FE-2565-11
DIST. CATEGORY UC-90c

AN ANALYSIS OF COAL HYDROGASIFICATION PROCESSES

Monthly Technical Progress Report for the Period 1 January - 31 January 1978

BECHTEL CORPORATION
San Francisco, California 94119
Date Published – February 1978

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY UNDER CONTRACT NO. EF-77-A-01-2565

ABSTRACT

This monthly Technical Progress Report covers work performed during the period 1 January 1978 to 31 January 1978 for a program entitled "An Analysis of Coal Hydrogasification Processes." This program is being performed in four sequential tasks: Tasks I — Data Collection; Task II — Data Analysis; Task III — Process Modeling and Reactor Design; and Task IV — Identification of Additional Data and Recommended Experimental Programs.

During January, substantial progress was made on Tasks I, II, and III. Data from four recent Rocketdyne hydropyrolysis tests with subbituminous coal and 24 recent Rocketdyne partial liquefaction tests with bituminous coal were entered into the computerized data base. The Rocketdyne data base was expanded to include calculated values for carbon selectivity to methane, ethane, and BTX. The PERC data base was also expanded to include calculated values for gas velocity, gas residence time, and carbon selectivity to gas, methane, and ethane.

During January, the semiempirical correlation for predicting carbon conversion efficiency was fitted to the Cities Service and Rocketdyne subbituminous coal data. The analysis showed that the Cities Service bench-scale reactor and the Rocketdyne 1/4-ton/hr reactor give similar carbon conversions under comparable operating conditions. Also during January, an improved semiempirical correlation was presented for predicting overall carbon conversion. The improved correlation accounts for thermodynamic equilibrium between the coal and reaction products.

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Section 1

OBJECTIVES AND SCOPE

This report is the January 1978 Monthly Technical Progress Report for a program entitled, "An Analysis of Coal Hydrogasification Processes." The program is being performed for DOE by Bechtel Corporation under DOE Contract No. EF-77-A-01-2565. Work on this program was initiated on February 1, 1977.

The major objective of the program is "to conduct an analytical study which will investigate the operability potential and scaleup feasibility of the Cities Service, Rocketdyne, and Pittsburgh Energy Research Center (PERC) coal hydrogasification processes, relative to DOE plans for a hydrogasification process development unit (PDU)." To accomplish the objective, four sequential program tasks have been established.

The primary objective of Task I is to conduct a survey of information in the public domain relative to the above three processes. This survey is to be supplemented with visits to the process contractors for discussion, expansion, and updating.

The primary objective of Task II is to perform a detailed analysis of the data, as required to evaluate the information for a pilot plant application. Consideration will be given to reactor heat and mass balances, reaction kinetics, actual or predicted data on the product gas yield and composition, and all other relevant factors. In addition, conceptual designs, where available, will be analyzed for potential operational problems and scaling.

Task III has two primary objectives: (1) to perform reactor model studies, where available data permit, for each of the three processes; and (2) to generate a conceptual, full-scale, optimum reactor design in consultation with DOE. The reactor model study will attempt to predict, where possible, overall carbon conversion, carbon selectivity to gas, and carbon selectivity to methane and ethane for the three processes. In conjunction with the modeling study, a sensitivity analysis will be performed that will determine the influence of the degree of uncertainty of the basic information used in the prediction of reactor performance.

The primary objectives of Task IV are to: (1) identify critical data gaps and point out specific data that are missing and are required for reliable pilot plant design; (2) recommend experiments to acquire the necessary data, and estimate the number of experiments and man-hours needed to obtain these data; and (3) assess the impact on the process design phase, in case the necessary data connot be experimentally determined.

Section 2

PROGRESS SUMMARY AND OPEN ITEMS

2.1 PROGRESS SUMMARY

Figure 2-1 summarizes the program progress between February 1, 1977 (the program start date) and January 31, 1978. As shown in Figure 2-1, the contract period has been extended through April 30, 1978, to reflect contract modification A001.

During January, substantial progress was made on Tasks I, II, and III. Actual manhour expended in January were 650; budgeted manhours were 700. As can be seen in Figure 2-1, actual manhours expended and program progress are on schedule.

2.2 OPEN ITEMS

At the end of the January 1978 reporting period, there were no significant open items.

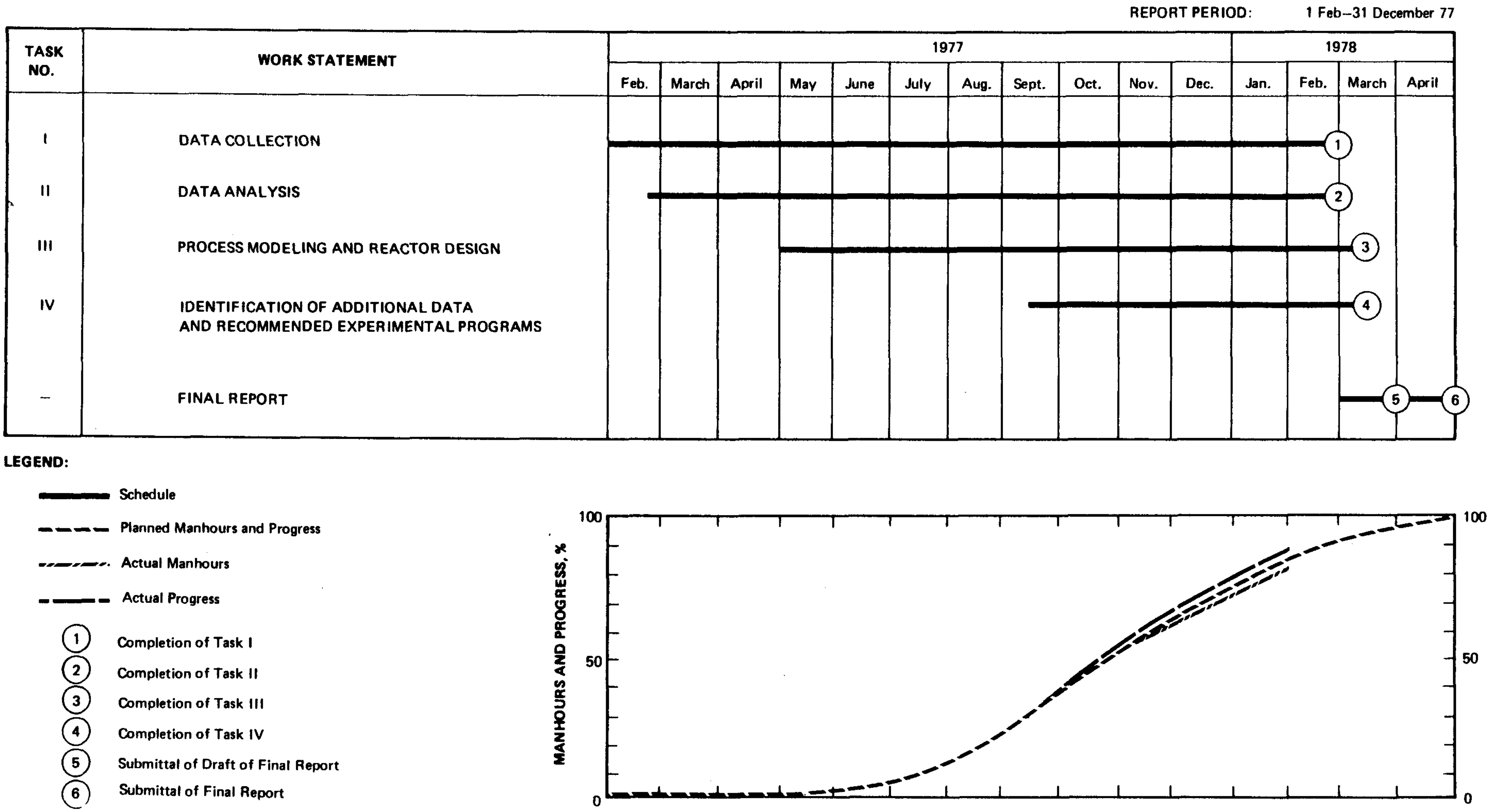

Figure 2-1. Progress and Performance Chart

Section 3

TECHNICAL PROGRESS

This section describes the technical progress for Tasks I, II, and III during the reporting period.

