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DEVELOPMENT OF BEACON TECHNOLOGY

Quarterly Report for the Period January—March 1982

Work Performed Under Contract No. FC21-80MC14400

For
Morgantown Energy Technology Center
Morgantown, West Virginia

By
TRW Energy Development Group
Redondo Beach, California

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

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

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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.

Process conditions favoring the production of hydrogen were explored this quarter. Excess steam was found to suppress methane formation, and reduction of catalyst methanation activity was demonstrated.

The effect of carbon loading on the physical stability of catalyst C77-K2 and the effect of trace sulfur levels on the chemical stability of the catalyst were examined. The carbon loading tests did not show the catalyst breakup that was expected. Tests of chemical stability of the catalyst in the presence of sulfur-containing gases showed a decline in performance even at levels as low as 4 ppm.

Experiments conducted using a Paraho-type oil shale retort offgas as a feedstock showed that acceptable performance could be obtained by removing carbon dioxide from the feedgas.

Design of the tandem two reactor system is continuing, along with cold flow testing of the proposed solids transfer system.

A simplified thermodynamic analysis of the BEACON process shows that BEACON's increased efficiency over competing processes results from more hot gas going to the turbine with less power required to compress the air for combustion.

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). This report covers the period from January through March 1982.

2. SUMMARY

CATALYST DEVELOPMENT AT TRW

The BEACON process for producing methane is being demonstrated successfully in laboratory and bench scale development tests. Other applications such as the production of hydrogen may also be attractive. Catalyst development at TRW this quarter explored conditions favoring the production of hydrogen. Operating conditions which favor hydrogen production over methane synthesis were identified. Enhanced hydrogen production results from suppressing methane formation and reacting carbon monoxide with water to form carbon dioxide and hydrogen. Both thermodynamic and kinetic approaches are possible. Thermodynamic approaches include a low pressure, high temperature gasification, and excess steam to increase the water-gas shift and methane-steam reforming reactions. Kinetic approaches for enhancing hydrogen production involve reducing the intrinsic catalyst activity for carbon methanation, reducing gas residence time, and lowering the process temperature to exploit reaction activation energy differences.

The use of excess steam and limited residence times for suppressing methane or increasing hydrogen production were tested in the laboratory. K1 and K2 catalysts were carburized at temperatures between 450°C and 600°C. The results show a reduction in gasification rates, steam utilization, methane production, and CO production with increasing carbon deposition temperature, while the production of CO₂ and hydrogen are increased. The data suggest that methane yield is a strong function of steam conversion. Increasing the carbon deposition temperature reduces catalytic activity and hence increases excess steam. At 600°C the methane yield from K1- and K2-based carbons is directly proportional to steam conversion.

CATALYST DEVELOPMENT AT SOHIO

Carbon loading tests with catalyst C77-K2 continued this quarter. The carbon loading experiments were conducted in a 1-inch quartz reactor, with carbon deposited at 450°C and gasified with steam at 550°C. No significant breakup of the catalyst was observed even at a 69% carbon loading level. However, catalyst agglomeration continued to be a problem in the 1-1/2 inch reactor, and the problem is not yet understood.

Experiments to improve the carbon deposition efficiency of the BEACON process when using oil shale retort offgas as a feedstock were carried out in one-inch quartz fluidized bed reactors. In the first set of experiments the tail gas from the first carbon deposition reactor at 450°C was fed to a second deposition reactor at 550°C. Another set of experiments was conducted using a single one-inch reactor with carbon deposition at 500°C and 550°C. In all the experiments the deposited carbon was removed from the catalyst by gasification at 550°C. During the first set of experiments in the series-connected reactors, it was expected that carbon would be deposited at 450°C in the first reactor from carbon monoxide and olefins, and at 550°C in the second reactor from methane and other saturated hydrocarbons. Most of the hydrocarbons with carbon numbers greater than one were removed in the first reactor but CH_4 and CO were increased. In the second reactor there was hardly any carbon deposition. The main reaction was the reduction of CO_2 with hydrogen to produce CO and water. In some of the experiments the CO_2 was removed from the feed and as a result the CO concentration decreased significantly. Reactions which were conducted in a single deposition reactor were initially run at 550°C. However, a large portion of the deposited carbon could not be gasified with steam at 550°C. In view of this result, the deposition temperature was lowered to 500°C, and for these runs it was possible to remove all the deposited carbon with steam at 550°C.

Further experiments were performed to test the resistance of catalyst C77-K2 to sulfur poisoning. They showed that the catalyst loses some of its activity after prolonged exposure to COS, regardless of whether the contaminant is in the carbon deposition feed or in the steaming feed.

BENCH SCALE TESTING

Thirty cycles of carbon deposition and steaming of K1-based BEACON solids at 100 psig pressure in the 4-inch reactor were completed this quarter. The only discernible effect of cycling on performance was on methane yield; the steam utilization and gasification rates indicated near equilibrium operation. A drop in methane yield from about 16% in cycle 1 to less than 13% in cycle 2 is believed to be due to contamination of the catalyst. The deactivation remained virtually constant during the remaining 29 cycles even though additional contamination occurred in subsequent cycles. The small reduction in methane yield observed at 100 psig in the 4-inch reactor became almost complete suppression of methane when samples of the solids were steamed at ambient pressure in a laboratory U-tube microreactor.

TANDEM REACTOR COLD FLOW TESTING

A cold flow test facility constructed last quarter was used to gather design information for the hot unit. Testing of the solids transfer system showed that solids transfer rates in the range of 10 to 30 grams per second can readily be achieved in horizontal transfer lines. Such rates are in the desirable operating range of the hot unit. It was also noted that poor gas distribution resulted in erratic solids transfer through the horizontal line nearest the bottom of the reactor.

TANDEM REACTOR DESIGN

The detailed design of the two tandem reactor vessels was completed this quarter and the reactor materials were procured. The gasification reactor is 7.5 centimeters in diameter and the carbon deposition reactor is 15 centimeters in diameter. The solids-transfer system will be designed after the results are in from the cold flow testing.

ENGINEERING ANALYSIS

A simplified engineering analysis indicates that BEACON systems utilizing medium pressure low-Btu gas as a feedstock and producing combined-cycle electric power and methane have a thermodynamic advantage over conventional systems producing the same products. The analysis makes use of models with simplified heat, material, and utility balances. The BEACON process and a competitive system are treated in an identical manner with respect to efficiency calculations. A thermodynamic "lost work" analysis of the model systems is used to calculate the maximum reversible work associated with each unit operation and to compare it to the actual work determined in the model system study. A nearly 25% increase in the efficiency of the BEACON process over its competitor results from the increase in the power delivered to the combined-cycle generating system and from the decrease in the power required to compress air for combustion.

3. CATALYST DEVELOPMENT

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

3.1 CATALYST DEVELOPMENT AT TRW

The technical viability of the BEACON process for producing substitute natural gas (SNG) is being demonstrated successfully in laboratory and bench scale development tests. The BEACON technology may also be attractive for the production of hydrogen. Catalyst development at TRW this quarter explored conditions favoring production of hydrogen. The findings and results of these investigations along with a brief background for the work and a short description of the experimental program are presented in this report.

3.1.1 Thermodynamic and Kinetic Considerations for Hydrogen Production

Enhanced hydrogen production from steam gasification of BEACON carbons must involve suppressing methane and other carbonaceous fuel gas formation. Nominal reactions involved in BEACON carbon-steam gasification include:

For enhanced hydrogen production, reactions (2) and (4) must be suppressed while reactions (3) and (5) should be accelerated and forced to the right.

* Catalytically active BEACON carbon

Several thermodynamic and kinetic approaches for increasing hydrogen production from carbon-steam gasification are possible. These are listed in Table 3-1.

