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GASIFICATION

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BEACON PROCESS

DEVELOPMENT OF BEACON TECHNOLOGY

QUARTERLY REPORT JULY — SEPTEMBER 1981

MASTER

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by

TRW ENERGY SYSTEMS GROUP

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
1. INTRODUCTION	1-1
2. SUMMARY	2-1
3. TASK 1 - CATALYST DEVELOPMENT	3-1
3.1 CATALYST DEVELOPMENT AT TRW	3-1
3.1.1 Experiment Description	3-1
3.1.2 Results and Preliminary Findings	3-3
3.2 CATALYST DEVELOPMENT AT SOHIO	3-8
3.2.1 Multiple-Cycle Testing of Catalyst C77-K2.	3-8
3.2.2 Alonized Stainless Steel Reactor Testing with Catalyst C77-K2	3-10
3.2.2.1 Experiment Description	3-10
3.2.2.2 Experiment Results.	3-14
3.2.2.3 Conclusions	3-15
3.2.3 Promoted Catalyst Screening Experiments.	3-18
3.2.4 Further Experiments with Catalyst C78-K1	3-18
3.2.4.1 Experiment Description.	3-20
3.2.4.2 Discussion of Experiment Results.	3-23
3.2.5 Bench-Scale Preparation of Catalyst C77-K2	3-24
3.2.6 Catalyst Preparation Modifications	3-28
4. TASK 2 - CARBON DEPOSITION AND GASIFICATION IN BATCH MODE BENCH-SCALE EQUIPMENT.	4-1
4.1 FOUR-INCH DIAMETER, HIGH PRESSURE, FLUID BED REACTOR TESTING	4-1
4.1.1 Fluid Bed C77 Multiple-Cycle Performance Tests	4-2
4.1.2 Cyclone Solids Return System Testing	4-6
4.1.3 "Huff-Puff" Tandem Reactor System	4-9
4.1.4 Testing of K2-Based BEACON Solids	4-10
4.1.4.1 Steaming Temperature Screening Tests.	4-10
4.1.4.2 Cycling Tests	4-12

FIGURES

	<u>Page</u>
3-1. Alonized Stainless Steel Reactor	3-13
3-2. Carbon Deposition Results	3-16
3-3. Accumulated Carbon Deposit at the End of Each Cycle. . .	3-17
3-4. Cycle Efficiency	3-17
3-5. Inconel Tube Fluid Bed Reactor	3-21
3-6. Gasification Reaction Selectivities and Steam Utilization Versus Reaction Time	3-26
4-1. Cyclone Solids Return Loop	4-6

TABLES

	<u>Page</u>
3-1. Reaction Conditions for Multiple-Cycle Performance Experiments	3-2
3-2. Multiple Cycle Steam Gasification Performance of the K1 Catalyst Through 30 Gasification-Carburization Cycles	3-4
3-3. Multiple Cycle Steam Gasification Performance of the K2 Catalyst Through 28 Gasification-Carburization Cycles	3-5
3-4. Multiple Cycle Re-Carburization Performance of the K1 Catalyst Through 30 Gasification-Carburization Cycles	3-6
3-5. Multiple Cycle Re-Carburization Performance of the K2 Catalyst Through 28 Gasification-Carburization Cycles	3-7
3-6. Multiple-Cycle Testing of Catalyst C77-K2 (Test 1)	3-9
3-7. Multiple-Cycle Testing of Catalyst C77-K2 (Test 2).	3-11
3-8. Reaction Conditions for C77-K2 Tests in Alonized Reactor	3-14
3-9. Data from Catalyst Screening Experiments	3-19
3-10. Catalyst C78-K1 Formulations and Fixed Experiment Conditions.	3-20
3-11. Catalyst C78 Experiment Results	3-25
3-12. Test Results of Bench-Scale Catalysts (C77-K2)	3-27
3-13. Product Gas Composition -- "Fixed Bed" Versus Fluidized Bed	3-27
4-1. C77 Multiple-Cycle Carbon Deposition/Gasification Performance Data	4-3
4-2. Product Gas and Feed Gas Composition Data from C77 Multiple-Cycle Testing	4-4
4-3. Summary of Cyclone Solids Return System Testing	4-8
4-4. Steaming Temperature Screening Test Results (K2-Based BEACON Carbon)	4-12
4-5. Nominal Conditions for Multiple-Cycle Testing of K2-Based BEACON Carbon	4-13

ABSTRACT

The BEACON process involves the catalytic deposition of carbon from a gas stream containing carbon monoxide, and subsequent exposure of this carbon to a gas stream containing hydrogen or steam at elevated temperature and pressure to produce methane. The steam gasification route currently is receiving the most attention.

Multiple-cycle tests with K1 and K2 catalysts showed sustained activity and stable performance through thirty of the planned forty cycles. The tests will be completed next quarter. Steaming temperature screening tests on K2-based BEACON carbon supported the conclusion based on earlier testing with K1-based BEACON carbon that steam gasification at two temperature levels has significant advantages over steam gasification at a single temperature in terms of gasification rates and methane yields. Multiple-cycle testing of K2-based BEACON carbon was started in the 4-inch bench-scale fluid bed reactor.

Catalyst C77 continued to have problems during multiple-cycle testing -- loss of catalytic activity, possibly due to overheating, and poor fluidizability.

Further modifications of the C77 catalyst preparation technique were tested. Catalyst C77-K2 showed no change in performance, and results with catalyst C77-K1 were generally disappointing. Laboratory experiments continued with catalyst C78.

A variable differential pressure concept which does not require gas/solids separation is now being considered for the transfer of BEACON solids between carbon deposition and carbon gasification reactors.

1. INTRODUCTION

The BEACON process converts low Btu gas into a substitute natural gas (SNG) and electric power. The original investigations of the chemistry and the necessary catalyst systems were performed by TRW. Since July 1978, the Standard Oil Company of Ohio (SOHIO) has joined with TRW to develop the process.

The joint TRW/SOHIO program has concentrated on the development of catalysts to perform the BEACON process chemistry, bench-scale testing to define suitable process conditions, reactor studies, and engineering analysis pertaining to the development of conceptual commercial designs and studies of their efficiencies, costs and economics. The reactor studies were undertaken under DOE Contract No. DE-AC01-79ER10032, "BEACON Reactor Design Modeling and Cold Flow Testing."

The current program operates under a cooperative agreement among DOE, SOHIO and TRW (Cooperative Agreement No. DE-FC21-80MC14400). The program is divided into five tasks: 1) Catalyst Development, 2) Carbon Deposition and Gasification in Batch Mode Bench-Scale Equipment, 3) Continuous Flow Bench-Scale Testing of Carbon Deposition and Gasification of the Deposited Carbon, 4) Engineering Analysis, and 5) Program Management. This report covers the period from July through September 1981.

2. SUMMARY

Carbon deposition/gasification multiple-cycle tests with catalyst C77 were continued in the 4-inch diameter, bench-scale, fluid bed reactor until catalytic activity dropped to an unacceptable level after 5-1/2 cycles. The spent catalyst is being examined to determine the probable cause(s) for the reduction in catalytic activity.

Further laboratory-scale, multiple-cycle testing of catalyst C77-K2 was conducted at atmospheric pressure during the quarter. The first test was terminated after 3-1/2 cycles due to an unexplained catalyst bed expansion. The catalyst performed well during the second test for 16 cycles, although catalyst bed expansion was observed during the first 9 cycles. After the loss of some carburized catalyst during cycle 16 due to a test error, the residual carbon on the remaining catalyst was removed at high temperature (up to 725°C) to establish a new baseline catalyst weight. This treatment severely reduced the activity of the catalyst, thereby supporting the belief that overheating may have been responsible for the loss of catalytic activity during the bench-scale tests in the 4-inch reactor.

Initial testing of one-kilogram batches of catalyst C77-K2, which were prepared using a scaled-up version of the laboratory preparation procedure, generally was satisfactory, although several batches had low steam gasification rates. The catalyst became stuck at the sparger during some of these tests, causing the reactor to behave as a fixed bed reactor instead of a fluidized bed reactor. It was noted that the product gas composition during steam gasification showed considerably more methane and less carbon monoxide and hydrogen in the "fixed bed" mode than in the normal fluidized bed mode. Further investigation of this phenomenon is planned.

A small Alonized stainless steel reactor was fabricated to investigate the problems encountered earlier with catalyst C77-K2 in the 1-1/2 inch Alonized stainless steel bench-scale reactor. Although the carbon deposition rate declined steadily during six cycles of testing, the cycle

efficiency averaged about 60% with no apparent time dependence. Calculated values of residual carbon based on gas chromatography indicated accumulated carbon equal to about 30% of catalyst weight at the end of six cycles, but the actual weight of solids recovered from the reactor at the end of six cycles was about 99% of the predicted value in the absence of residual carbon. Although no firm conclusion regarding inactive carbon can be made until the microanalysis of the solids recovered from the reactor is completed, cycle efficiencies did not indicate a severe problem with inactive carbon, and it must be tentatively concluded that the difficulties experienced in the 1-1/2 inch bench-scale reactor were not due to the Alon coating on the reactor. However, the poor fluidizability of catalyst C77-K2, experienced earlier in the 1-1/2 inch bench-scale reactor and again during these laboratory tests, poses a real difficulty. In conjunction with the poor performance in the 4-inch fluid bed reactor, real questions have been raised regarding the operability of the C77-K2 catalyst.