3.1 TASK I AND II — ROCKETDYNE DATA COLLECTION AND ANALYSIS

During this reporting period, Bechtel received additional hydropyrolysis data from Rocketdyne[1] for four recently completed tests (Runs 011-14, 15, 16, and 17) conducted in Rocketdyne's 1/4-ton/hr reactor test facility using Montana Rosebud subbituminous coal feed. A revised set of data was also received from Rocketdyne[1] for 10 earlier hydropyrolysis tests that were previously reported by Bechtel.[2]

During this reporting period, Bechtel also received additional data from Rocketdyne[3,4] for 24 coal partial liquefaction tests (Runs 16 through 42) conducted in Rocketdyne's 1-ton/hr reactor test facility using two Western Kentucky bituminous coal feeds. Analyses of these coals are given elsewhere.[3]

All the above acquired hydropyrolysis and partial liquefaction data were entered into the computerized data base. Table 3-1 gives a computer listing of all the available Rocketdyne data. The data base has been expanded during this reporting period to include data for additional operating and dependent variables. The additional variables are total reactor pressure, gas velocity, mean particle size, and carbon selectivities to methane, ethane, and BTX. Product selectivities were calculated from product gas and liquid analyses, where available, and overall carbon conversions.

Table 3-1

ROCKETDYNE HYDROPYROLYSIS DATA

RUN DESIG-NATION	DATE	COAL* TYPE	REACTOR	OVERALL FRACTION CARBON CONVERTED	CARBON SELEC-TIVITY TO GAS	CARBON SELEC-TIVITY TO METHANE	CARBON SELEC-TIVITY TO ETHANE	CARBON SELEC-TIVITY TO BTX	OUTLET GAS TEMP (DEG R)	REACTOR PRESSURE (PSIG)	HYDROGEN PARTIAL PRESSURE (PSIG)	GAS VEL-OCITY (FT/SEC)	GAS RESI-DENCE TIME (MSEC)	HYDROGEN TO COAL RATIO (LB/LB)	MEAN PARTICLE SIZE (MICRONS)
5	1/31/77	BTM-1	1 TPH	.382					1750.	1000.	940.	32.30	155.	.250	56.
6	2/ 3/77	BTM-1	1 TPH	.542	0.397			.089	2160.	1000.	930.	39.70	126.	.478	56.
7	2/ 7/77	BTM-1	1 TPH	.615	0.483			.013	2410.	1000.	920.	42.00	119.	.775	56.
8	2/17/77	BTM-1	1 TPH	.596	0.485			.089	2150.	1000.	920.	18.20	274.	.365	56.
9	2/22/77	BTM-1	1 TPH	.645	0.760			.002	2340.	1500.	1390.	12.20	410.	.365	56.
10	3/ 1/77	BTM-1	1 TPH	.609	0.782			.056	2030.	1500.	1400.	10.20	490.	.314	56.
11	3/ 4/77	BTM-1	1 TPH	.627	0.968			.027	2110.	1500.	1420.	7.90	634.	.334	56.
12	3/ 9/77	BTM-1	1 TPH	.576	0.672			.123	2140.	1000.	940.	11.80	424.	.333	56.
13	3/23/77	BTM-1	1 TPH	.560	0.334			.055	2180.	1000.	930.	79.40	63.	.292	56.
14	3/25/77	BTM-1	1 TPH	.597	0.472			.097	2230.	1500.	1400.	51.00	98.	.397	56.
15	3/29/77	BTM-1	1 TPH	.560	0.359			.066	2120.	700.	650.	111.00	45.	.403	56.
16	4/ 4/77	BTM-1	1 TPH	.573	0.412			.058	2150.	1000.	930.	72.50	69.	.443	56.
17		BTM-1	1 TPH	.592	0.434			.083	2200.	1010.	940.	78.10	64.	.507	56.
18		BTM-1	1 TPH	.519	0.343			.071	2090.	1000.	930.	74.60	67.	.409	56.
19		BTM-1	1 TPH	.562	0.256			.034	2050.	520.	480.	147.00	34.	.429	56.
20		BTM-2	1 TPH	.540	0.341			.085	2060.	1000.	930.	63.30	79.	.293	52.
21		BTM-2	1 TPH	.590	0.403			.132	2150.	1000.	930.	78.10	64.	.458	52.
22		BTM-2	1 TPH	.570	0.389			.047	2090.	500.	470.	87.70	57.	.370	52.
23		BTM-2	1 TPH	.600	0.355			.120	2100.	1000.	930.	79.40	63.	.469	36.
24		BTM-2	1 TPH	.638	0.434			.172	2230.	1000.	930.	82.00	61.	.528	36.
25		BTM-2	1 TPH	.630	0.365			.154	2380.	1000.	930.	41.30	121.	.656	36.
26	9/ 9/77	BTM-2	1 TPH	.615	0.382			.122	2180.	1000.	940.	39.10	128.	.485	36.
27	9/14/77	BTM-2	1 TPH	.571	0.366			.095	2070.	1000.	950.	37.30	134.	.472	36.
28	9/16/77	BTM-2	1 TPH	.587	0.433			.123	2230.	1000.	940.	39.70	126.	.491	52.
29	9/21/77	BTM-2	1 TPH	.576	0.477			.151	2180.	1500.	1400.	23.60	212.	.418	52.
30	9/23/77	BTM-2	1 TPH	.546	0.441			.097	2090.	1000.	940.	36.80	136.	.435	52.
31	9/27/77	BTM-2	1 TPH	.628	0.712			.135	2400.	1500.	1400.	23.90	209.	.505	52.
32	9/29/77	BTM-2	1 TPH	.622	0.441			.138	2300.	1000.	930.	39.40	127.	.452	52.
34	10/ 4/77	BTM-2	1 TPH	.479	0.378			.071	1990.	1000.	940.	75.80	66.	.414	52.
37	10/31/77	BTM-2	1 TPH	.482	0.427			.083	2030.	1000.	940.	19.60	255.	.304	52.
38	11/ 8/77	BTM-2	1 TPH	.462	0.329				1870.	1000.	950.	18.50	271.	.313	52.
39	11/ 9/77	BTM-2	1 TPH	.513	0.468			.105	2120.	1000.	940.	20.20	247.	.296	52.
40	11/10/77	BTM-2	1 TPH	.481	0.486			.098	2050.	1000.	950.	22.20	225.	.279	52.
41	11/11/77	BTM-2	1 TPH	.432	0.382			.049	1890.	1000.	950.	20.90	239.	.243	52.
42	11/14/77	BTM-2	1 TPH	.518	0.502			.139	2150.	1000.	950.	23.60	212.	.249	52.

Table 3-1 (Cont'd)

RUN DESIGNATION	DATE	COAL* TYPE	REACTOR	OVERALL FRACTION CARBON CONVERTED	CARBON SELECTIVITY TO GAS	CARBON SELECTIVITY TO METHANE	CARBON SELECTIVITY TO ETHANE	CARBON SELECTIVITY TO BTX	OUTLET GAS TEMP (DEG R)	REACTOR PRESSURE (PSIG)	HYDROGEN PARTIAL PRESSURE (PSIG)	GAS VELOCITY (FT/SEC)	GAS RESIDENCE TIME (MSEC)	HYDROGEN TO COAL RATIO (LB/LB)	MEAN PARTICLE SIZE (MICRONS)
011- 7	9/21/77	BTM-1	1/4 TPH	.473	0.421	.317	.044		2130.	1000.	950.	24.40	615.	.356	
011- 8	9/29/77	BTM-1	1/4 TPH	.535	0.583	.492	.009		2270.	1010.	950.	31.60	475.	.421	
011- 9	10/ 4/77	BTM-1	1/4 TPH	.588	0.724	.655	.002		2420.	1500.	1420.	21.60	695.	.499	
011-10	10/ 7/77	BTM-1	1/4 TPH	.588	0.707	.643	.0		2370.	1490.	1410.	21.70	690.	.506	
011- 2	8/30/77	SUBBTM	1/4 TPH	.289	0.495	.246	.118		1930.	1020.	960.	25.00	600.	.592	
011- 4	9/ 9/77	SUBBTM	1/4 TPH	.361	0.837	.640	.006		2360.	990.	930.	28.00	535.	.512	
011- 5	9/15/77	SUBBTM	1/4 TPH	.364	0.629	.451	.036		2190.	1000.	940.	26.10	575.	.401	
011-11	10/14/77	SUBBTM	1/4 TPH	.436	0.991	.819	.002		2300.	1500.	1410.	22.10	680.	.569	
011-12	10/18/77	SUBBTM	1/4 TPH	.392	0.714	.423	.140		2050.	1500.	1430.	18.60	805.	.559	
011-13	10/21/77	SUBBTM	1/4 TPH	.321	0.692	.330	.206		1930.	1500.	1440.	19.10	785.	.535	
011-14	10/28/77	SUBBTM	1/4 TPH	.278					2020.	1010.	790.	28.47	527.	.418	
011-15	11/ 2/77	SUBBTM	1/4 TPH	.298					2170.	1130.	840.	22.69	661.	.331	
011-16	11/21/77	SUBBTM	1/4 TPH	.470	1.000	.872	.0		2220.	1480.	1390.	10.60	1420.	.550	
011-17	11/28/77	SUBBTM	1/4 TPH	.407	0.860	.627	.081		1990.	1500.	1430.	8.70	1725.	.576	

