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PROCESS DESIGN AND DEVELOPMENT

PIPELINE GAS FROM OIL SHALE BY DIRECT HYDROGASIFICATION

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PIPELINE GAS FROM OIL SHALE BY DIRECT HYDROGASIFICATION

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The rate of hydrogasification of the organic matter in a Colorado oil shale was measured in a laboratory semiflow reactor at temperatures from 1100° to 1400° F. and pressures up to 2000 p.s.i.g. The kerogen hydrogenolysis reaction sequence was shown to involve initial formation of intermediates at least partially recoverable as liquids at very short residence times and/or low temperatures, followed by pyrolysis, hydrogenation, and hydrogenolysis reactions leading to gaseous aliphatic hydrocarbons of decreasing molecular weight. At sufficiently long gas residence times, the primary gaseous hydrocarbons were methane and ethane. Continuous operation at 1200° to 1400° F. was simulated in tests conducted at 1000 p.s.i.g. and at hydrogen-oil shale ratios ranging from 100 to 250% of the stoichiometric requirement for complete conversion of the organic matter to methane. At average oil shale residence times of about 5 minutes, the instantaneous organic carbon gasification averaged 63 to 64%.

THE gas industry has been studying methods for the production of natural gas substitutes from coal and petroleum oils. Processes for direct conversion of these fossil fuels to high heating value gases consisting largely of methane are in an advanced stage of development (6, 7). In the case of oil shale, existing technology would involve a preliminary retorting step to produce crude shale oil, and refining to prepare a suitable feed for continuous destructive hydrogenation (hydrogasification). It was reasoned that a direct oil shale hydrogasification process might be preferable because of potentially higher conversion of the organic matter to gas, and elimination of a number of process steps.

Feasibility was shown for direct hydrogasification of the organic matter in Green River oil shale. High heating value gases were produced (1, 8, 11) in batch reactor tests at 1300° F., at 1200 to 5500 p.s.i.g., and with 100% of the stoichiometric hydrogen requirement for complete conversion of the organic matter to methane. About 90% or more of the organic carbon plus hydrogen content of the oil shale was converted to methane and ethane.

In these tests, the path of the hydrogenolysis of kerogen was only partially indicated at the long heatup times and long gas residence times encountered in the batch reactor. Only the slower final breakdown of higher gaseous paraffins to methane and ethane could be observed. It was also not possible to measure over-all reaction rates and precisely determine the effects of temperature. Pressure effects were obscured by changes with temperature and degree of conversion.

The present work was conducted in a reactor system in which oil shale heatup times and exit gas holdup times in the heated portion of the reactor were of the order of a few seconds. After leaving the reactor, the reaction products were cooled rapidly to minimize further reactions.

The scope of this study was rather broad and three separate test programs are described. The objective of the first test series was to show the mechanism of the hydrogasification of oil shale kerogen, and to measure the rates of kerogen conversion to gaseous hydrocarbons and of mineral carbonate decomposition. In these first tests, product residence times in the heated portion of the reactor were small, so methane and ethane were not the only major gaseous products. The second test series was conducted over a range of hydrogen space velocities with a bed of inerts downstream of the oil shale

charge to simulate conditions conducive to vapor-phase hydrogenolysis of heavier hydrocarbons to methane and ethane in hot spent oil shale in a cocurrent flow reactor. Once the conditions necessary for producing primarily methane and ethane were found in the second test series, a third test series was conducted to show the effects of a major design parameter, hydrogen-oil shale ratio, on product distribution. Tests were made with continuous feeding of oil shale to simulate continuous operation and to provide data for pilot plant reactor design.

Experimental

Apparatus. A schematic diagram of the semiflow reactor system is shown in Figure 1.

The reactor contained a self-sealing, modified Bridgman closure at each end and was 2 inches in inside diameter, 4 inches in outside diameter, and 60 inches in inside length. The reactor barrel, constructed of Uniloy N-155 super alloy, was rated for operation at a maximum temperature of 1700° F at 1500 p.s.i.g. The closures were rated for a maximum temperature of 1400° F. at 1500 p.s.i.g. Satisfactory closure operation was obtained with both 16-25-6 and Inconel-X seal rings. A boundary lubricant of molybdenum disulfide, applied in aerosol form, was used on all closure threads and on the seal rings to prevent galling. This reactor has been completely described (9), along with design details of the use of externally heated reactors at combined high temperatures and high pressures.

An Inconel-X thermowell of 3/8-inch outside diameter, with a 12-gage wall thickness and 58 inches long, was mounted axially in the bottom closure. The thermowell could contain up to five 0.040-inch outside diameter thermocouples. Thermocouples were Chromel-Alumel, magnesium oxide insulated, and enclosed in a swaged Inconel sheath. To provide for complete containment and recovery of the oil shale residue, the reactor was provided with a removable stainless steel insert, 1 5/8 inches in inside diameter by 1.990 inches in outside diameter and containing a 1/2-inch outside diameter thermowell sleeve.

The reactor was heated by means of an electric resistance furnace containing four separately controlled heating zones, consisting of four rectangular heating elements, 7 inches wide and 12 inches long. Temperatures were controlled manually during tests but by pyrometric controllers during reactor heatup. Each temperature was recorded at approximately 3-second intervals by means of a high-speed potentiometric temperature recorder during the test period.

