DEVELOPMENT OF BEACON TECHNOLOGY

Quarterly Report for the Period April—June 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**

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
1. INTRODUCTION	1-1
2. SUMMARY	2-1
2.1 INTRODUCTION	2-1
2.2 CATALYST DEVELOPMENT (SOHIO).	2-1
2.3 BENCH-SCALE TESTING (TRW)	2-3
2.4 ENGINEERING ANALYSIS (TRW AND SOHIO).	2-3
3. CATALYST DEVELOPMENT	3-1
3.1 HYDROCARBON FEEDGAS EXPERIMENTS	3-1
3.1.1 Experimental Objectives and Description	3-1
3.1.2 Discussion of Experimental Results	3-1
3.2 EFFECT OF CARBON LOADING ON CATALYST PHYSICAL PROPERTIES.	3-14
3.2.1 Experimental Objectives and Description.	3-14
3.2.2 Discussion of Experimental Results	3-15
3.3 EFFECT OF PROCESS VARIATIONS ON CATALYST ACTIVITY AND PROPERTIES.	3-26
3.3.1 Experimental Objectives and Description.	3-26
3.3.2 Discussion of Experimental Results	3-28
4. BENCH-SCALE TESTING (4-INCH AND TANDEM REACTORS)	4-1
4.1 SECOND STAGE STEAMING TESTS	4-2
4.2 EFFECT OF CONTAMINANT ON SELECTIVITY OF K-1 SOLIDS.	4-4
4.3 TANDEM REACTOR CONSTRUCTION	4-5
5. ENGINEERING ANALYSIS	5-1
5.1 AN INTEGRATED TEST FACILITY	5-1
5.2 PRELIMINARY DESIGN OF THE ITF	5-2
5.2.1 Design Conditions.	5-2
5.2.2 Mode of Operation of the ITF	5-3
5.2.3 Site Specification	5-6
5.2.4 Description of Major Process Elements.	5-7
5.3 A RESEARCH PROGRAM USING THE ITF.	5-9

LIST OF FIGURES

	<u>Page</u>
3-1 Total Carbon Conversion vs Temperature (Single Reactor)	3-6
3-2 Carbon Monoxide Conversion vs Temperature (Single Reactor)	3-7
3-3 Hydrocarbon Conversion vs Temperature (Single Reactor)	3-8
3-4 Methane Conversion vs Reactor Temperature (Single Reactor)	3-9
3-5 MM Btu Gas Needed Per MM Btu H ₂ Produced, Temperature Effect (Single Reactor)	3-10
3-6 Volume Change of Labeled C77-K2 Catalyst (Labeled With Elements A and B)	3-16
3-7 Volume Change of Labeled C77-K2 Catalyst (Labeled With Element A Only)	3-18
4-1 Transfer of Fluidized BEACON Solids in 3-Inch Cold Flow Tandem Unit (Sloping Transfer Lines).	4-8
4-2 Tandem Reactor System	4-10
4-3 Carbon Deposition Reactor.	4-14
4-4 Steam Gasification Reactor	4-15
4-5 Solids De-entrainment Sections for Gasification and Deposition Reactors (Reactor Expander Sections).	4-16
4-6 Tandem Reactors Installed in Test Stand.	4-18
4-7 Tandem Reactor Control Panel (DEC Computer Not Shown).	4-19
4-8 Gas Analysis Instrumentation for Tandem System	4-20
4-9 Temperature Control System for Tandem Reactors	4-21
5-1 Process Flow Sheet for Preliminary Design of the Integrated Test Facility	5-4

LIST OF TABLES

		<u>Page</u>
3-1	Carbon Deposition From Butane	3-2
3-2	Summary of the Results Using Paraho Mixture	3-3
3-3	Summary of the Averages of the Results Using Paraho Mixture	3-5
3-4	Flow Rate vs Btu Ratio, Temperature Effect (Tandem Reactors)	3-11
3-5	Carbon Deposition Results Using Paraho Off-Gas Mixture as Feed (CO_2 Removed From Feed)	3-13
3-6	Particle Size Distribution (Eleven Cycle Series).	3-17
3-7	Particle Size Distribution (Twelve Cycle Series).	3-19
3-8	Carbon Contents of Various Fractions.	3-21
3-9	Particle Size Distribution Cycled C77-K2 Catalyst (Third Experimental Series)	3-24
3-10	Particle Size Distribution Cycled C77-K2 Catalyst (Fourth Experimental Series).	3-25
3-11	Deposition/Gasification of a C77-K2 Catalyst.	3-27
3-12	Analytical Inspection of a Used C77-K2 Catalyst	3-29
4-1	Methane Enrichment on K1 Based BEACON Solids.	4-3
4-2	Pressure Effect on Methane Suppression.	4-6

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.

