2642*60.)
C
C      20  CONTINUE
C
C      .....PRINT RESULTS
C
C      WRITE(4,600) RUNID,SAMPL
C      WRITE(6,600) RUNID,SAMPL
C      WRITE(4,660) TEMP
C      WRITE(6,660) TEMP
C      WRITE(4,670) RES
C      WRITE(6,670) RES
C      WRITE(4,680)
C      WRITE(6,680)
C      WRITE(4,610) OCC
C      WRITE(6,610) OCC
C
C      IF(IDEQ.EQ.1) GO TO 30
C
C      WRITE(4,620) SELECT
C      WRITE(6,620) SELECT
C
C      IF(IDEQ.EQ.2) GO TO 30
C
C      WRITE(4,630) HT
C      WRITE(6,630) HT
C      WRITE(4,640) HTS
```



```

        WRITE(6,640) HTS
        WRITE(4,650) HTO
        WRITE(6,650) HTO
C
30    CONTINUE
C
        WRITE(6,700)
        WRITE(6,720) SLURAT
        WRITE(6,725) FRAC
        WRITE(6,730) DEN
        WRITE(6,735) GASF
        WRITE(6,810) GFF
        WRITE(6,705) ASHF,ASHI
        WRITE(6,710) OCF,OCF
        IF(IDEQ.EQ.1) GO TO 40
        WRITE(6,715) TCS,TCSS
        WRITE(6,740) CH4
        WRITE(6,745) C2H4
        WRITE(6,805) C2H6
        WRITE(6,750) C3H6
        WRITE(6,755) C3H8
        WRITE(6,760) C4H8N
        WRITE(6,765) C4H8I
        WRITE(6,770) C4H10N
        WRITE(6,775) C4H10I
        WRITE(6,780) CO
        WRITE(6,785) CO2
        WRITE(6,790) ARF,AR
        WRITE(6,795) H2F,H2
C
        IF(IDEQ.EQ.2.) GO TO 40
C
        WRITE(6,800) NAFF,NAFF
C
40    CONTINUE
C
        WRITE(4,900)
        READ(4,405) IRUN
        IF(IRUN.EQ.1) GO TO 1
C
C.....FORMAT STATEMENTS
C
90    FORMAT(1X,5X,'ENTER REACTION TEMPERATURE (C):')
95    FORMAT(1X,5X,'ENTER SYSTEM PRESSURE (PSIG):')
100   FORMAT(1X,5X,'ENTER RUN NO. AND SAMPLE NO.:')
105   FORMAT(1X,5X,'SELECT ONE OF THE FOLLOWING:',
1     /1X,5X,'(1) ORGANIC CARBON CONVERSION',
2     /1X,5X,'(2) CARBON TO OIL SELECTIVITY',
3     /1X,5X,'(3) TOTAL HYDROGEN CONSUMPTION')
110   FORMAT(1X,5X,'ENTER PER CENT ASH IN FEED ',

```

```

1 'SHALE AND SPENT SHALE:')
115 FORMAT(1X,5X,'ENTER PER CENT ORGANIC CARBON ',
1 'IN FEED SHALE AND SPENT SHALE:')
120 FORMAT(1X,5X,'ENTER SLURRY FEED RATE (ML/MIN):')
125 FORMAT(1X,5X,'ENTER PARTS SOLVENT AND ',
1 'PARTS SHALE IN SLURRY:')
130 FORMAT(1X,5X,'ENTER SLURRY DENSITY:')
135 FORMAT(1X,5X,'ENTER PER CENT TOTAL CARBON ',
1 'IN FEED SHALE AND SPENT SHALE:')
140 FORMAT(1X,5X,'ENTER GAS FEED RATE (SCFH):')
145 FORMAT(1X,5X,'ENTER ARGON IN FEED AND ',
1 'PRODUCT GASES (MOLE %):')
150 FORMAT(1X,5X,'ENTER CH4 IN PRODUCT GAS (MOLE %):')
155 FORMAT(1X,5X,'ENTER C2H4 IN PRODUCT GAS (MOLE %):')
166 FORMAT(1X,5X,'ENTER C2H6 IN PRODUCT GAS (MOLE %):')
160 FORMAT(1X,5X,'ENTER C3H6 IN PRODUCT GAS (MOLE %):')
165 FORMAT(1X,5X,'ENTER C3H8 IN PRODUCT GAS (MOLE %):')
170 FORMAT(1X,5X,'ENTER N-C4H8 IN PRODUCT GAS (MOLE %):')
175 FORMAT(1X,5X,'ENTER I-C4H8 IN PRODUCT GAS (MOLE %):')
180 FORMAT(1X,5X,'ENTER N-C4H10 IN PRODUCT GAS (MOLE %):')
185 FORMAT(1X,5X,'ENTER I-C4H10 IN PRODUCT GAS (MOLE %):')
190 FORMAT(1X,5X,'ENTER CO IN PRODUCT GAS (MOLE %):')
195 FORMAT(1X,5X,'ENTER CO2 IN PRODUCT GAS (MOLE %):')
200 FORMAT(1X,5X,'ENTER NAPHTHALENE IN FEED SOLVENT ',
1 'AND PRODUCT LIQUID (MOLE %):')
205 FORMAT(1X,5X,'ENTER HYDROGEN IN FEED AND ',
1 'PRODUCT GASES (MOLE %):')
210 FORMAT(1X,5X,'ENTER MOLECULAR WEIGHT OF SOLVENT:')
C
400 FORMAT(2I)
405 FORMAT(1I)
500 FORMAT(2F)
505 FORMAT(1F)
C
600 FORMAT(///1X,5X,'RUN NUMBER:',23X,I10,
1 /1X,5X,'SAMPLE NUMBER:',22X,I8)
610 FORMAT(1X,5X,'ORGANIC CARBON CONVERSION (%):',4X,F10.2)
620 FORMAT(1X,5X,'CARBON TO OIL SELECTIVITY (%):',4X,F10.2)
630 FORMAT(1X,5X,'HYDROGEN CONSUMPTION (SCFH):',4X,F12.2)
640 FORMAT(1X,5X,'HYDROGEN CONSUMPTION (SCF/TON):',3X,F10.2)
650 FORMAT(1X,5X,'HYDROGEN CONSUMPTION (SCF/BBL):',3X,F10.2)
660 FORMAT(1X,5X,'REACTION TEMPERATURE (C):',9X,F10.2)
670 FORMAT(1X,5X,'RESIDENCE TIME (MIN):',13X,F10.2)
680 FORMAT(1X,5X,'*****')
C