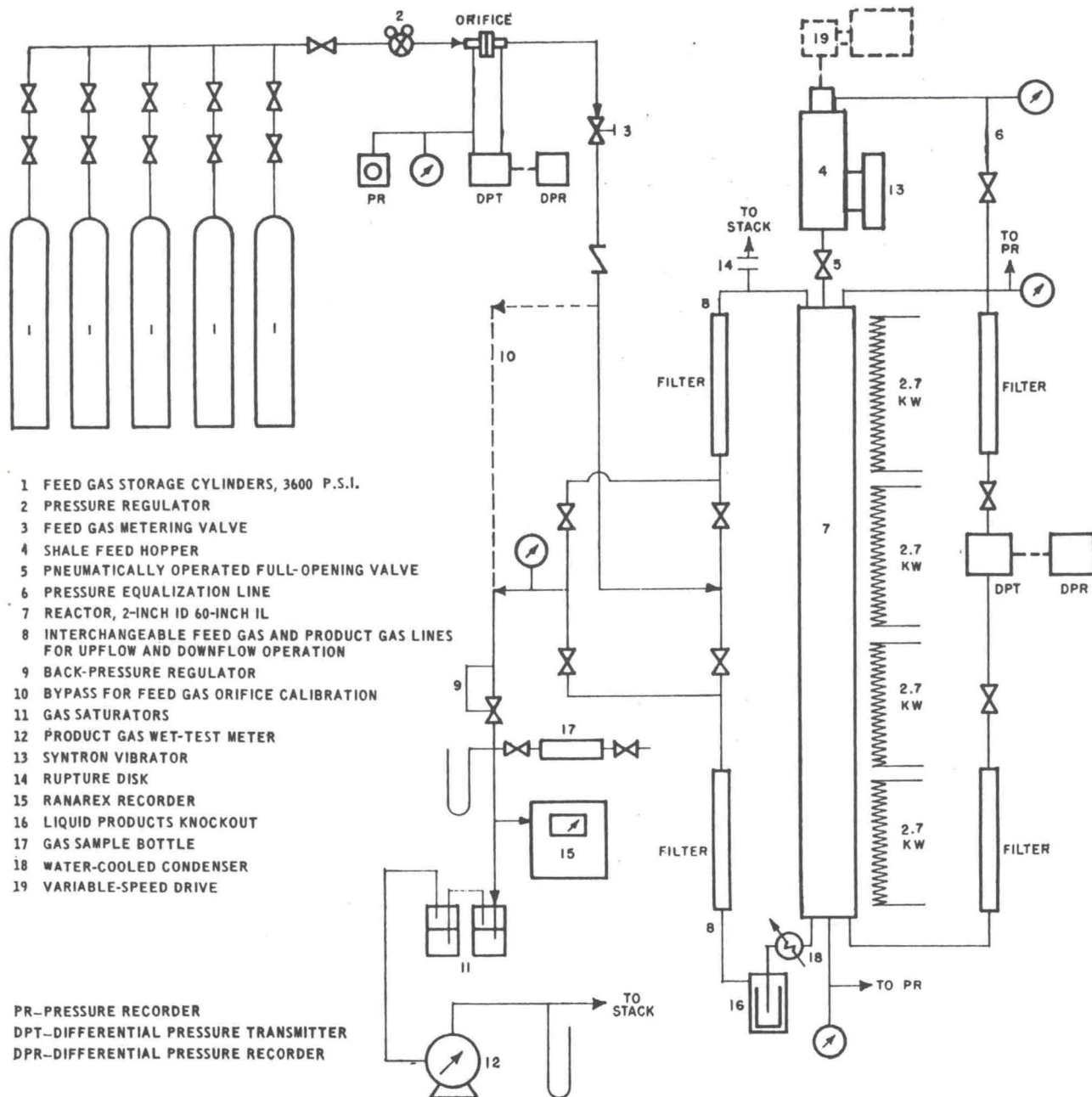


Figure 1. Semiflow reactor system for study of rates of hydrogasification of oil shale at temperatures to 1700° F. and pressures to 3000 p.s.i.g.

A feed hopper was mounted directly above the reactor and was provided with a vibrator to aid oil shale feeding. A full-opening, air-operated ball valve was installed between the hopper and the reactor. A second hopper contained a rotating-drum-type feeder, which was driven by a variable speed drive, for continuous oil shale feeding.

Feed hydrogen flow rates were controlled manually and were measured by means of an orifice meter. The orifice pressure and the reactor pressure were recorded continuously. The feed hydrogen was preheated to reaction temperature within the reactor. Exit gases passed through a water-cooled coil, a liquids knockout pot, a high-pressure filter, and a pressure-reducing back-pressure regulator, before being sampled, metered, and monitored. A sampling manifold was installed upstream of the metering and monitoring system. The exit gas specific gravity was monitored by means of a recording gravitometer.

Materials. In all tests, the feed hydrogen contained an accurately measured, small amount of helium, usually 1 to 2

Table I. Analysis of Colorado Oil Shale

Sample designation	4770
Type	Colorado, Mahogany Zone
Source	Union Oil Co.
Particle size, U. S. standard sieve	-8, +20
Analysis, wt. % (dry basis)	
Moisture	0.3 ^a
Organic carbon ^b	17.45
Mineral carbon ^c	4.84
Hydrogen ^b	2.36
Organic C/H wt. ratio	7.4
Fischer assay oil, gal./ton dry shale ^d	35.9

^a On oven-dry basis (dried for 1 hr. at 105–110° C.). ^b ASTM method D 271-58 adapted in accordance with technique of Grace and Gauger (3). ^c Method A-3, U. S. Bureau of Mines. ^d Modified method of Stanfield and Frost (14).

mole %, as a tracer for exit gas flow rate measurement. The gases were mixed during compression and stored in high-pressure cylinders at pressures up to 3000 p.s.i.g. Commercially available grades of electrolytic hydrogen (99.8% pure) and helium (99.99% pure) were used. The oil shale used in all semiflow tests was supplied by the Union Oil Co. An analysis of the oil shale is given in Table I.

Procedure. The semiflow experimental technique employed in the majority of the tests followed closely that employed in coal hydrogenolysis studies described recently (2, 9).

Most tests were of 15-minute duration or less. After the reactor was heated to the desired operating temperature, the unit was pressurized and gas flow was started. Heat inputs were then adjusted until all recorded reactor temperatures remained constant. When flow rates, temperatures, and pressures had been stabilized completely, the feed gas was sampled. Tests were initiated by opening the quick-opening ball valve connecting the hopper and the reactor. The vibrator mounted on the hopper was started only a few seconds before the start of the run to avoid compacting the oil shale charge.

The feed gas orifice calibration was checked before each run with a wet-test meter. Exit gases were also metered with the wet-test meter during each test, as a check on flow rates calculated using the helium tracer. Exit gas flow rates were calculated as follows:

$$\text{Exit gas flow rate} = \left[\frac{\% \text{ He in feed gas}}{\% \text{ He in exit gas}} \right] [\text{feed gas flow rate}] \left[\frac{100 - \% \text{ He in exit gas}}{100} \right]$$

All gas flow volumes are reported on a helium-free, saturated gas volume basis, in standard cubic feet (SCF) at 60° F. and 30.00 inches of Hg. The exit gas specific gravity record was used as an aid in selecting times for exit gas sampling; in tests conducted to simulate continuous operation, it was also used to check the length of the oil shale feeding period, since it was not always possible to obtain positive proof of the initiation

of solids feeding. Gas analyses were performed by mass spectrometer. Except for the last three tests conducted in the series to simulate continuous operation, combined values for nitrogen plus carbon monoxide are reported, because of the inability to distinguish precisely between these two gases by the mass spectrometer. In the last three tests, carbon monoxide was also determined by infrared spectrophotometer and nitrogen was obtained by difference.