Laboratory tests with K1 and K2 catalysts were started during this quarter to determine their multiple-cycle performance over forty carburization-gasification cycles. Approximately thirty of the planned forty reaction cycles with each catalyst were completed, and both catalysts remained active and stable. Good approaches to equilibrium-predicted performance were exhibited by both catalysts, although the K1 catalyst performed better than the K2 catalyst. The superior performance of the K1 catalyst during carbon deposition was consistent with earlier non-cyclic carburization tests which showed the K2 catalyst to be a less active carburization catalyst than either the baseline catalyst or the K1 catalyst.

Multiple-cycle carbon deposition/gasification testing of K2-based BEACON solids was started this quarter in the 4-inch fluid bed reactor. Four of the planned fifty cycles were completed with no indication of a decrease in catalytic activity. Steaming temperature screening tests were performed on the K2-based BEACON carbon before starting the multiple-cycle tests. As in the case of K1-based BEACON carbon, the test data suggest that two stage steam gasification will lead to higher gasification rates and higher conversions to methane than single stage gasification. The test series will include both single and two stage steam gasification.

The cyclone (lock-hopper type) solids return system for the 4-inch fluid bed reactor underwent further testing this quarter. It continued to perform satisfactorily with reactor gas velocities up to 23 cm/sec with a short bed (60 cm), which is adequate for current testing, but it was inefficient at gas velocities approaching 30 cm/sec with a tall bed (90 cm). So, a variable differential pressure ("huff-puff") concept which does not require gas/solids separation is now being considered for the transfer of BEACON solids between carbon deposition and carbon gasification reactors instead of the lock-hopper approach to solids feed and withdrawal under consideration previously. A cold flow unit is being designed to test the "huff-puff" concept.

The laboratory test series on promoted variations of the C78 catalyst was completed this quarter. The performance of the K2-P7 promoted catalyst was similar to that of the K2-P3 promoted catalyst tested last quarter.

The excellent performance of the unpromoted C78-K1 catalyst during last quarter's catalyst screening experiments motivated further work with this catalyst. Experiments were conducted to study 1) the effects of catalyst quantity, catalyst distribution (relative volumes of treated and untreated catalyst support in the bed), and total bed volume on carbon deposition and gasification performance, and 2) the effects of carbon deposition rate, and the amount of carbon deposited, on the reactivity of the carbon during gasification. The quantity of catalyst present affected the results only at the higher carbon monoxide feed rates (during carbon deposition); the system appeared to be feed limited at all other test conditions. The catalyst distribution and total bed volume appeared to affect gas-solids mixing, resulting in higher carbon gasification rates with the larger bed volumes. The amount of carbon present at the beginning of each carbon gasification run did not appear to affect the carbon gasification performance significantly, but the rate of carbon deposition did seem to affect the reactivity of the carbon during gasification, particularly at the higher deposition rates. The cycle efficiency remained high (over 80%) in all cases and appeared to be independent of variations in the carbon deposition parameters.

Reaction selectivities and steam utilization during gasification varied as a function of reaction time. Selectivities for CO and CH₄ were high during the early portion of a run when about 90% of the feed steam was converted. As the steam-to-carbon ratio increased during the run, the steam utilization decreased and reaction selectivities shifted to CO₂ and H₂. This behavior suggests that product gas composition is strongly influenced by the steam-to-carbon ratio.

Further modifications of the standard C77 catalyst preparation technique were testing during the quarter. The performance of the modified catalyst C77-K2 was unchanged. The modified C77-K1 catalyst was an improvement over the standard C77-K1 preparation, although it was less active than the K2 version and its fluidization properties deteriorated with cycling.

The new technique for catalyst preparation introduced last quarter was investigated further during this quarter with disappointing results. Catalyst C78-K2 showed no performance advantage over the standard C77 preparation. Catalyst C78-K1 could not be tested because of poor fluidization.

3. TASK 1 - CATALYST DEVELOPMENT

The catalysts appropriate for the BEACON chemistry are being developed at TRW and SOHIO.

3.1 CATALYST DEVELOPMENT AT TRW

The catalyst development effort at TRW this quarter was oriented toward demonstrating the stable, high activity of BEACON catalysts when alternately subjected to carburization (carbon deposition) and steam gasification. For commercial process economics it is essential that the catalyst be used in a cyclic manner. In this operational mode the catalyst must remain active for both carburization and gasification and have a relatively stable product distribution for each half-cycle reaction.

3.1.1 Experiment Description

Laboratory tests were conducted with unpromoted K1 and K2 catalysts using U-tube microreactors. The objective was to determine the multiple-cycle performance of these catalysts over forty carburization-gasification cycles. Forty cycles was considered to be a sufficient number to confirm sustained high catalyst activity and to detect developing trends in performance. After completion of the forty cycles, the results will be analyzed statistically to discern possible performance trends, and the catalysts will be examined to determine whether morphological and surface area changes have occurred.

Both the K1 and K2 catalysts were reacted in separate but similar quartz U-tube microreactors.* Reaction conditions are shown in Table 3-1. Two-gram samples of carburized catalysts were reacted with steam at 600°C. The steam feed rates were low enough that the carburized catalysts behaved as packed beds. Small differences in liquid water pump rates between the two microreactors resulted in slightly different steam feed rates for

* Previously described in "Development of BEACON Technology, Quarterly Report, October-December 1980", Report No. DOE/MC/14400-03, Published March 1981, section 3.1.1.

TABLE 3-1. REACTION CONDITIONS FOR MULTIPLE-CYCLE
PERFORMANCE EXPERIMENTS

	Gasification		Re-Carburization	
	Reactor #1 (K2)	Reactor #2 (K1)	Reactor #1 (K2)	Reactor #2 (K1)
Pressure	Atmospheric		Atmospheric	
Temperature, °C	600		450	400
Steam Feed Rate, moles/hour	0.16	0.13	--	--
Superficial Steam Velocity, cm/sec	1.6	1.3	--	--
Carburizing Gas Feed Rate, moles/hour	--	--	0.06-0.07	0.05

gasification. For each steam gasification reaction (half-cycle), product gas volume and composition were measured and recorded as a function of time. From these measurements together with the information concerning steam feed rate and initial carbon charge, steam utilization, percent carbon gasified, and global rates were computed. The steam gasification reaction for a given half-cycle was continued until approximately 25 to 30% of the initial carbon charge had been gasified, based on product gas composition and evolution measurements. After completion of each gasification half-cycle, the cooled U-tube microreactor with its residual contents was weighed to confirm the gasification extent and provide a material balance check. Typically the grams of carbon gasified as determined from product gas measurements agreed within 5% of the measured weight loss.

The K1 and K2 catalysts were re-carburized in the U-tube micro-reactors using an 85:15 mole percent CO:H₂ gas mixture. Somewhat different re-carburization conditions had to be used for the two catalysts because of the substantially higher CO disproportionation activity of the K1 catalyst. The K1 catalyst could be re-carburized at an acceptable rate at 400°C, but the less active K2 catalyst had to be re-carburized at 450°C.

Re-carburization was continued until the amount of carbon deposited equalled that which had been gasified in the previous steam gasification half-cycle. The actual weight of carbon deposited was checked at the end of the re-carburization period by weighing the microreactor tube containing the re-carburized catalyst. For each re-carburization half-cycle, values were determined for the carbon deposition rate, CO conversion, and CO selectivity to carbon. The carbon deposition rate was determined from carbon-catalyst weight measurements made before and after re-carburization prior to steam gasification. CO conversion and CO selectivity to carbon were determined from feed and exit gas composition and flowrate measurements.

3.1.2 Results and Preliminary Findings

Approximately thirty of the planned forty reaction cycles with each catalyst were completed. The additional reaction cycles will be completed next quarter. Through the thirty reaction cycles, both catalysts appeared to maintain both carburization and steam gasification activity.

Steam utilization and product gas composition remained nearly constant over each gasification period so that average values for the gasification parameters were meaningful. Similarly, CO conversion and selectivity measurements were relatively constant over each re-carburization period so that average values for the carburization parameters were meaningful. Gravimetrically determined carbon deposition and steam gasification rates were, by their nature, average values.

Average values for steam gasification parameters determined for each half-cycle are reported in Tables 3-2 and 3-3 for K1 and K2 catalysts, respectively. Both catalysts remained active through the number of reaction cycles completed, and both catalysts yielded a stable product gas composition.* Good approaches to equilibrium-predicted performance also are exhibited by both catalysts, although the K1 catalyst shows a closer approach to theoretically predicted performance. Average values for recarburization parameters for each half-cycle are reported in Tables 3-4 and 3-5 for K1 and K2 catalysts, respectively. Both catalysts remained

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* Early runs with the K2 catalyst show some instability in product gas composition.