Experiments were continued this quarter with the objective of improving the carbon deposition efficiency using a Paraho retort off-gas mixture. Analysis has shown that the use of the Paraho off-gas to make hydrogen would be attractive if the ratio of the heat content of the feedgas to the heat content of the hydrogen produced is less than 3. Experimental conditions to achieve this ratio have been established.

Recent work had shown that the volume of a BEACON supported catalyst bed increased with an increase in carbon loading level. Four series of experiments were performed where sieve analyses were made after one or more BEACON process cycles. These tests showed that the volume expansion is due to an increase in the number and size of the larger catalyst particles. Other recent work showed agglomeration and lump formation in a test series using the C77 supported BEACON catalyst. Process ranges producing this condition were identified.

The bench-scale testing of unsupported catalysts concentrated in two areas: a) the completion of batch testing in the 4-inch reactor, and b) the construction of the Tandem Reactor Unit which will permit the transfer of solids between the carbon deposition and steam gasification reactors during testing. It was found that a second stage of steaming enhanced the methane yield. Approximately 80% of the construction and instrumentation of the Tandem Reactor Unit was completed during the quarter.

A conceptual design was completed for an Integrated Test Facility (ITF) which would permit research on the BEACON process at a scale sufficient for scale-up.

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 April through June 1982.

2. SUMMARY

2.1 INTRODUCTION

The BEACON 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 to develop conceptual commercial designs and study their efficiencies, cost and economics. SOHIO has concentrated on the development of supported catalysts for the BEACON chemistry with TRW directing its attention to unsupported carbonaceous catalysts. During the quarter reported here all of the catalyst development activities were performed at SOHIO on supported catalysts.

The major bench-scale testing has been conducted at TRW using a 4-inch fluidized bed reactor. The construction of a bench-scale Tandem Reactor Unit was started at TRW. This unit permits the transfer of solids between the carbon deposition and steam gasification reactors during testing.

Both SOHIO and TRW personnel worked on defining an integrated test facility which would be the next scale up for the BEACON development.

2.2 CATALYST DEVELOPMENT (SOHIO)

The conversion of a low Btu off-gas mixture from a Paraho shale oil retort to hydrogen could be an attractive utilization of the BEACON process. Analysis has shown that the use of this off-gas to make hydrogen would be economical attractive if the ratio of the heat content of the feedgas to the heat content of the hydrogen produced is less than 3. Twenty-three experiments involving the use of the Paraho off-gas to produce hydrogen were conducted this quarter. This is in addition to the 17 reported for the last quarter. These 40 experiments have established that the best preliminary conditions to achieve the goal of a Btu ratio of 3 or less are as follows:

- Removal of CO₂ from the feed.

- Flow of the feedgas in a 1-inch quartz reactor of approximately 300-340 cc/min.
- Staged reactors with 500°C for the first reactor and 550°C or 600°C for the second reactor.

Four series of experiments were performed to study the effect of carbon loading on the physical properties of C77 catalysts. The experiments involved carbon deposition and steam gasification cycling and the performance of sieve analysis on the catalysts at various times in the cycled sequence.

Some conclusions from these four sets of experiments are:

- The volume expansion of the catalyst is due to an increase in the number and size of the larger catalyst particles.
- The growth of the particles is irreversible under the conditions used.
- The larger particles have higher carbon levels than the overall average of the bed.
- It was found that after removing the large particles hardly any small particles grew to replace them if the catalyst is exposed to the same carbon loading level as before.

A 1-1/2 inch diameter stainless steel laboratory reactor was used to perform tests studying the effect of some process variations on catalyst activity and properties. In all cases the catalysts studied were the C77 type of supported BEACON catalyst. The process variations studied did not prevent the agglomeration of the catalyst. It has been hypothesized that the agglomeration could be due to very poor fluidization of this catalyst in this reactor.

