2R-0208-9

DOE/MC/14400-1607
(DE84011423)

DEVELOPMENT OF BEACON TECHNOLOGY

Quarterly Report for the Period October—December 1982

Work Performed Under Contract No. FC21-80MC14400

For
Morgantown Energy Technology Center
Morgantown, West Virginia

By
TRW Energy Development Group
Redondo Beach, California

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

DEVELOPMENT OF BEACON TECHNOLOGY

**Quarterly Report for the Period
October—December 1982**

Work Performed Under Contract No. FC21-80MC14400

**Prepared for
U.S. Department of Energy
Assistant Secretary for Nuclear Energy**

**Prepared by
TRW Energy Development Group
Redondo Beach, California**

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
1. INTRODUCTION.	1-1
2. SUMMARY	2-1
2.1 CATALYST DEVELOPMENT AT SOHIO.	2-1
2.2 CATALYST DEVELOPMENT AT TRW FOR SELECTIVE HYDROGEN PRODUCTION	2-2
2.3 TANDEM REACTOR DEVELOPMENT	2-2
2.4 ENGINEERING ANALYSIS	2-3
3. CATALYST DEVELOPMENT	3-1
3.1 CATALYST DEVELOPMENT AT SOHIO.	3-1
3.1.1 Promoters for C77-K2 Catalyst to Suppress Methane Formation and Reduce Volume Expansion	3-1
3.1.2 Testing Large Scale Preparation of C77-K2 Catalyst	3-8
3.2 CATALYST DEVELOPMENT AT TRW FOR SELECTIVE HYDROGEN PRODUCTION.	3-10
3.2.1 Background	3-10
3.2.2 Test Matrix	3-13
3.2.3 Ambient Pressure Results	3-15
4. TANDEM REACTOR DEVELOPMENT.	4-1
4.1 APPARATUS SHAKEDOWN	4-1
4.2 TANDEM REACTOR TESTING	4-7
5. ENGINEERING ANALYSIS.	5-1

LIST OF FIGURES

	<u>Page</u>
3-1 Particle Size Distribution Before/After Loading Class IIB Promoter (Level 5) on C77-K2 Catalyst	3-6
3-2 Particle Size Distribution Before/After Loading Class IIA Promoter (Level 5) on C77-K2 Catalyst	3-7
3-3 Effect of Catalyst Preparation and Composition on Extent of BEACON Carbon Steaming to H ₂	3-20
4-1 Typical Solids Transfer Operation (Tandem Reactors) . . .	4-3
5-1 BEACON Steam-Carbon to Hydrogen Model System.	5-2
5-2 Hydrogen From BEACON Carbon Steaming Used in a Phosphoric Acid Fuel Cell.	5-3
5-3 BEACON - Hydrogen System, Performance With Fuel Cell. . .	5-4

LIST OF TABLES

		<u>Page</u>
3-1	Effect of Promoters on Methane Suppression During Steaming	3-3
3-2	Effect of Promoters on Reducing Volume Expansion	3-5
3-3	Reaction Rates - Pooled Sample of Pilot Plant Preparations of C77-K2 Catalyst.	3-9
3-4	Effect of "Thermal Soak" on Methanation Activity of K-1 BEACON Catalyst.	3-11
3-5	Steam Gasification of Modified K-1 BEACON Carbon (640°C, 1 Atm)	3-12
3-6	Hydrogen Production Catalyst Development Test Matrix (Laboratory Scale Testing)	3-14
3-7	Stability of Methane Suppression Catalyst (Type B, K-1 + 10% Additive F).	3-17
3-8	Stability Testing of Catalyst No. 11 (Type D, K-1 + 10% Additive F + 5% Additive X).	3-19
3-9	Effect of K-2 Additive on Methane Suppression (Type B, K-1 Catalyst).	3-22
3-10	Stability Testing of Catalyst No. 5 (K-1 + 20 Wt. Percent Additive F, Type B) - Ambient Pressure Steaming	3-23
4-1	Bed Weight Determination by DP Measurements.	4-4
4-2	Solids Entrainment Tests (100 Psig, 450°C and 650°C, 0.5 FPS)	4-6
4-3	Carbon Deposition/Steaming Test (Run T-1) - 100 Psig, 450°/650°C	4-8
4-4	Tandem Reactor Steam Gasification Data (600°C, 100 Psig).	4-9

ABSTRACT

The BEACON process involves the catalytic deposition of a highly reactive form of carbon from a gas stream which contains carbon monoxide. The carbon-depleted gas is combusted with air to produce power, and the carbon is reacted with steam to produce methane or hydrogen.

During the quarter both SOHIO and TRW worked on catalysts which would suppress methane formation during steaming thus increasing the amount of hydrogen formed. At SOHIO a C77-K2 catalyst promoted with a Class II compound showed promise in laboratory tests for suppressing methane. At TRW a K-1 unsupported catalyst promoted with 10% of Additive F maintained methane suppression over 30 cycles in laboratory scale tests.

SOHIO also identified some Class III compounds which suppressed the volume expansion of C77-K2 catalysts. Combining promoters for both methane suppression and prevention of volume expansion did not perform both functions. Holding the volume steady was achieved but the methane suppression was not.

A total of seven 4 kilogram batches of C77-K2 catalyst have been made at a pilot plant facility at SOHIO. Laboratory testing of the deposition and steaming rates of samples of each batch and a pooled sample of all batches show consistent rates.

At TRW a study of variables possibly important for reducing methane and increasing hydrogen formation was conducted. This led to the preparation and laboratory evaluation of 20 catalysts. Two of these catalysts show particular promise in that they have maintained their reaction rates, steam utilization and methane suppression in favor of hydrogen formation for more than 20 cycles.

Shakedown of the Tandem Reactor Apparatus was completed and testing was initiated under quasi-continuous transfer of solids between reactors. Nine short term tests were performed with K-1 based BEACON solids. The

data from these tests indicate that the Tandem Reactor concept is valid and BEACON solids can be transferred efficiently in the fluidized state between the deposition and gasification reactors.

A preliminary analysis of the potential of a BEACON combined cycle/hydrogen system with a hydrogen fuel cell has been performed. The BEACON process can be used to coproduce hydrogen and electric power, and the efficiency of the overall system is quite high when the electricity is produced by a combined cycle power system. If fuel cells are used to convert the hydrogen to electricity then a system for making only electricity results, and such a system gives an overall efficiency of 54%.

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 and engineering analysis pertaining to the development of conceptual commercial designs and studies of their efficiencies, costs and economics.

The current program operates under a cooperative agreement among DOE, SOHIO and TRW (Cooperative Agreement No. DE-FC-21-80MC14400). This report covers the period from October through December 1982.

2. SUMMARY

2.1 CATALYST DEVELOPMENT AT SOHIO

The C77 type catalysts prepared at SOHIO during this quarter can be divided into three groups. The first group consists of catalyst promoted to suppress methane formation during steaming thus increasing the amount of hydrogen formed. The second group of catalyst was promoted for the purpose of reducing volume expansion which has been a problem with C77 catalyst during fluidization. The third catalyst group contained promoters from the previous two groups for the purpose of suppressing methane formation and reducing volume expansion.