In the first series of tests, single charges of oil shale weighing from 10 to 200 grams were fed. These charges were allowed to fall freely from the hopper, which resulted in a charging rate of about 7 grams per second. Small amounts of high-purity alumina inerts, up to 4 inches in depth, were placed in the reactor before the run to support the shale charge and to position it in the center of the third reactor heating zone. Temperatures were recorded for thermocouples located at the center of the oil shale charge and at a point 6 inches above the charge to show whether the feed hydrogen was being preheated completely before reaching the charge. In this test series, as well as in the second test series, the specific rate of formation of carbon in the form of gaseous aliphatic hydrocarbons was calculated from the exit gas flow rate, the exit gas composition, and the weight of organic carbon fed. Organic carbon conversions to gaseous aliphatic hydrocarbons up to a given time were obtained by graphically integrating, from zero time, a plot of specific rate vs. time. In tests where insufficient liquid hydrocarbons were collected for analysis, carbon contents of these liquids were assumed to be 85 weight %, a typical value for liquids analyzed in these tests.

Since the void volume in the bed of inerts was small, exit gas holdup times in the system downstream of the reaction zone were small. At typical operating conditions of 1300° F., 1000 p.s.i.g., and 100 standard cu. feet per hour feed hydrogen flow rate, the total exit gas holdup time was only about 10 seconds, based on the appearance of the first hydrogasification products in the exit gas sample. Gas residence times in the reactor proper at these conditions were less than 5 seconds. During the initial period of high rate of hydrogasification, gas samples were taken at intervals as short as 5 seconds and thereafter at time intervals sufficiently small to delineate the entire course of the reaction. The last gas sample was usually taken

Table II. Typical Data of Exploratory Tests at 1300° F. and 1000 P.S.I.G.

Time of sampling, sec.	Shale sample weight, 25 grams										
	10	20	30	35	40	50	60	80	120	240	480
Temperature, °F.	1304	1280	1272	1271	1272	1272	1293	1280	1297	1300	1310
Feed hydrogen rate, SCF/hr	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0
Exit gas rate, SCF/hr.	98.5	99.2	98.8	97.3	96.6	97.3	96.6	95.5	95.2	96.3	98.1
Exit gas composition, mole %											
H ₂ S	0.01	...	0.01	0.01	0.01
N ₂ + CO	0.05	0.51	0.67	0.71	0.70	0.69	0.79	0.79	0.65	0.34	0.04
CO ₂	...	0.97	0.81	0.69	0.60	0.47	0.36	0.20	0.06	0.02	0.01
H ₂	99.93	86.10	82.03	85.13	88.88	95.56	97.76	98.09	98.36	99.06	99.90
CH ₄	0.01	6.29	8.53	7.07	5.14	1.79	0.74	0.68	0.80	0.52	0.03
C ₂ H ₆	...	3.66	5.30	4.42	3.26	0.96	0.18	0.07	0.04	0.02	0.01
C ₃ H ₈	...	1.54	1.69	1.35	0.96	0.33	0.05	0.02
Higher paraffins	...	0.25	0.25	0.19	0.13	0.06	0.02	0.02	0.02
C ₂ H ₄	...	0.25	0.29	0.15	0.10	0.01	...
C ₃ H ₆	...	0.23	0.24	0.16	0.09
C ₄ H ₈	...	0.08
Higher mono-olefins	0.01	0.04	0.04	0.03	0.03	0.02	0.02	0.03	0.02	0.01	0.01
Diolefins	...	0.03
Acetylene	...	0.02	0.02	0.02	0.02	0.02
Benzene	...	0.03	0.09	0.06	0.07	0.07	0.05	0.04	0.01
Toluene	0.02	...	0.01	0.01	0.01	0.03	0.02	0.01	...
Higher aromatics	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	...
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Rate of formation of gaseous hydrocarbon carbon, lb./lb. organic carbon fed/hr.	0.26	68.2	86.1	68.9	49.6	16.3	4.62	3.64	3.50	2.03	0.38
Conversion of organic carbon in feed, %											
To gaseous hydrocarbons	0	5.8	29.9	40.7	48.9	57.8	60.3	62.4	65.7	74.3	82.0
To oil	10.2
To solid residue	4.5
Total	96.7

at 480 seconds, at which time its methane content was less than 0.1 mole %.

The second series of tests was conducted with larger amounts of alumina inerts below the oil shale bed to provide sufficient residence time for the primary reaction products to undergo further hydrogasification after leaving the reaction zone. Sufficient alumina inerts, to simulate spent shale, were placed in the reactor prior to each test to give a total bed volume (oil shale plus inerts) of 0.02 cu. foot. Since gas flow rates were varied from 10 to 200 SCF per hour, the feed hydrogen space velocity varied from 500 to 10,000 SCF per cu. foot bed-hour, and exit gas holdup times ranged from about 200 to about 10 seconds, respectively. Temperatures of the center of the inerts and of the bottom of the oil shale charge were recorded. Here, as in earlier tests, gas samples were taken at those time intervals required to delineate the entire course of the reaction.

In the third series of tests, continuous operation was simulated by semicontinuous feeding of oil shale. In the first few tests, oil shale was fed by opening the ball valve, connecting the reactor and feed hopper, every 15 or 20 seconds for 1 second and for total charging times of from 465 to 840 seconds. In later tests, conducted with a rotating drum-type feeder, oil shale feed rates were about 5.5 pounds per hour. Approximately 0.01 cu. foot of alumina inerts was placed in the reactor prior to each of these tests to minimize changes in feed hydrogen space velocity accompanying bed volume changes, and to provide a zone simulating a bed of spent oil shale wherein primary reaction products could further react. This resulted in a total bed volume (oil shale plus inerts) which increased to a final value averaging about 0.02 cu. foot. Since, in these tests, the inlet hydrogen-to-oil shale ratio was varied by varying gas flow rates, the exit gas holdup times also varied. Temperatures of the bottom of the oil shale bed, of the bottom of the inerts, and of the center of the final oil shale bed were recorded. Gas samples were taken during and after the feeding period. The instantaneous fraction of organic carbon in the shale feed converted to gaseous aliphatic hydrocarbons was calculated from the exit gas rate, the exit gas composition, and the shale feed rate. The conversion of organic carbon to gaseous aliphatic hydrocarbons for the entire test was obtained by first graphically integrating from zero time a plot of rate of formation of gaseous aliphatic hydrocarbons *vs.* time, and then dividing the value thus obtained by the total organic carbon fed.

