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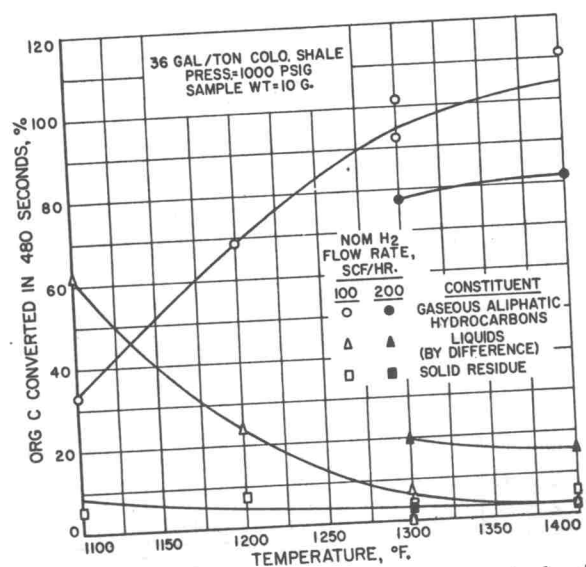

Figure 6. Effects of temperature and feed hydrogen flow rate on conversion of organic carbon to gaseous aliphatic hydrocarbons, liquids, and solid residue
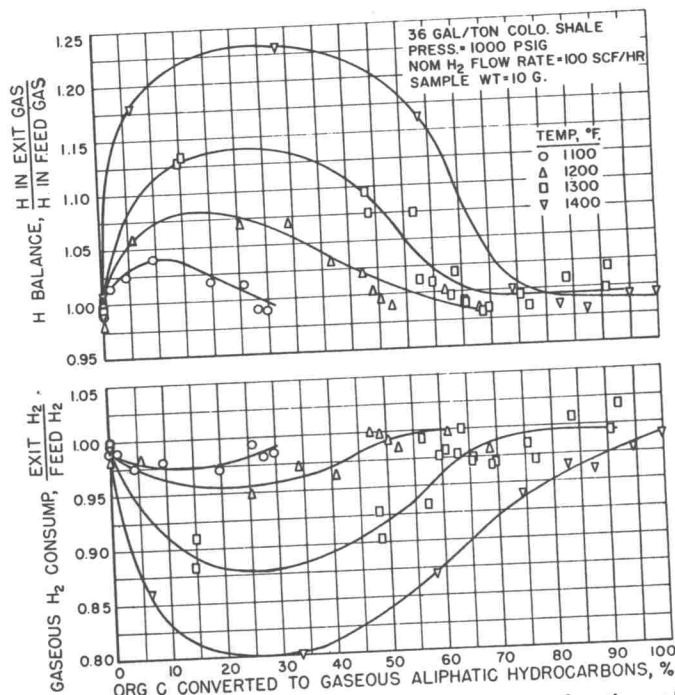

