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.

1 FEED GAS STORAGE CYLINDERS, 3600 P.S.I.
2 PRESSURE REGULATOR
3 FEED GAS METERING VALVE
4 SHALE FEED HOPPER
5 PNEUMATICALLY OPERATED FULL-OPENING VALVE
6 PRESSURE EQUALIZATION LINE
7 REACTOR, 2-INCH ID 60-INCH IL
8 INTERCHANGEABLE FEED GAS AND PRODUCT GAS LINES FOR UPFLOW AND DOWNFLOW OPERATION
9 BACK-PRESSURE REGULATOR
10 BYPASS FOR FEED GAS ORIFICE CALIBRATION
11 GAS SATURATORS
12 PRODUCT GAS WET-TEST METER
13 SYNTRON VIBRATOR
14 RUPTURE DISK
15 RANAREX RECORDER
16 LIQUID PRODUCTS KNOCKOUT
17 GAS SAMPLE BOTTLE
18 WATER-COOLED CONDENSER
19 VARIABLE-SPEED DRIVE

PR—PRESSURE RECORDER
DPT—DIFFERENTIAL PRESSURE TRANSMITTER
DPR—DIFFERENTIAL PRESSURE RECORDER

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 105–10° 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.

Shale sample weight, 25 grams

Time of sampling, sec.	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_2S	...	...	...	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_2H_6	...	3.66	5.30	4.42	3.26	0.96	0.18	0.07	0.04	0.02	0.01
C_3H_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_2H_4	...	0.25	0.29	0.15	0.10	...	...	...	...	0.01	...
C_3H_6	...	0.23	0.24	0.16	0.09	...	...	...	...	...	...
C_4H_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