Two types of promoters were used for methane suppression: a Class III promoter and a new Class IV promoter. As presented in the Third Quarter 1982 Report the Class III promoter had been shown to be capable of methane suppression. Two concentration levels of the Class III promoter were investigated during this quarter. To reduce volume expansion catalysts with Class IIA and Class IIB promoters were prepared. A third kind of catalysts used combinations of the above promoters. Specifically a Class III and Class IIB promoters were added to a catalyst support treated according to standard method. In all of the above cases the active catalyst was of the K-2 type. The Class III promoter is able to reduce methane formation at both concentrations tested. This confirms the work reported in the previous quarter. The Class IV promoter was a failure as it inhibited carbon deposition. Both the Class IIA and Class IIB promoted catalysts suppressed volume expansion. No change was observed between the particle size distribution of the catalyst after several cycles and the particle size distribution of the original support. The catalyst containing a methane suppression promoter and a volume expansion reducer was only half a success. It reduced the volume expansion but did not suppress methane formation.

During this quarter five additional 4 kilogram batches of C77-K2 catalyst have been made at a pilot plant facility at SOHIO. These are in addition to the two batches made and reported during the third quarter of 1982. Laboratory testing of the deposition and steaming rates of samples of

each batch and a pooled sample of all batches showed consistent rates.

2.2 CATALYST DEVELOPMENT AT TRW FOR SELECTIVE HYDROGEN PRODUCTION

In one recent BEACON SNG process development test at bench-scale an unsupported K-1 type BEACON catalyst was cycled at pressure in the 4-inch diameter reactor for a total of 30 cycles of carbon deposition and subsequent steam gasification. During these tests it was observed that although the overall carbon deposition and steam gasification global reaction rates at 100 psig remained nearly constant, there was a reduction in the activity of the catalyst for promoting methane formation during steaming cycles especially at the lower pressures. This led to a study and investigation of possible catalysts which would suppress methane during steaming and thus lead to a high yield of hydrogen. From this study 20 catalysts were defined which incorporated variations in catalyst composition, method of preparation and pretreatment. These catalysts were prepared and evaluated in the laboratory. Two catalysts met the established criteria of success.

Both of these catalysts are of the K-1 type but there was some variation in method of preparation. Both incorporate 10% of Additive F and one incorporates additionally 5% of Additive X. The catalyst with only the Additive F has maintained a steam utilization of 65% or greater over 20 cycles and has not built-up a carbon residue after steaming of more than .27 grams out of an original 1 gram starting carbon amount. The catalyst which has Additive F and Additive X also has shown comparable steam utilization over 30 cycles. It has however built-up almost twice as much carbon residue over these 30 cycles.

2.3 TANDEM REACTOR DEVELOPMENT

After completion of the shakedown of the Tandem Reactor apparatus, testing was initiated under quasi-continuous transfer of solids between reactors. Apparatus deficiencies identified during shakedown were corrected or ways were found around them which should permit the implementation of the test plan. Nine short term tests were performed during December with the No. 1 candidate catalyst for SNG production, a K-1 based BEACON solid.

The data from these tests indicate that the Tandem Reactor concept is valid when applied to BEACON solids. BEACON solids can be transferred efficiently in the fluidized state under reaction conditions quasi-continuously between the deposition and gasification reactors.

Apparatus shakedown and the needed modifications were completed in November. Empty reactor tests with reactive gases showed that the defects on the aluminized surface should not be a problem at least for the immediate objectives of the test program (a few hundred hours of testing). Problems with instrumentation were minor and easily correctable. During early fluidization tests with nitrogen, pressure plugging of the differential pressure leg was experienced but it was corrected by increasing the purge gas velocity. The use of the DP gauges to determine bed weight and the amount of material transferred was worked out. Some excessive entrainment losses were experienced initially and elimination of this problem was studied. The use of filters in the reactor appears to be a reasonable answer.

In the first test performed in the Tandem Reactor both product composition and steam utilization were close to thermodynamically predicted values and fuel conversion during deposition was excellent. In the remaining eight runs performed during the quarter the influence of some processing variables was investigated.

2.4 ENGINEERING ANALYSIS

A preliminary analysis of the potential of a BEACON combined cycle/hydrogen system with a hydrogen fuel cell has been performed. A model system for making hydrogen by the BEACON process was modified to operate with phosphoric acid fuel cells. The heat from the fuel cells was used to raise steam for the BEACON steaming step. Other heat integration steps were incorporated in the system for the BEACON process to be interconnected with a phosphoric acid fuel cell. The efficiency of the overall system from low Btu gas to electric power has been calculated and found to be 54%.

3. CATALYST DEVELOPMENT

Catalysts appropriate for the BEACON chemistry are being developed at SOHIO and TRW. SOHIO is concentrating on supported catalysts and TRW works on developing unsupported carbonaceous catalysts. During the quarter reported here both organizations worked on developing catalysts which would suppress methane formation during steaming thus increasing the amount of hydrogen formed.

3.1 CATALYST DEVELOPMENT AT SOHIO

3.1.1 Promoters for C77-K2 Catalyst to Suppress Methane Formation and Reduce Volume Expansion

The C77 type catalysts prepared at SOHIO during this quarter can be divided into three groups. The first group consists of catalysts promoted to suppress methane formation during steaming. The second group of catalysts was promoted for the purpose of reducing volume expansion which has been a problem with the C77 catalyst during fluidization. The third catalyst group contained promoters from the previous two groups for the purpose of suppressing methane formation and reducing volume expansion.

Two types of promoters were used for methane suppression: a Class III promoter and a new Class IV promoter. The Class III promoter had been shown to be capable of methane suppression as presented in the Third Quarter 1982 report (Section 3.1.1.3). The promoters were added to a batch of catalyst support after which the active catalyst was added to the support containing the promoter. From there on the standard catalyst preparation procedure was followed. The Class III catalyst was prepared to yield a Level 5 concentration of the active ingredient of the Class III promoter and another batch was prepared to have a Level 6 active promoter concentration. The Class IV promoter was formed in situ on the catalyst support and the active catalyst then was added to the support containing the promoter after which the standard catalyst preparation procedure was followed.

Catalysts with the promoters to reduce volume expansion were prepared by dissolving Class IIA and IIB promoters on the catalyst support. The active catalyst material then was added to the support containing the promoter after which the standard catalyst preparation procedure was followed. The Class IIA promoter was present at a Level 4 concentration and the Class IIB was present at a Level 5 concentration.

A third kind of catalyst, where combinations of promoters were used to suppress methane formation and decrease volume expansion, was prepared. For this purpose both Class III and Class IIB promoters were added to the catalyst support. The K-2 catalyst then was incorporated by the standard procedure. The final catalyst contained Level 2 concentrations of both the active ingredient of the Class III promoter and the active ingredient of the Class IIB promoter.

As reported in the last quarterly report (for July-September 1982, Section 3.1.1.3), the Class III compound was shown to be very effective in suppressing methane formation during steaming. It was desired to re-check the result obtained in the previous quarter and to see how effective the Class III promoter would be at a lower concentration (Level 6). These results along with those obtained in evaluating the Class IV promoter and the combination Class IIB/Class III promoter are presented in Table 3-1.