Figure 7. Gaseous hydrogen balances as a function of temperature and organic carbon conversion
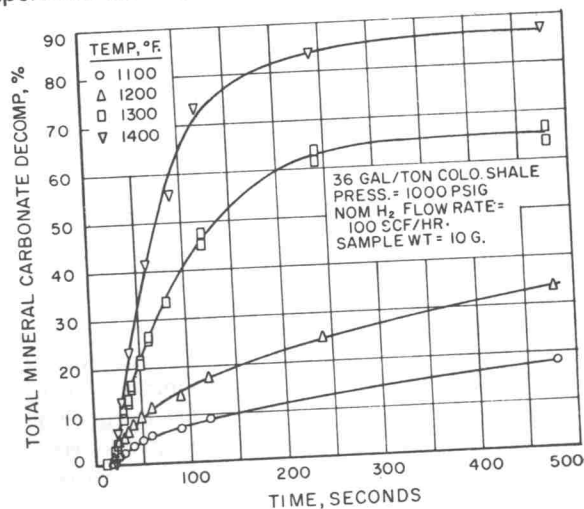
Figure 8. Effects of temperature and time on mineral carbonate decomposition
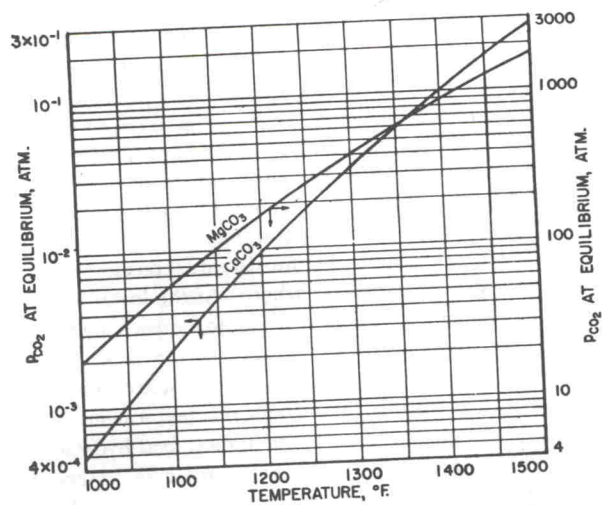
Figure 9. Effect of temperature on equilibrium carbon dioxide partial pressures for magnesium carbonate and calcium carbonate decomposition

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

Shale sample weight, 50 grams. Total bed volume, 0.02 cu. foot. Shale–inerts volume ratio, 0.0974.

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												
$H_2S + C_4H_4S$	...	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_2H_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_3H_8	0.21	0.10	0.08	0.03	0.01	...	...	...	...	...	...	...
Higher paraffins	...	...	...	...	...	...	...	...	...	...	...	...
C_2H_4	...	0.01	...	...	...	...	...	...	...	...	...	...
Higher mono-olefins	...	...	...	0.03	0.02	0.02	0.01	...	...	...	...	0.02
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	0.02	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
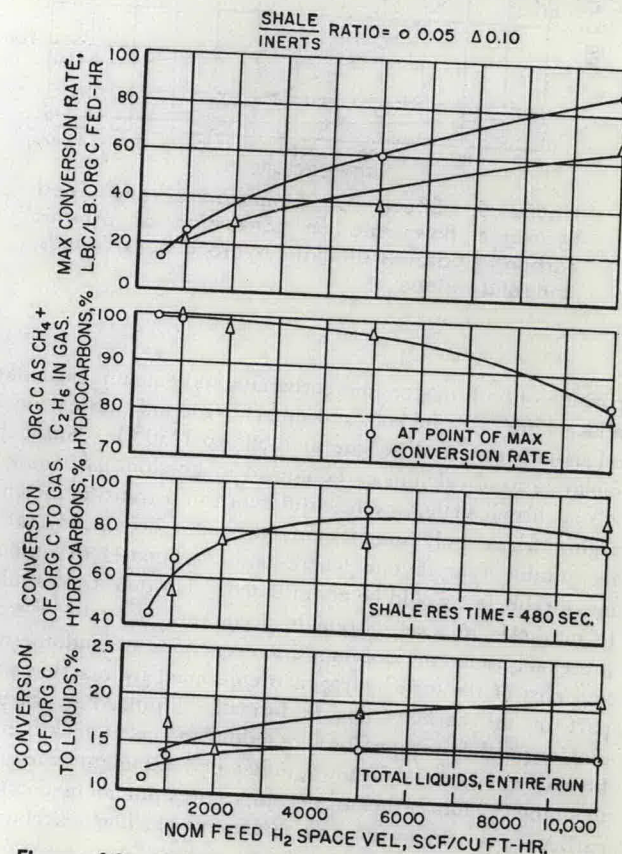

Figure 10. Effect of feed hydrogen space velocity on organic carbon converted to liquids and ethane plus methane and on maximum conversion rate