TABLE 3-1. THERMODYNAMIC AND KINETIC APPROACHES FOR ENHANCED HYDROGEN PRODUCTION (METHANE SUPPRESSION)

THERMODYNAMIC	KINETIC
<ul style="list-style-type: none"> • Utilize Low Pressure, High Temperature Gasification • Employ High Excess Steam (Increases Water-Gas Shift and Methane-Steam Reforming Reactions) 	<ul style="list-style-type: none"> • Reduce Catalyst/Carbon Methanation Activity • Reduce Residence Time • Lower Temperature (Exploit Reaction Activation Energy Differences)

The limits of the thermodynamic approaches are illustrated in Figure 3-1. As the equilibrium results in Figure 3-1 indicate, hydrogen production is favored by high temperature and low absolute reaction pressure. For atmospheric pressure gasification, hydrogen yield expressed as moles of H_2 produced per mole of carbon gasified is near its maximum value of 1 within a temperature range of 650° to 700°C. As can be seen from the figure, operating the gasification reaction at 10 atmospheres pressure substantially reduces hydrogen yield favoring instead the formation of methane. Methane production may be suppressed at this operating pressure, but temperatures significantly above 800°C are required. Processes which utilize these high temperatures to suppress methane formation (favor hydrogen production) suffer from costly materials problems and lower overall thermal efficiencies. Based on these analyses, kinetic based approaches for improved hydrogen production need to be explored.

Figure 3-1. Equilibrium Yields for Graphite-Steam Gasification

Packed bed microreactors were used to study the feasibility of various approaches for suppressing methane or increasing hydrogen production. Specific approaches explored included: (1) the utilization of excess steam during gasification to promote increased water-gas shift and methane-steam reforming reactions, (2) gas residence time reduction to limit methane production from the $C-H_2$ and $CO-H_2$ reactions, and (3) reduction of BEACON catalyst intrinsic methanation activity. Procedures and detailed results from these experiments are described in the following subsections of this report.

3.1.2 Standard Gasification Tests of BEACON Carbons

Standard gasification tests using 1-gram samples of carburized catalysts and a steam feed rate of 1 gram/hour were conducted. K1 and K2 catalysts carburized at temperatures of 450, 500, 550, and 600°C (see Table 3-2) were used. Gasification was carried out at 600°C under atmospheric pressure. The packed bed microreactor apparatus and test procedures were described in a previous quarterly report.* All tests were run in duplicate to check for repeatability of results.

TABLE 3-2. CARBON DEPOSITION PERFORMANCE OF BEACON CATALYSTS

	Carbon Deposition Temperature* (°C)			
	450	500	550	600
Carbon Deposition Rate, gC/hr/g K1 catalyst metal	0.47	0.36	0.21	0.18
Carbon Deposition Rate, gC/hr/g K2 catalyst metal	0.33	0.30	0.09	0.14

* Other Experiment Conditions: 1 atm pressure, 85:15 CO:H₂ mole ratio carburizing gas

Test results are summarized in Tables 3-3, 3-4, and 3-5. The data show a reduction in gasification rates, steam utilization, methane production, and CO production with increasing carbon deposition temperature, while the production of hydrogen and CO₂ are increased. The data clearly illustrate the non-equilibrium kinetics. The volume percentage of methane in the product decreased from 7 to 3, while the volume percentage of hydrogen increased from 53 to 59. The product composition data can be seen more clearly in the overall gasification stoichiometry equations presented in Table 3-5.

* "Development of BEACON Technology, Quarterly Report, July-September 1981," Report No. DOE/MC/14400-06, Published June 1982, Section 3.1.1

TABLE 3-3. GASIFICATION PERFORMANCE OF K1-BASED BEACON CARBONS

Parameter	Theoretical *	Carbon Deposition Temperature(°C)			
		450	500	550	600
Carbon Gasification Rate, gC/hr	0.35	0.30	0.27	0.21	0.20
Steam Utilization, %	71	64	61	52	49
Product Composition, mole % (dry)					
Hydrogen	49	53	55	59	59
Methane	9	7	5	3	3
Carbon Monoxide	17	14	13	10	10
Carbon Dioxide	25	26	27	28	28

TABLE 3-4. GASIFICATION PERFORMANCE OF K2-BASED BEACON CARBONS

Parameter	Theoretical *	Carbon Deposition Temperature (°C)			
		450	500	550	600
Carbon Gasification Rate, gC/hr	0.35	0.28	0.24	0.22	0.23
Steam Utilization, %	71	61	56	52	50
Product Composition, mole % (dry)					
Hydrogen	49	53	54	57	56
Methane	9	7	6	3	4
Carbon Monoxide	17	13	12	11	11
Carbon Dioxide	25	27	28	29	29

* Equilibrium predicted for 600°C, 1 atm pressure, graphite-steam gasification

TABLE 3-5. GASIFICATION. STOICHIOMETRIES FOR BEACON CARBONS

CARBON DEPOSITION TEMPERATURE (°C)	STOICHIOMETRY*
	$C \text{ (GRAPHITE)} + 1.32 H_2O \rightarrow 0.98 H_2 + 0.17 CH_4 + 0.33 CO + 0.50 CO_2$
K1-BASED CARBONS	
450	$CH_{0.11} + 1.42 H_2O \rightarrow 1.10 H_2 + 0.14 CH_4 + 0.30 CO + 0.56 CO_2$
500	$CH_{0.10} + 1.48 H_2O \rightarrow 1.20 H_2 + 0.12 CH_4 + 0.28 CO + 0.60 CO_2$
550	$CH_{0.09} + 1.61 H_2O \rightarrow 1.40 H_2 + 0.076 CH_4 + 0.25 CO + 0.68 CO_2$
600	$CH_{0.08} + 1.62 H_2O \rightarrow 1.42 H_2 + 0.070 CH_4 + 0.24 CO + 0.69 CO_2$
K2-BASED CARBONS	
450	$CH_{0.11} + 1.44 H_2O \rightarrow 1.10 H_2 + 0.14 CH_4 + 0.28 CO + 0.58 CO_2$
500	$CH_{0.10} + 1.50 H_2O \rightarrow 1.18 H_2 + 0.12 CH_4 + 0.26 CO + 0.62 CO_2$
550	$CH_{0.09} + 1.59 H_2O \rightarrow 1.36 H_2 + 0.082 CH_4 + 0.25 CO + 0.67 CO_2$
600	$CH_{0.09} + 1.57 H_2O \rightarrow 1.31 H_2 + 0.095 CH_4 + 0.25 CO + 0.66 CO_2$

* 600°C, 1 atm pressure, steam gasification

Methane yield correlates well with steam conversion as shown in Figure 3-2. Two parallel straight lines were obtained for the K1 and K2 catalysts. The K2 catalyst appears to be a slightly better methanation catalyst. The data of Figure 3-2 suggest that methane yield is a strong function of steam conversion and hence the available excess steam. It appears that increasing the carbon deposition temperature resulted in reduced catalytic activity and hence increased the excess steam, at a constant steam feed rate of 1 gram/hour. To test this hypothesis one gasification test was done with a steam feed rate of 8 grams/hour with K1-based carbon prepared at 450°C. The methane yield dropped to 0.025 mole/mole C gasified. This data point is shown in Figure 3-2 as

Figure 3-2. Correlation of Methane Yield With Steam Conversion

[450°C(HSF)]. In summary, we can conclude that methane yield from K1- and K2-based carbons is directly proportional to steam conversion at a gasification temperature of 600°C.