TABLE 3-2. MULTIPLE CYCLE STEAM GASIFICATION PERFORMANCE OF THE K1 CATALYST THROUGH 30 GASIFICATION-CARBURIZATION CYCLES

REACTION CYCLE	GLOBAL GASIFICATION RATE (g CARBON/HR)	STEAM UTILIZATION (%)	DRY PRODUCT GAS COMPOSITION (MOL %)			
			H ₂	CO	CH ₄	CO ₂
Theoretical*	0.86	71	49	17	9	25
1	0.30**	62	50	23	9	18
2	0.81	66	49	16	9	26
3	0.80	67	43	3	18	36
4	0.73	62	46	5	16	33
5	0.91	71	51	11	9	30
6	0.83	65	48	7	13	31
7†	0.47	40	59	2	6	33
8	0.76	66	49	4	14	33
9	0.83	68	52	10	10	28
10	0.88	75	51	11	10	28
11	0.81	71	51	11	10	28
12	0.79	70	51	10	10	29
13	0.81	72	51	10	10	29
14	0.79	72	51	9	11	30
15	0.76	74	50	9	11	30
16	0.71	67	53	7	9	30
17	0.83	77	51	8	11	30
18	0.82	74	51	8	10	30
19	0.78	71	50	8	11	31
20	0.77	72	50	8	11	31
21	0.75	76	50	8	11	31
22	0.73	72	47	6	14	33
23	0.80	74	49	8	12	31
24	0.81	74	50	8	11	31
25	0.79	71	50	8	11	31
26	0.80	74	48	5	14	33
27	0.77	73	49	8	12	31
28	0.71	69	55	8	7	30
29	0.76	75	54	8	8	30
30‡	0.50	58	61	4	4	32

*Theoretically predicted values for equilibrium controlled, steam feed limited, graphite-steam reaction under prevailing experiment conditions.

**Sample mistakenly gasified at lower steam feed rate than planned.

†Bed separation observed due to steam feed surge.

‡Gasification temperature inadvertently set at 500°C instead of 600°C.

TABLE 3-3. MULTIPLE CYCLE STEAM GASIFICATION PERFORMANCE OF THE K2 CATALYST THROUGH 28 GASIFICATION-CARBURIZATION CYCLES

REACTION CYCLE	GLOBAL GASIFICATION RATE (g CARBON/HR)	STEAM UTILIZATION (%)	DRY PRODUCT GAS COMPOSITION (MOL %)			
			H ₂	CO	CH ₄	CO ₂
Theoretical*	1.04	71	49	17	9	25
1	.67	50	53	15	5	27
2	.73	54	52	15	5	28
3	.58	49	53	15	5	28
4	.84	62	52	15	6	27
5	.66	53	52	16	5	26
6	.68	53	54	15	5	27
7	.66	49	53	15	5	27
8	.71	55	53	15	5	27
9	.88	54	51	15	6	28
10	.65	53	56	17	5	22
11	.71	57	52	15	5	28
12	.70	51	50	17	5	28
13	.67	50	54	14	4	28
14	.65	48	53	13	5	29
15	.73	50	53	13	5	29
16	.66	48	53	15	4	28
17	.63	52	51	14	4	31
18	.63	46	55	12	4	29
19	.69	54	53	16	4	27
20	.66	48	52	15	5	28
21	.70	52	53	15	4	28
22	.73	51	54	14	5	28
23	.67	49	53	14	5	28
24	.59	48	53	12	4	31
25	.64	52	54	13	5	29
26	.68	51	52	15	5	28
27	.64	50	54	13	4	29
28	.61	49	53	14	4	29

*Theoretically predicted values for equilibrium controlled, steam feed limited, graphite-steam reaction under prevailing experiment conditions.

TABLE 3-4. MULTIPLE CYCLE RE-CARBURIZATION PERFORMANCE OF THE K1 CATALYST THROUGH 30 GASIFICATION-CARBURIZATION CYCLES

REACTION CYCLE	SPECIFIC CARBON DEPOSITION RATE (g CARBON/HR/ g CATALYST METAL)	CO CONVERSION (%)	CO SELECTIVITY TO CARBON (MOLE CARBON/MOLE CO CONVERTED)
Theoretical*	2.5	99.56	.563
1	1.056	40	.463
2	1.240	66	.475
3	1.376	63	.482
4	1.384	68	.454
5	1.731	89	.459
6	1.614	85	.443
7	1.526	74	.476
8	1.438	64	.459
9	1.631	75	.468
10	1.597	80	.451
11	1.571	77	.462
12	1.837	87	.454
13	1.620	78	.466
14	1.857	85	.470
15	1.701	91	.432
16	1.727	80	.475
17	1.651	86	.462
18	1.603	90	.442
19	1.959	92	.492
20	1.689	83	.436
21	1.461	92	.413
22	1.436	75	.433
23	1.846	91	.460
24	1.644	90	.428
25	1.690	87	.459
26	1.658	86	.445
27	1.798	93	.469
28	1.879	94	.473
29	1.686	90	.445
30	1.629	92	.445

*Theoretically predicted values for deposition of graphite from an 85:15 mole ratio CO:H₂ gas mixture under prevailing experiment conditions.

TABLE 3-5. MULTIPLE CYCLE RE-CARBURIZATION PERFORMANCE OF THE K2 CATALYST THROUGH 28 GASIFICATION-CARBURIZATION CYCLES

REACTION CYCLE	SPECIFIC CARBON DEPOSITION RATE (g CARBON/HR/ g CATALYST METAL)	CO CONVERSION (%)	CO SELECTIVITY TO CARBON (MOLE CARBON/MOLE CO CONVERTED)
Theoretical*	1.8	99.997	.557
1	.508	61	.334
2	.602	69	.403
3	.476	61	.359
4	.507	59	.352
5	.440	54	.308
6	.464	41	.346
7	.533	45	.341
8	.623	46	.387
9	.553	38	.392
10	.594	42	.382
11	.676	44	.379
12	.700	47	.360
13	.613	43	.341
14	.647	47	.352
15	.677	47	.376
16	.617	41	.356
17	.680	47	.357
18	.714	46	.401
19	.732	48	.405
20	.783	52	.388
21	.676	48	.432
22	.784	52	.387
23	.765	47	.408
24	.738	58	.381
25	.745	52	.396
26	.698	49	.383
27	.639	48	.364
28	.705	44	.398

*Theoretically predicted values for deposition of graphite from an 85:15 mole ratio CO:H₂ gas mixture under prevailing experiment conditions.

active and stable throughout the number of reaction cycles completed. Under the carburization conditions employed (see Section 3.1.1), the K1 catalyst showed a better approach to equilibrium-predicted performance than the K2 catalyst despite a lower carburization temperature. The carbon deposition rate, CO conversion, and CO selectivity to carbon were all higher with the K1 catalyst. The superior performance of the K1 catalyst is consistent with earlier non-cyclic carburization tests which showed the K2 catalyst to be a less active carburization catalyst than either the baseline catalyst or the K1 catalyst.

3.2 CATALYST DEVELOPMENT AT SOHIO

During this quarter, laboratory work continued with both C77-K1 and C77-K2 catalysts. In one experiment, the catalyst preparation procedure was modified in an attempt to improve the stability of the C77 catalysts, especially the K1 version. Multiple-cycle testing of laboratory prepared catalyst C77-K2 was conducted in the one-inch quartz fluid bed reactor and in a new Alonized stainless steel laboratory reactor. Twenty one-kilogram batches of C77-K2 were prepared, and samples were tested for catalytic activity. The test series on promoted variations of the new C78 catalysts was completed, and further experiments were conducted with the C78 catalysts.

3.2.1 Multiple-Cycle Testing of Catalyst C77-K2

Forty cycles of carbon deposition and gasification (steaming) were planned to determine the performance characteristics of catalyst C77-K2 under repetitive cycling conditions. Testing was done in the one-inch diameter quartz fluid bed reactor* at atmospheric pressure starting with 40 cc samples of uncarburized catalyst.

Results of the first test are shown in Table 3-6. During the first three cycles, the catalyst bed expanded from 40 cc to 70 cc. There was no evidence of carbon accumulation in the bed or on the exterior of the

* Previously described in "Development of BEACON Technology, Quarterly Report, April-June 1980," Report No. DOE/MC/14400-01, Published November 1980, Section 3.1.2.

TABLE 3-6. MULTIPLE-CYCLE TESTING OF CATALYST C77-K2 (TEST 1)

CYCLE	OPERATION	TEMPERATURE (°C)	SPECIFIC REACTION RATE (g carbon/hr/g catalyst metal)	CARBON DEPOSITED (+) OR REMOVED (-) (grams)	RESIDUAL CARBON* (grams)	VOLUME OF CATALYST BED (cc)
1	Carburization	450	0.64	+4.63	4.63	52
	Methanation	550	0.31	-1.93	2.70	53
2	Carburization	450	0.71	+2.38	5.08	53
	Steaming	650	1.01	-3.22	1.86	60
3	Carburization	450	0.69	+3.19	5.05	70
	Steaming	550	0.56	-2.74	2.31	70

* At the end of each operation (half-cycle)

catalyst. The catalyst volume was reduced to 52 cc after soaking the catalyst in distilled water and drying it. However, during the next carburization half-cycle the catalyst volume expanded again and the test was terminated. At present we have no reasonable explanation for the bed expansion.

Another forty-cycle test was started using a fresh batch of catalyst. For 16 cycles the catalyst performed well (see Table 3-7). By the third cycle the catalyst bed had expanded to 53 cc. By cycle nine the bed expansion reached a maximum of 69 cc. During cycle 16, some carburized catalyst was lost due to a test error. To determine the weight of the remaining catalyst without carbon, the carbon was removed with steam and hydrogen at high temperature (550 to 725°C). This treatment reduced the activity of the catalyst severely and the test was stopped after 20 cycles.