Exploratory Tests. Exploratory tests to select the proper combinations of oil shale sample weights and feed hydrogen flow rates were made at 1300° F. and 1000 p.s.i.g. Typical test data are shown in Table II.

To approach isothermal as well as differential reactor conditions, it was necessary to use the smallest oil shale sample weights for a given feed gas flow rate which still permitted accurate product analysis. However, it was also necessary to maintain a sufficient sample size so that representative samples of the highly heterogeneous feed could be prepared by riffing of larger batches. In this work the minimum sample size used was 10 grams.

Feed gas flow rates were set as high as possible to keep the residence time of the reaction products in the exit gas system small, so as to minimize secondary vapor phase reactions. This also minimized backmixing of reaction products in the exit gas system and oil shale particle heatup times. A feed hydrogen flow rate of 100 SCF per hour was calculated to be the minimum gas flow rate which could be used in the differential reactor of the first series of experiments, assuming complete mixing in the exit gas system, without distorting the true relationship between reaction rate and time.

With 50- and 25-gram samples, the maximum exit gas hydrocarbon concentration was too high at this hydrogen feed rate, and temperatures changed too greatly to allow the assumption of differential and isothermal reaction conditions. In tests with 10-gram samples, exit gas hydrocarbon concentrations and reaction zone temperature changes approached practical limiting values. With such small samples, however, quantitative recovery of liquids was not possible.

The observed rates of conversion may have been largely a function of heat transfer. The lack of accurate thermophysical data for oil shales makes calculation of particle temperatures difficult. However, heat transfer calculations indicated that the -8, +20 U.S.S. size oil shale particles would be preheated to at least 1100° F. in falling from the hopper through the top two reactor heating zones.

As shown in Figure 2, there were large increases in the specific rate with decreases in sample weight. Therefore, to obtain differential rates of reaction, it was necessary to prepare a cross plot of reaction rates *vs.* sample weight at selected

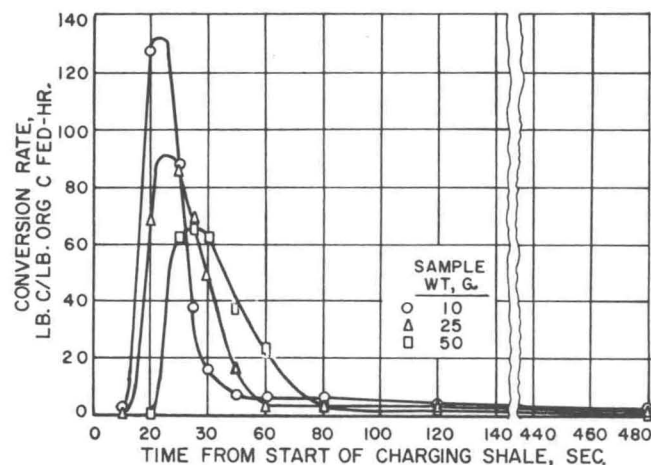


Figure 2. Effects of sample weight and time on rate of conversion of organic carbon in oil shale to gaseous aliphatic hydrocarbons

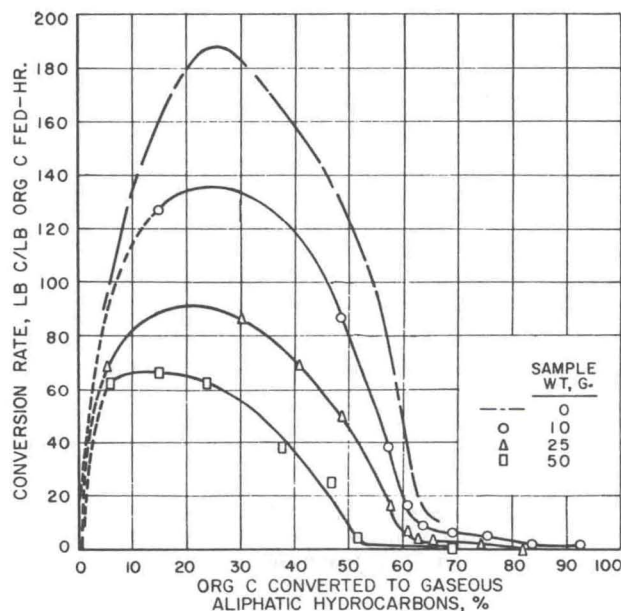


Figure 3. Effects of oil shale sample weight and organic carbon converted to gaseous aliphatic hydrocarbons on conversion rate

levels of organic carbon gasification. By plotting on semi-logarithmic coordinates (logarithm of reaction rate *vs.* sample weight) a family of curves was obtained for the parameter, per cent conversion. These curves approached straight lines as sample weights approached zero, so that reasonably good rate values for zero sample weight could be obtained by linear extrapolation. Reaction rates obtained by this cross-plotting technique are shown in Figure 3, as a function of conversion.

Table III. Typical Test Data on Mechanism of Oil Shale Hydrogasification

	Shale sample weight, 10 grams										
Time of sampling, sec.	10	20	30	35	40	50	60	80	120	240	480
Temperature, ° F.	1297	1291	1290	1290	1290	1290	1290	1291	1293	1296	1303
Feed hydrogen rate, SCF/hr.	98.8	98.8	98.8	98.8	98.8	98.8	98.8	98.8	98.8	98.8	98.8
Exit gas rate, SCF/hr.	99.9	97.6	96.9	96.1	99.1	100.7	97.6	96.9	98.4	99.9	100.7
Exit gas composition, mole %											
H ₂ S
N ₂ + CO	0.30	0.68	0.68	0.73	0.78	0.78	0.74	0.70	0.63	0.30	0.24
CO ₂	...	0.54	0.45	0.35	0.21	0.13	0.05	0.06
H ₂	99.68	89.37	92.16	95.87	97.63	98.41	98.59	98.59	98.86	99.59	99.66
CH ₄	0.01	4.72	3.43	1.62	0.80	0.47	0.48	0.51	0.45	0.07	...
C ₂ H ₆	...	2.85	2.17	0.94	0.36	0.09	0.05	0.03	0.02	0.01	0.02
C ₃ H ₈	...	1.25	0.77	0.33	0.08
Higher paraffins	...	0.20	0.10	0.04	0.03	0.03	0.02	0.01	0.01
C ₂ H ₄	...	0.12	0.04
C ₃ H ₆	...	0.16	0.08	0.02
C ₄ H ₈	...	0.03
Higher mono-olefins	0.01	0.03	0.03	0.02	0.02	0.02	0.02	0.03	0.01	0.01	0.02
Diolefins
Acetylene	...	0.03	0.02	0.02	0.01
Benzene	...	0.02	0.05	0.05	0.04	0.02	0.01	0.01
Toluene	0.01	0.01	0.02	0.02	0.02	0.03	0.01	...	0.01
Higher aromatics	0.01	...	0.02	0.03	0.02	0.03	0.02	0.02	0.04
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Rate of formation of gaseous hydrocarbon, lb./lb. organic carbon fed/hr.	0.64	127.2	86.7	38.2	16.6	7.61	6.35	6.46	4.48	1.30	1.39
Conversion of organic carbon in feed, %											
To gaseous hydrocarbons	0	14.8	48.7	57.4	60.7	63.7	65.6	69.2	75.5	83.7	92.3
To oil	ND
To solid residue	0.4
Total	92.7