Table 3-1 shows the results obtained with the lower concentration of the Class III promoter (Batch No. 148). The promoter was efficient even at this level and the methane concentration generally is zero after the first cycle. The rates were somewhat lower but this probably is due to a fluidization problem in the small laboratory reactor. The next catalyst in Table 3-1 is a repeat of the catalyst reported in the last quarterly report. As with the first preparation no methane was observed after the first cycle.

The Class IV promoter was unsuccessful as it completely inhibited the carbon deposition. The combination of Class IIB and Class III promoters at a Level 2 concentration for each did not sufficiently suppress the formation of methane during steaming although rates were satisfactory.

Table 3-1. Effect of Promoters on Methane Suppression During Steaming.
Catalyst: C77-K2

Batch Number	Promoter(s)	Steaming Temperature (°C)	Cycle Number	Rate gC/Hr/g Active Cat.	Mole % H ₂ Mole % CH ₄	In Product Gases			
148	Class III Level 6	550	1	0.65	<u>36.1</u> 0.3	<u>34.6</u> 0.2			
			2	0.64	<u>48.8</u> 0.4	<u>44.5</u> 0	<u>43.0</u> 0		
			3	0.49	<u>42.0</u> 0.2	<u>42.9</u> 0	<u>33.1</u> 0	<u>24.3</u> 0	
			4	0.20	<u>27.9</u> 0	<u>22.1</u> 0	<u>34.7</u> 0		
153	Class III Level 5	550	1	0.72	<u>43.6</u> 0.6	<u>50.2</u> 0.8	<u>44.3</u> 0.3	<u>45.3</u> 0.3	<u>48.0</u> 0.2
			2	0.52	<u>39.2</u> 0	<u>39.4</u> 0	<u>23.1</u> 0		
			3	0.66	<u>34.7</u> 0	<u>35.8</u> 0			
142	Class IV	Carbon Deposition Was Approximately 0							
145	Class IIB/ Class III Level 2 Each	550	1	0.70	<u>35.5</u> 1.5	<u>28.4</u> 0.1			
			2	-	-	-			
			3	0.49	<u>36.5</u> 3.2	<u>35.2</u> 0.5	<u>34.4</u> 0.1		
			4	0.70	<u>37.8</u> 4.3	<u>39.2</u> 0.7			

Table 3-2 compares the results obtained using Class IIA and Class IIB promoters with the C77-K2 catalyst. Without a promoter the volume expanded after the first deposition and kept on increasing until it leveled off after 15-1/2 cycles (see Batch No. 91). However with the Class IIA and Class IIB promoters the volume increased only moderately. Even increasing the carbon loading level to 30% did not expand the volume much further.

It had been reported previously that volume expansion is connected to an increase of the weight percent of the large particles. Sieve analysis of the Class IIA and Class IIB promoted C77-K2 catalyst show why the volume expanded only moderately. Figure 3-1 is a plot of particle diameter vs weight percent of the Class IIB promoted catalyst. The support (without active catalyst), the unused catalyst (0% carbon) and the catalyst after five cycles (7.5% carbon) have almost identical particle size distributions. In contrast the weight percent of large particles increases significantly with unpromoted C77-K2 catalyst as the volume expands.

In a similar manner the particle size distribution of the Class IIA promoted C77-K2 catalyst is shown in Figure 3-2. The particle size distributions are not in as close agreement as that experienced with Class IIB promoters shown in Figure 3-1. With the Class IIA promotion (Figure 3-2) it appears that during the catalyst preparation large particles were created at the expense of the fine particles. However after six cycles the weight percent of the large particles decreased and the particle size distribution profile was approaching the distribution observed with the support alone.

A catalyst which was promoted with a proven methane suppression component and with an effective volume expansion reducer was tested. Table 3-1 shows that this catalyst (Batch No. 145) failed as a methane suppressor. The 3.2% and 4.3% methane levels are higher than with unpromoted C77-K2 catalyst. It appears that the promoters are working against each other. However the results in Table 3-2 indicate that this combination promotion reduces volume expansion as effectively as the one with only Class IIB promoter.

٧١

Batch Number	Promoter	Number of Cycles	Loading Level (%)	Volume (cc)		Volume Increase (%)
				Before Reaction	After Reaction	
137	Class IIB Level 5	4	21.5	20	25	25
		5	29.7	20	28	40
146	Class IIA Level 4	5	22.2	20	25.5	28
		6	30.4	20	28	40
91 (40 Steaming Cycles)	None	1/2	20.1	20	29	45
		5	23.6	20	43	115
		15-1/2	23.6	20	56	180
145	Class IIB/Class III Level 2 Each	4	26.7	20	25	25

Figure 3-1. Particle Size Distribution Before/After Loading Class IIB Promoter (Level 5) on C77-K2 Catalyst

Figure 3-2. Particle Size Distribution Before/After Loading Class IIA Promoter (Level 5) on C77-K2 Catalyst

The work reported in the previous quarter has been confirmed by showing that the Class III promoter is able to reduce methane formation both at Level 5 and Level 6. The Class IV promoter was a failure as it inhibited carbon deposition. Both the Class IIA and Class IIB promoters effectively reduced volume expansion of the C77-K2 catalyst.

Correlation has been established between particle size distribution and volume expansion. The weight percent of large particles greatly increases and weight percent of the fine particles decreases when the volume expands significantly. With the Class IIA and Class IIB promoted catalyst hardly any change was observed between the particle size distribution of the catalyst after cycling and the particle size distribution of the support.

The catalyst containing a methane suppression promoter and a volume expansion reducer was only half a success. It reduced the volume expansion but did not suppress methane formation.

3.1.2 Testing Large Scale Preparation of C77-K2 Catalyst

In the last quarterly report (Section 3.1.1.1) it was reported that two 4 kilogram batches of C77-K2 catalyst were prepared in a 5-gallon reactor at the SOHIO pilot plant. Samples from the two batches were subjected to 4 cycles of carbon deposition and steaming in laboratory scale equipment using a standard laboratory procedure which has been discussed in previous reports. Good reactivities for both carbon deposition and steaming were maintained through four cycles with these catalysts prepared on a much larger scale. The large scale preparation was duplicated in this quarter and a pooled sample was obtained by taking equal portions from each of the batches prepared in the third and fourth quarters and combining them. The catalysts were evaluated in a 1-inch quartz reactor using the standard laboratory procedure. Similar performances were observed for the batches prepared in the fourth quarter as compared with those produced during the third quarter of 1982. The results obtained with the pooled sample are presented in Table 3-3 and as expected the reaction rates are very good and similar to those observed with individual batches. The rates of deposition varied from 1.3 to 1.54 grams of carbon deposited per hour per gram of active catalyst. The rates of steaming varied from 0.77

Table 3-3. Reaction Rates - Pooled Sample of Pilot Plant Preparations of C77-K2 Catalyst

Cycle	Steps	Temperature (°C)	Time Hrs-Min	Total gC Moved	Rate gC/Hr, g Active Cat.	% Loading of Total Cat. Weight
1	C Dep	450	1 - 2	+1.69	1.13	17.5
1	Steam	550	- 29	-0.59	0.84	11.4
2	C Dep	450	- 29	+1.07	1.54	22.4
2	Steam	550	- 43	-0.80	0.77	14.2
3	C Dep	450	- 36	+1.23	1.41	26.9
3	Steam	550	1 - 0	-1.40	0.97	12.4
4	C Dep	450	- 27	+0.86	1.32	21.3
4	Steam	550	- 55	-1.31	0.99	7.7

Catalyst Volume: 20 cc

Catalyst Weight: 9.68g !

to 0.99 grams of carbon removed per hour per gram of active catalyst. These rates are similar to those reported in the third quarter 1982 report.