700 FORMAT(/1X,/1X,/1X,/1X,5X,33X,'FEED',5X,'PRODUCT')
705 FORMAT(1X,5X,'ASH (WT %):',16X,F10.3,2X,F10.3)
710 FORMAT(1X,5X,'ORGANIC CARBON (WT %):',5X,F10.3,2X,F10.3)
715 FORMAT(1X,5X,'TOTAL CARBON (WT %):',7X,F10.3,2X,F10.3)
720 FORMAT(1X,5X,'SLURRY FEED RATE (ML/MIN):',1X,F10.3)
725 FORMAT(1X,5X,'FRACTION OF SHALE IN SLURRY:',1X,F8.4)

```

```
730   FORMAT(1X,5X,'SLURRY DENSITY (GM/ML):',5X,F9.4)
735   FORMAT(1X,5X,'GAS RATE (SCFH):',11X,F10.3)
740   FORMAT(1X,5X,'CH4 (MOLE %):',15X,11X,F10.4)
745   FORMAT(1X,5X,'C2H4 (MOLE %):',14X,11X,F10.4)
750   FORMAT(1X,5X,'C3H6 (MOLE %):',14X,11X,F10.4)
755   FORMAT(1X,5X,'C3H8 (MOLE %):',14X,11X,F10.4)
760   FORMAT(1X,5X,'N-C4H8 (MOLE %):',23X,F10.4)
765   FORMAT(1X,5X,'I-C4H8 (MOLE %):',23X,F10.4)
770   FORMAT(1X,5X,'N-C4H10 (MOLE %):',11X,11X,F10.4)
775   FORMAT(1X,5X,'I-C4H10 (MOLE %):',11X,11X,F10.4)
780   FORMAT(1X,5X,'CO (MOLE %):',15X,12X,F10.4)
785   FORMAT(1X,5X,'CO2 (MOLE %):',14X,12X,F10.4)
790   FORMAT(1X,5X,'AR (MOLE %):',15X,F10.4,2X,F10.4)
795   FORMAT(1X,5X,'H2 (MOLE %):',15X,F10.4,2X,F10.4)
800   FORMAT(1X,5X,'NAPHTHALENE (MOLE %):',7X,F10.4,2X,F10.4)
805   FORMAT(1X,5X,'C2H6 (MOLE %):',25X,F10.4)
810   FORMAT(1X,5X,'HYDROGEN FEED RATE (SCF/TON):',1X,F7.0)
900   FORMAT(/1X,/1X,/1X,5X,'SELECT ONE OF THE FOLLOWING:',
1     /1X,5X,'(1) CALCULATE ANOTHER POINT',
2     /1X,5X,'(2) END CALCULATIONS')
C
      STOP
      END
```

APPENDIX B
MINITAB SAMPLE PROGRAM

Minitab Example Input File

<u>Y</u>	<u>X</u>
1.3215	.7990
1.2850	.8051
1.0697	.7791
.6785	.7738
.3102	.6956

```

READ C1 C2
-- 1.3215 .7990
-- 1.2850 .8051
-- 1.0697 .7791
-- 0.6785 .7738
-- 0.3102 .6956
-- NOBRIEF
-- NOCONSTANT
-- REGRESS Y IN C1 USING 1 PREDICTOR IN C2

```

THE REGRESSION EQUATION IS
 $Y = + 1.23 X1$

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
NOCONSTANT				
X1	C2	1.2313	0.2219	5.55

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = 0.3828$
 WITH (5- 1) = 4 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	4.5123	4.5123
RESIDUAL	4	0.5861	0.1465
TOTAL	5	5.0984	

ROW	X1 C2	Y C1	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
1	0.799	1.322	0.984	0.177	0.338	1.00
2	0.805	1.285	0.991	0.179	0.294	0.87
3	0.779	1.070	0.959	0.173	0.110	0.32
4	0.774	0.678	0.953	0.172	-0.274	-0.80
5	0.696	0.310	0.856	0.154	-0.546	-1.56

DURBIN-WATSON STATISTIC = 0.44

(X-PRIME X)INVERSE

	1
1	0.335998

--

APPENDIX C
RUN SUMMARY SHEETS

Sample Number: CR1-1

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	79.20
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.10
Actual residence time (min):	8.48

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.250	21.500	.734	20.766
Spent	75.520	16.530	.547	15.983

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,546
Organic Carbon Conversion (%):	32.48
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR ²	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR1-2

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	79.20
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.10
Actual residence time (min):	8.48

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.250	21.500	.734	20.766
Spent	77.184	15.880	.598	15.282

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,546
Organic Carbon Conversion (%):	36.83
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR1-3

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	79.20
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.10
Actual residence time (min):	8.48

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.250	21.500	.734	20.766
Spent	76.707	16.000	.576	15.424

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,546
Organic Carbon Conversion (%):	35.85
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR1-4

Run Conditions:

Temperature (°C):	425