3.2.2 Alonized Stainless Steel Reactor Testing with Catalyst C77-K2

A small Alonized stainless steel reactor was fabricated to investigate the problems encountered earlier with the 1-1/2 inch Alonized stainless steel bench-scale reactor. Six test cycles were completed with catalyst C77-K2. The carbon deposition rate declined steadily with each succeeding cycle, and the carbon deposit appeared to steadily accumulate on the catalyst. Cycle efficiency averaged about 60% with no apparent time dependence. At the end of the six cycles the catalyst was non-fluidizable.

3.2.2.1 Experiment Description

The reactor and inlet arm (Figure 3-1) were fabricated from 304 stainless steel. After welding the inlet arm to the reactor body, the assembly was treated at the Alon Processing Company. Then the top portions were cleaned and Swagelok connectors were welded to the tubing. The completed reactor assembly was installed in the laboratory setup used earlier for the 1/2-inch microreactor studies.*

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* op cit, DOE/MC/14400-01, Section 3.1.4.1

TABLE 3-7. MULTIPLE-CYCLE TESTING OF CATALYST C77-K2 (TEST 2)

CYCLE	OPERATION	TEMPERATURE (°C)	SPECIFIC REACTION RATE (g carbon/hr/g catalyst metal)	CARBON DEPOSITED (+) OR REMOVED (-) (grams)	RESIDUAL CARBON* (grams)
1	Carburization	450	0.65	+4.35	4.35
	Steaming	550	0.70	-2.24	2.11
2	Carburization	450	0.65	+2.25	4.36
	Steaming	550	0.64	-2.03	2.33
3	Carburization	450	0.70	+2.22	4.55
	Steaming	550	0.61	-1.94	2.61
4	Carburization	450	0.62	+1.98	4.59
	Steaming	550	0.55	-1.77	2.82
5	Carburization	550	0.63	+2.07	4.89
	Steaming	550		-2.63	2.26
6	Carburization	450	0.67	+2.14	4.40
	Steaming	550	0.54	-2.59	1.81
7	Carburization	450	0.60	+2.23	4.04
	Steaming	550	0.70	-2.61	1.43
8	Carburization	450	0.65	+2.70	4.13
	Steaming	550	0.53	-1.64	2.49
9	Carburization	450	0.61	+1.96	4.45
	Steaming	550	0.58	-1.85	2.60
10	Carburization	450	0.63	+1.92	4.52
	Steaming	550	0.58	-2.08	2.44

*At the end of each operation (half-cycle)

TABLE 3-7. MULTIPLE-CYCLE TESTING OF CATALYST C77-K2 (TEST 2) cont

CYCLE	OPERATION	TEMPERATURE (°C)	SPECIFIC REACTION RATE (g carbon/hr/g catalyst metal)	CARBON DEPOSITED (+) OR REMOVED (-) (grams)	RESIDUAL CARBON* (grams)
11	Carburization	450	0.63	+1.84	4.28
	Steaming	550	0.59	-2.06	2.22
12	Carburization	450	0.78	+2.68 [†]	4.90 [†]
	Steaming	550	0.82	-2.40 [†]	2.50 [†]
13	Carburization	450	0.67	+2.11 [†]	4.61 [†] 4.19
	Steaming	550	0.62	-2.10	2.09
14	Carburization	450	0.53	+1.70 [†]	3.79 [†]
	Steaming	550	0.70	-2.22	1.57
15	Carburization	450	0.58	+2.16	3.73
	Steaming	550	0.72	-2.12	1.61
16	Carburization	450	0.64	+2.54	4.15
	AFTER THE LOSS OF SOME CARBURIZED CATALYST				3.86
	Steaming	550	0.73	-1.98	1.88
17	AFTER GASIFICATION/METHANATION OF RESIDUAL CARBON				
	Carburization	450	0.36	+3.48	3.48
	Steaming	550	0.72	-2.15	1.33
18	Carburization	450	0.33	+2.40	3.73
	Steaming	550	0.62	-1.83	1.90
19	Carburization	450	0.31	+1.52	3.42
	Steaming	550	0.54	-1.25	2.17
20	Carburization	450	0.31	+1.51	3.68
	Steaming	550	0.18	-0.52	3.16

* At the end of each operation (half-cycle)

[†] Calculated values

Figure 3-1. Alonized Stainless Steel Reactor

The reactor was charged with 5 cc of C77-K2 and 2.5 cc of untreated carrier. Six carbon deposition/steaming cycles were performed. Reaction conditions are shown in Table 3-8. During each cycle, 250-350 mg of fresh carbon was deposited.

Carbon was removed during steaming until the reactor effluent reached 98% nitrogen on a moisture-free basis. After six cycles, the catalyst-carbon residual was removed from the reactor for physical examination and chemical analysis.

3.2.2.2 Experiment Results

The experiment results are summarized in Figures 3-2 through 3-4. As shown in Figure 3-2, the specific carbon deposition rate (grams carbon/liter catalyst/hour) declined with each succeeding cycle, except for cycle 1 which had an unusually high steam fraction in the deposition feed gas. The carbon monoxide conversion also generally declined with each succeeding

TABLE 3-8. REACTION CONDITIONS FOR C77-K2
TESTS IN ALONIZED REACTOR

	<u>Carbon Deposition</u>	<u>Steaming</u>
Reactor Pressure, psig	40	40
Reactor Temperature, °C	455 - 465	600
Feed Gas Composition	30% CO 6 - 8% H ₂ O* Balance N ₂	25% H ₂ O Balance N ₂
Feed Gas Flow Rate, ml/minute (STP)	180	250

* Cycle 1 had about 20% H₂O in the feed gas.

cycle and exhibited abnormally low values. Again, the first cycle is unique. Carbon deposition reaction selectivities were inconsistent. Excluding cycle 1, whose high steam fraction could be expected to enhance selectivities for the shift and methanation reactions (R1 and R2 in Figure 3-2), it is not clear why the reaction selectivities changed dramatically in cycles 5 and 6.

The carbon deposit accumulated on the catalyst with each succeeding cycle as shown in Figure 3-3, expressed as a percentage of the catalyst weight. The rate of carbon accumulation is consistent with the cycle efficiency which averaged about 60% over the six cycles (Figure 3-4). The data presented in Figures 3-3 and 3-4 are calculated from material balances based on gas chromatograph samples. Since the microanalysis of the spent catalyst is not complete, the actual carbon accumulated on the catalyst is not known at this time.

The spent catalyst removed from the reactor was a black, sticky solid. The material could not be poured from the reactor and had to be tapped out. About 10% of the solids was found lodged against the various filters in the reactor system. Including the estimate of residual carbon, the solids balance was 81%.

X-ray diffraction tests on the recovered solids indicated only catalyst and amorphous carbon as identifiable crystalline phases. Scanning electron micrographs showed undisturbed catalyst carrier and a lot of debris. Surfaces were rough. The debris could have been responsible for the poor fluidizability of the spent catalyst.

3.2.2.3 Conclusions

No firm conclusion regarding inactive carbon can be made until the microanalysis of the solids recovered from the reactor is completed. The actual weight of the solids recovered was about 99% of the predicted value in the absence of residual carbon. However, calculated values based on gas chromatography indicated accumulated carbon equal to about 30% of catalyst weight at the end of six cycles. In any event, cycle efficiencies did not

Figure 3-2. Carbon Deposition Results

indicate a severe problem with inactive carbon, and it must be tentatively concluded that the difficulties experienced in the 1-1/2 inch bench-scale reactor were not due to the Alon coating on the reactor.

The poor fluidizability of catalyst C77-K2, experienced earlier in the 1-1/2 inch bench-scale reactor* and again during these laboratory tests, poses a real difficulty. In conjunction with the poor performance in the 4-inch fluid bed reactor (Section 4.1.1 of this report), real questions have been raised regarding the operability of the C77-K2 catalyst.

* "Development of BEACON Technology, Quarterly Report, April-June 1981," Report No. DOE/MC/14400-05, Published December 1981, Section 4.2

Figure 3-3. Accumulated Carbon Deposit at the End of Each Cycle

Figure 3-4. Cycle Efficiency

3.2.3 Promoted Catalyst Screening Experiments

One additional promoted catalyst was prepared and testing during this quarter. The experiment procedures were described in the previous quarterly report.* Experiment data are reported in Table 3-9; data on the catalyst compositions tested last quarter are repeated for comparison. The performance of K2-P7 was similar to that of K2-P3, ranking slightly above K2-P3 for average carbon monoxide conversion rate during carbon deposition, and slightly above unpromoted K2 for selectivity for the methane reaction during gasification. Using the scoring scheme devised last quarter for ranking catalysts with respect to carbon deposition capability,** the catalysts ranked as follows:

Catalyst: K1 > K2-P10 > K2-P3 > K2-P7 > K2 > K1-P14 > K2-P14

Score: (24 points max)   22   18   14   12   7   6   5

3.2.4 Further Experiments with Catalyst C78-K1

The excellent performance of the unpromoted C78-K1 catalyst during last quarter's catalyst screening experiments* motivated further work with this catalyst. Two questions addressed during this quarter were 1) how much catalyst must be used to obtain interpretable results, and 2) does the amount of carbon deposited or the rate of carbon deposition affect the reactivity of the carbon during gasification?