* BTM-1 is Kentucky bituminous HvAb coal from the Colonial Mine of the Pittsburgh and Midway Mining Co.

BTM-2 is Kentucky bituminous HvAb coal from the Hamilton No. 2 Mine of the Island Creek Coal Co.

The additional partial liquefaction bituminous tests shown in Table 3-1 were conducted at reactor pressures of 500 to 1,000 psig, outlet gas temperatures of approximately 1,410°F to 1,940°F (1,870°R to 2,400°R), and gas (or particle) residence times of approximately 45 to 275 milliseconds. Results indicate a maximum carbon conversion to gas of 45 percent (selectivity of 71 percent) at a hydrogen partial pressure of 1,400 psig, nominal gas temperature of 1,940°F, and gas residence time of approximately 200 milliseconds. Lower temperatures and/or residence times decrease the carbon conversion to gas. Maximum carbon conversion to BTX of about 10 percent (selectivity of 17 percent) was obtained at a hydrogen partial pressure of 930 psig, nominal gas temperature of 1,770°F, and gas residence time of about 60 milliseconds.

The recent hydrogasification data were generated in two entrained downflow reactors; one is 1.88 inches I.D. by 15 feet long (Runs 011-14 and 15) and the other is 2.83 inches I.D. by 15 feet long (Runs 011-16 and 17). These data were obtained at reactor pressures of 1,000 to 1,500 psig, outlet gas temperatures of 1,530°F to 1,760°F (1,990°R to 2,220°R), and gas (or particle) residence times of approximately 530 to 1,730 milliseconds. Overall carbon conversion for these tests ranged from 28 to 47 percent, and carbon selectivities to methane and ethane ranged from 63 to 87 percent and zero to 8 percent, respectively. (Product gas analyses were not reported for Runs 011-14 and 15.)

Methane was mixed with the hydrogen gas stream fed to the reactor in Runs 011-14 and 011-15 to simulate the recycle of raw product gases. Since the measured reactant flow rates and product gas analyses for the two runs were inconsistent with C, H, and O material balances,[1] the results obtained from these two tests are uncertain. Significant fluctuations in reactant flows, particularly in Run 011-14, remains essentially unexplained.

Insufficent information was available to calculate carbon selectivity to BTX for the four recent hydropyrolysis tests and 10 earlier hydropyrolysis tests given in Table 3-1.

3.2 TASK I AND II — PERC DATA COLLECTION AND ANALYSIS

In an earlier report,[5] Bechtel presented and analyzed the data from 42 hydropyrolysis tests conducted at the Pittsburgh Energy Research Center (PERC) in a free-fall, dilute-phase (FDP) reactor using bituminous and lignite coal feeds. During this February 1978 reporting period, the PERC computerized data base was expanded to include additional operating and dependent variables for the above 42 tests.

Table 3-2 gives an updated computer listing of the available PERC data. This listing presents additional data for carbon selectivities to gas, methane, and ethane; gas velocity; gas residence time; and mean particle size. Carbon selectivities to gaseous products were computed from PERC-reported product gas analyses and overall carbon conversion;[6,7] gas velocity was computed using the average of the reported inlet and outlet gas flow rates and the reactor cross-sectional area; and gas residence time was computed using the reactor heated length and the gas velocity.

Insufficient data were available to calculate carbon conversions and selectivities to liquid products. Particle residence time data were also unavailable.

Table 3-2

PITTSBURGH ENERGY RESEARCH CENTER
HYDROPYROLYSIS DATA

RUN DESIGNATION	DATE	COAL TYPE	OVERALL FRACTION CARBON CONVERTED BASED ON GAS ANALYSIS	OVERALL FRACTION CARBON CONVERTED BASED ON CHAR ANALYSIS	CARBON SELECTIVITY TO GAS	CARBON SELECTIVITY TO METHANE	CARBON SELECTIVITY TO ETHANE	REACTOR WALL TEMP (DEG R)	REACTOR PRESSURE (PSIG)	MEAN HYDROGEN PARTIAL PRESSURE (PSIG)	GAS VELOCITY (FT/SEC)	GAS RESIDENCE TIME (SEC)	HYDROGEN TO COAL RATIO (LB/LB)
IHR-178	1974	BTM-1	.135	.281	0.473	0.420	0.025	1930.	1000.	853.	.0401	124.7	.0718
IHR-167	1974	BTM-1	.141	.250	0.556	0.488	0.040	1930.	1000.	368.	.0420	119.1	.0298
IHR-156	1974	BTM-1	.168	.250	0.660	0.556	0.020	2020.	1000.	340.	.0447	111.9	.0320
IHR-176	1974	BTM-1	.173	.240	0.700	0.617	0.008	2020.	1000.	339.	.0448	111.5	.0319
IHR-190	1974	BTM-1	.182	.220	0.809	0.723	0.009	2020.	1000.	347.	.0475	105.2	.0333
IHR-183	1974	BTM-1	.189	.362	0.517	0.470	0.0	2020.	1000.	454.	.0412	121.3	.1051
IHR-177	1974	BTM-1	.240	.308	0.773	0.724	0.006	2020.	1000.	737.	.0416	120.1	.0701
IHR-166	1974	BTM-1	.162	.256	0.625	0.563	0.004	2020.	1200.	411.	.0368	135.8	.0321
IHR-165	1974	BTM-1	.180	.242	0.744	0.682	0.004	2020.	1500.	516.	.0300	166.5	.0335
IHR-157	1974	BTM-1	.208	.300	0.737	0.663	0.003	2020.	2000.	627.	.0232	215.3	.0329
IHR-172	1974	BTM-1	.185	.280	0.650	0.629	0.004	2020.	2000.	665.	.0228	219.0	.0355
IHR-186	1974	BTM-1	.221	.334	0.671	0.614	0.0	2110.	500.	361.	.0415	120.6	.0547
IHR-173	1974	BTM-1	.164	.314	0.516	0.478	0.006	2110.	1000.	371.	.0442	67.9	.0330
IHR-147	1974	BTM-1	.189	.250	0.736	0.628	0.016	2110.	1000.	388.	.0463	108.0	.0372
IHR-146	1974	BTM-1	.182	.256	0.691	0.621	0.012	2110.	1000.	348.	.0459	109.0	.0338
IHR-182	1974	BTM-1	.144	.260	0.550	0.488	0.008	2110.	1000.	393.	.0934	53.6	.0374
IHR-181	1974	BTM-1	.269	.332	0.804	0.729	0.0	2110.	1000.	680.	.0458	109.2	.0695
IHR-151	1974	BTM-1	.160	.242	0.802	0.744	0.012	2110.	1100.	369.	.0422	118.4	.0342
IHR-153	1974	BTM-1	.269	.233	0.773	0.708	0.004	2110.	1100.	783.	.0380	131.7	.0727
IHR-149	1974	BTM-1	.192	.250	0.852	0.816	0.004	2110.	1200.	436.	.0399	125.4	.0366
IHR-160	1974	BTM-1	.196	.242	0.802	0.744	0.012	2110.	1500.	509.	.0310	161.5	.0374
IHR-158	1974	BTM-1	.214	.250	0.852	0.816	0.004	2110.	2000.	640.	.0240	208.7	.0352
IHR-154	1974	BTM-1	.200	.240	0.700	0.617	0.008	2110.	2000.	671.	.0241	207.3	.0368
IHR-192	1974	BTM-2	.081	.191	0.398	0.298	0.063	1660.	1000.	561.	.0437	114.5	.0501
IHR-191	1974	BTM-2	.137	.251	0.514	0.343	0.116	1800.	1000.	494.	.0435	115.0	.0411
IHR-161	1974	BTM-2	.237	.298	0.755	0.708	0.0	2110.	1000.	397.	.0482	103.8	.0432
IHR-164	1974	BTM-2	.262	.278	0.888	0.813	0.0	2110.	1200.	409.	.0431	116.0	.0373
IHR-162	1974	BTM-2	.233	.278	0.781	0.723	0.0	2110.	1500.	488.	.0322	155.3	.0326
IHR-163	1974	BTM-2	.248	.263	0.924	0.833	0.008	2110.	2000.	670.	.0248	201.9	.0343
120	1976	LIGNITE	.379	.409	0.961	0.597	0.024	2110.	1000.	679.	.0595	84.1	.0578
122	1976	BTM-2	.321	.337	0.955	0.834	0.033	2110.	1000.	736.	.0525	95.2	.0800
124A	1976	BTM-2	.256	.316	0.810	0.671	0.041	2110.	1000.	669.	.0404	123.6	.0490
124B	1976	BTM-2	.240	.272	0.890	0.768	0.011	2110.	1000.	601.	.0338	147.7	.0420
128A	6/76	BTM-2	.337	.360	0.933	0.825	0.0	2110.	1000.	705.	.0402	124.5	.0727
128B	6/76	BTM-2	.321	.298	1.067	0.943	0.0	2110.	1000.	655.	.0345	145.0	.0640
130	12/ 7/76	LIGNITE	.430	.434	0.827	0.532	0.0	2110.	1000.	738.	.0533	93.9	.0670
131	12/ 7/76	LIGNITE	.663	.332	1.669	1.151	0.0	2110.	1000.	752.	.0660	75.7	.1240
132	1/11/77	LIGNITE	.493	.317	1.297	0.842	0.0	2110.	1000.	714.	.0515	97.1	.0863
133	3/77	LIGNITE	.546	.330	1.182	0.948	0.0	2110.	1000.	755.	.0565	88.5	.0850
134	3/77	LIGNITE	.509	.442	0.826	0.652	0.0	2110.	1000.	748.	.0570	87.7	.0823
135A	4/77	LIGNITE	.650	.440	1.232	0.730	0.0	2110.	1000.	708.	.0752	119.7	.0899
135B	4/77	LIGNITE	.481	.507	0.791	0.454	0.0	2110.	1000.	664.	.0481	187.1	.0560