3.1.3 Gasification Tests with Excess Steam

To verify the result suggested by the tests described in the previous section, 1-gram samples of K1-based carbon prepared at 450°C were gasified with steam feed rates of 1-13 grams/hour at a temperature of 600°C. The

packed bed microreactor apparatus was modified to allow for the high steam feed rates and the trapping of condensed steam. The data are shown in Figure 3-3. Once again, a linear relationship was found between methane yield and steam conversion. Extrapolation of these data suggests that methane production would be completely suppressed by using enough excess steam. The same data, when plotted as shown in Figure 3-4, suggest that about 4.9 moles of steam are required for each mole of gasified carbon to completely suppress methane production. Of course this result is applicable only to the K1 catalyst at a gasification temperature of 600°C.

Figure 3-3. Correlation of Methane Yield With Steam Feed Rate and Steam Conversion

The experimental data with excess steam suggested a method of using the packed bed microreactor as a differential reactor to study gasification kinetics. Again, 1-gram samples of K1-based carbon prepared at 450°C were

Figure 3-4. Correlation of Methane Yield With Excess Steam

used. Steam feed rate was increased until the carbon gasification rate reached a constant value. These data, plotted in Figure 3-5, show that a steam feed rate of about 20 grams/hour is needed to obtain a constant gasification rate of about 1.3 grams/hour.

Figure 3-5. Effect of Steam Feed Rate on Gasification

3.1.4 Summary

During the present quarter, we have examined the effects of carbon deposition temperature and excess steam on the production of methane, when K1- and K2-based carbons are gasified with steam at 600°C and atmospheric pressure. It was found that methane yield is directly related to steam conversion. This approach can be used to completely suppress methane production, if maximum hydrogen yield is desired.

3.2 CATALYST DEVELOPMENT AT SOHIO

The 1-1/2 inch diameter laboratory reactor was down most of the quarter. It is again operable and data are being generated. The problem of catalyst agglomeration in this reactor has continued, and it is not yet understood. The thermocouple centered in the reactor was not the source of the problem. Variables such as gas velocity, temperature of the incoming feed, and feed composition will be explored during the coming quarter.

Carbon loaded catalyst samples from the tests conducted in the 1-1/2 inch diameter laboratory reactor last quarter were subjected to further tests and analyses this quarter. A description of the 1-1/2 inch diameter laboratory reactor and the experiment conditions employed to obtain the carbon loaded samples of C77-K2 were presented in the previous quarterly report.* There was no evidence of catalyst breakup.

Carbon loading tests with catalyst C77-K2 continued this quarter in the one-inch quartz reactor. Carbon was deposited on the catalyst at 450°C and then gasified with steam at 550°C. No significant breakup of the catalyst was observed even at a 69% carbon loading level.

*"Development of BEACON Technology, Quarterly Report, October-December 1981," Report No. DOE/MC/14400-07, Published September 1982, Section 3.2.3

Experiments to improve the carbon deposition efficiency of the BEACON process when using oil shale retort offgas as a feedstock were performed this quarter. Significant improvement was obtained by removing CO₂ from the carbon deposition feedgas.

Further experiments were performed to test the resistance of catalyst C77-K2 to sulfur poisoning. These experiments showed that the catalyst loses some of its activity after prolonged exposure to carbonyl sulfide, regardless of whether the contaminant is in the carbon deposition feed or in the steaming feed.

3.2.1 Hydrocarbon Feedgas Experiments

Earlier experiments using simulated oil shale retort offgas as a BEACON feedstock were conducted to determine the influence of temperature on the rate of carbon deposition.* The maximum carbon deposition rate was obtained when the carbon was deposited at 450°C. The experiments this quarter were conducted to see whether the carbon deposition efficiency could be improved by using tandem deposition reactors operating at different temperatures and by removing the CO₂ in the feedgas mixture.

3.2.1.1 Experiment Description

The experiments were carried out in one-inch quartz fluid bed reactors. In the first set of experiments two one-inch reactors were connected in series. The tailgas of the first reactor was fed to the second reactor. The carbon deposition temperature of the first reactor was 450°C while the second reactor was held at 550°C. Carbon was deposited from a mixture having the composition of a typical Paraho retort offgas but without water, sulfur and ammonia. In subsequent experiments CO₂ also was removed from the feed.

*"Development of BEACON Technology, Quarterly Report, April-June 1981", Report No. DOE/MC/14400-05, Published December 1981, Section 3.2.4

Experiments also were carried out using a single one-inch reactor at deposition temperatures of 550°C and 500°C.

To better understand the role of hydrocarbons in the feed, carbon was deposited from ~3 and ~6 mole % propane in N₂ feed at 450°C.

In all the experiments the deposited carbon was removed from the catalyst by steam gasification at 550°C using steam/N₂ feed at atmospheric pressure.

3.2.1.2 Discussion of Experiment Results

Table 3-6 summarizes the results obtained with the Paraho mixture as the feed for carbon deposition. During the first four experiments in the series-connected reactors, it was expected that carbon would be deposited at 450°C in the first reactor from carbon monoxide and olefins, and at 550°C in the second reactor from methane and other saturated hydrocarbons. In Table 3-7 the typical composition of tailgas samples from the first and second reactors are compared with the composition of the feed. While most of the hydrocarbons with C>1 were removed, CH₄ and especially CO were increased. Actually, in the second reactor there was hardly any carbon deposition. The main reaction taking place in the second reactor was the reduction of CO₂ with H₂ (formed from the higher hydrocarbons) to produce CO and water. In experiment 4 the CO₂ was removed from the feed. The gas compositions of the feed and tailgases are presented in Table 3-8. In the absence of CO₂ the CO concentration decreased significantly. Interestingly, even the very small amount of CO₂ formed (approximately 0.5%) in the first reactor was reduced in the second reactor. Table 3-9 compares the carbon deposition with and without CO₂. The most obvious difference is that while there was hardly any carbon deposition in the second reactor with CO₂ in the feed there was very good carbon deposition without CO₂.

After seeing the advantages of removing CO₂ from the feed, we carried out experiments 5 thru 11 in a single reactor at the higher deposition temperature (550°C). However, a large portion of the deposited carbon

TABLE 3-6. SUMMARY OF RESULTS USING PARAHO FEED MIXTURE

Experiment Number	Reactor Configuration and Run Number	Carbon Deposition Temperature (°C)	CO ₂ in Feedgas?	Catalyst Volume (cc)	Carbon Deposition Rate (gC/gCatalyst Metal/Hr)	-----Conversions (%)*-----				Material Balance Closure (%)
						C _{Total}	CO	C ₂	CH ₄	
1	Tandem: 1A	450/550	Yes	40.0	0.110	10.3	-227	84.3	4.85	97.4
2	Tandem: 1B	450/550	Yes	40.0	0.123	11.5	-216	91.1	-19.4	97.0
3	Tandem: 2	450/550	Yes	40.0	0.130	11.8	-186	91.8	-14.7	97.5
4	Tandem: 3	450/550	No	40.0	0.266	54.5	46.9	98.0	-98.3	108.7
5	Single: 1	550	No	20.0	0.499	51.8	33.0	99.5	-46.8	98.3
6	Single: 2	550	No	20.0	0.534	58.2	34.3	98.5	-32.2	99.5
7	Single: 3	550	No	20.0	0.525	53.8	33.0	97.3	-38.2	99.1
8	Single: 3-X	550	No	20.0	0.453	45.5	34.9	87.8	-56.5	100.3
9	Single: 4	550	No	20.0	0.473	47.6	25.9	91.4	-44.5	98.3
10	Single: 5A	550	No	20.0	0.549	55.4	23.9	95.7	-28.5	99.3
11	Single: 5B	550	No	20.0	0.492	54.6	13.0	96.1	-38.0	101.1
12	Single: 6A	500	No	20.0	0.310	34.2	43.1	81.3	-106	100.6
13	Single: 6B	500	No	20.0	0.323	36.0	40.5	83.0	-123	102.0
14	Single: 7	500	No	20.0	0.415	46.6	52.9	87.4	-80.4	101.2
15	Single: 8	500	No	20.0	0.397	43.7	50.4	88.3	-83.3	100.4
16	Single: 9A	500	No	20.0	0.417	45.7	52.8	77.7	-56.4	100.4
17	Single: 9B	500	No	20.0	0.409	45.4	53.5	85.4	-73.8	100.7