For carbon deposition, the quantity of catalyst present definitely affected the results, but only at the higher CO feed rate where the system appeared to be catalyst limited. For carbon gasification, gas-solids mixing appeared to have a greater influence on the results than the quantity of catalyst (carbon) present. The rate of carbon deposition appeared

* op cit, DOE/MC/14400-05, Section 3.2.3

** ibid, Section 3.2.3.2

TABLE 3-9. DATA FROM CATALYST SCREENING EXPERIMENTS

Series	9180										9356									
Run Number	37	52	54A	54B	66	70	80	88	94	97	102	15	19	23	26	29	34	43	47	50
Catalyst	K2	K2	K2	K2	K2*	K2*	K2-P14*	K2-P14*	K1*	K1*	K1-P14*	K2-P10*	K2-P10*	K2-P3*	K2-P3*	K2-P3*	K2-P3*	K2-P7*	K2-P7*	K2-P7*
CARBON DEPOSITION																				
Temperature (°C)	458	470	457	459	450	470	453	470	443	447	461	470	471	471	455	450	448	457	459	456
CO Partial Pressure (psia)	10	14	17	13	10	29	11	22	11	22	11	11	22	11	22	11	11	12	22	12
H ₂ /CO Ratio	0	0	.15	.55	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H ₂ O/CO Ratio	.51	.74	0	0	.64	.66	.45	.18	.42	.27	.34	.42	.22	.44	.28	1.12	.62	.68	.45	.57
CO Conversion (%)	75	80	19	30	76	78	49	12	84	78	58	85	71	59	49	67	68	69	59	63
Reaction Selectivity (%)																				
CO + H ₂ O = CO ₂ + H ₂	38	65	**13	**29	73	67	75	64	40	32	54	20	12	36	45	65	45	39	18	34
4CO + 2H ₂ O = 3CO ₂ + CH ₄	27	35	**45	**71	27	33	25	7	11	7	18	33	24	12	12	10	11	23	11	28
2CO = CO ₂ + C	35	0	**41	**0	0	0	0	29	48	61	28	48	64	52	43	25	44	38	71	38
H ₂ Conversion (%)	—	—	79	69	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Selectivity to H ₂ O (%)	—	—	13	17	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
H ₂ O Conversion (%)	52	68	—	—	62	77	79	36	63	54	87	68	83	49	54	36	46	43	34	52
Selectivity to H ₂ (%)	42	38	—	—	31	18	57	84	60	56	61	18	19	66	51	79	71	46	45	38
Average Reaction Rate (mol/kg catalyst metal/hr)																				
CO	-160	-340	-75	-97	-200	-780	-121	-61	-233	-427	-133	-273	-440	-193	-280	-173	-173	-27.3	-43.9	-26.4
H ₂ O	-70	-187	7	21	-87	-360	-79	-34	-70	-71	-70	-90	-113	-75	-79	-107	-75	-11.9	-13.6	-13.2
H ₂	29	73	-51	-114	27	65	44	29	41	39	43	17	22	49	41	83	53	5.3	11.8	7.2
CH ₄	19	58	22	48	31	148	17	3	13	17	13	36	44	13	19	12	10	3.1	2.8	3.7
C	25	0	10	0	0	0	0	12	61	147	21	53	120	53	66	27	43	5.1	10.6	2.3
Carbon Deposited (mg)	283	0	117	0	0	0	0	232	302	547	260	235	275	173	189	106	322	326	206	211
GASIFICATION																				
Average Carbon Reaction Rate (mol/kg catalyst metal/hr)	-46				-37	-37	-36	-3	-5	-75	-90	-5	-49	-46	-27	-34	-27	-43	-4.9	-6.8
H ₂ O Selectivity to CH ₄ (%)	8				11	10	9	0	0	15	20	0	22	19	5	4	2	5	11	21
Reaction Selectivity (%)																				
C + H ₂ O = CO + H ₂	16				1	6	5	0	0	4	10	0	3	9	5	12	9	16	12	21
C + 2H ₂ O = CO ₂ + 2H ₂	79				95	85	87	100	100	82	72	100	78	75	90	84	89	80	80	66
2C + 2H ₂ O = CO ₂ + CH ₄	5				5	8	7	0	0	14	18	0	20	16	5	4	2	4	9	13
Carbon Removed (mg)	223				207	98	99	6	13	193	333	18	122	176	66	124	79	163	132	191
NET CARBON																				
Cycle Efficiency (%)	79	NM	NM	NM	NM	NM	NM	6	64	61	7	52	64	38	66	75	51	40	73	91
Net Deposit This Cycle (mg)	60	0	117	-207	-98	-99	-6	219	109	214	242	113	99	107	65	27	159	194	56	20
Net Deposit Cumulative (mg)	60	60	177	-30	-98	-187	-6	213	109	323	242	113	212	107	172	199	358	194	250	270
Carbon on Catalyst *** (mg)	—	—	—	140	—	86	—	12	—	270	166	—	†	—	—	—	†	—	—	†

* Diluted with untreated bulk carrier

*** From laboratory analysis

** H₂ Reactions: CO + H₂ = H₂O + C
2CO + 2H₂ = CO₂ + CH₄
2CO = CO₂ + C

† Laboratory analysis not yet available

NM Not meaningful

to affect the reactivity of the carbon during gasification, particularly at the higher deposition rates. The cycle efficiency remained high in all cases.

3.2.4.1 Experiment Description

The C78-K1 catalyst and additional catalyst carrier were used to prepare three catalyst samples for testing. These samples differed in volume and catalyst distribution as shown in the upper portion of Table 3-10.

The experiments were conducted in a 1-inch diameter Inconel fluid bed reactor (Figure 3-5). Reactor pressure, temperatures, and feed gas flow rate for the carbon deposition and gasification reactions are shown in the lower portion of Table 3-10.

TABLE 3-10. CATALYST C78-K1 FORMULATIONS AND
FIXED EXPERIMENT CONDITIONS

CATALYST FORMULATIONS		
<u>Designator</u>	<u>Volume</u>	<u>Composition</u>
A	40 cc	100 vol % C78-K1
B	40 cc	30 vol % (12 cc) C78-K1; 70 vol % (28 cc) inert bulk carrier
C	12 cc	100 vol % C78-K1
FIXED EXPERIMENT CONDITIONS		
	<u>Carbon Deposition</u>	<u>Gasification</u>
Reactor Pressure, psig	5	5
Reactor Temperature, °C	450	600
Feed Rate, cc/minute	200	200

Figure 3-5. Inconel Tube Fluid Bed Reactor.

The initial carbon deposition feed gas composition (before H_2O augmentation) was either 57% CO in N_2 (low level) or 100% CO (high level). On the way to the reactor this feed gas was passed through a humidifier where it was saturated with water vapor. The actual feed gas composition for each cycle is shown in Table 3-11. Total flow was 200 cc/minute.

For gasification, a nitrogen gas stream was passed through the humidifier where it was saturated with water vapor (approximately 20% absolute humidity). The actual H_2O fraction for each cycle is shown in Table 3-11. Total flow was 200 cc/minute.

The reactor temperature was reduced to ambient between runs, i.e., between each carbon deposition and gasification half-cycle. A constant N_2 purge was used at all times that reactant gases were not passing through the reactor.

During each run, product gas composition was measured with a gas chromatograph at 20-minute intervals, and product gas flow was measured continuously using a wet test meter.

Quantities of CO, CO_2 , H_2 , CH_4 and other product gas constituents were calculated from product gas composition and volume data. CO_2 was also adsorbed on Ascarite. In most cases, the calculated weight of CO_2 was within a few percent of the measured weight (Ascarite weight gain).

Water was condensed from the product gas stream and collected in a graduated glass tube. Any residual water vapor in the gas stream was adsorbed on Drierite and weighed.

3.2.4.2 Discussion of Experiment Results

Referring to Table 3-11, the carbon deposition rates were approximately the same (12 mg/minute average) for all runs at the lower CO feed rate (53% CO fraction in the feed gas). There was a substantial increase in the carbon deposition rate for all runs at the higher CO feed rate (approximately 83% CO fraction in the feed gas). The average carbon deposition rate doubled to 24 mg/minute at the higher feed rate. This suggests that the system was feed gas limited rather than catalyst limited, although the substantially larger increase in carbon deposition rate for sample A (which had 3.3 times the amount of catalyst of samples B and C) suggests that the quantity of catalyst may have limited the carbon deposition rates of samples B and C at the higher CO feed rate.

However, there was no corresponding decrease in CO conversion for samples B and C (CO conversions actually increased), although the increase in CO conversion for samples B and C was much less than for sample A. It is also interesting to note that H₂O conversions increased for samples B and C at the higher CO feed rate, whereas for sample A the H₂O conversion decreased at the higher CO feed rate.