Pressure (psig):	1500
Slurry feed rate (ml/min):	80.258
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml):	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	9.97
Actual residence time (min):	8.28

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.250	21.500	.734	20.766
Spent	84.703	10.350	.606	9.744

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,394
Organic Carbon Conversion (%):	63.30
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR ₂	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR1-5

Run Conditions:

Temperature (°C):	425
Pressure (psig):	1500
Slurry feed rate (ml/min):	80.258
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	9.97
Actual residence time (min):	8.28

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.250	21.500	.734	20.766
Spent	85,615	9.860	.629	9.231

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,394
Organic Carbon Conversion (%):	65.60
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR1-6

Run Conditions:

Temperature (°C):	425
Pressure (psig):	1500
Slurry feed rate (ml/min):	80.258
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	9.97
Actual residence time (min):	8.28

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.250	21.500	.734	20.766
Spent	84.638	10.350	.614	9.736

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,394
Organic Carbon Conversion (%):	63.30
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR2-1

Run Conditions:

Temperature (°C):	355
Pressure (psig):	1500
Slurry feed rate (ml/min):	75.04
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.66
Actual residence time (min):	9.04

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	65.830	21.790	.718	21.072
Spent	72.278	19.160	.675	18.485

Calculated Yields:

Hydrogen feed rate (SCF/ton):	12,186
Organic Carbon Conversion (%):	20.10
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	99.500	n-C ₄ H ₈	--
CH ₄	0.020	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	0.050
C ₃ H ₈	--	CO ₂	0.400
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR2-2

Run Conditions:

Temperature (°C):	355
Pressure (psig):	1500
Slurry feed rate (ml/min):	75.04
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.475
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.66
Actual residence time (min):	9.04

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	65.830	21.790	.718	21.072
Spent	72.685	19.400	.669	18.731

Calculated Yields:

Hydrogen feed rate (SCF/ton):	12,186
Organic Carbon Conversion (%):	19.49
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	99.320	n-C ₄ H ₈	--
CH ₄	0.030	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	0.090
C ₃ H ₈	--	CO ₂	0.560
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR3-1

Run Conditions:

Temperature (°C):	355
Pressure (psig):	1200
Slurry feed rate (ml/min):	56.045
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.863
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	14.274
Actual residence time (min):	12.39

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.970	19.823	0.711	19.112
Spent	74.575	17.197	0.616	16.581

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,208
Organic Carbon Conversion (%):	22.09
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	99.610	n-C ₄ H ₈	--
CH ₄	0.020	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	0.004	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	0.040
C ₃ H ₈	--	CO ₂	0.320
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR3-2

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	54.52
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.863
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	14.674
Actual residence time (min):	12.62

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.970	19.823	0.711	19.112