* Negative (-) conversions indicate net production species

TABLE 3-7. GAS COMPOSITIONS AND FLOW RATES DURING CARBON DEPOSITION
(Feedgas Contains CO₂)

	Feedgas	After 450°C Reactor	After 550°C Reactor
H ₂	4.0	4.6	4.3
CO ₂	24.9	23.0	19.5
C ₂	0.6	0.3	0.2
N ₂	62.3	63.2	63.0
CH ₄	2.3	3.4	2.8
CO	2.9	4.3	9.0
C ₂ ⁼	0.9	0	0
C ₃	0.3	<0.1	0
C ₃ ⁼	0.3	0	0
n-C ₄	0.5	<0.1	0
Total Flow (cc/min)	335	328	325

could not be gasified with steam at 550°C. In view of this result, we lowered the deposition temperature to 500°C (experiments 12 thru 17). In these runs we were able to consistently remove all the deposited carbon with steam at 550°C.

To gain more insight into the deposition of carbon from higher hydrocarbons, some deposition experiments were done with propane. The products of deposition were carbon, CH₄ and H₂. Carbon can be deposited from propane by the following primary reaction pathways:

TABLE 3-8. GAS COMPOSITIONS AND FLOW RATES DURING CARBON DEPOSITION
(Feedgas Does Not Contain CO₂)

	Feedgas	After 450°C Reactor	After 550°C Reactor
Experiment No. 4; Deposition No. 1			
H ₂	5.87	6.24	12.25
CO ₂	0	0.52	0.17
N ₂	81.34	80.84	78.52
CH ₄	3.06	7.76	5.04
CO	2.50	0.91	1.23
C ₂	0.98	0.34	0
C ₂ ⁼	1.25	0	0
C ₃	0.63	0.11	0
C ₃ ⁼	0.67	0	0
n-C ₄	0.50	0.03	0
Total Flow (cc/min)	335	333	327

Experiment No. 4; Deposition No. 2			
H ₂	5.89	N	13.20
CO ₂	0	0	0.16
N ₂	82.92		79.85
CH ₄	3.19	D	4.91
CO	2.57	A	1.27
C ₂	0.99	T	0
C ₂ ⁼	1.27	A	0
C ₃	0.63		0
C ₃ ⁼	0.67		0
n-C ₄	0.50		0
Total Flow (cc/min)	333		333

TABLE 3-9. COMPARISON OF TANDEM REACTOR RESULTS WITH AND WITHOUT CO₂ IN THE FEEDGAS

Feed: Paraho Mixture		Temperature: Reactor No. 1--450°C, Reactor No. 2--550°C					
Step	Reactor	With CO ₂ in Feedgas (Experiment Nos. 1-3)			Without CO ₂ in Feedgas (Experiment No. 4)		
		Rate (gC/gCatalyst Metal/Hr)	Carbon	H ₂ O	Rate (gC/gCatalyst Metal/Hr)	Carbon	H ₂ O
			Loading (%)	Generated (g)		Loading (%)	Generated (g)
			Runs 1A + 1B			Cycle 1	
Carbon	1	0.23	21.2	1.89	0.28	20.2	0.45
Deposition	2	0.012	1.5	1.39	0.21	14.7	0.21
Steam	1	1.03	8.7	--	0.99	8.8	--
Gasification	2	--	--	--	--	--	--
			Run 2			Cycle 2	
Carbon	1	0.26	21.2	1.48	0.28	21.1	0.28
Deposition	2	0.002	1.6	0.95	0.24	24.9	0.18
Steam	1	1.11	9.0	--	1.02	10.6	--
Gasification	2	--	--	--	0.87	13.0	--

Secondary reactions involve the formation and cracking of methane with 2H₂ being formed. At 450°C the secondary reactions are probably not significant when compared to the main reactions (1 and 2). We found that when approximately 6 mole % propane was used in the feed the CH₄/H₂ ratio was about 1 in the effluent gas. This indicates that both primary pathways are used. However, when the propane concentration was only about 3 mole % the ratio was increased to 2. This suggests that both pathways are used but a lower concentration of reactant favors reaction 2. The deposited carbon was active in steam gasification at 550°C.

3.2.2 Sulfur Tolerance Testing of Catalyst C77-K2

Further experiments were performed to test the resistance of catalyst C77-K2 to sulfur poisoning.* The experiments were carried out in a one-inch quartz fluid bed reactor. Standard reaction conditions were used with one modification: COS was added to the feed. In the first experiment, 4 ppm COS was added to the feed during steaming for several cycles; then the level of COS was raised to 12 ppm for a few additional cycles. In the second experiment, using a fresh batch of catalyst, carbon was deposited from a feed containing 12 ppm COS. In the third experiment, another fresh batch of catalyst was used to deposit carbon from a feed containing 4 ppm COS.

In the first experiment we wanted to investigate the effect of sulfur introduced during steaming. Figure 3-6(a) shows the carbon gasification rate for each cycle. The first cycle had no COS in the steam feed. This established a base value. The next five cycles (X) had 4 ppm COS in the steam feed. The next three cycles had 12 ppm COS in the steam feed. The gasification rates for cycles 3 and 4 are lower than the base case (cycle 1). Surprisingly, the rates for cycles 2, 5 and 7 are the same as for cycle 1. From these data we cannot conclude that there is any significant deterioration of steaming efficiency. However, after only one cycle with 12 ppm COS in the steam feed, the gasification rates went well below the rate of the base case. The last two (Δ) points are fairly close together, indicating that after the initial drop in rate the decrease is very gradual. During the last cycle, steaming was performed with no COS present. The rate remained about the same as the previous two cycles, suggesting that the catalyst degeneration is irreversible under these experiment conditions.

Figure 3-6(b) shows the carbon deposition rate for each cycle. Although there is considerable scatter in the data, the conclusion is the same as that drawn from the gasification rates. There was no significant

*For earlier work, refer to "Development of BEACON Technology, Quarterly Report, January-March 1981," Report No. DOE/MC/14400-04, Published July 1981, Section 3.2.4.1

(a) Carbon Gasification Rates

(b) Carbon Deposition Rates

Figure 3-6. Carbon Gasification and Deposition Rates with Carbonyl Sulfide Added to the Steam Feed

change in the carbon deposition rate when only 4 ppm COS was added to the steam feed. However, 12 ppm COS in the steam feed lowered the catalyst's activity for carbon deposition.

Since we can expect COS contaminants in the carbon deposition feed rather than in the steaming feed, the next two experiments were more important from the practical point of view. Figure 3-7 shows the carbon gasification and deposition rates for each cycle when the deposition feed contained 12 ppm COS. After the catalyst was exposed to sulfur for only two cycles the gasification rates declined rapidly.

Figure 3-8 shows the carbon gasification and deposition rates for each cycle when only 4 ppm COS was present in the deposition feed. For the first 13 cycles the gasification rates with COS in the deposition feed were about the same as those for the base case without COS (cycles 1 and 2). However, starting with cycle 14 the rates dropped to a lower level. The carbon deposition rates also were unaffected for a while, but started to decrease a few cycles earlier than the gasification rates. During this last experiment we periodically analyzed for sulfur in the feed and tailgas samples collected during both steaming and carbon deposition. No sulfur was found above the detection limit of 1 ppm in the tailgas samples.