A batch of C77-K2 catalyst was prepared and subjected to carbon deposition until a high carbon loading of 50.6% carbon was achieved. Half of this carbon containing catalyst was gasified with steam and the other half was subjected to sieve analysis. Three of the cuts from the sieve analysis were large enough that steam gasification was feasible. The steam gasification rates for the different fractions are reported along with the results obtained with the unsieved material.

2.3 BENCH-SCALE TESTING (TRW)

The bench-scale effort concentrated in two areas namely the completion of batch testing in the 4-inch reactor and the construction of the Tandem Reactor Unit. Second stage steaming tests were performed in the 4 inch unit. It was demonstrated that the methane yield from the steam gasification of BEACON carbon is enhanced if the gasification product gas is brought into contact with a K-1 based BEACON catalyst (e.g. feed solids to the first stage) in the 500-550°C temperature range prior to cooling and steam recovery. Better than 85% conversion efficiency of fuel to methane was achieved. Near equilibrium yields were obtained from the second stage. Some possible contaminants also were identified.

The effect of Additive F on the selectivity of K-1 based BEACON solids toward the promotion of methane production was examined. The influence of pressure on the effect of Additive F was studied. It was found that at the concentration level tested Additive F had a pronounced effect on methane selectivity at ambient pressures but virtually no effect at 100 psig.

Approximately 80% of the construction and instrumentation of a bench-scale Tandem Reactor Unit was completed during the quarter. This unit will permit the transfer of solids between the carbon deposition and steam gasification reactors during testing. Solids will be transferred in the fluidized state by means of changing pressure drops between the deposition and steaming reactors ("huff-puff" concept). Once the transfer concept is shown to be valid the apparatus will be used to test the long term physical and chemical stability of BEACON catalyst. The Tandem Reactor Unit will be used for the testing of both methane and hydrogen production catalysts.

2.4 ENGINEERING ANALYSIS (TRW AND SOHIO)

Conceptual designs and independent cost estimates were made on a Integrated Test Facility (ITF). This facility was designed to be of sufficient size so that bundles of heat transfer tubes could be placed in the reactors so that their influence on fluidization quality and heat transfer rates could be determined.

3. CATALYST DEVELOPMENT

The catalyst appropriate for the BEACON chemistry are being developed at TRW and SOHIO. TRW is developing an unsupported carbon based catalyst and SOHIO is developing a supported catalyst system. During the quarter reported here all of the catalyst development work was performed at SOHIO on the supported catalyst system.

3.1 HYDROCARBON FEEDGAS EXPERIMENTS

The off-gas from a Paraho shale oil retort is a source of a low Btu gas suitable for processing by the BEACON technology. This off-gas does contain some hydrocarbons as well as carbon monoxide and hydrogen. Conditions for decomposing these by hydrocarbons received attention this quarter. Economic analysis has shown that the use of the Paraho off-gas to make hydrogen would be attractive if the ratio of the heat content of the feedgas to the heat content of the hydrogen produced is less than 3. This was taken as an objective for the work during this quarter.

3.1.1 Experimental Objectives and Descriptions

The same single and two stage reactor systems were used as described in the last quarterly report (Section 3.2.1.1). One set of experiments was intended to continue the investigation of the role of hydrocarbons in the feed and to do this the carbon was deposited from approximately 10% n-butane in nitrogen at 450° and 550°C. Another twenty-three deposition experiments have been performed during this quarter using a simulated Paraho off-gas as feed. These experiments involved a variety of changes in the process conditions.

3.1.2 Discussion of Experimental Results

To gain more insight into the deposition of carbon from the higher hydrocarbon component of Paraho off-gas some deposition experiments were performed with approximately 10% n-butane diluted with nitrogen. Table 3-1 shows the results obtained.

