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.	30	80	150	250	350	450	550	600	660	800	1000
Temp. at final center of shale, ° F.	1349	1310	1290	1308	1220	1235	1273	1280	1285	1306	1350
Temp. at bottom of shale, ° F.	1350	1298	1290	1298	1246	1266	1299	1302	1310	1326	1364
Temp. at bottom of inerts, ° F.	1407	1412	1420	1430	1440	1450	1458	1450	1445	1445	1435
Feed hydrogen rate, SCF/hr.	88.6	88.6	88.6	88.6	88.8	89.0	89.0	89.4	89.8	90.2	90.4
Feed hydrogen space velocity, SCF/cu. ft.-hr.	10,030	8880	7660	6400	5510	4840	4500	4520	4540	4560	4570
Exit gas rate, SCF/hr.	88.1	85.1	85.1	85.6	84.8	85.0	84.4	83.2	84.1	82.9	82.5
Total bed volume, cu. ft.	0.0088	0.0100	0.0116	0.0138	0.0161	0.0184	0.0198	0.0198	0.0198	0.0198	0.0198
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_2H_6	0.06	4.95	4.45	4.27	4.05	3.93	3.95	0.45	0.23	0.15	0.11
C_2H_4	...	0.21	0.05	0.09	0.08	0.07	0.09	0.02	0.01	...	...
C_3H_6	...	...	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
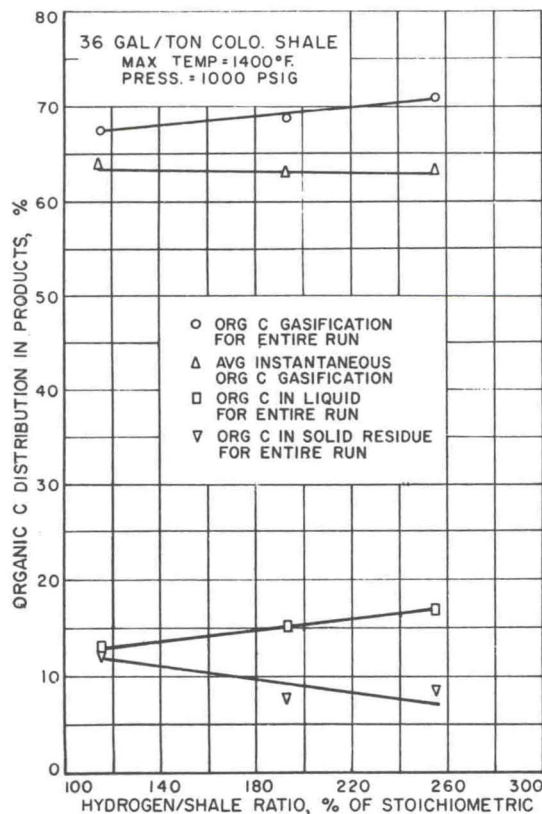

Figure 11. Effect of hydrogen-shale ratio on carbon distribution in products and average instantaneous carbon gasification
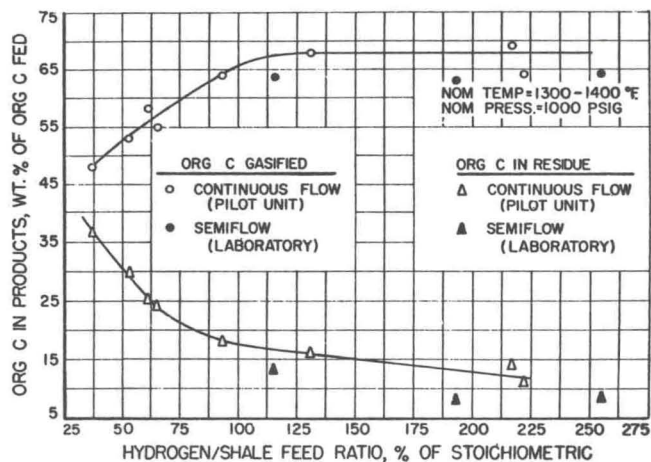

Figure 12. Comparison of laboratory and pilot plant test results

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.

Acknowledgment

Literature Cited

(1) Elliott, M. A., Linden, H. R., Shultz, E. B., Jr., U. S. Patent **2,991,164** (July 4, 1961).
(2) Feldkirchner, H. L., Linden, H. R., Division of Fuel Chemistry, 142nd Meeting, ACS, Atlantic City, N. J., September 1962.
(3) Grace, R. J., Gauger, A. W., *Ind. Eng. Chem., Anal. Ed.* **18,** 563–5 (1946).
(4) Jukkola, E. E., Denilauler, A. J., Jensen, H. B., Barnet, W. I., Murphy, W. I. R., *Ind. Eng. Chem.* **45,** 2711–14 (1953).
(5) Levenspiel, O., Bischoff, K. B., *Ibid.*, **51,** 1431–4 (1959).
(6) Linden, H. R., 48th National Meeting, American Institute of Chemical Engineers, Denver, Colo., August 1962; Preprint 14, pp. 17–52.
(7) Linden, H. R., Elliott, M. A., *Am. Gas J.* **186,** 34–8 (January 1959), 22–7 (February 1959), 39–41 (March 1959), 26–7 (April 1959), 50–6 (May 1959).
(8) Shultz, E. B., Jr., 48th National Meeting, American Institute of Chemical Engineers, Denver, Colo., August 1962; Preprint 9, pp. 44–57.
(9) Shultz, E. B., Jr., Feldkirchner, H. L., Pyrcioch, E. J., *Chem. Eng. Progr. Symp. Ser.* **57,** No. 34, 73–80 (1961).
(10) Shultz, E. B., Jr., Linden, H. R., *Ind. Eng. Chem.* **49,** 2011–16 (1957).
(11) *Ibid.*, **51,** 573–6 (1959).
(12) Shultz, E. B., Jr., Linden, H. R., Ind. Eng. Chem. Process Design Develop. **1,** 111–16 (1962).
(13) Shultz, E. B., Jr., Mechales, N., Linden, H. R., *Ind. Eng. Chem.* **52,** 580–3 (1960).
(14) Stanfield, K. E., Frost, I. C., U. S. Bur. Mines, Rept. Invest. **4477** (1949).