These experiments show that catalyst C77-K2 loses some of its activity after prolonged exposure to COS, regardless of whether the contaminant is in the carbon deposition feed or in the steaming feed.

(a) Carbon Gasification Rates

(b) Carbon Deposition Rates

Figure 3-7. Carbon Gasification and Deposition Rates with 12 ppm Carbonyl Sulfide in the Deposition Feed

(a) Carbon Gasification Rates

(b) Carbon Deposition Rates

Figure 3-8. Carbon Gasification and Deposition Rates with 4 ppm Carbonyl Sulfide in the Deposition Feed

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

Bench scale testing in the 4-inch reactor continued during the quarter. The major accomplishment was the successful completion of the planned 30 cycles of carbon deposition/steaming with K1-based BEACON solids. These tests demonstrated the stability of the catalytic activity of K1-based solids for both the deposition and steaming reactions. Steam utilization and methane production approached equilibrium throughout these tests.

Contamination of the K1-based solids suppressed methane production at ambient or near ambient pressure but had very little effect on either conversion rates (deposition or gasification) or product gas composition at 100 psig.

An internal stainless steel filter was installed in the reactor to permit reactor operation at velocities up to 12 cm/sec (0.4 ft/sec). The filter reduced solids entrainment to virtually zero and increased operating efficiency.

The multicycle 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 monitored continuously using calibrated orifices. Product gas compositions were measured every 8-1/2 minutes using a 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 was also measured using a dry gas meter. The test procedures used and measurements performed in steaming tests have been described in detail in previous quarterly reports.

* "Development of BEACON Technology, Quarterly Report, October-December 1980", Report No. DOE/MC/14400-03, Published March 1981, Section 4.2

4.1 K1-BASED BEACON SOLIDS MULTICYCLE TESTING IN 4-INCH REACTOR

The K1-based BEACON solids multicycle tests which were started last quarter were concluded during the current quarter with the completion of 30 carbon deposition/steam gasification cycles. The nominal test conditions -- temperature, pressure, linear gas velocity, and feed gas composition -- used during these multicycle tests are shown in Table 4-1. The results obtained are summarized in Figure 4-1 and Table 4-2.

TABLE 4-1. NOMINAL MULTICYCLE TEST CONDITIONS

Reactor Pressure	115 psia
Reactor Temperature	
Carbon Deposition	450°C
Steaming	650°C
Linear Gas Velocity	10 cm/sec (0.3 ft/sec)
Feed Gas Composition (mol %)	
Carbon Deposition	30% CO 15% H ₂ 50% N ₂ 5% CO ₂
Steaming	90% H ₂ O - 10% N ₂

Figure 4-1 presents the steam utilization and carbon gasification rates as a function of cycle number. Two conclusions can be drawn from these data concerning gasification performance: (a) steam gasification of

* Equilibrium predicted values for graphite-steam reaction at 100 psig and 650°C.

Figure 4-1. Steam Gasification of K1-Based BEACON Solids
(100 psig, 650°C)

TABLE 4-2. STEAM GASIFICATION OF K1-BASED BEACON SOLIDS
AT 100 PSIG AND 650°C

Product Gas Composition (vol %)						
	<u>Cycle 1</u>	<u>Cycle 6</u>	<u>Cycle 11</u>	<u>Cycle 14</u>	<u>Cycle 25</u>	<u>Cycle 30</u>
CH ₄	15.7 (17.8)*	10.4	9.2	12.9	10.6	10.4
CO	8.6 (13.6)	8.4	16.8	14.5	16.9	8.7
CO ₂	31.7 (30.2)	31.3	26.2	28.0	25.6	31.0
H ₂	44.1 (38.3)	49.9	47.8	44.6	46.7	49.8

*Equilibrium composition based on thermodynamic data for steam gasification of graphite at 100 psig and 650°C.

K1-based BEACON carbon took place virtually at equilibrium and (b) there was no discernible effect of cycling on performance. The data show appreciable scatter, but the scatter does not seem to be masking deterioration of catalytic activity.

The data scatter was due to two types of "experimental error" in the control and measurement of operating parameters, and the data have been grouped accordingly in Figure 4-1. The circles represent the data within the expected deviation about the mean, which in the case of steam utilization is virtually identical to the equilibrium line. The mean deviation is less than 10% and can be easily justified by an error analysis of the measurements (e.g., a $\pm 5^\circ\text{C}$ variation in reaction temperature caused a variation of ± 2 percentage points in steam utilization). The Xs represent data generated under operational upsets where an appreciable fraction of the solids were outside the reaction zone. The majority of these upsets occurred between cycles 15 and 25 when we experienced problems with automatic flow control of the feed gases. Electronic noise resulted in very large errors in feed gas temperature measurements which affected

feedgas control (especially that of steam). These stray electronic signals were intermittent and very infrequent but it took only a few seconds of higher flow to entrain the solids out of the reactor and into the filter housing. Until the problem was corrected by going to manual steam feed control and by the installation of an internal filter into the reactor which kept the solids within the reactor vessel, several tests were performed with less than the needed quantity of solids present in the reaction zone for the usual near-equilibrium performance (not enough residence time and appreciable steam bypass). It should be noted, however, that steam gasification performance always returned to virtual equilibrium when upsets were avoided.*

Similar conclusions can be drawn from the product gas composition data (data from selected cycles are presented in Table 4-2). The methane concentration dropped from approximately 16 percent by volume to 13 percent between the first and second cycles and then fluctuated between 9 and 13 percent during the 30 cycles.** It is believed that the fluctuations in product gas composition are due principally to small variations in bed temperature from cycle to cycle. An effort was made to maintain the bed temperature to within $\pm 5^{\circ}\text{C}$ of the desired value (650°C) and to reproduce the temperature profile within a couple of degrees during succeeding runs; it was not always possible to attain these limits during high heat demand (high reaction rates), but the deviations were small. Other operating variables -- e.g., poor fluidization, fluctuations in steam feed, and fluctuations in reactor pressure -- also could have contributed to the

* It is believed that the source of the "noise" was one or two defective channels in the Doric Digitrend 220 data logger used to store thermocouple data prior to transmittal to the computer. This problem will be investigated more thoroughly when the 4-inch reactor testing concludes next quarter.

** In runs where steam utilization dropped below 50% because of solids entrainment out of the reaction zone, the methane concentration in the product gas dropped appreciably below 10%.

observed variations in product gas composition. It is important to note, however, that the product gas composition from the 30th cycle is virtually identical to that of the 6th cycle; the same was true of other cycles not presented in Table 4-2.

The initial drop in methane yield, from about 16 percent in cycle 1 to just under 13 percent in cycle 2 (cycle 2 data are not included in Table 4-2), is believed to be due to contamination of the catalyst. Based on the fact that the methane concentration in the product gas remained within a stable range after the second cycle and the fact that 40 cycles in laboratory scale, ambient pressure testing showed no drop in methane yield when uncontaminated catalyst was used,^{*} it is speculated that enough contamination of the K1-based solids occurred during the first cycle to cause the indicated small catalyst deactivation. The deactivation remained virtually constant during the remaining 29 cycles, even though additional contamination of the catalyst occurred in subsequent cycles.

4.2 LABORATORY TESTING OF 4-INCH REACTOR SAMPLES

The small reduction in methane yield observed during steaming at 100 psig in the 4-inch reactor became almost complete suppression of methane when these solids were steamed at ambient pressure. During the 30 carbon deposition/steaming cycles performed at 100 psig pressure in the 4-inch fluidized bed reactor, samples of solids were withdrawn at frequent intervals for characterization testing. These samples were subjected to chemical and physical analyses and to activity tests at laboratory scale to verify catalyst performance in the 4-inch reactor. The laboratory-scale tests were performed in a U-tube microreactor (1 to 2 gram beds) at ambient pressure. It was during these tests that the virtually complete suppression of methane was observed. It should be noted that the only discernible effect of cycling on performance was on methane yield; the steam utilization and gasification rates indicated near equilibrium operation.