3.2 CATALYST DEVELOPMENT AT TRW FOR SELECTIVE HYDROGEN PRODUCTION

The catalyst development effort at TRW during this reporting period was devoted to identification and testing of a stable catalyst system based on BEACON solids that will inhibit methane formation and promote hydrogen production at near equilibrium steam utilization rates. Such a catalyst would increase the flexibility of the BEACON SNG system by permitting the production of hydrogen as an alternate product. This effort was initiated at the end of last quarter (September) and continued with appreciable success during the current quarter.

3.2.1 Background

In one recent BEACON SNG Process development bench-scale test, an unsupported K-1 type BEACON catalyst was cycled at pressure in the 4-inch diameter reactor for a total of thirty cycles of carbon deposition and subsequent steam gasification. During these tests it was observed that although the overall carbon deposition and steam gasification global reaction rates at 100 psig remained nearly constant, there was a reduction in the activity of the catalyst. At lower pressures methane formation was decreased during the steaming cycles; at ambient pressure methane suppression was appreciable. This reduction in methane activity was traced to two most likely causes: a) a change in catalyst composition, and b) effect of possible localized thermal exposures above the nominal 650°C steaming operating temperature. Post test analysis of the cycled catalyst material did show a significant change in chemical composition. These two hypotheses were briefly evaluated in laboratory tests as described below.

Fresh type K-1 catalyst was first run through five cycles of carbon deposition and 750°C steaming at atmospheric pressure to simulate abnormal thermal exposures (750°C). This catalyst was then run through a steaming cycle at 640°C. The data are shown in Table 3-4. It is apparent that the 750°C steaming cycles (thermal soak) did not adversely affect the ability of the catalyst to form methane at 640°C. Indeed, at 640°C the steam gasification product composition and steam utilization very closely

Table 3-4. Effect of "Thermal Soak" on Methanation Activity of K-1 BEACON Catalyst*

Steam Gasification Product Gas Composition, Mole % Dry								
	750°C Steaming Cycles**					750°C Equilibrium Composition	640°C Steaming	640°C Equilibrium Composition
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5			
CH ₄	2.4	2.1	1.9	1.9	2.2	1.8	6.4	5.9
H ₂	47.4	46.8	46.8	46.8	46.5	50.3	50.4	50.9
CO	41.0	43.4	44.5	43.8	44.3	41.9	23.8	23.8
CO ₂	9.1	7.6	6.5	7.3	7.3	6.0	20.2	19.4
N ₂	0.1	0.1	0.2	0.2	0.2	-	0.3	0
% Steam Utiliz.	85	91	90	83	91	90.7	76	77

* Tests were initiated with fresh type K-1 BEACON solids. Carbon was deposited at 450°C in between steamings.

** The 750°C steaming cycles were performed as a catalyst "thermal soak."

approached equilibrium. Thus abnormal thermal exposure did not appear to be the cause of the change in catalyst methanation activity.

The second hypothesis was tested by the performance of a carbon deposition-steaming cycle with a K-1 catalyst modified by the addition of the major "contaminant" found in the 4-inch reactor sample after 30 cycles of bench scale testing. The results are summarized in Table 3-5, first row, and are compared to the product gas composition and steam utilization of unmodified K-1 catalyst and to the same quantities predicted by thermodynamics. The data in Table 3-5 show that the modified catalyst suppressed methane formation severely.

Comparison of the data in Tables 3-4 and 3-5 led to the tentative conclusions that the "in situ" compositional modification of the K-1 catalyst during the thirty-cycle test was the primary cause for the change in its activity toward methane formation at low pressures. Furthermore, the data in Table 3-5 revealed that methane suppression occurred at a small penalty in steam utilization; that is, the "modified K-1 catalyst" appeared to be a very promising catalyst for hydrogen production by selective steam gasification of BEACON solids, if its activity proved to be stable. Later testing revealed that this particular "modified K-1 catalyst" was not very stable, but others of similar composition proved very promising.

Table 3-5. Steam Gasification of Modified
K-1 BEACON Carbon (640°C, 1 atm)

	Product Gas Composition, % V/V Dry				Steam Utilization %
	CH ₄	H ₂	CO	CO ₂	
Modified K-1 Catalyst	1.5	57	21	20	68
Unmodified K-1 Catalyst	6.4	50.4	23.8	20.2	76
Predicted by Equilibrium	5.9	50.9	23.8	19.4	77

3.2.2 Test Matrix

The background information presented above, the experience gained in the development of the K-1 solids as a BEACON SNG catalyst, and open literature data on synthesis gas processing (e.g., Fischer-Tropsch synthesis) led to the formulation of the fractional factorial test matrix presented in Table 3-6. The screening matrix is based on five composition variables (including the base component K-1) and four concentration levels, five methods of preparation variables, and three methods of pretreatment; at least two of the most promising catalysts will be subjected to two additional variables: steam feedrate and pressure. Twenty catalysts were prepared to cover the composition variables and levels and the various methods of preparation; seven of these catalysts were also "pretreated" prior to testing, generating another ten samples for testing. These thirty samples will permit the scanning of all the variables at one to four levels at a minimum number of tests.

Emphasis was placed on modifying the most active of the BEACON SNG catalysts, K-1,* and an Additive F which the test described in the "Background" section revealed to be an effective methane suppressant. Additives K-2, X, and Y were selected either because they were present as "contaminants" in the bench scale, thirty-cycle sample which exhibited methane suppression tendencies, or because the open literature suggested them to be methane suppressants. The methods of preparation were selected because of expected influence on the degree of mixing of the catalyst components and on "crystal" site. The pretreatment techniques were selected principally for their potential effect on catalytic sites (valence, defects, elemental arrangement). Most tests were planned at low levels of additive under the assumption that methane suppression sensitivity to parametric changes will be highest at low concentrations of additive. The data presented in Tables 3-4 and 3-5, above, were generated with Catalysts No. 1 and No. 3, respectively.

* K-1 based BEACON solids exhibited the highest BEACON carbon gasification rate.