Results

Mechanism of Oil Shale Hydrogasification. A series of tests was conducted at 1100°, 1200°, 1300°, and 1400° F. to measure the effect of temperature and conversion to gaseous aliphatic hydrocarbons on the rate of gasification of organic carbon (Figure 4). These results show a large increase in rate with increases in temperature. Typical test data are given in Table III. The effects of increases in temperature and hydrogen flow rate on gaseous and total product distribution are shown in Figures 5 and 6. The gaseous aliphatic hydrocarbon yields and the percentage of paraffins increased with increases in temperature and decreased with increases in feed hydrogen flow rate. The variation of liquid yields was the opposite of gas yields. These results indicate that the major steps in the hydrogenolysis of kerogen are:

Kerogen decomposition with initial formation of intermediates at least partially recoverable as liquids at very short residence times and/or low temperatures.

Pyrolysis, hydrogenation, and hydrogenolysis reactions leading to gaseous aliphatic hydrocarbons of decreasing molecular weight and, finally, ethane and methane, along with some aromatic liquids.

The gaseous molecular hydrogen consumption is compared with the elemental gaseous hydrogen balance in Figure 7. At low levels of organic carbon conversion to gaseous aliphatic hydrocarbons, the amount of hydrogen donated by the oil shale is approximately equal to the amount of feed hydrogen consumed. Thus, pyrolysis and hydrogenation reactions probably occur simultaneously. At high conversion levels, accurate measurement was not possible.

Rates of carbonate decomposition were also measured, although separate infrared spectrophotometer analyses were not performed for carbon monoxide. Mass spectrometer analyses indicated, however, that nitrogen was negligible in

comparison to carbon oxides. The strong increase in decomposition rate with increase in temperature is shown graphically in Figure 8. These rates are much higher than those measured by Jukkola and others (4) in nitrogen or carbon dioxide at 1 atm. This may be due to the more rapid oil shale heatup and the lower concentration of carbon dioxide in these tests. The large increase in decomposition rate between 1200° and 1300° F. is probably due to the combined decom-

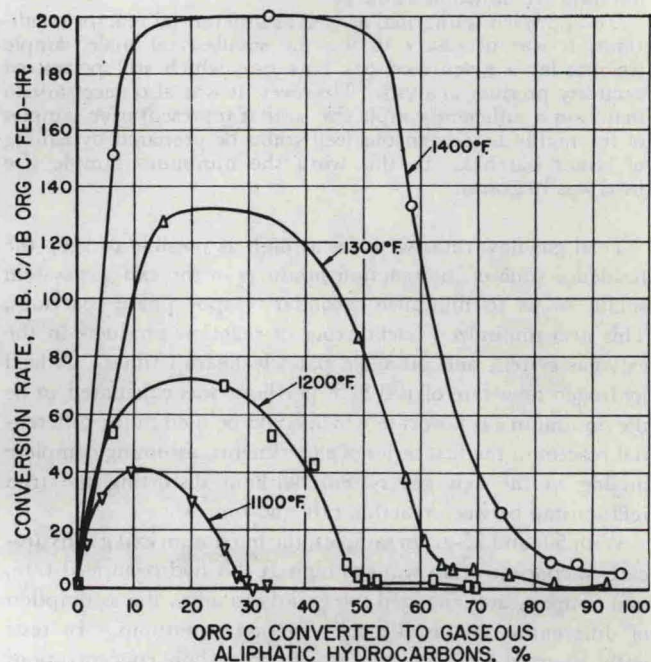


Figure 4. Effects of temperature and organic carbon conversion to gaseous aliphatic hydrocarbons on conversion rate

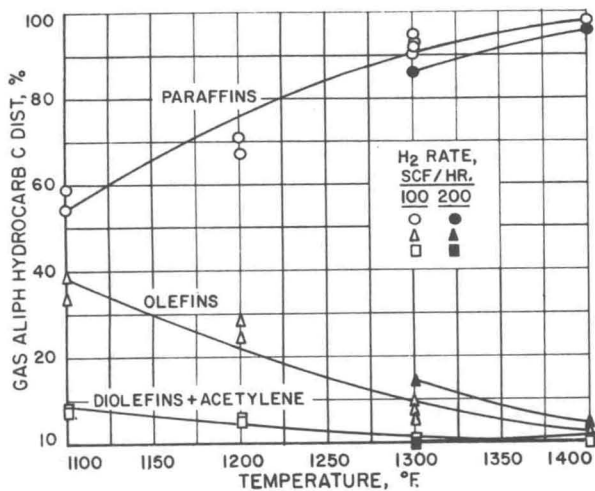


Figure 5. Effects of temperature and feed hydrogen flow rate on average gaseous aliphatic hydrocarbon distribution during first minute of gasification