^{*}op cit, DOE/MC/14400-07, Section 3.1.1

The laboratory-scale data are summarized in Table 4-3. The first column shows the dry product gas composition obtained from steaming a sample of the K1-based BEACON solids before they were subjected to the 30 cycle testing in the 4-inch reactor. The measured composition is virtually identical to that expected from equilibrium operation (predictable from thermodynamic data).^{*} The first solids sample drawn from the 4-inch reactor for performance verification testing at laboratory scale was after 11 cycles were completed. The sample was steamed at laboratory scale at 600°C and 650°C. Steaming performance was virtually that predicted by equilibrium but with almost complete suppression of methane. Samples drawn after 14, 18, 22, 26, and 30 cycles and steamed at laboratory scale furnished identical results to those described for the cycle 11 sample, i.e., high gasification rate but low methane yield.

4.3 4-INCH REACTOR MODIFICATION TO ACCOMMODATE HIGHER GAS VELOCITIES

The 4-inch reactor was modified slightly to accommodate the installation of the internal stainless steel filter depicted schematically in Figure 4-2. The filter is equipped with on-line backflushing capability which permits the "cleaning" of the filter element with minimum (short term disturbance to the cycling operation. Nitrogen cooling gas insures that the filter element remains appreciably below reaction temperature. The internal filter has been operated successfully at gas velocities up to 12 cm/sec (0.4 ft/sec) for several cycles; data deviations due to flow upsets have been virtually eliminated since the installation of the internal filter (solids have been kept within the reaction zone).

^{*} This fresh sample was cycled at laboratory scale in glass equipment for 12 cycles prior to using this batch of solids as the starting material for the 30 cycle testing in the 4-inch reactor. There was no change in either product gas composition or steam utilization during the laboratory-scale cycling.

TABLE 4-3. LABORATORY-SCALE STEAM GASIFICATION OF K1-BASED BEACON
SOLIDS CARBURIZED DURING CYCLING IN THE 4-INCH REACTOR

Product Gas Composition, Mole Percent Dry						
	Fresh	After 11		After 14		After 18
	Sample 600°C**	Cycles* 600°C**	Cycles* 650°C**	Cycles* 600°C**	Cycles* 650°C**	Cycles* 650°C**
CH ₄	9	<1	<1	<1	<1	<1
CO	16	14	23	10	18	18
CO ₂	29	25	20	27	22	23
H ₂	46	59	56	63	59	59

	After 22		After 26	After 30
	Cycles* 600°C**	Cycles* 650°C**	Cycles* 600°C**	Cycles* 600°C**
CH ₄	<1	<1	<1	<1
CO	12	20	14	16
CO ₂	27	21	27	25
H ₂	61	59	59	58

* At 100 psig pressure in the 4-inch reactor

** Laboratory steam gasification temperature

Figure 4-2. Reactor Internal Filter Flow Diagram

4.4 STATUS OF 1-1/2 INCH DIAMETER PROCESS DEVELOPMENT REACTOR

Alterations were made to the 1-1/2 inch diameter, process development, fluid bed reactor system to improve its performance. The earlier distributor, a simple perforated plate, was replaced with a sintered ceramic plate, and a vibrator was attached to the top flange of the reactor to discourage catalyst fines from sticking to the surfaces of the disengagement section of the reactor. These alterations, together with the correction of a feedgas problem, have resulted in smooth operation and good reaction rates. About 50 hours of smooth operation have been logged to date.

5. TANDEM REACTOR DEVELOPMENT

Work continued this quarter on the tandem reactor concept which includes a variable differential pressure ("huff-puff") transfer line for the transfer of BEACON solids between carbon deposition and gasification reactors.* Testing was started in the cold flow test facility constructed last quarter, and design work started on the hot flow unit.

5.1 COLD FLOW TESTING

A cold flow test facility (Figure 5-1) was constructed last quarter** to confirm the viability of the tandem reactor concept and to provide design information for the hot flow unit. After shakedown testing, additional horizontal transfer lines were installed. Further testing verified that solids transfer rates in the range 10-30 grams/sec could readily be achieved in the horizontal transfer lines. Such rates are in the desirable range of operation of the hot unit. During these initial tests it was observed that the diagnostic pressure lines plugged with carbon and that poor gas distribution at the test unit inlets resulted in poor solids transfer through the horizontal line closest to the inlets. As a result of these difficulties plus an interest in investigating solids transfer through a sloped line, further modifications were made in the cold flow unit including installation of a continuous purge on the diagnostic pressure lines and installation of a sloping transfer line. A system schematic is shown in Figure 5-2. Testing will continue next quarter.

5.2 HOT FLOW REACTOR DESIGN

The detailed design of the hot flow tandem reactor vessels was completed this quarter and reactor materials were procured. Design criteria for the tandem reactors are listed in Table 5-1. Based on

* op cit, DOE/MC/14400-06, Section 4.1.3

** op cit, DOE/MC/14400-07, Section 5

Figure 5-1. Cold Flow Tandem Reactor Test Facility

Figure 5-2. Cold Flow Tandem Reactor Unit

TABLE 5-1. DESIGN CRITERIA FOR HOT FLOW TANDEM REACTOR VESSELS

GASIFICATION REACTOR	
Temperature	500-750°C
Pressure	1-7 atmospheres
Superficial Velocity	10-45 cm/sec
Steam Feed	50-100%
Nitrogen Feed	0-50%
Reactor Materials	Type 316 Stainless Steel with Inside Surfaces Aluminized
DEPOSITION REACTOR	
Temperature	400-600°C
Pressure	1-7 atmospheres
Superficial Velocity	10-45 cm/sec
Carbon Monoxide	20-50%
Hydrogen	5-40%
Carbon Dioxide	0-10%
Nitrogen	20-65%
Reactor Materials	Type 316 Stainless Steel with Inside Surfaces Aluminized

trade-offs between fluid bed dynamics and operating costs, the gasification reactor was sized at 7.5 cm diameter and the carbon deposition reactor was sized at 15 cm diameter. (Given equal superficial velocity, pressure, and bed height in each reactor, the deposition reactor must be twice the diameter of the gasification reactor to obtain equal carbon deposition and gasification rates.) Design of the solids transfer geometry and control system will be done after further results are available from the cold flow testing.

6. ENGINEERING ANALYSIS

BEACON systems utilizing medium pressure (150-250 psig) low Btu gas as a feedstock and producing combined-cycle electric power and methane as products have a unique thermodynamic advantage over conventional systems producing the same products. In this section we present two forms of analysis to demonstrate this advantage.

The first form of analysis we call "model system studies." These are simplified process heat, material and utility balances for competitive cases in which we select a simple model feedstock composition and rigorously treat the competitive cases in an identical manner with respect to efficiency calculations. The advantage of this approach is that we can see very rapidly what aspects of a particular case are important in determining the overall system efficiency and the relative efficiency of one process concept (or case) versus another.

In the second type of evaluation we perform a thermodynamic "lost work" analysis around each of the model systems by constructing a theoretical, reversible, process model that starts with the same feedstock and ends up with the same products as the model system case. In the reversible process we calculate the maximum (reversible) work associated with each unit operation and compare it to the actual work determined in the model system study. The difference between the reversible work and the work calculated for the model system is the "lost work" which is an accurate measure of the degree of inefficiency (or efficiency) of a particular process flow sheet.