3.3 TASK III — AN IMPROVED SEMIEMPIRICAL CORRELATION FOR PREDICTING CARBON CONVERSION

This subsection presents:

- An improved semiempirical correlation that predicts overall carbon conversion efficiency and accounts for thermodynamic equilibrium effects
- Predictions of carbon conversion at thermodynamic equilibrium
- A comparison between the original and improved correlations for predicting carbon conversion

3.3.1 Derivation of the Improved Model

The following model was previously proposed by Bechtel[5] for correlating overall carbon conversion to the reactor operating variables:

$$X = 1 - \exp\left[-\alpha_1 (t_{RG})^{\alpha_2} (t_{RP})^{\alpha_3} (u_G)^{\alpha_4} (P)^{\alpha_5} (P_{H_2})^{\alpha_6} (H_2/\text{coal})^{\alpha_7} (d_P)^{\alpha_8} \exp(-\alpha_9/T)\right] \quad (1)$$

where,

X = weight fraction overall carbon conversion

$\alpha_1, \alpha_2, \ldots \alpha_9$ = fitted coefficients

t_{RG} = gas residence time

t_{RP} = particle residence time

u_G = superficial gas velocity

P_{H_2} = hydrogen partial pressure

P = total reactor pressure

H_2/coal = hydrogen-to-coal ratio

d_P = mean particle diameter

T = reaction temperature

The coefficients, α_1 through α_9, have been fitted to the data using a computerized multiple regression statistical analysis. The choice for the exponential form for Equation 1 was influenced by the similar form for an integrated, first-order, irreversible kinetic model.[5] The boundary conditions for the proposed correlation are zero carbon conversion at time zero and unity (100 percent conversion) at infinite time.

Hydropyrolysis of coal, however, is an extremely complex process, involving a number of reversible heterogeneous and homogeneous reactions.[8] Because of this reversibility, the maximum carbon conversion for a given set of operating conditions is limited by the thermodynamic equilibrium between the carbon in the coal, the oxygen, hydrogen, and reactant products. Since the overall hydropyrolysis reaction is exothermic, this equilibrium limit of carbon conversion, X^*, should decrease with increasing temperature. Furthermore, since there are fewer product gas moles than reactant gas moles, X^* should increase with increasing pressure.

To satisfy this equilibrium boundary condition, the following model has been proposed for correlating carbon conversion to the operating variables:

$$X = X^* \left\{ 1 - \exp \left[-\alpha_1 (t_{RG})^{\alpha_2} (t_{RP})^{\alpha_3} (u_G)^{\alpha_4} (P)^{\alpha_5} (P_{H_2})^{\alpha_6} (H_2/\text{coal})^{\alpha_7} (d_P)^{\alpha_8} \exp(-\alpha_9/T) \right] \right\} \tag{2}$$

where X^* is the equilibrium conversion, i.e., conversion at $t = \infty$

The form of Equation 2 has been influenced by the similar form of an integrated, first-order kinetic model for the reversible homogeneous reaction, $A \rightleftharpoons B$, where one mole of reactant produces one mole of product. For this reaction, the analytical expression for conversion of A to B, X_A, is

$$X_A = X_A^* \left[1 - e^{-(k_1 + k_2)t} \right] \tag{3}$$

with

$$X_A^* = k_1/(k_1 + k_2) = K/(1 + K) \tag{4}$$

where,

X_A^* = equilibrium fraction conversion of A

k_1 = forward reaction rate constant

k_2 = reverse reaction rate constant

t = time

K = equilibrium constant = k_1/k_2

3.3.2 Prediction of Fraction Carbon Conversion at Equilibrium

Owing to the complexity of the coal hydropyrolysis process, a thermodynamic equilibrium computer model, PEP[9] (Propellant Evaluation Program), has been used to predict the thermodynamic equilibria. PEP considers a reaction system of carbon (β-graphite), hydrogen, oxygen, and hydrocarbon gases within a temperature and pressure range normally encountered in coal hydropyrolysis.

At a given temperature, pressure, and relative weights of initial reactants, PEP predicts the concentration of species that appear in significant amounts at equilibrium. The equilibrium fraction of carbon converted, X^*, for the bituminous and subbituminous coals used by Cities Service and Rocketdyne[1] are shown in Figures 3-1 through 3-6 for various levels of temperature, pressure, and hydrogen-to-coal ratio.

For both types of coal, the results from PEP indicate that methane is the major hydrocarbon product at equilibrium. Higher hydrocarbon products, such as ethane and ethylene, are present only in trace amounts. PEP predicts that significant quantities of CO and CO_2 are also present in the gas phase at equilibrium. For the bituminous coal (Figures 3-1 through 3-3), the predicted amount of CO and CO_2 present is small relative to methane. For the subbituminous coal (Figures 3-4 through 3-6), which contains higher fractions of oxygen and moisture, the predicted quantities of CO and CO_2 can be significant relative to the methane.

