

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

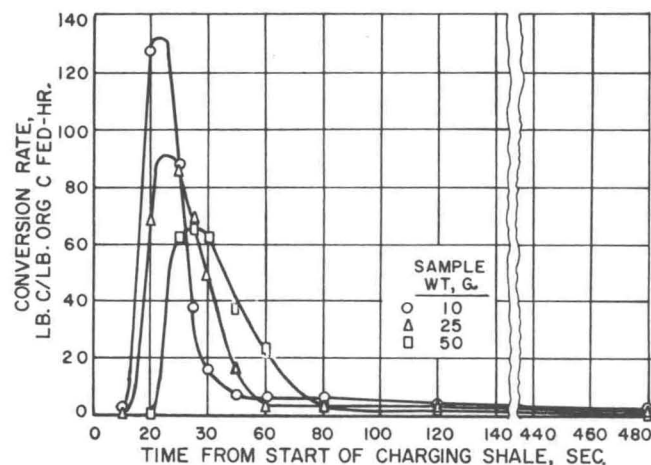


Figure 2. Effects of sample weight and time on rate of conversion of organic carbon in oil shale to gaseous aliphatic hydrocarbons

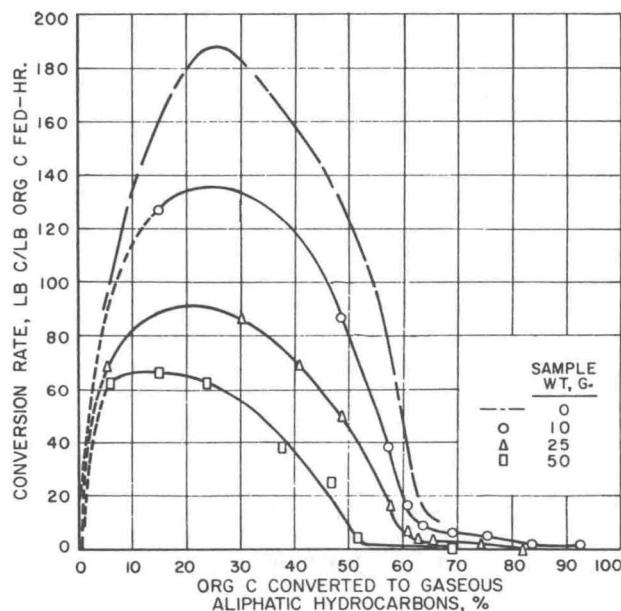


Figure 3. Effects of oil shale sample weight and organic carbon converted to gaseous aliphatic hydrocarbons on conversion rate

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 <sub>2</sub> S	...	...	...	...	...	...	...	...	...	...	...
N <sub>2</sub> + CO	0.30	0.68	0.68	0.73	0.78	0.78	0.74	0.70	0.63	0.30	0.24
CO <sub>2</sub>	...	0.54	0.45	0.35	0.21	0.13	0.05	0.06	...	...	...
H <sub>2</sub>	99.68	89.37	92.16	95.87	97.63	98.41	98.59	98.59	98.86	99.59	99.66
CH <sub>4</sub>	0.01	4.72	3.43	1.62	0.80	0.47	0.48	0.51	0.45	0.07	...
C <sub>2</sub> H <sub>6</sub>	...	2.85	2.17	0.94	0.36	0.09	0.05	0.03	0.02	0.01	0.02
C <sub>3</sub> H <sub>8</sub>	...	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 <sub>2</sub> H <sub>4</sub>	...	0.12	0.04	...	...	...	...	...	...	...	...
C <sub>3</sub> H <sub>6</sub>	...	0.16	0.08	0.02	...	...	...	...	...	...	...
C <sub>4</sub> H <sub>8</sub>	...	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-

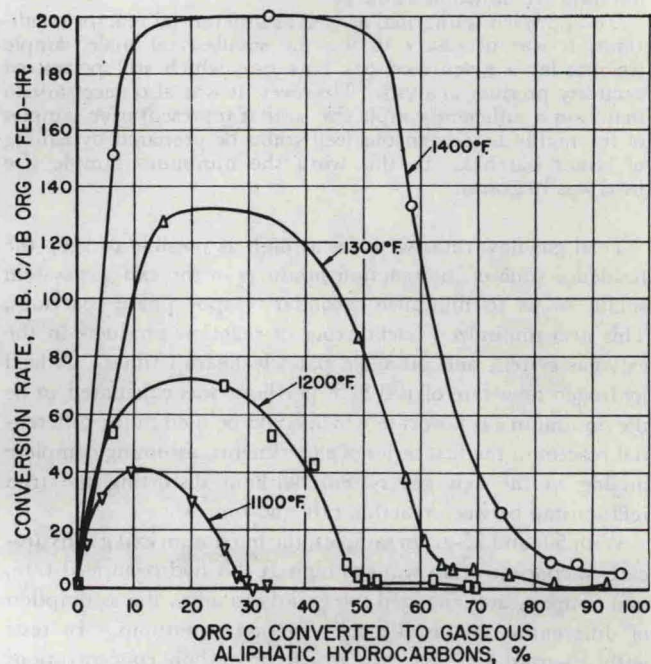


Figure 4. Effects of temperature and organic carbon conversion to gaseous aliphatic hydrocarbons on conversion rate