Table 3-6. Hydrogen Production Catalyst Development Test Matrix
(Laboratory-Scale Testing)

Catalyst No.	Catalyst Composition, Wt %					Method of Preparation					Pretreatment			
	K-1	K-2	F	X	Y	A	B	C	D	E	None	Steam 750°C	350°C	Hydrogen 750°C
1	100					X					X			
2	100						X				X			
3	60		40				X				X	X		
4	70		30				X				X	X		
5	80		20				X				X	X	X	X
6	90		10				X				X			
7	80		20					X			X		X	X
8	80		20						X		X			X
9	90		10						X		X			X
10	88		10	2					X		X			
11	85		10	5					X		X			
12	80		20							X	X			
13	90		10							X	X			
14	88		10	2			X				X			
15	80	20					X				X			
16	90			10			X				X			
17	95				5		X				X			
18	98				2		X				X			
19		95			5		X				X			
20		98			2		X				X			

- At least two "solids charge-to-steam feedrate ratios" will be tested.
- At least two promising candidate catalysts will be subjected to 50 carbon deposition/steaming cycles to verify stability.
- Nominal test conditions: Deposition - Ambient pressure, 450°C
Steaming - Ambient pressure, 600°C
Quantity of solids cycled between 1.0g → 0.2g → 1.0 grams
- The most promising candidate catalyst will be tested under pressure to determine its effect on methane suppression.

Each catalyst will be subjected to carbon deposition (450°C)-steaming (600-650°C) cycles during the screening tests. A minimum of two cycles will be performed on every sample; every catalyst that shows promise will be subjected to long term testing. The two most promising catalysts will be selected for fifty-cycle stability testing and for pressure parametric testing. In each cycle, carbon will be gasified until steam utilization (gasification rate) drops below 40%; that is, virtually all the active carbon will be gasified in each cycle. This "deep" cycling aims to quickly identify catalyst activity deterioration and the build up of inactive or less active carbon (to be labeled here as "residue"). The criteria for success during the ambient pressure screening tests are: near equilibrium steam utilization (gasification rate) at 600° to 650°C temperature range, greater than 80% methane suppression, and at least 50 cycle stability with or without catalyst regeneration. It is assumed that the catalyst can be regenerated by higher temperature gasification of the carbon residue or some other simple regeneration procedure.*

3.2.3. Ambient Pressure Results

Fifteen of the twenty catalysts listed in Table 3-6 were prepared during the quarter and most of them have already been screened. Results to date have identified two catalyst compositions which appear to be strong candidates to meet all of the success criteria listed in the previous section; these are Catalysts Nos. 6 and 11 in Table 3-6. Multi-cycle stability testing is underway with them and it looks very promising. Other observations and/or tentative conclusions drawn from these screening tests include the following:

- The method of preparation (A versus B, at least) of the K-1 catalyst or its pretreatment up to 750°C with steam has no influence on its catalytic activity in steam gasification of

*Fifty cycles represent a yield of 500 lbs carbon per lb of catalyst in the reactor (approximately 25×10^3 SCF H_2). Under less extreme cycling conditions than those used in these tests (less carbon removal per cycle) the carbon deposited and gasified could easily be more than 1,000 times the weight of catalyst to be removed from the reactor for reprocessing. Thus, under this criterion, catalyst make up costs will be almost insignificant.

BEACON carbon to methane. Catalysts Nos. 1 and 2, pretreated or not, yielded near equilibrium concentrations of methane in the 600°-650°C temperature range (e.g. data in Table 3-4).

- Additive F when incorporated into K-1 modifies the latter from an excellent methanation promoter to a potentially excellent selective hydrogen catalyst. Methane suppression occurs at all levels of F tried to date in the 600-650°C temperature range (Catalyst Nos. 3 through 6); however, the degree of suppression and the stability of catalytic activity at this temperature range depend on the concentration of F in the catalyst and probably to a smaller extent on the method of preparation. Testing continues to verify these observations/conclusions.
- Method of preparation appears to influence performance to varying degrees; the influence is near zero between A and B but appreciable between B and C. Catalysts prepared by method C exhibited appreciably poorer performance (higher methane yield and less stability) than those prepared by method B. Differences between B, D, and E appear to be less significant.
- Catalyst pretreatment, as defined in these tests, does not appear to influence performance.
- The K-2 additive does not suppress methane.

Table 3-7 summarizes the data obtained during multi-cycle testing of Catalyst No. 6 (Type B, K-1 + 10% Additive F BEACON catalyst).^{*} For the sake of brevity, only data from Cycles 1, 5, 10, 15, and 20 are presented in Table 3-7, but the in-between cycles are easily interpolable. This

^{*}The catalyst stability tests consist of carbon deposition/steaming cycles and the aim is to demonstrate stable catalytic activity for at least 50 cycles. Activity is measured against three criteria: methane suppression, steam utilization, and inactive carbon built-up on the catalyst. Carbon deposition is performed at 450°C and steaming at 600°C; both operations are conducted at ambient pressure. Deposition is stopped when the BEACON solids weight (principally carbon) reaches approximately one gram and steaming is stopped when steam utilization drops below 50%. The solids weight remaining in the reactor at the conclusion of steaming is called the "residue;" it consists of the catalyst and the carbon which does not steam gasify at practical steam utilization rates at the indicated temperature. The residue will gasify further at higher temperatures but the resulting catalyst does not appear to be as active as the starting catalyst. In these tests we aim to identify catalysts that will exhibit stable activity at the 600°C to 650°C for at least 50 cycles without the need of regeneration; it is also required that methane suppression is 80% or better and that steam utilization is near the equilibrium value (>60%).

Table 3-7. Stability of Methane Suppression Catalyst (Type B, K-1 + 10% Additive F)

Specie	Compos. Predicted By Thermod. (600°C)		Product Gas Composition, % V/V, Versus Cycle No. Steaming at 600°C, Ambient Pressure *				
	Normal	Zero Methane	Cycle 1	Cycle 5	Cycle 10	Cycle 15	Cycle 20***
CH ₄	8.8	0	4	2	2	1.5	2
H ₂	49.3	61.3	56	59	59	60	59
CO	16.7	16.1	17	16	16	16	16
CO ₂	25.2	22.6	23	23	23	23	23
% Steam Utiliz.	71	66	66	65	65	65	65
Residue** (Grams)	-	-	0.17	0.23	0.27	0.20	0.24

* Between steamings, carbon was deposited at 450°C.

** Solids residue at end of steaming (solids wt prior to steaming was approximately 1 gram).

*** Last cycle during December 82; cycle testing continues into January 83 with the goal of 50 cycles.

catalyst exhibited excellent stability to date as indicated by very low residue weight, high steam utilization, and appreciable methane suppression after the first cycle. The methane value indicated is the maximum or very near maximum methane concentration obtained at the start of steaming; as carbon was consumed (lower steam residence time) the methane concentration dropped closer to 1% without a measurable drop in steam utilization. Steaming performance was virtually constant and near thermodynamic equilibrium through 20 cycles. The 2nd and 3rd columns of Table 3-7 list the expected product gas compositions and steam utilizations under equilibrium conditions when a) methane is permitted to form, and b) methane is not allowed to form (complete suppression); these compositions were computed from thermochemical data. Testing is continuing with this catalyst.