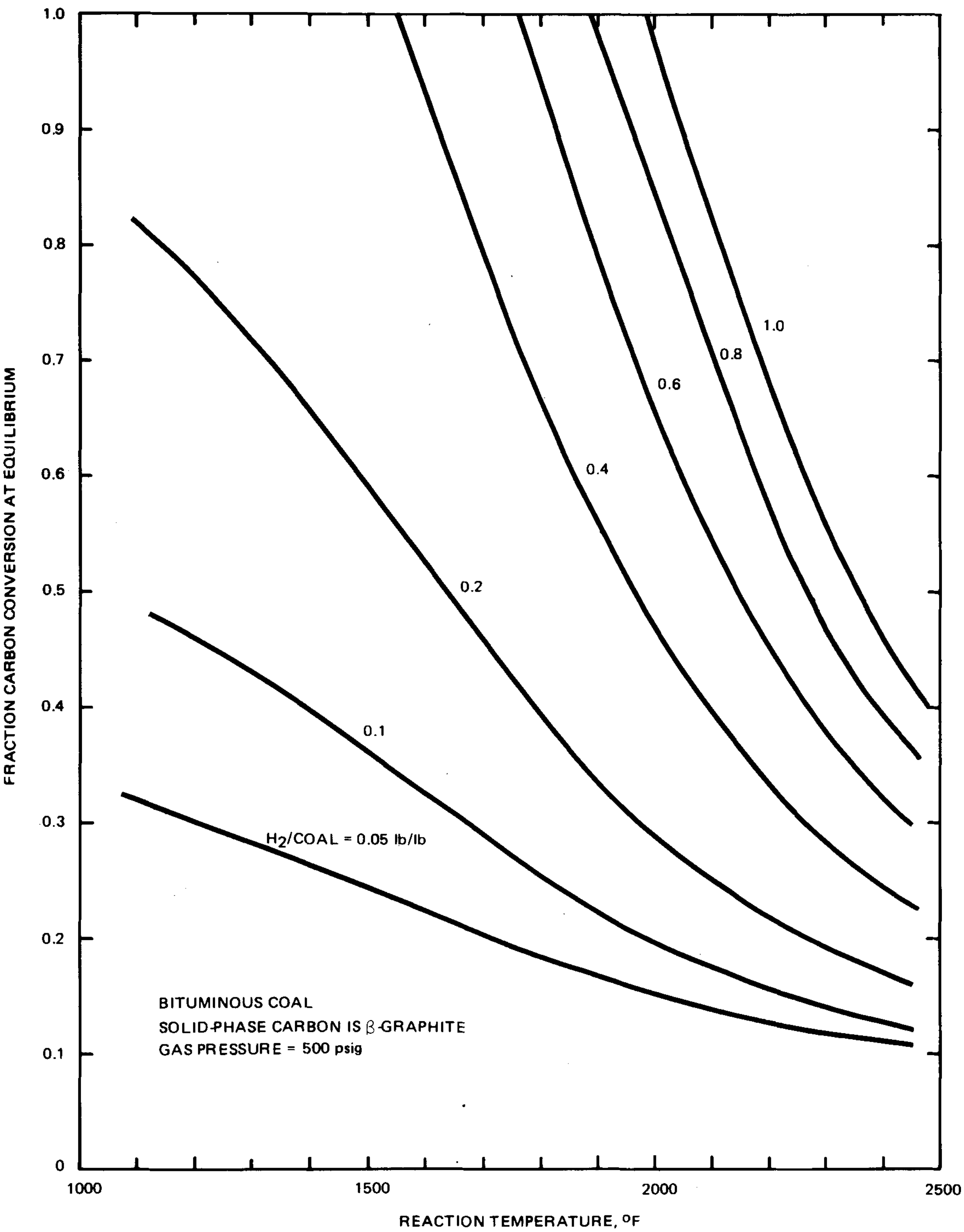

Figure 3-1. Fraction Carbon Conversion at Equilibrium — Bituminous Coal at 500 psig

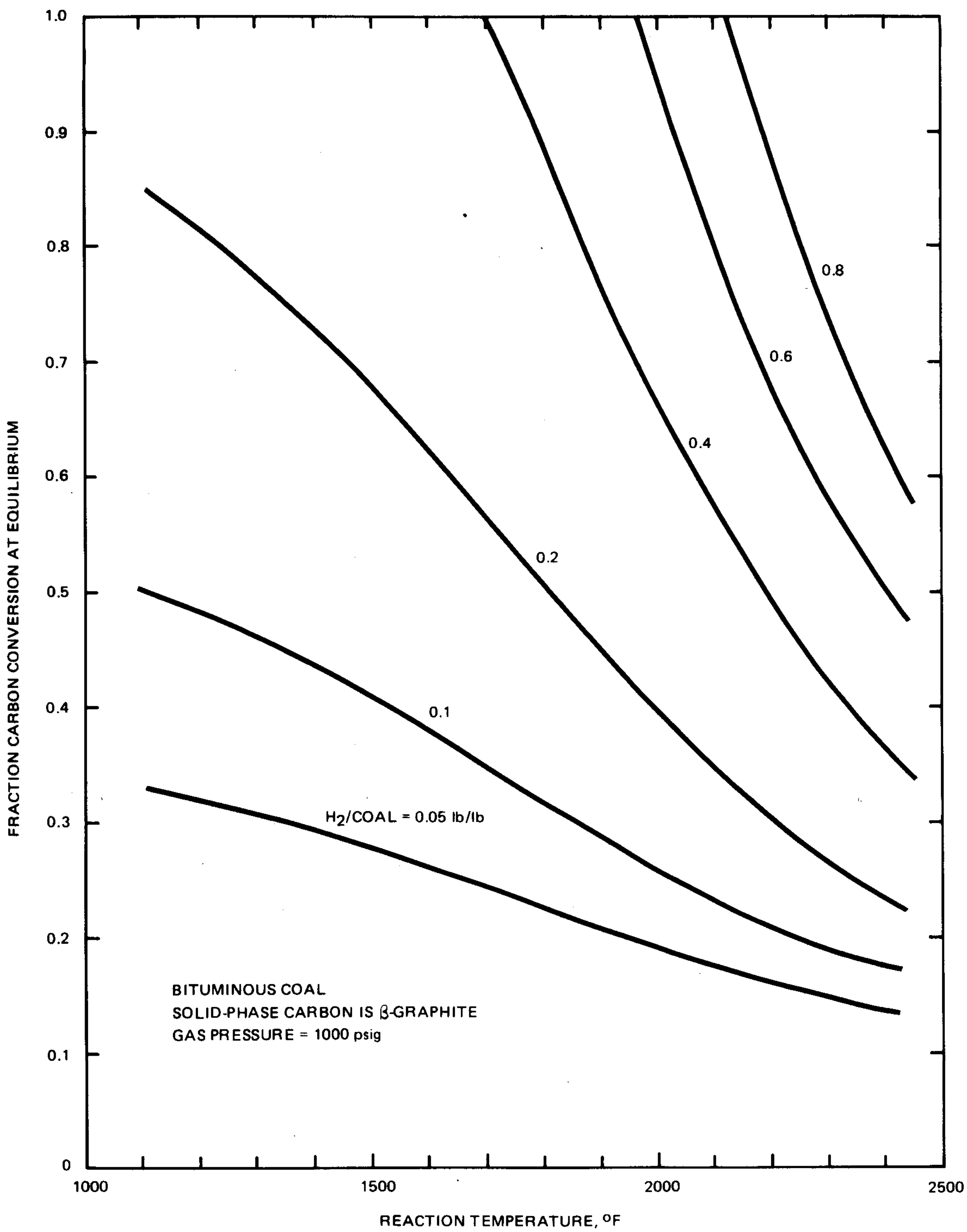

Figure 3-2. Fraction Carbon Conversion at Equilibrium — Bituminous Coal at 1,000 psig