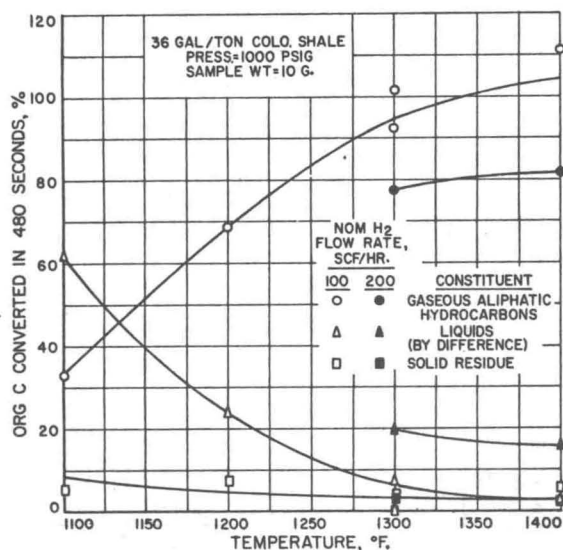


Figure 6. Effects of temperature and feed hydrogen flow rate on conversion of organic carbon to gaseous aliphatic hydrocarbons, liquids, and solid residue

position of both magnesium carbonate and calcium carbonate above 1200° F. Jukkola and others (4) found that calcite in oil shale begins to dissociate at 1150° to 1250° F. Since the molar ratio of calcium carbonate to magnesium carbonate is 2.3 in this oil shale, any rate difference in a transition from a region where only magnesium carbonate decomposes at a measurable rate to one where both carbonates decompose measurably fast would be accentuated. It would be desirable to minimize mineral carbonate decomposition in large-scale processing, since the decomposition reactions are endothermic and part of the feed hydrogen is consumed by reaction with part of the carbon dioxide formed. Equilibrium carbon dioxide partial pressures for magnesium and calcium carbonate breakdown, shown in Figure 9, indicate that it might be feasible to inhibit calcium carbonate decomposition, but not magnesium carbonate decomposition, by maintaining a high carbon dioxide partial pressure.

Effect of Process Variables on Product Distribution and Gasification Rate. There were several shortcomings in the

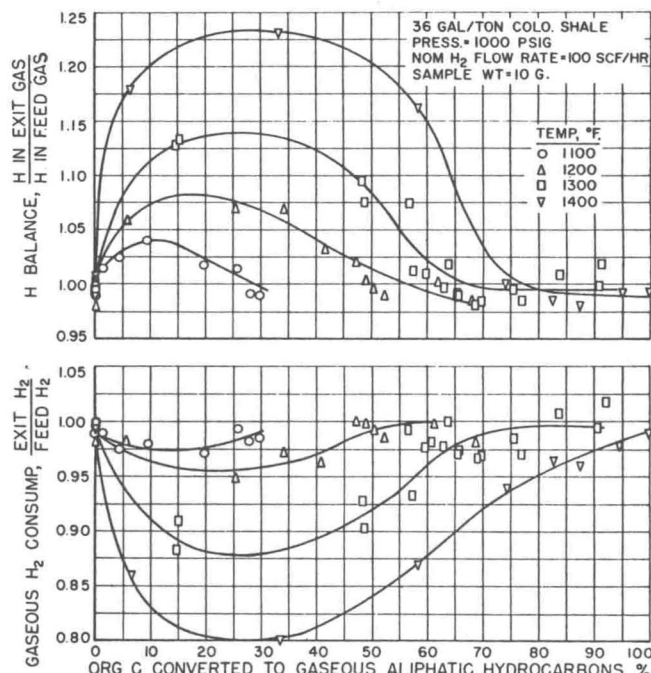


Figure 7. Gaseous hydrogen balances as a function of temperature and organic carbon conversion

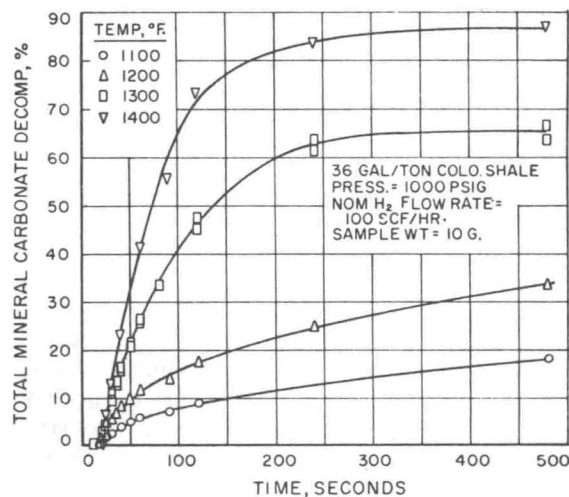


Figure 8. Effects of temperature and time on mineral carbonate decomposition

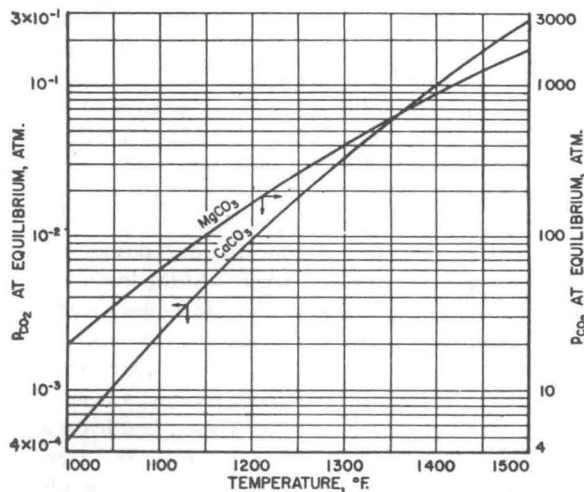


Figure 9. Effect of temperature on equilibrium carbon dioxide partial pressures for magnesium carbonate and calcium carbonate decomposition

Table IV. Typical Test Data on Effect of Process Variables on Product Distribution and Gasification Rate