Table 3-8 presents multi-cycle data on Catalyst No. 11 (Type D, K-1 BEACON catalyst modified by 10% Additive F plus 5% Additive X). Very good performance stability was obtained with this catalyst through 30 cycles. Actually, this catalyst exhibited a higher degree of methane suppression than the Type B catalyst without Additive X but the "steaming residue" on the average increased slightly with increasing cycle number. The difference in residue build-up between the two catalysts is better illustrated by the data in Figure 3-3 which represents least square plots of the steaming residues versus cycle number for the Type B and Type D catalysts of Tables 3-7 and 3-8. Residues from a third catalyst, represented by triangles, are also shown in Figure 3-3. (The two Type D catalysts differ only in pretreatment; the one represented by the triangles was reduced by hydrogen prior to the first cycle, the other was cycled "as prepared." Cycling of the "pretreated catalyst" was discontinued after the 8th Cycle because the data being generated were virtually identical to that generated with the "as prepared" catalyst; the agreement can be considered as a good reproducibility check.) Extrapolation of the data in Figure 3-3 and Tables 3-7 and 3-8 seem to indicate that these two catalysts should meet the criteria as candidate hydrogen catalysts for above ambient pressure testing. Testing continues until the 50 cycle performance criterion is met or until activity failure occurs.

Table 3-8. Stability Testing of Catalyst No. 11 (Type D,
K-1 + 10% Additive F + 5% Additive X)

Species	Compos. Predicted By Thermod. (600°C)		Product Gas Composition, % V/V, Versus Cycle No. Steaming at 600°C, Ambient Pressure*						
	Normal	Zero Methane	Cycle 1	Cycle 2	Cycle 10	Cycle 15	Cycle 20	Cycle 25	Cycle 30***
CH ₄	8.8	0	7	1.5	<1	<1	<1	<1	<1
H ₂	49.3	61.3	52	59	60	60	60	60	60
CO	16.7	16.1	16	16	17	16	17	17	16
CO ₂	25.2	22.6	25	23	22	23	22	22	23
% Steam Utiliz.	71	66	69	65	66	65	66	65	65
Residue** (Grams)	-	-	~0.10	0.13	0.34	0.45	0.46	0.48	.52 [†]

* Between steamings, carbon was deposited at 450°C.

** Solids Residue at end of steaming (solids wt prior to steaming was approximately 1 gram).

*** Last cycle during December 82; cycle testing continues into January 83 with the goal of 50 cycles.

[†] Residue from Cycle 29; steaming residue value for Cycle 30 is not available because steaming was not taken to completion.

Figure 3-3. Effect of Catalyst Preparation and Composition on Extent of BEACON Carbon Steaming to H_2

Table 3-9 presents the data on Catalyst No. 15 (Type B, K-1 + 20% K-2). This catalyst failed to suppress methane; it appears to be a very good methanation catalyst. Even after subjecting the catalyst to 800°C temperature for over one hour (Cycle 3), there was no hint of methane suppression. There was a 20% drop in product gas methane concentration between the 1st and 2nd Cycles at 600°C, but then methane stabilized at a very high value. In fact, above 600°C steam gasification yielded equilibrium product compositions (compare first 6 columns of Table 3-9 to the last 3). Testing with this catalyst was discontinued.

Catalysts Nos. 3, 4, and 5 exhibited good methane suppression but poor stability. Stability in catalytic activity decreased with increasing level of Additive F. Catalyst No. 3 lasted 6 cycles before the build-up in inactive carbon reached an unacceptable level; Catalyst No. 4 lasted 14 cycles and Catalyst No. 5 lasted twenty. Table 3-10 summarizes the data generated with Catalyst No. 5 (K-1 + 20% Additive F, Type B catalyst). The data show that the "residues" remained tolerable through 15 cycles but by the 20th cycle approximately 90 percent of the deposited carbon could not be steam gasified at acceptable steam utilization rates at the 600° to 650°C temperature range. The catalyst was regenerated by steam gasification of the residue at 750°C, but after an additional four cycles in the 600°-650°C range the residue increased to 0.9 grams again (it was up to 0.5 grams after two cycles). Tests with these catalysts have been discontinued, but the cycled samples were stored for possible additional testing on regeneration at some future date.

Three samples of Catalyst No. 7 (Type C, K-1 + 20% Additive F) were tested: One "as prepared" sample, one pretreated (reduced) with hydrogen at 350°C, and one pretreated with hydrogen at 750°C. All three of them yielded more than 3 percent methane and high residues by the 3rd cycle (>0.5 grams at 600°C). Tests were discontinued with this catalyst.

Table 3-9. Effect of K-2 Additive on Methane Suppression (Type B, K-1 Catalyst)*

	Ambient Pressure Cycling						Equil. Compositions		
	1st Cycle		2nd Cycle	3rd Cycle		4th Cycle			
	600°C	650°C	600°C	600°C	800°C	600°C	600°C	650°C	800°C
CH ₄	8.1	5.4	6.6	6.6	1.2	6.5	8.8	5.3	1.1
H ₂	50.9	51.8	51.9	51.7	49.1	52.6	49.3	51.0	49.8
CO	16.3	25.3	15.6	17.5	46.3	16.6	16.7	25.7	46.1
CO ₂	24.6	18.2	25.1	24.0	3.4	24.2	25.2	18.0	3.0
N ₂	.1	.1	.1	.2	-	.1	-	-	-
	100.-	100.8	99.3	100.-	100.-	100.-	100.-	100.-	100.-
% Steam Utiliz.	61	74	59	52	80	55	71	78	94
Residue** (Grams)	-	0.10	0.13	-	0.10	0.13	-	-	-

* Between steamings carbon was deposited at 450°C.

** Solids residue at end of steaming at the indicated conditions (solids wt prior to steaming was approximately 1 gram).

Table 3-10. Stability Testing of Catalyst No. 5 (K-1 + 20 Wt % Additive F, Type B) - Ambient Pressure Steaming*

Specie	Compos. Predicted By Thermod. (625°C)		Product Gas Composition, % V/V, Versus Cycle No.					
	Normal	Zero Methane	Cycle 1 625°C	Cycle 10 620°C	Cycle 20 650°C	Regen. Steam AT 750°C	Cycle 24	
							600°C	650°C
CH ₄	6.9	0	2	1	<1	<1	<1	<1
H ₂	50.5	59.9	57	56	59	51	62	59
CO	21.0	20.3	22	22	16	42	16	25
CO ₂	21.6	19.8	19	21	22	6	22	16
% Steam Utiliz. }	74	70	65	68	62	90	42	67
Residue** (Grams)	-	-	0.3	0.4	0.9	0.15		0.9

* Between steamings carbon was deposited at 450°C.

** Solids residue at end of steaming at the indicated conditions (feed solids approximately 1 gram).

4. TANDEM REACTOR DEVELOPMENT

During the current reporting period shakedown of the tandem reactor apparatus was completed and testing was initiated under quasi-continuous transfer of solids between reactors. Apparatus deficiencies identified during shakedown were corrected or ways were found around them which should permit the implementation of the test plan presented in the previous quarterly report. Nine short term tests were performed during December with K-1 based BEACON solids; the number one candidate catalyst for SNG production. The data from these tests appear to indicate that the tandem reactor concept is valid when applied to BEACON solids; that is, BEACON solids can be transferred efficiently in the fluidized state under reaction conditions quasi-continuously between the deposition and gasification reactors. Detailed description of the apparatus was presented in the previous quarterly report.