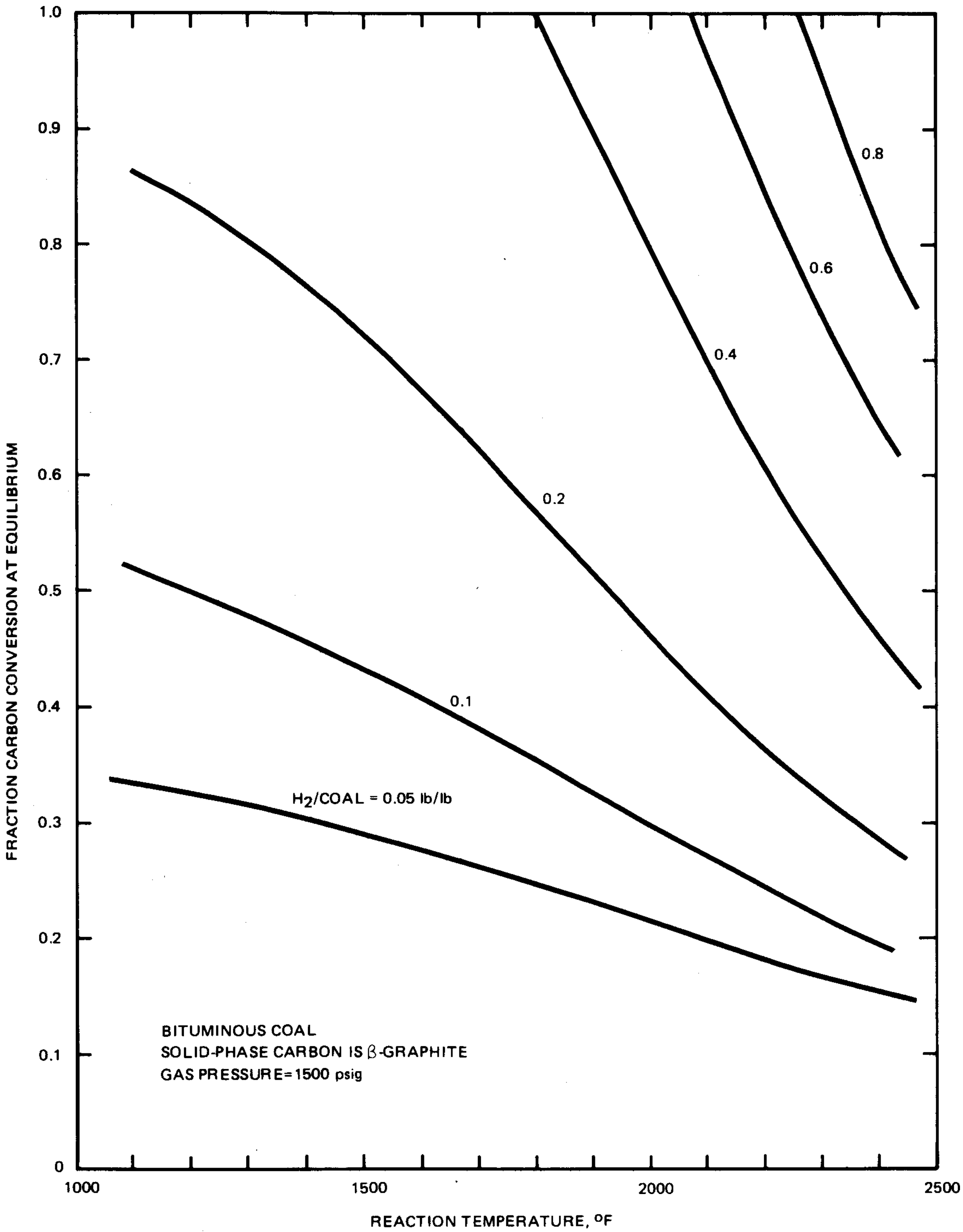

Figure 3-3. Fraction Carbon Conversion at Equilibrium — Bituminous Coal at 1,500 psig

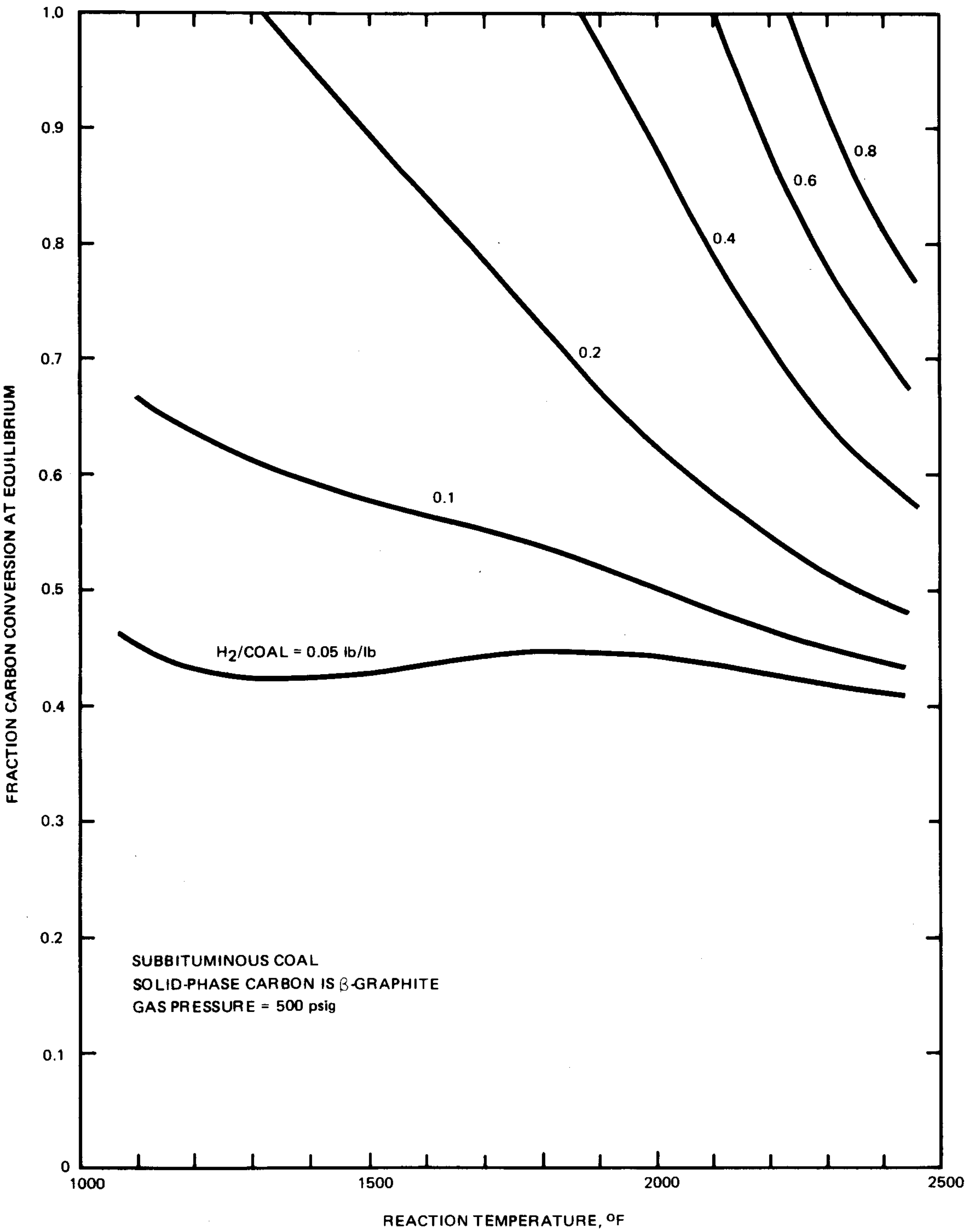

Figure 3-4. Fraction Carbon Conversion at Equilibrium — Subbituminous Coal at 500 psig