Table 3-1. Carbon Deposition From Butane

Temperature (°C)	% Carbon Loading on Catalyst		Rate of Carbon Deposition gC/hr	n-butane Conversion (%)	Average H ₂ :CH ₄
	Start	End			
450	0	→ 6.1	0.81	Slow	0.00
450	6.1	→ 41	2.06	85	1.73
500	0	→ 19.5	1.92	99	1.52

At 450°C the reaction started slowly, but after some carbon had been deposited a good rate was obtained. At the higher temperature of 500°C no induction period was observed. Interestingly almost complete conversion was obtained at 500°C, but the carbon deposition rate was about the same as obtained at 450°C. The reason is that more methane is produced at the higher temperature instead of being deposited as carbon. If one considers the possibility of all the reactions that may occur there are nine different ways n-butane can decompose. However, just as with propane the tailgas coming from the reactor contained only methane and hydrogen besides the nitrogen diluent. This indicates that only three reaction paths are possible:

Since the average hydrogen to methane ratio is 1.73 at 450°C and 1.52 at 500°C the reaction probably is proceeding by all of the three equations shown. From this experiment and the previous ones having hydrocarbon as feed we have concluded that the only products that can be found are carbon, hydrogen and methane.

In the last quarterly report Table 3-6 contained the summary of the results of 17 experiments using a Paraho mixture feedgas. Table 3-2 of this report contains the results from 23 new experiments run during this

Table 3-2. Summary of the Results Using Paraho Mixture

Run Type	Run Number	Temp (°C)	CO ₂ in Feedgas	Cat Vol, cc	Feedgas cc/Min	Average Deposit Rate gC/g Cat./Hr	Total Carbon	Conversion (%) [*]			Btu Ratio Feedgas/H ₂	Elemental Losses, %				Overall Closure, %
								CO	C ₂ +	CH ₄		N	C	H	O	
I	DEP 31	400	No	20	335.0	0.227	25.3	59.5	53.4	-64.8	6.22	0.14	0.52	-1.82	-9.58	100.3
II	DEP 34	450	No	20	335.0	0.316	35.3	56.9	73.8	-78.4	4.51	-0.19	1.64	-1.70	-9.94	100.5
	DEP 35	450	No	20	337.5	0.302	33.5	67.5	76.2	-103.8	4.76	0.30	-0.14	-1.60	20.14	99.9
	DEP 36	450	No	20	340.0	0.299	34.9	57.7	69.9	-74.7	4.59	0.24	0.10	-8.20	-40.96	101.9
III	DEP 19	500	No	20	333.3	0.434	47.9	55.3	83.9	-76.9	3.36	-0.26	-3.92	-5.19	-6.11	101.6
IV	DEP 32	525	No	20	337.5	0.369	42.1	46.0	90.1	-83.4	3.76	1.16	0.10	-4.89	22.57	99.8
	DEP 37	525	No	20	340.0	0.357	41.5	52.3	100.0	-109.1	3.38	0.28	1.12	-6.36	24.55	100.7
VI	DEP 20	550	No/H ₂ O	20	371.4	0.208	21.6	-38.4	71.8	-25.9	8.25	2.76	-1.32	-0.08	4.48	98.2
	DEP 21	550	No/H ₂ O	20	373.1	0.208	21.5	-71.4	93.4	-41.2	8.25	1.63	4.16	1.27	3.49	98.2
VII	DEP 33	400/525	No	20/20	340.0	0.230	50.6	49.9	95.8	-69.9	3.16	0.11	1.41	1.88	23.96	99.2
XI	DEP 41	450/500	No	20/20	340.0	0.188	46.5	57.0	89.4	-82.4	3.47	1.58	-4.44	-12.09	-31.01	101.7
	DEP 22	500/500	No	20/20	329.0	0.200	42.2	72.1	100.0	-95.9	3.77	7.71	13.53	7.03	8.84	92.0
X	DEP 23	500/500	No	20/20	333.3	0.192	40.0	74.3	99.9	-85.6	3.98	14.58	18.05	15.84	25.12	84.8
	DEP 24	500/500	No	20/20	331.0	0.222	45.6	73.3	98.2	-103.9	3.47	1.27	8.40	1.60	-0.14	98.2
XV	DEP 39	450/600	No	20/20	338.0	0.227	52.6	25.7	99.4	-3.9	2.99	1.25	9.89	-4.30	-31.70	99.6
	DEP 25	500/500	No	20/20	500.0	0.308	43.5	69.3	93.3	-91.0	3.64	2.37	9.52	-2.41	-13.02	98.3
XI	DEP 26	500/500	No	20/20	505.0	0.338	46.1	67.1	94.7	-90.0	3.46	0.67	6.75	0.99	-4.37	98.9
	DEP 27	500/550	No	20/20	327.0	0.272	62.7	54.1	100.0	-43.0	2.52	-0.98	-2.26	-6.56	-2.43	102.2
XII	DEP 23	500/550	No	20/20	335.0	0.271	61.1	53.8	100.0	-38.3	2.59	0.02	0.02	-4.56	10.20	100.7
	DEP 29	500/550	No	20/20	342.0	0.261	56.2	50.1	100.0	-37.7	2.31	1.14	5.53	-1.08	-4.03	99.1
XIII	DEP 38	500/550	No	20/20	505.0	0.372	58.6	52.1	100.0	-34.1	2.74	1.04	2.57	-7.85	-28.12	100.9
XIV	DEP 30	500/600	No	20/20	331.0	0.285	65.0	20.9	100.0	-7.5	2.45	-0.33	-0.31	-3.50	-2.81	101.0
	DEP 40	500/600	No	20/20	338.0	0.245	57.7	34.9	100.0	-17.2	2.79	1.13	4.16	-8.29	-17.51	100.7