4.1 APPARATUS SHAKEDOWN

Apparatus shakedown and the needed modifications were completed in November. Mechanical shakedown of the system was virtually uneventful. The most serious mechanical problem was the defective Alon coating of the deposition reactor and of the solids transfer lines alluded to in the previous quarterly report. Empty reactor tests with reactive gases showed that the defects on the aluminized surface should not be a problem, at least for the immediate objectives of the test program (a few hundred hours of testing). Problems with instrumentation were minor and easily correctable. During early fluidization tests with nitrogen gas under pressure (nominal 100 psig) plugging of the differential pressure legs was experienced, but it was corrected by increasing the purge gas velocity from one to ten feet per second. Debugging of the software for the data acquisition system went very smoothly but two hardware related problems, interphase problems between the gas chromatographs and the computer and problems with computer scanning of temperatures, still persist. Ways around these difficulties have been found so that they do not interfere with testing (the GC data are inputted manually into the computer every 10 or 20 minutes,

and the temperatures are scanned and recorded by a DORIC data logger rather than the computer). Minor problems with temperature and pressure controllers were easily corrected.

The solids transfer system and its monitoring and recording instrumentation were tested successfully under nominal operating conditions (450°C, 100 psig deposition reactor and 600°C, 100 psig steam gasification reactor conditions); the system performed well from the start. Initial tests were conducted with nitrogen feeds at nominal reaction temperatures and pressures. BEACON solids were transferred back and forth between the deposition and gasification reactors by both manual and automatic manipulation of the transfer valves with no apparent problems. The transfer of solids was tracked well by changes in reactor bed differential. Transfer system performance was subsequently verified with reactive gas; it has operated trouble free through hundreds of transfers since then. The transfer lines and valves were visually inspected recently for evidence of carbon deposits; none was found.

Figure 4-1 depicts a typical solids transfer cycle during tandem testing of the carbon deposition and steaming operations of the BEACON Process (the curves are actual recorder traces). At the "start" of the transfer cycle carbon lean solids were transferred from the bottom of the gasifier (right trace in Figure 4-1) to the top of the deposition reactor. In this case, approximately 150 grams of the lean solids were transferred from the gasifier to the deposition unit in about 20 seconds (each inch of horizontal scale represents 2.7 inches of water pressure drop which corresponds to 1300 grams of solids in the deposition reactor - 6 inches ID - and 325 grams of solids in the steamer - 3 inches ID); the reactors were allowed to equilibrate for about 2.5 minutes and then approximately 400 grams of high carbon solids were transferred from the deposition to the steam gasification reactor in about 30 seconds. The traces in Figure 4-1 show that the DP system tracked very well the transfer of solids between the reactors of the tandem system. Table 4-1 presents data which correlates the weight of solids in the bed to bed DP values. Determinations performed at ambient pressure showed that the weight of solids in the

BG = Bottom of Gas Bed; TD = Top of Deposition Bed
 BD = Bottom of Depositor Bed; TG = Top of Gasification Bed

Figure 4-1. Typical Solids Transfer Operation (Tandem Reactors)

Table 4-1. Bed Weight Determination by DP Measurements

Test No.	Actual Solids In Reactors, Grams		Estimated Solids In Reactors at 100 Psig, Hot (Based On Bed ΔP)		Correction Factor (Actual/Measured)	
	Gasif.	Dep.	Gasif.	Dep.	Gasif.	Dep.
S-1	1,394	5,984	1,044	5,123	1.33	1.17
S-2	1,394	5,854	1,056	5,029	1.32	1.16
S-3	1,321	5,883	948	5,029	1.39	1.16
S-4	7,028 TOTAL		1,596 (7,295)*	4,418	--	--

* Total solids calculated using average correction factors of 1.35 for gasification and 1.16 for deposition reactor beds.

reactor bed can be computed directly and accurately from differential pressure measurements when the gas velocity in the reactor is above the minimum fluidization value for the reactor solids. However, with increasing reactor pressure the computed weight of solids dropped below the actual weight; also the drop was larger in the smaller reactor.* Fortunately, a very reproducible "correction factor" was determined which permitted the correlation of reactor bed weight to reactor bed DP for each of the two reactors (last two columns of Table 4-1). Bed differential pressures correlated very well also with the quantity of solids transferred and with the quantities of carbon deposited and gasified in tests with reactive gases described in the next section.

Table 4-2 presents data on solids entrainment obtained with and without cyclones installed in the de-entrainment section of each reactor. During Test S-5 cyclones of the size indicated (2nd and 3rd columns) were installed in the reactors; in Tests S-6 and S-7 there were no cyclones in the reactors; in Test S-8 the larger cyclone (originally installed in the deposition reactor) was installed in the gasification reactor.** It is evident that the cyclones did not assist the retention of solids in the reactor during these particular tests. In fact, Test S-5 indicates that these cyclones - possibly because they were undersized - increased the solids entrainment rate. (It is believed that solids escaped up the dipleg of the cyclone.) Additional work is needed in the future to design appropriate cyclones for the tandem system. However, the solids entrainment rates obtained without cyclones are adequate if the system could be operated without upsets. For added protection during start-up, solids transfer, or other potential system pressure upsets internal filters - instead of cyclones - will be installed in the expander section of the Tandem reactors.

* The difference between actual weight and "DP weight" is probably due to wall effects which become more pronounced under pressure (more dense gas) and are larger the smaller the reactor diameter gets.

** The deposition reactor has twice the diameter of the gasification reactor; it was believed that the larger cyclone may prove effective in the smaller reactor.

Table 4-2. Solids Entrainment Tests (100 Psig, 450°C and 650°C, 0.5 FPS)

Test No.	Cyclone ID Inches		Time Of Test, Min.	Solids In Filters, Grams		Avg Entrainment Rate Grams/Min	
	Dep.	Gasif.		Dep.	Gasif.	Dep.	Gasif.
S-5	1.49	1.06	308	846	465	2.7	1.5
S-6	None	None	525	633	182	1.2	0.3
S-7	None	None	458	680	190	1.5	0.4
S-8	None	1.49	535	676	283	1.3	0.5

4.2 TANDEM REACTOR TESTING

Tandem Reactor testing with K-1 type BEACON methanation catalyst was initiated in the last week of November and continued during December. Eight tests were run during the Holidays shortened month for a total of 30 hours of steaming operation and slightly fewer hours of deposition operation (the carbon deposition rate was somewhat higher than the steaming rate in a few of the tests). In addition to accumulating carbon deposition/steaming time on a given batch of catalyst in order to test its stability during tandem operation (simultaneous deposition and steaming operation) data are being generated on the ranges of operability of the tandem apparatus and on the viability of the tandem reactor concept itself as it applies to BEACON type solids. Table 4-3 presents the data obtained during the first test with reactive gases in the tandem apparatus. The data show that the catalyst performed very well even though the charge of BEACON solids loaded to the tandem apparatus to start these tests was prepared more than a year ago and was stored in ambient air during the interim. Both product composition and steam utilization were close to thermodynamically predicted values; also, fuel conversion during deposition was excellent even though a high hydrogen, low CO content low Btu gas was used in this first test in order to make sure that the deposition reactor temperature could be controlled; later tests showed that deposition temperature was no problem at appreciably higher deposition rates.