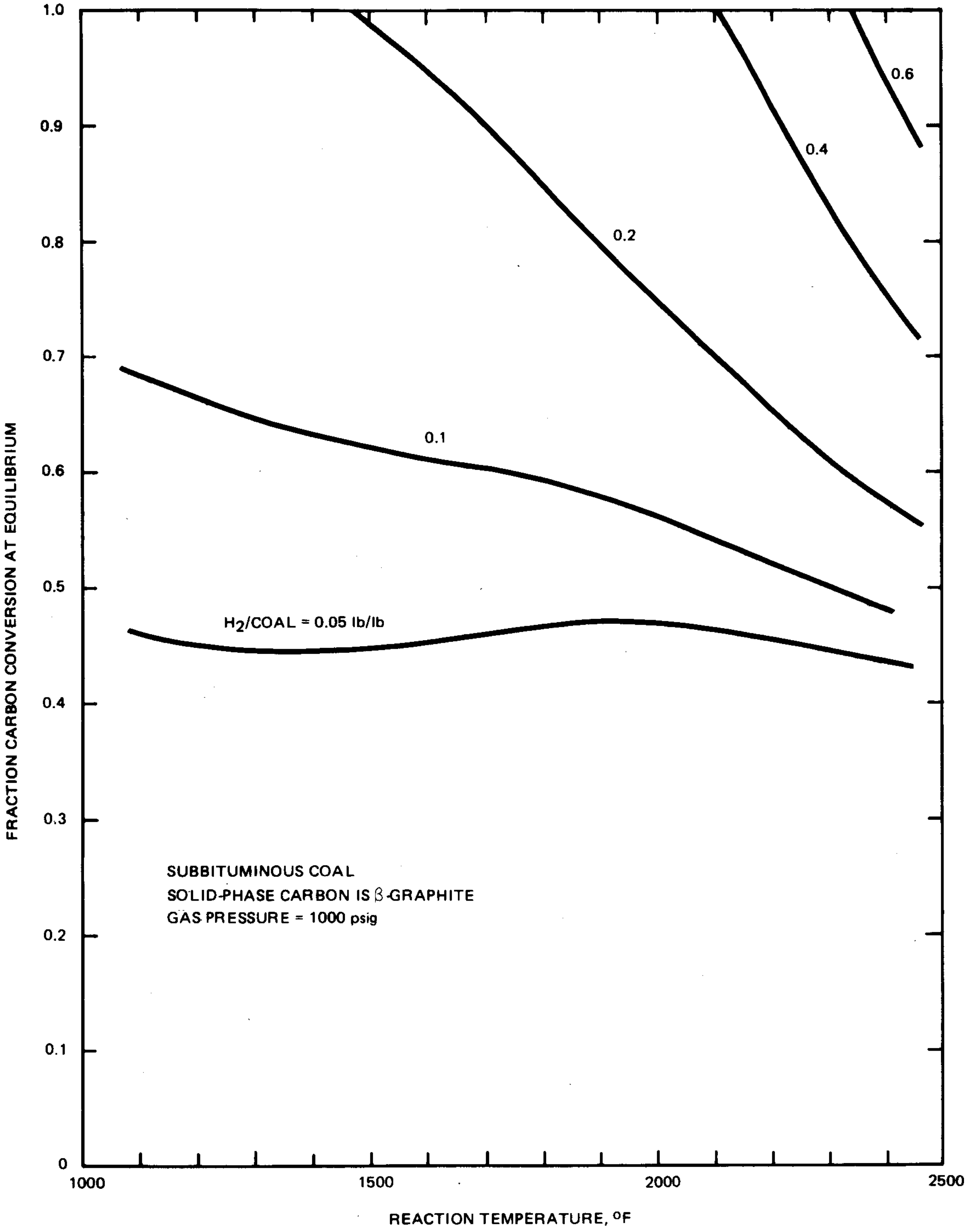

Figure 3-5. Fraction Carbon Conversion at Equilibrium — Subbituminous Coal at 1,000 psig

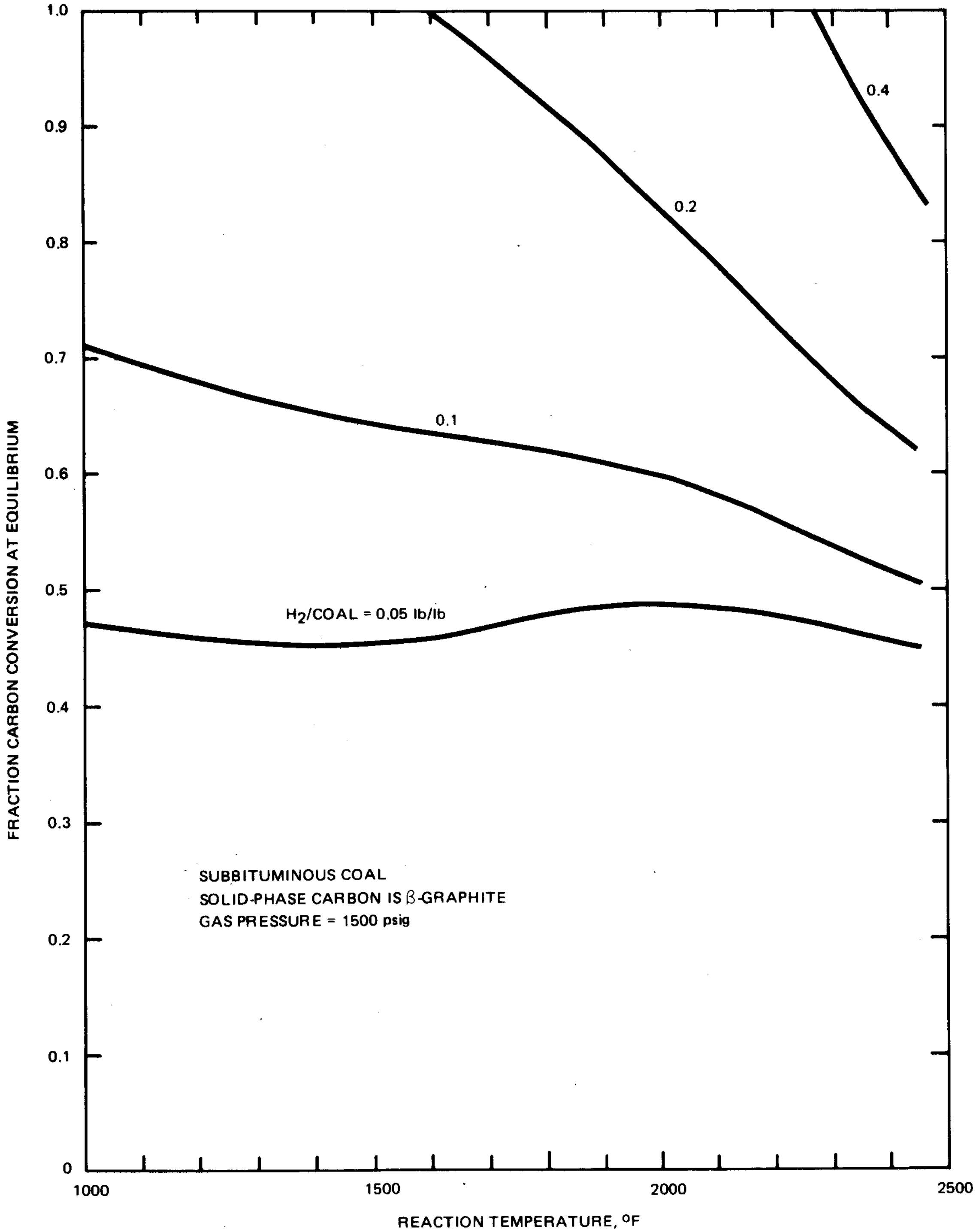

Figure 3-6. Fraction Carbon Conversion at Equilibrium — Subbituminous Coal at 1,500 psig

The equilibrium distribution of oxygen in coal to H_2O, CO, and CO_2 exhibits the following temperature dependence. At low temperatures, the oxygen in the coal reacts with hydrogen to form additional water. As the temperature increases, (1) the amount of this additional water decreases and the production of CO and CO_2 increases (indicating that the oxygen in coal preferentially reacts with carbon instead of hydrogen as the temperature is raised), and (2) CO production predominates over CO_2 production. At very high temperatures, the water present at equilibrium may be less than the water contained in the coal feed. Presumably, at these high temperatures, water reacts with carbon to form additional CO. These temperature effects are the opposite of the effects due to increasing hydrogen partial pressure or hydrogen-to-coal ratio.

As can be seen in Figures 3-1 through 3-6, the fraction carbon conversion at equilibrium is unity at low temperature, decreases below unity at higher temperatures, and increases with increasing pressure and hydrogen-to-coal ratio. Also, subbituminous coal gives larger values of X^* than bituminous coal at comparable hydrogen-to-coal ratios. This observation is attributed to the following:

- The carbon content of the subbituminous coal is less than the carbon content of the bituminous coal. Therefore, more hydrogen is available for conversion of the subbituminous coal at the same level of hydrogen-to-coal ratio
- The oxygen content of the subbituminous coal is greater than the oxygen content of the bituminous coal, resulting in larger conversions of carbon to CO and CO_2 for the subbituminous coal

As mentioned previously, PEP assumes that the carbon present is β-graphite. Because observations[10] have indicated that carbon in coal has a higher reactivity than β-graphite, the predictions of X^* in Figures 3-1 through 3-6 should be considered as approximate, and probably on the low side.