	Shale sample weight, 50 grams.			Total bed volume, 0.02 cu. foot.			Shale-inerts volume ratio, 0.0974.					
	60	70	80	100	120	140	160	180	240	360	480	720
Time of sampling, sec.	60	70	80	100	120	140	160	180	240	360	480	720
Temp. at bottom of shale, °F.	1215	1223	1227	1236	1243	1254	1259	1266	1270	1282	1290	1294
Temp. at center of inerts, °F.	1253	1256	1258	1262	1267	1271	1274	1277	1280	1287	1291	1294
Feed hydrogen rate, SCF/hr.	100.1	102.5	104.9	105.0	104.5	102.8	100.7	99.1	98.8	98.9	99.0	99.2
Feed hydrogen space velocity, SCF/cu. ft.-hr.	5000	5130	5250	5250	5230	5140	5040	4950	4940	4950	4950	4960
Exit gas rate, SCF/hr.	104.3	107.6	110.8	110.9	111.1	108.6	105.7	105.3	103.7	103.1	105.3	104.0
Exit gas composition												
H ₂ S + C ₄ H ₄ S	...	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.01
N ₂ + CO	0.78	0.69	0.70	0.80	0.86	0.88	0.87	0.80	0.66	0.38	0.17	0.12
CO ₂	0.52	0.47	0.43	0.37	0.33	0.23	0.02	0.13	0.06	0.02	0.01	...
H ₂	82.38	84.68	87.72	94.33	97.27	97.80	98.04	98.03	98.15	98.69	99.25	99.76
CH ₄	10.01	8.87	7.00	2.82	1.06	0.78	0.85	0.84	0.92	0.85	0.54	0.06
C ₂ H ₆	5.99	5.03	3.76	1.35	0.26	0.06	0.09	0.04	0.04	0.03	0.02	0.01
C ₃ H ₈	0.21	0.10	0.08	0.03	0.01
Higher paraffins	...	0.01	0.02
C ₂ H ₄	0.03	0.02	0.02	0.01
Higher mono-olefins
Acetylene
Benzene	0.10	0.12	0.28	0.19	0.14	0.16	0.09	0.11	0.11	0.01	0.01	0.01
Toluene	0.01	0.01	0.01	0.03	0.02	0.03	0.01	0.02	0.03	0.01	...	0.01
Ethylbenzene	...	0.01	0.01	0.03	0.02	0.02	0.01	0.02	0.02	0.01	...	0.01
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Rate of formation of gaseous hydrocarbon carbon, lb./lb. organic carbon fed/hr.	38.4	33.7	26.6	10.2	2.98	1.66	1.80	1.58	1.69	1.53	0.99	0.34
Conversion of organic carbon in feed, %												
To gaseous hydrocarbons	29.4	39.6	47.9	58.2	61.5	62.8	63.8	64.7	67.4	72.8	77.1	81.6
To oil	19.0
To solid residue	4.3
Total	104.9

above tests. First, product residence times were short and liquid and olefinic gaseous hydrocarbons were major products. Second, product residence times in the reactor could not be practically controlled, since they were a function of many other variables—e.g., temperature, pressure, flow rate, and oil shale sample size. For process design purposes, it is necessary to show the effects of variables under conditions where gaseous paraffins are the primary products.

Therefore, the test program was supplemented by tests using a bed of inerts downstream from the oil shale bed to simulate spent oil shale in a practical reactor system, which would allow further conversion of higher molecular weight hydrocarbons to gaseous paraffins. Typical test data are shown in Table IV. As can be seen in Figure 10, the above objective was met in these tests. The fraction of gaseous hydrocarbon carbon appearing as methane plus ethane was about 80% or more over the entire range of space velocities employed. In addition, only about 2% or less of the gaseous hydrocarbon carbon was nonparaffinic.

The results shown in Figure 10 are consistent with the reaction sequence described earlier. At the lower feed hydrogen space velocities, the conversion to gaseous hydrocarbons was reduced by coke formation due to the lack of sufficient hydrogen. At the higher feed hydrogen space velocities, the conversion to gaseous hydrocarbons reached a nearly constant value. The slight decrease at the highest feed hydrogen space velocities was accompanied by an increase in liquids, which indicates that products residence times were insufficient for conversion of liquid intermediates to gaseous hydrocarbons. The apparent increase in the maximum rate of conversion to gaseous hydrocarbons with increases in feed hydrogen space

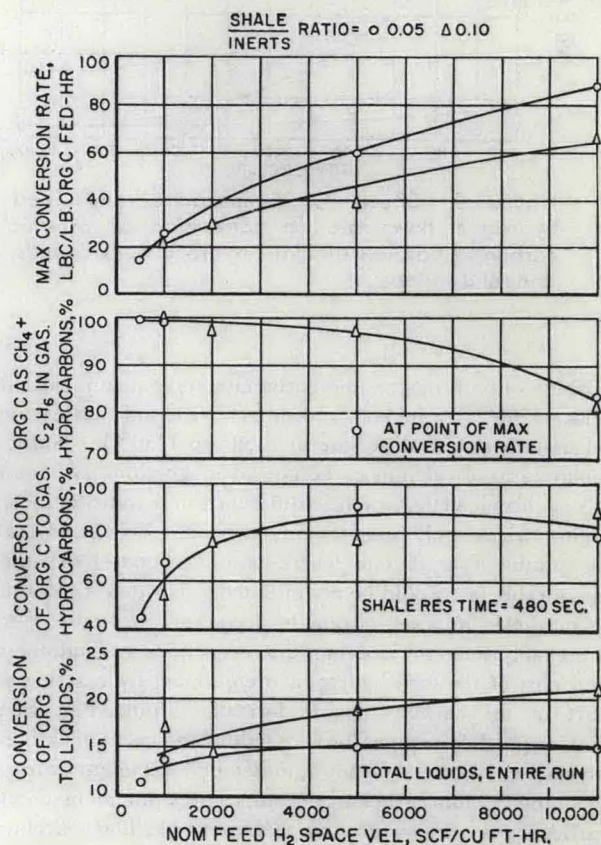


Figure 10. Effect of feed hydrogen space velocity on organic carbon converted to liquids and ethane plus methane and on maximum conversion rate

Table V. Typical Test Data on Effect of Hydrogen-Shale Ratio on Product Distribution