Spent	80.500	14.157	0.595	13.562

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,605
Organic Carbon Conversion (%):	40.97
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	98.830	n-C ₄ H ₈	--
CH ₄	0.070	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	0.002
C ₂ H ₆	0.020	i-C ₄ H ₁₀	--
C ₃ H ₆	0.010	CO	0.150
C ₃ H ₈	0.010	CO ₂	0.920
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR3-3

Run Conditions:

Temperature (°C):	425
Pressure (psig):	1500
Slurry feed rate (ml/min):	54.52
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.863
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	14.674
Actual residence time (min):	12.52

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.970	19.823	0.711	19.112
Spent	85.570	9.070	0.585	8.485

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,605
Organic Carbon Conversion (%):	65.25
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	98.200	n-C ₄ H ₈	0.001
CH ₄	0.180	i-C ₄ H ₈	--
C ₂ H ₄	0.010	n-C ₄ H ₁₀	0.020
C ₂ H ₆	0.080	i-C ₄ H ₁₀	0.005
C ₃ H ₆	0.020	CO	0.270
C ₃ H ₈	0.040	CO ₂	1.190
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR4-1

Run Conditions:

Temperature (°C):	425
Pressure (psig):	1500
Slurry feed rate (ml/min):	50.94
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.54
Hydrogen in feed gas (%):	95.01
Nominal Residence time (min):	15.70
Actual residence time (min):	13.46

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.130	21.350	0.731	20.619
Spent	86.975	8.400	0.629	7.771

Calculated Yields:

Hydrogen feed rate (SCF/ton):	15,167
Organic Carbon Conversion (%):	70.91
Oil/gas selectivity (%):	95.7

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	93.970	n-C ₄ H ₈	--
CH ₄	0.160	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	0.010
C ₂ H ₆	0.070	i-C ₄ H ₁₀	0.003
C ₃ H ₆	0.020	CO	0.230
C ₃ H ₈	0.040	CO ₂	1.090
		AR	4.420

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR4-2

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	51.81
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.54
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	15.44
Actual residence time (min):	13.35

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.130	21.350	0.731	20.619
Spent	81.135	13.280	0.633	12.647

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,168
Organic Carbon Conversion (%):	49.25
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	98.890	n-C ₄ H ₈	--
CH ₄	0.080	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	0.020	i-C ₄ H ₁₀	0.001
C ₃ H ₆	0.010	CO	0.170
C ₃ H ₈	0.010	CO ₂	0.830
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR5-1

Run Conditions:

Temperature (°C):	355
Pressure (psig):	1500
Slurry feed rate (ml/min):	12.44
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	7.63
Hydrogen in feed gas (%):	94.37
Nominal Residence time (min):	64.31
Actual residence time (min):	58.33

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.784	20.923	0.670	20.253
Spent	76.696	16.533	0.593	15.940

Calculated Yields:

Hydrogen feed rate (SCF/ton):	42,428
Organic Carbon Conversion (%):	30.44
Oil/gas selectivity (%):	95.9

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	94.080	n-C ₄ H ₈	--
CH ₄	0.020	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	0.020	i-C ₄ H ₁₀	--
C ₃ H ₆	0.002	CO	0.040
C ₃ H ₈	0.002	CO ₂	0.230
		AR	5.600

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR6-1

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	12.985
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	7.63
Hydrogen in feed gas (%):	94.416
Nominal Residence time (min):	61.61
Actual residence time (min):	55.56

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.605	20.943	0.710	20.233
Spent	86.430	9.023	0.486	8.537

Calculated Yields:

Hydrogen feed rate (SCF/ton):	40,667