3.3.3 Comparison Between Original and Improved Models

The Rocketdyne and Cities Service test programs have been conducted to date within a temperature range of 1,400°F to 2,000°F, a hydrogen partial pressure range of 500 to 1,600 psig, and a hydrogen-to-coal ratio range of 0.5 to 1.2 lb/lb. As shown in Figures 3-1 through 3-6, the equilibrium conversions predicted by PEP for these conditions all have a value of unity (100 percent conversion). For this case, Equation 2 reduces to Equation 1, the original proposed model. This may explain why the original model, which did not take the equilibrium limitation into account, has successfully correlated the Cities Service and Rocketdyne carbon conversion data.

The equilibrium limitation, however, must be taken into consideration when extrapolating the results of the fitted Cities Service and Rocketdyne model to a commerical-scale reactor. The reason for this is that a commercial-scale reactor will operate at a hydrogen-to-coal ratio less than 0.5 lb/lb. For this lower hydrogen-to-coal ratio, X^* falls below unity for the normal operating levels of reactor temperature and pressure (see Figures 3-1 through 3-6).

The equilibrium limitation must also be considered for an evaluation of the PERC hydrogasification data. This is due to the fact that the PERC reactor has operated with extremely low hydrogen-to-coal ratios, varying between 0.03 and 0.12 lb/lb (see Table 3-3 in Bechtel's June-August 1977 Quarterly Progress Report[5]). It is expected that X^* is less than 0.5 for most of the PERC data.

3.4 TASK III — ROCKETDYNE AND CITIES SERVICE REACTOR MODELING

In Bechtel's November 1977 Monthly Progress Report,[11] a correlation was presented for predicting overall carbon conversion based on the Cities Service subbituminous data available at that time. In Bechtel's December 1977 Progress Report,[12] the Cities Service subbituminous correlation was used to predict the overall carbon conversion for the six Rocketdyne subbituminous tests that had been conducted in the 1/4-ton/hr reactor. The predicted and measured conversions for the Rocketdyne tests were in excellent agreement.

During this reporting period, carbon conversion efficiency for the Cities Service and Rocketdyne subbituminous tests were correlated to the reactor operating variables using the semiempirical model (Equation 2) proposed earlier in the report. The Rocketdyne data are shown in Table 3-1 of the report, while the Cities Service data are shown in Table 3-1 of Bechtel's December 1977 Progress Report.[12]

Rocketdyne Runs 011-14 and 011-15 have not been included in the analysis, owing to the uncertainty in the results from these tests, as discussed in Subsection 3.1. It should be noted that, within the region of the Rocketdyne and Cities Service subbituminous data, the equilibrium conversion of carbon to products, X^*, is unity (see Figures 3-1 through 3-6) and Equation 2 reduces to Equation 1.

A statistical analysis of the fitted data indicated that carbon conversion for the Montana Rosebud coal was a significant function of gas residence time, maximum gas temperature, and hydrogen partial pressure. Carbon conversion was not significantly affected by reactor size, hydrogen-to-coal ratio, or gas velocity within the region investigated. The correlation fitted to the Rocketdyne and Cities Service subbituminous carbon conversion data is:

$$X = 1 - \exp\left[-0.267(P_{H_2})^{0.120}(t_R)^{0.236}\exp(-3{,}850/T_G)\right] \quad (5)$$

where,

X = overall carbon conversion, weight fraction

P_{H_2} = hydrogen partial pressure, psig

t_R = gas (or particle) residence time, milliseconds

T_G = maximum gas temperature, ^{o}R

Equation 5 has a standard error of estimate of 3.7 percent in the predicted percent carbon conversion. The measured and predicted carbon conversions are shown in Figure 3-7. The statistics and Figure 3-7 indicate that the Cities Service bench-scale reactor and the Rocketdyne 1/4-ton/hr reactor achieve similar carbon conversions under comparable operation conditions within the region investigated.

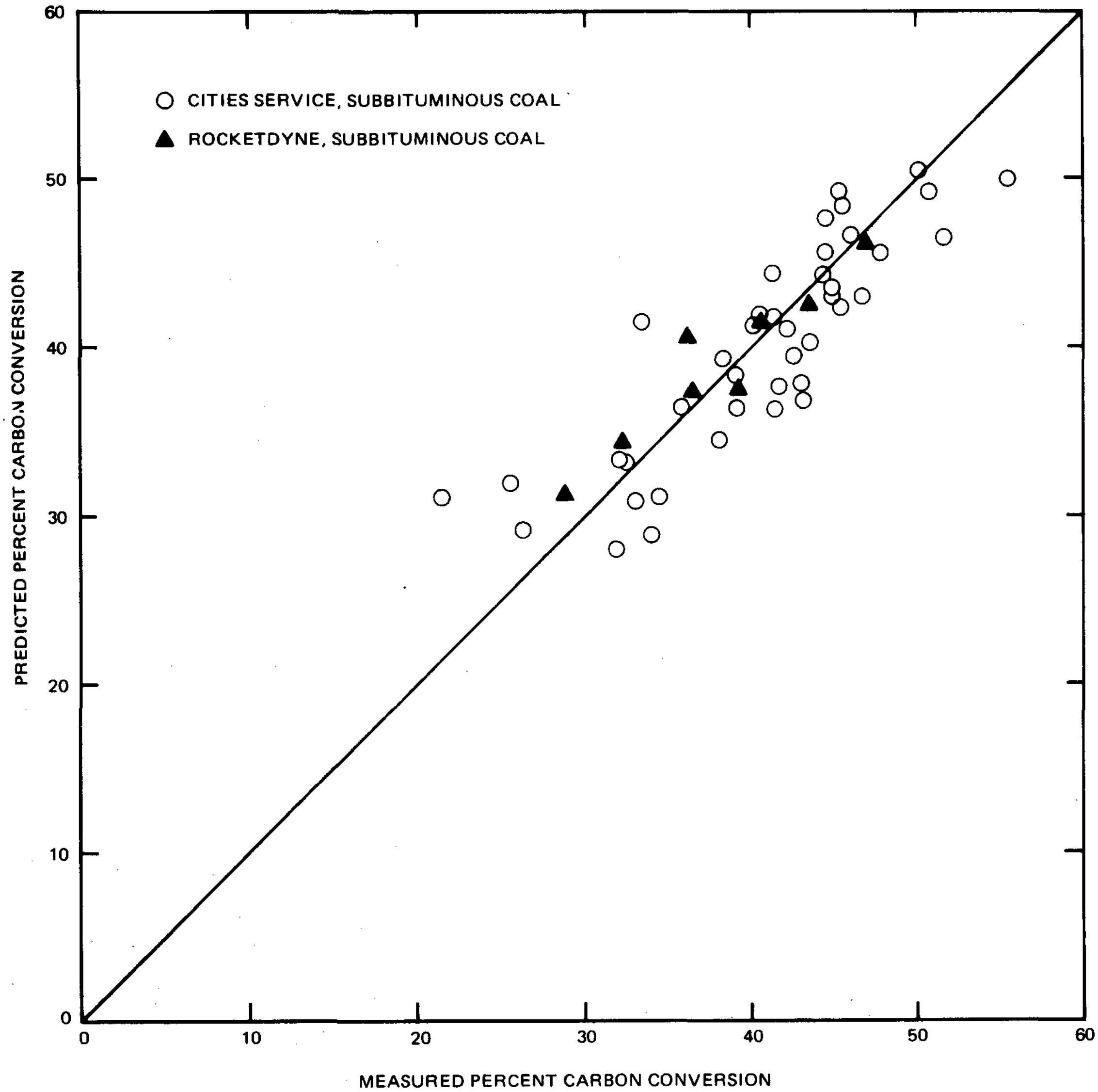

Figure 3-7. Comparison of Measured and Predicted Carbon Conversion for the Cities Service and Rocketdyne Reactors

3.5 FUTURE WORK

During the next reporting period, work will be conducted in the areas discussed below.

Models developed for correlating the Rocketdyne and Cities Service carbon conversion and carbon selectivity data will be updated and improved upon as further tests results are obtained with Montana Rosebud subbituminous coal and with Western Kentucky bituminous coal.

Models developed for correlating the carbon conversion and carbon selectivity data received to date from the Pittsburgh Energy Research Center and the Brookhaven National Laboratory will be updated and improved upon.

Additional data that may be required for reliable pilot plant design will be identified, and experimental programs necessary for the generation of the additional data will be recommended.

Section 4

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