Table 4-4 summarizes the results obtained from the remaining eight tandem runs performed during the quarter. Lower steaming temperatures and steam partial pressures were tried in these tests. The temperature and, to a lesser degree, the steam partial pressure demonstrated the expected effects on rates and on product composition. Catalyst activity remained constant (within experimental uncertainty). The carbon gasification rate normalized to steam feed rate was approximately 250 grams per hour per SCFM steam feed and changed by about 20% with 15°C change in temperature, up or down (reference column 3, Table 4-4). The proportionality to steam feed rate implied near or at equilibrium operation; the two thermodynamic compositions presented under the experimental data verify this expectation (compare T-4 to 620°C equilibrium data and T-6 or T-8 to the 600°C equilibrium data).

Table 4-3. Carbon Deposition/Steaming Test (Run T-1) - 100 Psig, 450°/650°C

	Gas Veloc., FPS	Steam Feedrate Lbs/Hr	Product Composition, % V/V						Steam Utiliz. %	% Fuel Conversion	
			CH ₄	H ₂	CO	CO ₂	N ₂	H ₂ O		H ₂	CO
Gasif.	0.5	8.5	8.2	28.2	5.1	18.9	6.1	33.5	57	-	-
			(11.9	25.6	9.0	20.1	5.8	27.5)*	(64)	-	-
Dep.	0.4	-	5.1	8.1	2.0	10.9	70.4	3.5		57	93
Gasification Feed (Composition, % V/V)			93% H ₂ O/7% N ₂								
Deposition Feed (Composition, % V/V)			14.7% H ₂ /22.9% CO/62.3% N ₂								

* Values in parentheses indicate thermodynamically predicted compositions (operation at equilibrium).

Table 4-4. Tandem Reactor Steam Gasification Data (600°C, 100 Psig)

Run No.	Steam Partial Pressure, Psia	Gasif. Rate ^(a)	Product Gas Composition, % V/V Dry				% Steam Utilization
			CH ₄	H ₂	CO	CO ₂	
T-2	80	242	14	47	1	38	40
T-3	100	189 ^(b)	10	54	1	36	34
T-4	100	293 ^(c)	23	37	2	39	44
T-5	100	258	17	45	2	36	42
T-6	60	268	17	44	1	38	43
T-7	50	230	16	48	1	36	39
T-8	60	244	17	43	2	39	47
T-9	70	208 ^(b)	10	54	1	34	38
● 620°C Equilibrium Composition (For 100 Psia P _{H₂O})			21	35	10	34	61
● 600°C Equilibrium Composition (For 60 Psia P _{H₂O})			19	38	10	33	61
● Typical Fuel (CO & H ₂) utilization during deposition: CO = 90 ± 5%							
● Nominal deposition feed: 30% CO/15% H ₂ /5% CO ₂ /50% N ₂							

(a) Grams/Hour/SCFM steam feed

(c) 615 ± 10°C reactor temperature

(b) 585 ± 10°C reactor temperature

However, comparison between experimental and predicted data reveals that most of the CO is shifted principally to hydrogen and carbon dioxide during these tests.

Steam utilization was appreciably below the expected (predicted by thermodynamics) values probably due to some steam bypassing because of reactor pressure fluctuations. In order to retain the solids in the reactor during system upsets, the external filter was transferred into the expander section of the gasification reactor. The filter was both too small and too fine. Excessive pressure drop was created across it, especially during transfer operations, which rendered pressure control difficult and rough. In turn the pressure fluctuations caused surges in flow, poor fluidization, and the transfer of solids to the expander section; the return of these solids to the reaction zone was slow. The poor fluidization and the fluctuating quantity of solids in the reaction zone are believed to have been responsible for the obtained low steam utilizations. The problem has now been corrected through the installation of a larger and coarser filter and through the use of somewhat lower steam feed rates. More recent runs show equilibrium steam utilizations.

The last two items in Table 4-4 refer to deposition performance. As the fuel utilization values indicate, carburization performance to date has been very good and stable. Testing to meet the dual objective of determining catalyst stability and apparatus operability continues with the original charge of K-1 solids.

5. ENGINEERING ANALYSIS

A very preliminary analysis of the potential coupling of a BEACON combined cycle/hydrogen system with a hydrogen fuel cell was performed during the reporting period. The results are described below.

The BEACON process can be used to coproduce hydrogen and electric power. The efficiency of the overall system is quite high when the electricity is produced by a combined cycle power system. If fuel cells are used to convert the hydrogen to electricity, then an efficient overall system for making only electricity results.

The model system for making hydrogen shown in Figure 5-1 was modified to operate with phosphoric acid fuel cells. The heat from the fuel cells was used to raise steam for the BEACON steaming step.

Figure 5-2 shows how a phosphoric acid fuel cell could be interconnected with the BEACON process. The heat generated in fuel cells and also the heat obtained from cooling the effluent gases from the carbon steaming reactor are used to evaporate and preheat the steam which is used for carbon gasification. Only one stage of shifting would be necessary because of the relatively high conversion to hydrogen expected in the carbon steaming step. The system shown does not take advantage of any exhaust turbines which could recover useful energy from the fuel cells exhaust gases. This keeps the system simple, and leads to a conservative efficiency estimate.

The efficiency of the overall system from low Btu gas to electric power is calculated in Figure 5-3. The hydrogen produced in the BEACON hydrogen-electric coproduction case is converted to electricity at 50% efficiency, resulting in the increased electric power output of 1439 MW. In addition, there is a credit for the steam which was not used. It is assumed that it could be used to generate electricity at 25% efficiency, which gives an additional 192 MW of electric power. Thus the total of electric power is 2469 MW, which when divided by the higher heating value of the inlet gas, gives an overall efficiency of 53.8%.

Figure 5-1. BEACON Steam - Carbon to Hydrogen Model System

Figure 5-2. Hydrogen From BEACON Carbon Steaming Used In a Phosphoric Acid Fuel Cell

BASE CASE:

	BTU/HR	MW
INLET GAS HHV	15.67×10^9	(4598)
ELECTRIC POWER	(2.86×10^9)	838
H ₂ PRODUCT HHV	9.83×10^9	(2879)

FUEL CELL SYSTEM:

ELECTRIC POWER FROM FUEL CELL (50% EFFICIENCY)	$\left(\frac{9.83 \times 10^9}{2} \right)$	1439
ADDITIONAL ELECTRIC POWER FROM HRSG (25% EFFICIENCY)	$\left(\frac{2.618 \times 10^9}{4} \right)$	192

TOTAL ELECTRIC POWER:

	838
	1439
	192
	<u>2469</u>
(8.43×10^9)	

OVERALL EFFICIENCY:

$$\frac{\text{ELECTRIC POWER}}{\text{INLET GAS HHV}} = \frac{8.43 \times 10^9}{15.67 \times 10^9} = 53.8\%$$

Figure 5-3. BEACON Hydrogen System
Performance With Fuel Cell