6.1 MODEL SYSTEM STUDIES

Figure 6-1 presents a simple model system for a process competitive with BEACON for producing combined-cycle power and substitute natural gas (SNG) from a clean, synthesis gas fuel. For simplicity we model the synthesis gas fuel as consisting of equal moles of carbon monoxide and hydrogen. The steam systems for power generation and shift-methanation are integrated; i.e., the exothermic shift-methanation system produces both

process steam and steam which is used for power generation. The high temperature combined shift and methanation process (RMP Process) was chosen as being representative of the best evolving competitive SNG technology.

Figure 6-2 presents a block diagram of the BEACON model system producing combined-cycle power and SNG. In this system we use a simplified BEACON feed gas consisting of equal moles of carbon monoxide and hydrogen diluted to producer gas volumetric heating value levels with nitrogen. Identical feedstock molar inputs of carbon monoxide and hydrogen are used in the BEACON (Figure 6-2) and conventional (Figure 6-1) cases, and the total hourly higher heating value of the feedstock fed to each process is also identical (15.66×10^9 Btu/hr). Both the conventional and BEACON systems have been constrained to produce the same quantities of methane (20,000 moles/hr, 7.66×10^9 Btu/hr HHV). Therefore, the total hourly input heating value is the same in both cases and the total hourly methane output is the same, leaving the net power generated in each case to be the floating variable which measures the comparative overall efficiency in each system.

Identical gas turbine/compressor/generator systems and efficiencies are used in the two cases with a turbine inlet temperature of 1970°F assumed. The heat recovery steam generator (HRSG) systems are assumed to be capable of converting the sensible heat remaining in the turbine exhaust gases to electric power at 25% overall efficiency, a number which is consistent with several detailed studies of the power recovery from HRSG systems. Part of the HRSG heat available in the BEACON case is used to raise process steam for the carbon-steam reaction, and the remainder is converted to electric power at 25% efficiency.

In the conventional system the high temperature shift-methanation process produces 1.21×10^9 Btu/hr of excess heat which is convertible to superheated steam and then to electric power at 35% efficiency. In the BEACON carbon deposition reactor a small amount of the exothermic heat of reaction is taken out as superheated steam (0.176×10^9 Btu/hr) and converted to electric power at 35% efficiency. The remainder of the exothermic heat from carbon deposition remains as sensible heat in the

working fluid of the gas turbine system. In the BEACON case the steam-carbon reaction is endothermic overall, and hence no net power is produced in this part of the system. Rather, heat must be imported from the combined-cycle burner and from the HRSG system.

In the BEACON system (Figure 6-2) we see that we pull 40,000 moles/hr of carbon ($\text{HHV} = 6.77 \times 10^9 \text{ Btu/hr}$) and $1.621 \times 10^9 \text{ Btu/hr}$ of heat out of the incoming fuel gas to the combined-cycle system to make the 20,000 moles/hr of CH_4 ($\text{HHV} = 7.66 \times 10^9 \text{ Btu/hr}$). Hence, the overall efficiency of methane production is 7.66 divided by $6.77 + 1.621$ or 91.3%. In the conventional system (Figure 6-1), $9.78 \times 10^9 \text{ Btu/hr}$ of synthesis gas feedstock produces $7.66 \times 10^9 \text{ Btu/hr}$ of methane plus $1.21 \times 10^9 \text{ Btu/hr}$ of high level heat available for power generation. Hence, the overall efficiency of methane production in the conventional case is $7.66 + 1.21$ divided by 9.78, or 90.7%. Thus, the efficiency of methane production in the two cases is essentially identical.

Although methane production in the two cases has about the same efficiency, on the power generation side we see that we have dramatic differences. The BEACON system produces 262 more MW than the conventional system or 31.6% more power. The reasons for this major improvement in power production and hence in overall efficiency in the BEACON case relative to the conventional case begins to become apparent from the model system block flow diagrams. In the conventional system, 434,800 moles of air are compressed for 458,800 moles of hot combustion gases entering the turbine or a ratio of 0.947 moles of air compressed per mole of combustion gas. In the BEACON system, only 285,352 moles of air are compressed for 549,352 moles of hot combustion gases entering the turbine at the same temperature or a ratio of 0.519 moles of air compressed per mole of combustion gas. Each mole of air compressed per hour consumes 1.38 KW of power, so the predominant difference in power production in the two systems boils down to the difference in power required to compress combustion air.

The question now comes down to why there should be so much more air compressed in the conventional system than in the BEACON system. In the conventional system, we feed a fuel to the burner in which all of the

energy content of the fuel is derived from the heat of combustion of the carbon monoxide and hydrogen and none of the energy content is yet in the form of sensible heat. Thus, in the burner we convert all of the chemical energy of the fuel to sensible heat and, in order to do this and still meet the system constraint of a 1970°F entrance temperature at the turbine, we must dilute the combustion product gases with a great deal of excess compressed air in order to hold the final temperature at 1970°F.

In the BEACON system, we initially extract from the fuel gas over 40% of its total heating value in the form of solid carbonaceous material which is subsequently converted to methane product at very high efficiency. In addition, a significant amount of the remaining heating value of the fuel is converted to sensible heat during carbon extraction, prior to entering the burner, and hence without compression of air. This can readily be understood when we recognize that the deposition of one mole of carbon from two moles of carbon monoxide also produces one mole of carbon dioxide and a large amount of heat. In effect what we have done is deposited one mole of carbon from carbon monoxide and burned one mole of carbon monoxide to carbon dioxide without ever compressing any air. The nitrogen diluent present in the low heating value fuel serves to take up the great majority of the heat of reaction during carbon deposition. Thus, in the BEACON case we enter the burner with a very lean fuel in which much of the heating value is already present as sensible heat. Hence, relatively little air must be compressed to burn the remaining carbon monoxide and hydrogen and to dilute the total combustion product to a turbine inlet temperature of 1970°F. In the limit, if there were no equilibrium constraints, all of the heating value of the depleted gas after carbon deposition would be in the form of sensible heat in the hot nitrogen plus carbon dioxide and water vapor.

Thus, through the mechanism of extracting energy from a low heating value feedstock in the form of a solid carbonaceous material, we convert the remaining energy in the feedstock to a form where it can be more efficiently converted to electric power in a combined-cycle system. This

CONVENTIONAL MODEL SYSTEM (SYNTHESIS GAS FEED)

Figure 6-1. Conventional Model System

BEACON STEAM-CARBON MODEL SYSTEM (PRODUCER GAS FEED)

Figure 6-2. BEACON Steam-Carbon Model System

energy extraction and concentration in the form of carbon provides the basis for the unique thermodynamic synergism of the BEACON combined-cycle power system.

6.2 LOST WORK ANALYSIS

In this section, the thermodynamic efficiency of the BEACON combined-cycle/methane system (Figure 6-2) is compared with the thermodynamic efficiency of the competing system providing combined-cycle power and SNG (Figure 6-1). The feed to the BEACON process is producer gas (64,000 moles per hour of CO, 64,000 moles per hour of H₂, and 200,000 moles per hour of N₂, at a total pressure of 17 atm). The conventional competitive process uses a synthesis gas feed (64,000 moles per hour of H₂, and 64,000 moles per hour of CO, at 17 atm pressure). Both processes produce the same amount of methane (20,000 moles per hour).

The basis of this analysis is the statement of the Second Law of Thermodynamics that no process can be more efficient in producing useful work than a reversible process. In order to see where useful work is lost in a real process, we construct a reversible process that has the same reaction conditions as the actual one. We compare the work which would be available from the reversible process with the actual work available from the real process. The difference is called "lost work." In this analysis, the essential features of the real process are duplicated with reversible operations. Each chemical reaction is assumed to occur at equilibrium. As the reaction proceeds, the heat of reaction is evolved and is converted into work by means of a heat pump operating with Carnot efficiency. Reactants transferred between vessels leave and enter reactors at equilibrium temperatures and partial pressures. Changes in temperatures and pressures of flow streams are accomplished by reversible compressors and reversible heat engines.