Turning now to the gasification portion of the cycle, the mean carbon gasification rate over all four runs for samples A and B was nearly the same (12 mg/minute) whereas the rate for sample C was somewhat lower (9 mg/minute). Samples A and B had the same total volume (40 cc) but different quantities of catalyst, whereas samples B and C had the same quantity of catalyst (12 cc) but different total volumes. Thus, the mean carbon gasification rate appears to be more closely related to the total sample volume than to the quantity of catalyst (and hence the quantity of carbon) present. The higher mean carbon gasification rate for sample B compared with sample C may have been due to better gas-solids mixing in the larger volume. The similarity in mean carbon gasification rates for samples A and B, which had substantially different catalyst (carbon) content, suggests that the system was feed gas (steam) limited within the range of parameters tested.

Reaction selectivities and steam utilization during gasification varied as a function of reaction time (Figure 3-6). Selectivities for CO and CH₄ were high during the early portion of the run when about 90% of the feed steam was converted. As the steam-to-carbon ratio increased during the run, the steam utilization decreased and reaction selectivities shifted to CO₂ and H₂. This behavior suggests that product gas composition is strongly influenced by the steam-to-carbon ratio.

Comparing gasification performance with carbon deposition parameters, the data suggest that some relationship exists between the carbon deposition rate and the carbon gasification rate. The mean carbon gasification rate had a positive correlation with the mean carbon deposition rate for all cycles in the case of sample A, and for cycles 1 and 3 versus cycles 2 and 4 for samples B and C. Cycles 1 and 3 were run at the higher CO feed rate and had substantially higher carbon deposition rates than cycles 2 and 4. The mechanism for such a relationship is not apparent from the data.

The cycle efficiency remained high (over 80%) in all cases and appeared to be independent of variations in the carbon deposition parameters.

3.2.5 Bench-Scale Preparation of Catalyst C77-K2

One-kilogram batches of catalyst C77-K2 were prepared using a scaled-up version of the laboratory preparation procedure. The catalytic activity of these batches for carbon deposition, steaming, and methanation was tested in the one-inch quartz fluid bed reactor.* The test results are shown in Table 3-12.

The first batch had to be discarded because of problems that occurred during preparation. With the exception of combined batch 12, 13, 14 and batch 17, all batches gave satisfactory results. Combined batch 12, 13 and 14 had a low steam gasification rate at 650°C, and batch 17 had a low steam gasification rate at 550°C.

* op cit, DOE/MC/14400-01, Section 3.1.2

TABLE 3-11. CATALYST C78 EXPERIMENT RESULTS

CATALYST AND CYCLE NUMBER	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3	C4
CARBON DEPOSITION												
Feed Gas Composition, % CO (balance N ₂ and H ₂ O)	83.6	52.7	84.3	52.7	82.1	52.8	85.1	52.8	80.3	52.6	84.1	52.2
Feed Gas Composition, CO/H ₂ O Ratio	5.1	5.4	5.4	5.9	4.6	5.3	5.7	5.4	3.8	5.3	5.3	5.3
CO Conversion, %	86.3	74.6	85.8	73.1	76.5	71.8	71.0	59.8	78.6	78.4	69.3	63.8
Selectivity to C, %	35.1	35.1	36.2	33.9	31.3	36.4	35.1	33.2	25.5	35.3	31.3	27.6
Selectivity to CH ₄ , %	4.9	3.7	4.6	4.0	5.2	2.3	3.6	2.4	9.7	4.6	4.6	4.1
Selectivity to CO ₂ , %	60.0	61.3	59.1	62.1	63.6	61.3	61.3	64.4	64.8	60.1	63.1	68.3
H ₂ O Conversion, %	79.9	81.1	79.7	85.9	88.1	79.4	87.6	82.1	90.2	83.3	89.2	81.9
Carbon Deposition Rate												
Average Rate (up to 12% carbon deposit*), mg/minute	35.8	13.8	28.9	12.3	19.1	13.8	23.4	8.5	17.3	14.2	18.6	10.0
Average Rate (12% to 23% carbon deposit*), mg/minute	-	-	30.4	13.9	-	-	23.4	11.7	-	-	21.0	9.8
Carbon Deposit on Catalyst at End of Carbon Deposition*, %	10.7	10.1	24.0	24.6	13.7	12.8	20.8	23.2	11.4	13.6	23.0	20.0
GASIFICATION												
Feed Gas Composition, % H ₂ O (balance N ₂)	21.6	19.0	21.1	19.1	21.4	19.6	22.1	19.1	20.9	21.1	21.9	20.8
Carbon Gasification Rate												
Peak Rate, mg/minute	25.3	19.9	22.7	19.1	22.7	21.5	33.3	24.1	17.5	19.7	18.9	18.1
Mean Rate, mg/minute	15.1	9.8	12.8	9.3	10.9	9.1	14.0	14.0	8.8	7.7	10.3	8.2
CYCLE EFFICIENCY**, %	95.8	98.4	82.6	84.8	85.3	86.0	87.3	91.3	115.4	90.6	81.9	102.0
* Carbon Deposit = $\frac{\text{Weight of Carbon Deposit}}{\text{Weight of Catalyst Metal}} \times 100$ ** Cycle Efficiency = $\frac{\text{Weight of Carbon Gasified During the Cycle}}{\text{Weight of New Carbon Deposited During the Cycle}} \times 100$												

Figure 3-6. Gasification Reaction Selectivities and Steam Utilization Versus Reaction Time

An interesting observation was made during these runs. Once the catalyst became stuck at the sparger the reactor became fixed bed. The product gas composition during steaming in this "fixed bed" mode is compared with a typical well-fluidized run in Table 3-13. Considerably more methane was formed in the "fixed bed" mode than in the well-fluidized bed. On the other hand, the carbon monoxide level was very low in the "fixed bed" mode. Further investigation is planned.

TABLE 3-12. TEST RESULTS OF BENCH-SCALE CATALYSTS (C77-K2)

Run	Batch	Specific Rates (g carbon/g catalyst metal/hour)		
		Carbon Deposition at 450°C	Methanation at 550°C	Steaming at 650°C
75A	1 (Discarded)	---	---	---
75B	2	0.62	0.21	0.98
75C	3,4,5,6	0.70	0.23	0.85
75D	7,8	0.62	0.20	0.77
75E	9,10,11	0.65	0.22	0.75
75F	12,13,14	0.66	0.19	0.63
75G	15,16	0.57	---	0.72
75H	17	0.62	0.16	0.49 (@ 550°C)
75I	18	0.70	0.17	0.64 (@ 550°C)
75J	19,20	0.58	---	0.73

TABLE 3-13. PRODUCT GAS COMPOSITION -- "FIXED BED"
VERSUS FLUIDIZED BED

Component	"Fixed Bed" (Mole %)	Well-Fluidized Bed (Mole %)
Hydrogen	20.21	33.26
Carbon Dioxide	22.88	15.84
Nitrogen	39.82	34.24
Methane	13.52	4.68
Carbon Monoxide	3.58	11.97

3.2.6 Catalyst Preparation Modifications

K1 and K2 versions of the C77 catalyst were prepared using a modified carrier. The activity of the modified C77-K2 catalyst was equal to that of the standard C77-K2 preparation. This indicated that the modification did not interfere with the catalyst performance. The K1 version of the modified catalyst was less active than the K2 version, and the fluidization properties of the K1 catalyst deteriorated with cycling. However, the modified C77-K1 catalyst was an improvement over the standard C77-K1 preparation.

The new technique for catalyst preparation introduced last quarter* was investigated further during this quarter. K1 and K2 catalysts were prepared using the new technique. The results were disappointing. The K2 version of the catalyst showed no performance advantage over the standard C77 preparation. The K1 version could not be tested because of poor fluidization.

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* op cit, DOE/MC/14400-05, Section 3.2.3

4. TASK 2 - CARBON DEPOSITION AND GASIFICATION IN BATCH MODE BENCH-SCALE EQUIPMENT

4.1 FOUR-INCH DIAMETER, HIGH PRESSURE, FLUID BED REACTOR TESTING

During the quarter, carbon deposition/gasification multiple-cycle tests with catalyst C77 were continued until catalytic activity dropped to an unacceptable level after 5-1/2 cycles. The spent catalyst is being examined to determine the probable cause(s) for the reduction in catalytic activity.

The cyclone (lock-hopper type) solids return system underwent further testing this quarter. It continued to perform satisfactorily with reactor gas velocities up to 23 cm/sec (0.75 ft/sec) with a short bed -- 60 cm (2 feet), which is adequate for current testing, but it was inefficient at gas velocities approaching 30 cm/sec (1 ft/sec) with a tall bed -- 90 cm (3 feet). So, a variable differential pressure ("huff-puff") concept which does not require gas/solids separation is now being considered for the transfer of solids between carbon deposition and carbon gasification reactors instead of the lock-hopper approach to solids feed and withdrawal under consideration previously. A cold flow unit is being designed to test the "huff-puff" concept.

Multiple-cycle carbon deposition/gasification testing of K2-based BEACON solids was started this quarter. The test series will include both single and two stage steam gasification.

Testing was performed in the 4-inch diameter, 12-foot long, high pressure fluid bed reactor system described in detail in the quarterly report covering the period October-December 1980.* The tests were conducted in batch mode with respect to solids and in continuous, steady feed mode with respect to gases. Reaction temperature and pressure were kept constant during each run. Individual gas feed and product gas flow rates were continuously monitored using calibrated orifice meters. Product gas

* op cit, DOE/MC/14400-03, Section 4.2

compositions were measured every 8-1/2 minutes using an on-line gas chromatograph. In addition, the CO, CO₂, and CH₄ components of the product gas were monitored continuously using NDIR analyzers. The product gas flow rate also was measured using a dry gas meter. The procedure used in the multiple-cycle testing of catalyst C77 was described in the previous quarterly report.* The test procedures used and measurements performed in first and second stage steaming were described in a previous quarterly report.** The procedure used in testing the cyclone solids return system is described in Section 4.1.2 of this report.