Organic Carbon Conversion (%):	67.00
Oil/gas selectivity (%):	96.9

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	94.044	n-C ₄ H ₈	--
CH ₄	0.053	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	0.017	i-C ₄ H ₁₀	--
C ₃ H ₆	0.008	CO	0.119
C ₃ H ₈	0.007	CO ₂	0.321
		AR	5.431

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR7-1

Run Conditions:

Temperature (°C):	355
Pressure (psig):	1500
Slurry feed rate (ml/min):	36.36
Solvent:	Tetralin
Solvent/shale ratio:	6.5/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	7.63
Hydrogen in feed gas (%):	94.416
Nominal Residence time (min):	22.00
Actual residence time (min):	19.96

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	68.823	20.277	0.713	19.564
Spent	76.071	17.353	0.619	16.734

Calculated Yields:

Hydrogen feed rate (SCF/ton):	22,371
Organic Carbon Conversion (%):	22.62
Oil/gas selectivity (%):	97.8

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	94.285	n-C ₄ H ₈	--
CH ₄	0.014	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	0.002	CO	0.037
C ₃ H ₈	--	CO ₂	0.190
		AR	5.472

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR7-2

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	25.37
Solvent:	Tetralin
Solvent/shale ratio:	6.5/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	7.63
Hydrogen in feed gas (%):	94.416
Nominal Residence time (min):	31.53
Actual residence time (min):	28.44

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	68.823	20.277	0.713	19.564
Spent	86.373	9.100	0.705	8.395

Calculated Yields:

Hydrogen feed rate (SCF/ton):	32,062
Organic Carbon Conversion (%):	65.81
Oil/gas selectivity (%):	97.8

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	94.226	n-C ₄ H ₈	--
CH ₄	0.038	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	0.007	CO	0.095
C ₃ H ₈	0.004	CO ₂	0.312
		AR	5.319

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR8-1

Run Conditions:

Temperature (°C):	425
Pressure (psig):	1500
Slurry feed rate (ml/min):	25.42
Solvent:	Tetralin
Solvent/shale ratio:	9/1
Slurry density (gm/ml)	0.987
Gas feed rate (SCFH):	7.63
Hydrogen in feed gas (%):	94.402
Nominal Residence time (min):	31.47
Actual residence time (min):	28.22

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.509	20.453	0.719	19.734
Spent	90.576	4.403	0.789	3.614

Calculated Yields:

Hydrogen feed rate (SCF/ton):	43,350
Organic Carbon Conversion (%):	86.35
Oil/gas selectivity (%):	96.3

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	93.955	n-C ₄ H ₈	0.003
CH ₄	0.088	i-C ₄ H ₈	--
C ₂ H ₄	0.006	n-C ₄ H ₁₀	--
C ₂ H ₆	0.034	i-C ₄ H ₁₀	--
C ₃ H ₆	0.015	CO	0.195
C ₃ H ₈	0.015	CO ₂	0.333
		AR	5.356

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR9-1

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	51.91
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.54
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	15.41
Actual residence time (min):	13.32

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.929	20.910	0.729	20.181
Spent	80.103	13.750	0.426	13.324

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,883
Organic Carbon Conversion (%):	44.84
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR9-2

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	51.91
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.54
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	15.41
Actual residence time (min):	13.32

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.929	20.910	0.729	20.181
Spent	81.485	12.465	0.403	12.062

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,883
Organic Carbon Conversion (%):	50.91
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₈	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	C ₄ H ₁₀	--
C ₃ H ₈	--	CO	--
		CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR9-3

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	51.91
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	10.54
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	15.41
Actual residence time (min):	13.32

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.929	20.910	0.729	20.181
Spent	81.326	13.135	0.455	12.680

Calculated Yields:

Hydrogen feed rate (SCF/ton):	14,883
Organic Carbon Conversion (%):	48.29
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR9-4

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	77.99
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.48
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.26
Actual residence time (min):	8.61

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.929	20.910	0.729	20.181
Spent	76.439	15.895	0.565	15.330

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,730
Organic Carbon Conversion (%):	33.49
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR ₂	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR9-5

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	77.99
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.48
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.26
Actual residence time (min):	8.61

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.929	20.910	0.729	20.181
Spent	76.423	16.000	0.597	15.403

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,730
Organic Carbon Conversion (%):	33.16
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	CO	--
C ₃ H ₈	--	CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR9-6

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	77.99
Solvent:	Tetralin
Solvent/shale ratio:	4/1
Slurry density (gm/ml)	1.030
Gas feed rate (SCFH):	12.48
Hydrogen in feed gas (%):	100
Nominal Residence time (min):	10.26
Actual residence time (min):	8.61

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	66.929	20.910	0.729	20.181
Spent	77.030	16.060	0.500	15.560

Calculated Yields:

Hydrogen feed rate (SCF/ton):	11,730
Organic Carbon Conversion (%):	33.01
Oil/gas selectivity (%):	--

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	--	n-C ₄ H ₈	--
CH ₄	--	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	--
C ₂ H ₆	--	i-C ₄ H ₁₀	--
C ₃ H ₆	--	C ₄ H ₁₀	--
C ₃ H ₈	--	CO	--
		CO ₂	--
		AR	--

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR11-1

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	54.84
Solvent:	#2 Diesel Fuel
Solvent/shale ratio:	7/1
Slurry density (gm/ml)	0.888
Gas feed rate (SCFH):	8.90
Hydrogen in feed gas (%):	94.451
Nominal Residence time (min):	14.60
Actual residence time (min):	12.92

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.696	20.667	0.713	19.954
Spent	81.884	12.440	0.602	11.838

Calculated Yields:

Hydrogen feed rate (SCF/ton):	21,042
Organic Carbon Conversion (%):	50.95
Oil/gas selectivity (%):	97.3

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	94.192	n-C ₄ H ₈	--
CH ₄	0.069	i-C ₄ H ₈	--
C ₂ H ₄	0.004	n-C ₄ H ₁₀	0.009
C ₂ H ₆	0.020	i-C ₄ H ₁₀	--
C ₃ H ₆	0.009	CO	0.097
C ₃ H ₈	0.011	CO ₂	0.409
		AR	5.179

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

Sample Number: CR11-2

Run Conditions:

Temperature (°C): 390
 Pressure (psig): 850
 Slurry feed rate (ml/min): 57.83
 Solvent: #2 Diesel Fuel
 Solvent/shale ratio: 7/1
 Slurry density (gm/ml) 0.888
 Gas feed rate (SCFH): 8.90
 Hydrogen in feed gas (%): 94.451
 Nominal Residence time (min): 13.80
 Actual residence time (min): 12.25

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	67.696	20.667	0.713	19.954
Spent	80.788	13.033	0.581	12.452

Calculated Yields:

Hydrogen feed rate (SCF/ton): 19,954
 Organic Carbon Conversion (%): 47.71
 Oil/gas selectivity (%): 96.5