* Negative conversion (-) indicates net production of species.

quarter. The averages of the multiple runs for each type of experiment were calculated and presented in Table 3-3. The averages included all 40 runs as reported in the last quarterly and in this quarterly.

The types of runs designated in Tables 3-2 and 3-3 are used to indicate some independent variable that was varied. For example Types I to V are studies of the influence of temperature from 400° to 550°C in a single reactor without carbon dioxide in the feed.

The conversion of all carbon containing species to deposited carbon (called total carbon conversion) was plotted against temperature and is shown in Figure 3-1. There is a fairly good straight-line relationship between conversion and temperature. The higher the temperature the higher the total carbon conversion. Figure 3-2 is the graph of carbon monoxide conversion vs temperature. It shows the opposite trend. The plot of hydrocarbon ($C>1$) conversion vs temperature can be seen in Figure 3-3. The higher temperatures favor higher conversions. The conversion of methane is plotted against temperature in Figure 3-4 and notice that these are negative numbers. Positive numbers represent actual conversion of the components, a zero value would mean no change from the amounts in the feed-gas but a negative number indicates there actually is more in the tailgas than in the feed.

From a Paraho mixture there 14 possible different reactions producing methane and 5 reactions are possible describing the conversion of methane to other products. From previous experience it is known that carbon deposition from methane increases with increasing temperature. However, carbon removal by hydrogen to form methane also increases with increasing temperature. The rate of the latter is slower than the rate of the former. Hydrocarbon conversion ($C>1$) also increases with increasing temperatures thus producing more methane.

Our goal is to reduce the ratio of heat input from the feedgas to the heat produced in the hydrogen product to below 3. The plot of this Btu ratio vs temperature is shown in Figure 3-5. The lowest value obtained was at the highest temperature, 550°C, however experiments had repeatedly

Table 3-3. Summary of the Averages of the Results Using Paraho Mixture

Run Type	Temperature (°C)	CO ₂ In Feedgas	Cat Vol, cc	Feedgas cc/Min	Average Deposit Rate gC/g Active Cat.	Total Carbon	Conversion (%)*			Btu Ratio Feedgas/H ₂	Overall Closure, %
							CO	C ₂ +	CH ₄		
I	400	No	20	335.0	0.227	25.3	59.5	53.4	-64.8	6.22	100.3
II	450	No	20	337.5	0.306	34.6	60.7	73.3	-85.6	4.62	100.8
III	500	No	20	333.3	0.386	42.8	49.8	83.9	-85.8	3.51	100.9
IV	525	No	20	338.8	0.363	41.8	49.2	95.1	-96.3	3.80	100.3
V	550	No	20	333.5	0.504	52.4	28.3	95.2	-40.7	3.07	99.4
VI	550	No/H ₂ O	20	372.3	0.208	21.6	-54.9	82.6	-33.6	8.25	98.2
VII	400/525	No	20/20	340.0	0.230	50.6	49.9	95.8	-69.9	3.16	99.2
VIII	450/500	Yes	20/20	333.3	0.121	11.2	-209.8	89.1	-9.8	3.45	97.3
IX	450/500	No	20/20	336.2	0.224	50.0	54.3	94.7	-69.7	3.23	99.0
X	500/500	No	20/20	331.0	0.222	45.6	73.3	98.2	-103.9	3.47	98.2
XI	500/500	No	20/20	502.3	0.232	44.8	68.2	94.0	-90.5	3.55	99.6
XII	500/500	No	20/20	334.7	0.268	60.0	52.7	100.0	-39.7	2.64	100.7
XIII	500/550	No	20/20	505.0	0.377	58.6	52.1	100.0	-34.1	2.74	100.9
XIV	500/600	No	20/20	334.5	0.265	61.4	65.8	100.0	-12.4	2.62	100.9
XV	450/600	No	20/20	338.0	0.227	52.7	25.7	99.4	-3.9	2.99	99.6

* Negative conversion (-) indicates net production of species.