4.1.1 Fluid Bed C77 Multiple-Cycle Performance Tests

Multiple-cycle performance tests on catalyst C77, which were initiated at the end of last quarter, were completed during the current quarter. The tests involved repeated carbon deposition/gasification operations between 5 and 20% by weight carbon loadings (nominal values) at 450° and 550°C, respectively. Testing was terminated prior to completion of the test matrix published in the previous quarterly report* because of deterioration in catalytic activity. Attempts to reactivate the catalyst were not successful. The spent catalyst is undergoing physical and chemical examinations at SOHIO to determine the probable cause(s) for the observed reduction in activity. Preliminary data also indicate appreciable catalyst breakup. It has been decided to discontinue large batch life testing of C77 until additional laboratory-scale data on its multiple-cycle performance justifies the larger scale tests. The data generated during the multiple-cycle tests are summarized in Tables 4-1 and 4-2. Data from the first four cycles were presented in the previous quarterly report;* they are repeated here for the sake of completeness.

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* op cit, DOE/MC/14400-05, Section 4.1.3.

** "Development of BEACON Technology, Quarterly Report, January-March 1981," Report No. DOE/MC/14400-04, Published July 1981, Section 4.1.

**TABLE 4-1. C77 MULTIPLE-CYCLE CARBON DEPOSITION/GASIFICATION
PERFORMANCE DATA**

CYCLE	OPERATION*	REACTION INTERVAL (MINUTES)	TEMP (°C)	LINEAR GAS VELOCITY (FT/SEC)	REACTION RATE	
					(gC/hr)	(gC/hr/gCAT METAL**)
1	CD-1A	24	450	0.39	413	0.55
	1B	84	480	0.49	460	0.62
	M-1	330	547	0.40	274	0.39
2	CD-2	170	454	0.31	228	0.31
	M-2	112	550	0.40	285	0.39
3	CD-3	52	454	0.32	235	0.32
	S-1	42	564	0.39	328	0.47
4	CD-4	64	443	0.31	227	0.31
	S-2	95	554	0.48	359	0.48
5	CD-5	129	454	0.36	250	0.42
	S-3	41	550	0.54	337	0.49
6	CD-6	145	450	0.36	266	0.39
	S-4	147	552	0.53	208	0.30
7	CD-7	218	450	0.26	67	0.22
	S-5	75	545	0.44	248	0.37
8	CD-8	369	450	0.35	131	0.20
	M-3A	274	550	0.40	126	0.19
	M-3B	199	550	0.39	58	0.09
9	CD-9	140	463	0.36	185	0.28
	S-6	320	560	0.44	247	0.38

*CD denotes carbon deposition, M denotes methanation by H₂, and S denotes gasification by steam

**Based on weight of catalyst metal in the reactor at start of operation. (Note: carbon/catalyst collected in filter was not returned to the reactor at the end of every run)

TABLE 4-2. PRODUCT GAS AND FEED GAS COMPOSITION DATA FROM C77 MULTIPLE-CYCLE TESTING

CYCLE	OPERATION **	PRODUCT GAS COMPOSITION, % V/V DRY BASIS *					FEED, V/V%		
		CH ₄	H ₂	CO	CO ₂	N ₂	N ₂	CO	H ₂ OR STEAM
1	CD-1A	0	0	8.3(1.5)	52.4(60.0)	38.6(38.5)	24	76	0
	1B	3.8(0.4)	1.9(3.0)	7.1(2.8)	51.7(57.9)	35.5(35.9)	20	72	8
	M-1	34.6(38.7)	52.8(48.1)	0	0	12.6(12.5)	9	0	91
2	CD-2	6.5(1.3)	2.6(4.0)	2.9(1.3)	39.1(38.6)	48.9(54.8)	32	55	13
	M-2	34.7	53.4	0	0	11.8	9	0	91
3	CD-3	6.0	2.7	2.8	39.0	49.6	32	55	13
	S-1	6.5(13.1)	46.9(34.4)	3.0(7.2)	27.3(26.7)	16.3(18.5)	16	0	84
4	CD-4	6.5	2.0	2.5	39.4	49.7	32	55	13
	S-2	7.5	40.5	5.0	26.5	20.5	16	0	84
5	CD-5	6.6	2.5	3.7	38.2	49.0	32	55	13
	S-3	3.1(16.2)	44.5(37.8)	4.0(7.4)	25.8(31.4)	22.5(7.3)	6	0	94
6	CD-6	7.1(1.5)	2.3(4.4)	2.6(1.4)	39.0(41.2)	49.0(51.5)	29	57	14
	S-4	2.4(15.2)	43.2(36.8)	1.6(7.4)	22.5(29.9)	30.3(10.7)	9	0	91
7	CD-7	3.9(1.9)	7.8(4.3)	42.0(1.2)	9.1(40.4)	37.2(52.3)	29	56	15
	S-5	2.0(15.6)	44.6(37.0)	4.1(7.3)	26.0(30.5)	23.3(9.6)	8	0	92
8	CD-8	2.6(1.3)	6.8(4.2)	36.1(1.6)	13.5(43.4)	41.0(49.6)	28	59	13
	M-3A	12.2(39.6)	77.8(49.3)	0.0	0.0	10.0(11.2)	8	0	92
	M-3B	5.2	85.8	0.0	0.0	8.9	8	0	92
9	CD-9	4.4(1.3)	9.3(4.5)	23.2(1.7)	22.3(41.9)	40.8(50.6)	29	58	13
	S-6	1.8(13.6)	51.0(36.6)	4.4(8.0)	25.1(28.0)	17.7(13.8)	12	0	88

*VALUES IN PARENTHESES REPRESENT EQUILIBRIUM COMPOSITIONS FOR THE INDICATED FEED.

**CD DENOTES CARBON DEPOSITION, M DENOTES METHANATION BY H₂, AND S DENOTES GASIFICATION BY STEAM.

The tests were performed at 10 psig reactor pressure under fluid bed conditions; the linear gas velocity in the reactor was approximately 12 cm/sec (0.4 ft/sec) and the bed height at rest was approximately 120 cm (4 feet). In three of the cycles carbon removal was performed with hydrogen and in the remaining six with steam.

Through the first 5-1/2 cycles the specific reaction rates for carbon deposition, methanation, and steam gasification remained virtually unchanged within each operational group (the carbon deposition rate in the first cycle was higher because of higher CO feedrate). These rates were obtained at near equilibrium feed utilizations and were not affected by temperature cycling due to start-ups and shutdowns or by a five week interruption in testing (between cycles 4 and 5) to modify the apparatus in order to eliminate solids emissions to the environment. During the second half of the sixth cycle the steam gasification rate dropped by approximately 40%; the same drop was experienced in the carbon deposition rate in the next cycle (cycle 7). The rates stabilized at the reduced values through cycle 8. In cycle 9, the carbon deposition rate recovered substantially; the steam gasification rate started at its normal value but dropped quickly to below 100 grams/hour (0.13 grams per hour per gram catalyst metal). Attempts to regenerate the catalyst through methanation with hydrogen and carbon burn-off with air were not successful. The system acted as if a substantial portion of the catalyst had been lost. Chemical analysis of the solids recovered from the reactor did not indicate appreciable changes in the composition of the catalyst during testing. It is believed that appreciable changes occurred in the active surface area of the catalyst (possibly due to overheating). Laboratory-scale testing is underway to determine the multiple-cycle performance of the catalyst under ambient pressure (see Section 3.2.1). If these tests are successful, additional large scale testing will be performed under fluidized bed conditions and pressure at a future date.

4.1.2 Cyclone Solids Return System Testing

The cyclone solids return system was tested at high reactor superficial gas velocities -- up to 30 cm/sec (1 ft/sec) -- to determine solids return efficiency and the feasibility of operating a lock-hopper system as a means of continuously feeding solids to the reactor.

The cyclone solids return loop is shown schematically in Figure 4-1. Valves V1 and V2 are air-operated ball valves which cycle open and closed according to the sequence shown in the figure. First V1 is open and V2 is closed for seven seconds. During this time the solids collected in the cyclone drop into the tube between V1 and V2. Then V1 closes. Four seconds later V2 opens for seven seconds to allow solids to drop into the tube below V2. At the bottom of the tube the solids are entrained by the feed gases and returned to the reactor inlet. Then V2 closes and both valves remain closed for four seconds before the sequence repeats itself.

Figure 4-1. Cyclone Solids Return Loop

The recycle efficiency of the system was tested in two steps as follows. In step 1, at the selected reactor pressure, temperature, rest bed height and gas velocity, the cyclone was bypassed by closing V3 and opening V4. This allowed all entrained solids to pass directly to the filter. The entrainment rate was determined by recovering and weighing the amount of solids collected in the filter during the time span of step 1. Next, in step 2, the same conditions of temperature, pressure, and gas velocity were established with V3 open and V4 closed to include the cyclone and recycle loop in the flow system (two cyclones, one having a 4" diameter and the other a 2" diameter, were tested individually). The amount of material collected by the filter during the time span of step 2 was determined as in step 1. The cyclone solids recycle rate was calculated by subtracting the filter solids collection rate in step 2 from the rate measured in step 1.