The essential thermodynamic features of the BEACON process and of the conventional competitor process are shown in Figures 6-3 and 6-4. Reactors are shown as large squares with material flow from left to right. Heavy vertical arrows represent work outputs. The vertical arrow above each

square indicates the work that could be obtained by a Carnot engine processing the heat of reaction. Each specie in a flow stream is considered to be removed from one reactor or put into another reactor through a semipermeable membrane at its equilibrium partial pressure. Between reactors, each specie is cooled by a reversible heat pump to room temperature, compressed or expanded as needed isothermally and reversibly at room temperature, then heated to reaction temperature by another reversible heat pump. The net work available from the expansion of all the species in a flow stream is shown issuing from a turbine (shown as a trapezoid), and the net work from all the heat engines required to bring all the species in a flow stream down to room temperature and then back to reaction temperature is shown issuing from a rectangle. It should be pointed out that the reversible expansion process could also be carried out adiabatically. In such a case, the split between expansion work and heat engine work would be different, but the sum would be the same.

Each part of the conceptual processes shown in Figures 6-3 and 6-4 operates reversibly; hence, a negative sign for the expansion work indicates a net input of power. Similarly, a negative sign for the work from the ideal heat engines indicates a net flow of power into the system. Power (work) values are given in millions of Btu per hour. The values in boldface type are for the reversible process. The sum of these values is the maximum possible useful work which could be obtained from the system. The values in italic type represent the actual work inputs and outputs of the model system. The sum of these values represents the actual work output from the model process.

In the BEACON process, all the producer gas entering the system is fed to the carburizer. For the reversible case, each specie in the entering producer gas is expanded to its equilibrium partial pressure in the carburizer and then heated to the temperature of the carburizer. The carburization reaction is exothermic and, in the reversible case, the reaction produces a net work output. In the real process, the heat of reaction irreversibly supplies the heat needed to bring the reactants up to temperature, and the small amount which is left over is used to generate electricity (63 million Btu per hour).

Two streams leave the carburizer reactor: one contains carbon which goes to the steamer, and the other contains carbon-depleted gases which go to the combustor. For the reversible case, the gases are first expanded to the very low equilibrium partial pressures which they would have in the combustor and are then heated to combustion temperature. Air must also be brought into the combustor in excess of that which is required for stoichiometric conversion in order to keep the temperature down to an acceptable level, and flow work is required to move the air into the combustor. As the combustion proceeds, the heat of reaction produces work by a Carnot engine. In the actual process, of course, the heat of reaction is used irreversibly for heating the gases up to exhaust temperature.

The hot combustion gases are expanded and cooled to produce useful work. In the reversible case, the exhaust gases from the combustor are dropped to atmospheric pressure through an expander and cooled to room temperature. In the actual process, an adiabatic turbine expands the gases until their temperature drops to approximately 1000°F, and 25% of the residual enthalpy is removed by a heat recovery steam generator (HRSG). The total amount of work actually available from this combined-cycle expansion step is 5,164 million Btu per hour, approximately 20% less than the value for the reversible process.

Carbon from the carburizer enters the steamer where it reacts with water. In the reversible case, the water is heated at room temperature from a liquid to a vapor; the vapor is then compressed isothermally to its partial pressure in the steamer reactor and is then heated to the temperature of the steamer reactor. The steaming reaction is endothermic. In the reversible case, the heat of reaction is supplied by a reversible heat pump; thus, a power input is necessary at this point. Two streams leave the steamer reactor: one is byproduct CO_2 at 70°F and one atmosphere, and the other is CH_4 at 70°F and one atmosphere. The equilibrium partial pressure of the methane in the steamer is less than one atmosphere; hence, in the reversible case it is compressed to atmospheric pressure. A small amount of work is recovered by cooling the methane and the carbon dioxide to room temperature. In the actual process, some of the

heat from the combustion of the carbon-depleted gases is used in preheating the input to the steamer and in supplying the endothermic heat of reaction, and no output of useful work is obtained.

In the non-BEACON system with parallel conventional processes for combined-cycle power generation and for methane production, the incoming synthesis gas is split into two streams: 24,000 moles each of CO and H₂ are sent to the combustor. In the reversible case, these gases are expanded and then heated to their equilibrium partial pressures and temperature that would occur in the combustor. The nitrogen and oxygen which make up the air stream are compressed from their ambient partial pressures and heated to their equilibrium partial pressures and temperature in the combustor. Useful work is obtained from the heat of reaction through a Carnot heat engine. In the real process, the heat of reaction in the combustor raises the temperature of the inlet gases to the combustion temperature. The overall power requirement for the real combustion process is 2,155 million Btu per hour. The hot combustion gases are then expanded to produce useful work. In the reversible case, the exhaust gases are expanded to atmospheric pressure and then cooled to room temperature by a reversible heat engine. The real system uses an adiabatic expansion followed by partial recovery of the enthalpy in the heat recovery steam generator (HRSG) producing 4,619 million Btu per hour. This is about 15% less work than is produced in the reversible case.

In the non-BEACON system, the larger part of the synthesis gas, 40,000 moles each of CO and H₂, is put through a conventional shift-methanation process to produce CH₄ and byproduct CO₂ at the same exit conditions as were assumed for the BEACON process. The overall work which could be obtained from such a process, if it were operated reversibly with heat exchanged to the surroundings at room temperature, is 1,637 million Btu per hour. This is the difference between the free energy of the incoming stream and the exiting streams. The actual amount of work obtained is calculated by assuming that the heat rejected in the process can be converted to electricity at 35% overall efficiency. This gives 433 million Btu per hour, which is about 26% of the maximum amount which could be obtained from a reversible process.

Comparison of the BEACON process with its competitor shows that BEACON produces 915 million Btu per hour more electrical power. The BEACON process extracts 51.8% of the possible available power in the form of electricity, whereas the conventional combined-cycle and shift-methanation process extracts only 41.8% of the possible available power in the form of electricity.

The nearly 25% increase in the efficiency of the BEACON process over its competitor results directly from the increase in the power delivered to the combined-cycle generating system and from the decrease in the power required to compress air for combustion. So much is obvious--but there is an underlying and not so obvious reason for why this is so. It comes from a fortuitous utilization of heat in a different part of the system. The First Law of Thermodynamics requires that when chemical energy is released, it must appear in the surroundings either as heat or work. It follows that if some of the heat that otherwise would be exported could be effectively reabsorbed by the system and partially converted to work, then the overall efficiency could be increased.

In the BEACON process, the use of low-level heat from the HRSG to raise steam for the carbon steaming reaction has the effect of reducing the net heat export from the system. In effect, by using the thermal energy remaining in the exhaust gases to raise steam for the steaming reactor feed, we are putting energy back into the system and giving the gas turbine another chance to turn it into useful work. This is a key feature of the BEACON process which allows it to have a higher efficiency than conventional processes. It is also necessary to operate the carbon deposition and steaming reactors at conditions close to equilibrium to minimize the lost work in these steps. Comparing the actual and reversible work figures for the carbon deposition and steaming reactors in Figure 6-3, we see that there is little lost work in these steps; thus, we are able to harvest much of the recycled energy, and the overall increase in efficiency results from this accomplishment.

BEACON STEAM-CARBON MODEL SYSTEM (PRODUCER GAS FEED)

Figure 6-3. BEACON Steam-Carbon Model System (Lost Work Analysis)

CONVENTIONAL MODEL SYSTEM (SYNTHESIS GAS FEED)

Figure 6-4. Conventional Model System (Lost Work Analysis)

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