	Shale feed rate, 5.47 lb./hour. Hydrogen-shale ratio, 255% of stoichiometric. Total shale charging time, 510 seconds										
	30	80	150	250	350	450	550	600	660	800	1000
Time of sampling, sec.	1349	1310	1290	1308	1220	1235	1273	1280	1285	1306	1350
Temp. at final center of shale, ° F.	1350	1298	1290	1298	1246	1266	1299	1302	1310	1326	1364
Temp. at bottom of shale, ° F.	1407	1412	1420	1430	1440	1450	1458	1450	1445	1436	1435
Temp. at bottom of inerts, ° F.	88.6	88.6	88.6	88.6	88.8	89.0	89.0	89.4	89.8	90.2	90.4
Feed hydrogen rate, SCF/hr.	10,030	8880	7660	6400	5510	4840	4500	4520	4540	4560	4570
Feed hydrogen space velocity, SCF/cu. ft.-hr.	88.1	85.1	85.1	85.6	84.8	85.0	84.4	83.2	84.1	82.9	82.5
Exit gas rate, SCF/hr.	0.0088	0.0100	0.0116	0.0138	0.0161	0.0184	0.0198	0.0198	0.0198	0.0198	0.0198
Total bed volume, cu. ft.											
Exit gas composition, mole %											
N ₂	0.09	0.01	0.70	0.40	0.53	0.46	0.40	0.56	0.58	0.39	...
CO	...	1.20	1.60	2.90	3.10	3.30	3.60	3.10	2.30	1.50	1.14
CO ₂	...	0.24	0.20	0.33	0.46	0.57	0.62	0.46	0.32	0.19	0.09
H ₂	99.75	81.67	80.44	78.06	77.31	76.66	75.71	92.39	93.91	94.81	95.53
CH ₄	0.10	11.54	12.37	13.77	14.27	14.74	15.47	2.75	2.51	2.80	2.97
C ₂ H ₆	0.06	4.95	4.45	4.27	4.05	3.93	3.95	0.45	0.23	0.15	0.11
C ₂ H ₄	...	0.21	0.05	0.09	0.08	0.07	0.09	0.02	0.01
C ₃ H ₈	0.07
Acetylene	0.01	0.01
Benzene	...	0.18	0.11	0.17	0.20	0.27	0.16	0.27	0.14	0.16	0.16
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Conversion of organic carbon to hydrocarbon carbon, lb./lb. organic carbon fed	0.006	0.613	0.606	0.627	0.629	0.636	0.655	0.101	0.082	0.084	0.086
Distribution of organic carbon in products, %											
As gaseous hydrocarbons	70.9
As liquids	16.9
As solid residue	8.5
Total											96.3

velocity above 5000 SCF/cu. foot-hour was primarily the result of increased linear velocity of the rapidly formed intermediate reaction products. Backmixing effects were found to be negligible over most of the range of flow rates studied (5).

Effect of Hydrogen-Shale Ratio on Product Distribution.

In view of the important effect of the hydrogen-oil shale feed ratio on product distribution, the semiflow techniques were

modified to permit control of this variable. Initially, small batches of oil shale were fed at frequent intervals onto a fixed bed of inerts. Results still showed an apparent effect of feed ratio above 100% of the stoichiometric requirements for conversion of the organic matter to methane, which was unexpected on the basis of oil hydrogasification results (10, 12, 13). However, these tests showed the expected negligible effect of an increase in total pressure from 1000 to 2000 p.s.i.g.

Further tests at 1200° to 1400° F. and 1000 p.s.i.g. were then conducted with a continuous feeding system in which oil shale was charged at a nearly constant rate for 510 seconds, corresponding to an average oil shale residence time of about 5 minutes. Thus, the hydrogen flow rate increased linearly with hydrogen-oil shale ratio. Typical test data are shown in Table V. As shown in Figure 11, instantaneous organic carbon gasification at hydrogen-oil shale feed ratios ranging from about 100 to 250% of stoichiometric remained nearly constant and averaged 63 to 64%. Total organic carbon gasification measured during the 1000- to 1100-second run

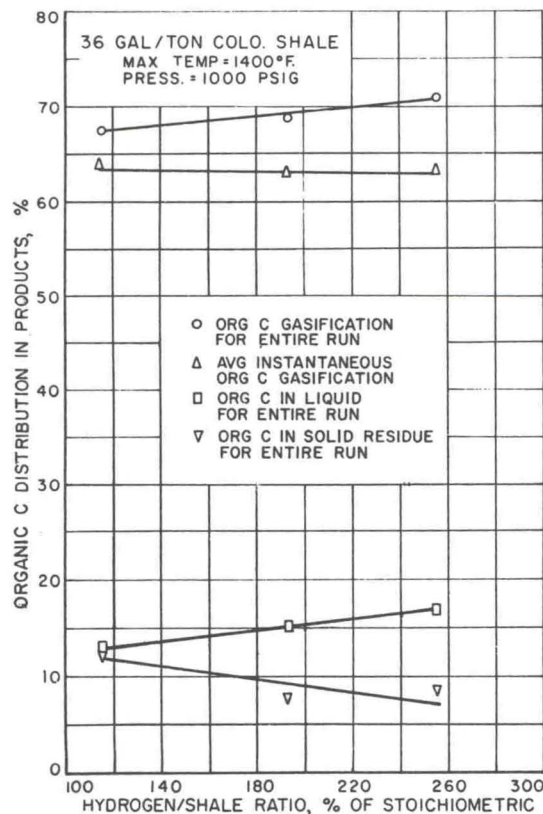


Figure 11. Effect of hydrogen-shale ratio on carbon distribution in products and average instantaneous carbon gasification

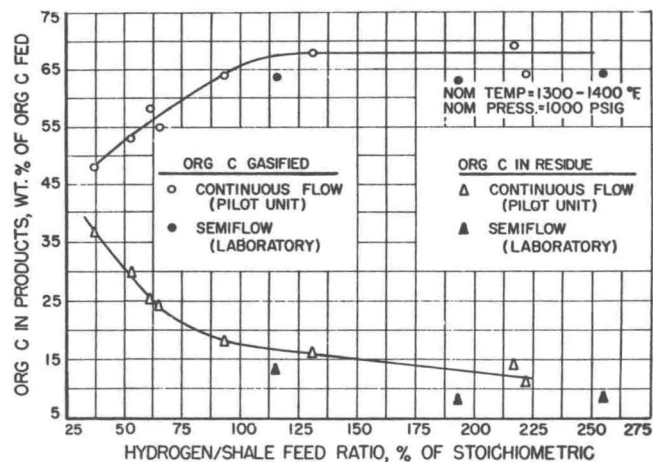


Figure 12. Comparison of laboratory and pilot plant test results

period was about 70%. The organic carbon distribution in the residue and the aromatic liquid products was about 13% each, at the lowest gas rate. The organic carbon in the residue decreased with an increase in hydrogen feed rate, as would be expected. All yield and organic carbon distribution data are uncorrected for low carbon balances (92 to 96%).

Higher conversions to gaseous hydrocarbons could, of course, be obtained by increasing oil shale residence times, although the maximum would be about 85 to 90%, since a minimum yield of aromatic liquids of 10 to 15% would be expected from previous experience in hydrogasification of petroleum hydrocarbons similar in composition to kerogen (10, 12, 13).

These test results have been verified by pilot-plant-scale tests. Although the pilot plant test program has not yet been completed, preliminary results are given in Figure 12 along with part of those shown in Figure 11. Good agreement in the two sets of data is apparent. Complete results from the pilot plant test program will be reported when the pilot plant test program is completed.

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