The results of the cyclone solids return system testing are summarized in Table 4-3. In this table, the rates of entrainment, return to the reactor, and carry-over to the filter are listed in columns A, B, and C, where $A = B + C$. A carry-over rate to the filter of 1 gram/minute was established as the maximum acceptable rate for long term cycling tests.

As indicated by the low carry-over rates measured for tests 4 and 7, the cyclone solids return system recycle efficiency was shown to be acceptable under certain conditions. At a reactor gas velocity of 23 cm/sec (0.75 ft/( )), the maximum tolerable rest bed height in the 4-inch reactor was found in tests 3, 5, 6 and 7 to be 60 cm (2 feet). In tests 1 through 5, for a 90 cm (3 foot) rest bed height, the system was found to operate acceptably only at a reactor gas velocity of 15 cm/sec (0.50 ft/sec). The occurrence of high carry-over rates at reactor gas velocities greater than 15 cm/sec (0.50 ft/sec) with a 90 cm (3 foot) rest bed height is believed to be attributable to the cycling action of the valves which may have disturbed the solids flow out of the bottom of the cyclone, thereby reducing its efficiency under conditions of high solids flows. The effect of cyclone diameter on recycle efficiency could not be determined from these tests.

TABLE 4-3. SUMMARY OF CYCLONE SOLIDS RETURN SYSTEM TESTING

TEST NO.	REACTOR		REACTOR GAS VELOCITY		REST BED HEIGHT		CYCLONE DIAMETER (inches)	TEST DURATION (minutes)	(A) MEASURED ENTRAINMENT STEP 1 (grams/minute)	(B) ESTIMATED RETURN TO REACTOR (grams/minute)	(C) MEASURED CARRY-OVER TO FILTER STEP 2 (grams/minute)
	PRESSURE (psig)	TEMP (°C)	(cm/sec)	(ft/sec)	(cm)	(ft)					
1	113	Amb.	28.3	0.93	90	3	4	8	96.6	49.6	47.0
2	107	Amb.	26.5	0.87	90	3	4	9	96.6	59.3	37.3
3	51	Amb.	22.6	0.74	90	3	4	33	5.4	3.2	2.2
4	55	538	15.2	0.50	90	3	4	60	2.1	1.4	0.7
5	66	538	22.9	0.75	90	3	2	30	30.3	4.4	25.9
6	58	538	22.9	0.75	60	2	2	60	2.6	1.3	1.3
7	61	538	22.9	0.75	60	2	2	480	-	-	0.42

It was decided to proceed with the K2-based BEACON solids cycling tests with the reactor system as presently configured. Modifications to the reactor to reduce entrainment, and changes in the cyclone solids return system design are being considered as methods for increasing the maximum acceptable reactor gas velocity to a target of 30 cm/sec (1 ft/sec).

As a prototype lock-hopper system for continuous feed of solids, the return loop did demonstrate the capability of transporting solids. During tests 1 and 2, recycle solids flows of 50 to 59 grams/minute were observed. However, a variable differential pressure transport system which does not require gas/solids separation is currently being considered as a simpler concept for the transfer of solids between the carbon deposition and carbon gasification (steaming) reactors (see Section 4.1.3). Lock-hoppers will be the backup concept.

4.1.3 "Huff-Puff" Tandem Reactor System

A variable differential pressure transfer line ("huff-puff") concept was formulated for the transfer of solids between BEACON carbon deposition and carbon gasification reactors instead of the lock-hopper type of solids feed and withdrawal system under consideration previously. The "huff-puff" transfer system does not require gas/solids separation prior to transfer, and therefore it is simpler than a lock-hopper type system for fluidized bed operations.

In the current BEACON operational concept, carbon deposition and carbon gasification operations take place in separate reactors at operating conditions optimized for each operation. With the "huff-puff" transfer system, operating conditions can be substantially different in the two reactors except for pressure; it is required that both reactors operate at nearly the same pressure and under fluidized bed conditions. The only other requirement is that the relative size of the two reactors be such that the quantity of carbon deposited per unit time in the deposition reactor equal the quantity consumed in the gasification reactor.

The two reactors are connected with a fluid bed transfer line located below the top of the beds. Transfer is accomplished by establishing a small differential pressure between the two reactors at the frequency required. Solids are transferred back and forth by changing the sign of the differential pressure. Less than 5% of the bed is transferred each time. Monitoring and control of the quantity of solids transfer can be accomplished by bed level or pressure monitors and by pressure or flow control valves.

A cold flow unit is being designed to test this concept. The unit will be constructed with clear plastic pipe and will be capable of sustaining one atmosphere pressure (15 psig); it is designed to simulate the future hot flow unit. Because carbon deposition and carbon gasification rates are appreciably different, the size of the two reactors must be different. Based on the anticipated size of the hot flow unit, the cold flow unit will consist of a 10-centimeter (4-inch) diameter column and a 5-centimeter (2-inch) diameter column simulating the carbon deposition and carbon gasification reactors, respectively; the height of the columns will be 2.4 meters (8 feet).

4.1.4 Testing of K2-Based BEACON Solids

In preparation for the K2-based BEACON solids carburization/ steaming multiple-cycle testing, approximately 11 kg of BEACON solids were produced in the ambient pressure reactor. Screening tests were performed in the 4-inch fluid bed reactor to determine the best temperature for the first stage gasification portions of the subsequent cycling tests, and four of the planned fifty cycles were completed.

4.1.4.1 Steaming Temperature Screening Tests

Before starting the cycling tests, the steaming performance of the K2-based BEACON carbon was checked at 650 and 600°C in the 4-inch fluid bed reactor. The reactor was operated at 7.8 atm (100 psig) pressure with a linear gas velocity of approximately 6.1 cm/sec (0.2 ft/sec).

The maximum specific gasification rate for the 650°C run (K2-5) was 3.27 grams/hour per gram carbon in the reactor, which was close to the rate of 4.0 grams/hour per gram carbon measured during K1-based BEACON carbon testing at 650°C. The maximum specific gasification rate could not be calculated for the 600°C run (K2-6) due to uncertainty in the amount of carbon present in the reactor at the time. Maximum steam utilizations were 58% and 54% at 650 and 600°C, respectively.

The 650°C run was repeated with good reproducibility. Upon repeating the 600°C run, however, substantially lower steam utilizations and gasification rates were measured, possibly due to a leak in the apparatus. The 600°C run will be repeated again during the cycling tests.

The compositions of the product gas obtained at 650 and 600°C are summarized in Table 4-4, which includes the equilibrium values in parentheses. These data show that a reactor temperature of 650°C is required for near equilibrium steaming; steam utilization is also higher at the higher temperature. Thus, just as in the case of K1-based BEACON carbon a second, lower temperature gasification stage where the fuel (CO and H₂) in the product gas from the first stage is converted to methane, is suggested by the data. During the cycling tests, a second stage operation will be inserted in the carbon deposition/steaming cycles once every 4 or 5 cycles to assess the effects of processing time and cycling on the catalytic activity of K2-based BEACON solids toward the methanation reaction.

TABLE 4-4. STEAMING TEMPERATURE SCREENING TEST RESULTS
(K2-BASED BEACON CARBON)

7.8 atm (100 psig), Feed 90% H₂^{0/10%} N₂
Linear Gas Velocity = 6.1 cm/sec (0.2 ft/sec)

Test No.	Temp. (°C)		Product Gas Composition (% v/v, dry, N ₂ -free)			
			CH ₄	H ₂	CO ₂	CO
K2-5	650	Measured	13.7	44.9	29.7	11.6
		Equilibrium	(17.8)	(38.3)	(30.2)	(13.6)
K2-6	600	Measured	13.4	48.7	34.3	3.6
		Equilibrium	(23.3)	(32.9)	(35.7)	(8.1)

4.1.4.2 Cycling Tests

The planned reaction conditions for the carburization/steaming cycling tests are summarized in Table 4-5. The spent solids from the earlier steaming runs are being used as the starting material. Fifty cycles are planned, unless the catalyst activity drops substantially, at which time an attempt will be made to regenerate the material by complete gasification of the remaining carbon. If the catalyst cannot be regenerated, cycling testing will be performed with K1-based solids.

Four carburization/steaming cycles have been completed successfully to date with no indication of a decrease in catalytic activity. Reaction rates for both carburization and steaming are remaining high. Data will be reported next quarter.

TABLE 4-5. NOMINAL CONDITIONS FOR MULTIPLE-CYCLE TESTING
OF K2-BASED BEACON CARBON

Reactor Pressure	7.8 atm (100 psig)
Reactor Temperature	
Carburization	450°C
First Stage Gasification (Steaming)	650°C
Second Stage Gasification	500°C
Linear Gas Velocity	9.1 cm/sec (0.3 ft/sec)
Feed Gas Composition (Mol %)	
Carburization	30% CO
	15% H ₂
	50% N ₂
	5% CO ₂
First Stage Gasification (Steaming)	90% H ₂ O - 10% N ₂
Second Stage Gasification	Composition of first stage product gas