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	93.814	n-C ₄ H ₈	--
CH ₄	0.091	i-C ₄ H ₈	--
C ₂ H ₄	--	n-C ₄ H ₁₀	0.007
C ₂ H ₆	0.027	i-C ₄ H ₁₀	--
C ₃ H ₆	0.014	CO	0.136
C ₃ H ₈	0.015	CO ₂	0.542
		AR	5.354

Additional Information

Napthalene in (mole %): --
 Napthalene out (mole %): --

Sample Number: CR12-1

Run Conditions:

Temperature (°C): 390
 Pressure (psig): 850
 Slurry feed rate (ml/min): 57.53
 Solvent: #2 Diesel Fuel
 Solvent/shale ratio: 7/1
 Slurry density (gm/ml) 0.888
 Gas feed rate (SCFH): 8.90
 Hydrogen in feed gas (%): 49.860
 Nominal Residence time (min): 13.90
 Actual residence time (min): 11.10

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	68.077	20.430	0.722	19.708
Spent	78.044	15.813	0.574	15.239

Calculated Yields:

Hydrogen feed rate (SCF/ton): 10,588
 Organic Carbon Conversion (%): 32.55
 Oil/gas selectivity (%): 95.6

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	50.011	n-C ₄ H ₈	0.007
CH ₄	0.080	i-C ₄ H ₈	0.003
C ₂ H ₄	0.006	n-C ₄ H ₁₀	--
C ₂ H ₆	0.023	i-C ₄ H ₁₀	--
C ₃ H ₆	0.013	CO	0.116
C ₃ H ₈	0.014	CO ₂	0.451
		AR	49.276

Additional Information

Napthalene in (mole %): --
 Napthalene out (mole %): --

Sample Number: CR12-2

Run Conditions:

Temperature (°C):	390
Pressure (psig):	1500
Slurry feed rate (ml/min):	58.34
Solvent:	#2 Diesel Fuel
Solvent/shale ratio:	7/1
Slurry density (gm/ml)	0.888
Gas feed rate (SCFH):	8.90
Hydrogen in feed gas (%):	49.860
Nominal Residence time (min):	13.70
Actual residence time (min):	12.14

Chemical Analysis:

<u>Shale</u>	<u>% Ash</u>	<u>% Total C</u>	<u>% Inorg. C</u>	<u>% Org. C</u>
Feed	68.077	20.430	0.722	19.708
Spent	82.200	12.400	0.627	11.773

Calculated Yields:

Hydrogen feed rate (SCF/ton):	10,441
Organic Carbon Conversion (%):	50.53
Oil/gas selectivity (%):	95.4

Product Gas Analysis:

<u>Component</u>	<u>Mole %</u>	<u>Component</u>	<u>Mole %</u>
H ₂	50.250	n-C ₄ H ₈	0.019
CH ₄	0.113	i-C ₄ H ₈	0.003
C ₂ H ₄	0.009	n-C ₄ H ₁₀	0.012
C ₂ H ₆	0.037	i-C ₄ H ₁₀	--
C ₃ H ₆	0.019	CO	0.122
C ₃ H ₈	0.025	CO ₂	0.724
		AR	48.668

Additional Information

Napthalene in (mole %):	--
Napthalene out (mole %):	--

APPENDIX D
MINITAB INPUT FILES

MINITAB Input File
Organic Carbon to Conversion Products

	<u>x/(1-x)</u>	<u>T</u> <u>(hr)</u>
355°C	.2516	.1507
	.2421	.1507
	.2835	.2065
	.2923	.3327
	.4376	.9805
390°C	.4810	.1413
	.5830	.1413
	.5588	.1413
	.6941	.2103
	.9704	.2225
	1.9248	.4740
2.0303	.9260	
425°C	1.7248	.1380
	1.9070	.1380
	1.7248	.1380
	2.4376	.2243
	6.3260	.4703

MINITAB Input File

Total Carbon to Conversion Products

	<u>x/(1-x)</u>	<u>T</u> <u>(hr)</u>
355°C	.2486	.1507
	.2401	.1507
	.2835	.2065
	.2915	.3327
	.4318	.9805
390°C	.4826	.1413
	.5773	.1413
	.5559	.1413
	.6832	.2103
	.9433	.2225
	1.7964	.4740
	1.9674	.9260
425°C	1.6560	.1380
	1.8177	.1380
	1.6539	.1380
	2.4376	.2243
	6.3260	.4703

MINITAB Input File
Total Carbon to Oil

	<u>S₁x/(1-x)</u>	<u>T (hr)</u>
355°C	.2441 *	.1507
	.2319 *	.1507
	.2773 *	.2065
	.2851	.3327
	.4141	.9805
390°C	.6566 *	.2103
	.9159 *	.2225
	1.7568	.4740
	1.9064	.9260
425°C	2.3328	.2243
	6.0919	.4703

* Estimated from gas production data on Tables 9 and 10

MINITAB Input File
Total Carbon to HC Gas

	<u>S₂x/(1-x)</u>	<u>T (hr)</u>
355°C	.0002486 *	.1507
	.0004802 *	.1507
	.0005670 *	.2065
	.0005830	.3327
	.003886	.9805
390°C	.004099 *	.2103
	.004717 *	.2225
	.005389	.4740
	.013772	.9260
425°C	.02565	.2243
	.08224	.4703

* Estimated from gas production data on Tables 9 and 10

MINITAB Input File
Total Carbon to CO_x Gas

	<u>S₃x/(1-x)</u>	<u>T (hr)</u>
355°C	.004226 *	.1507
	.007683 *	.1507
	.005670 *	.2065
	.005830	.3327
	.013818	.9805
390°C	.02254 *	.2103
	.02264 *	.2225
	.03413	.4740
	.04722	.9260
425°C	.07557	.2243
	.15182	.4703

* Estimated from gas production data on Tables 9 and 10