Figure 3-1. Total Carbon Conversion vs Temperature
(Single Reactor)

Figure 3-2. Carbon Monoxide Conversion vs Temperature
(Single Reactor)

Figure 3-3. Hydrocarbon Conversion vs Temperature
(Single Reactor)

Figure 3-4. Methane Conversion vs Reactor Temperature
(Single Reactor)

Figure 3-5. MM Btu Gas Needed Per MM Btu H_2 Produced
(Single Reactor)

shown that not all of the carbon produced at that temperature could be removed by steaming. Therefore, 500°C was considered to be the best operating temperature.

Experiments were conducted to see whether carbon could be deposited at 550°C at a low Btu ratio and still remove it by adding water to the feed. In Table 3-3 Type VI represents the average of these reactions with water. While most of the carbon deposited could be removed, the 8.25 Btu ratio is the worst yet. Results obtained under the same conditions but without water (shown as Type V) yielded a Btu ratio of 3.07.

In another set of experiments the effect of increasing flow rate of the feed was studied. The results are shown in Table 3-4 as experiments of Type X, XI, XII and XIII. The two temperature accommodations were tried in staged reactors. It was expected that the higher flow rates would minimize secondary reactions and thus improve Btu ratios, but in both cases the higher flows produced higher Btu ratios than the normal flows. The effects of temperature variations of the tandem reactors were studied and the results are shown as run types VII, IX, X, XII, XIV and XV. In the first reactor the temperatures range from 400°C to 500°C. The reason for not going to higher temperatures is to prevent the formation of "dead carbon." In the second reactor the temperatures ranged from 500°C to

Table 3-4. Flow Rate vs Btu Ratio, Temperature Effect (Tandem Reactors)

Run Type	Temperature	Flow Rate Feed (cc/Min)	Btu Ratio
X	500/500	333	3.47
XI	500/500	505	3.55
XII	500/500	335	2.64
XIII	500/550	505	2.74

600°C. In this reactor very little carbon is being deposited from carbon monoxide since the main source of the carbon is methane. Previous experiments has shown that higher temperature favors carbon deposition from methane and it has been found that carbon deposited from methane at these higher temperatures can be removed by steam.

The best results were obtained with Run Types XII and XIV which gave Btu ratios of 2.64 and 2.62 respectively.

Table 3-5 shows the typical tailgas composition of some of the key experiments together with the composition of the feedgas.

The series of experiments performed during the last quarter and this one has established that the best preliminary conditions to achieve the goal of a Btu ratio of three or less are as follows:

- Removal of CO₂ from the feed.
- Flow of the feed gas approximately 300-340 cc/min.
- Staged reactors with 500°C for the first reactor and 550°C or 600°C for the second reactor.

Our second best condition would be the same as above but with a single reactor operating at 500°C.

The use of a faster flow rate of feed or the addition of water to the feed did not improve the Btu ratio. It is concluded that all the hydrocarbons of carbon content greater than 1 in the Paraho mixture give carbon, hydrogen and methane as the only products.

Table 3-5. Carbon Deposition Results Using Paraho Off-Gas Mixture
as Feed (CO₂ Removed From Feed)

Temp. (°C)	Reactor	Variations		Typical Gas Composition (Mole %)*									Btu Ratio (Average)
				H ₂	CH ₄	CO ₂	CO	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	C ₄ H ₁₀	
500	Single	--	F	6.07	3.16	0.0	2.56	1.03	1.31	0.53	0.56	0.42	3.51
			T	10.81	4.64	0.35	1.20	0.58	0.0	0.24	0.0	0.14	
550	Single	--	F	5.92	3.17	0.0	2.56	1.03	1.30	0.69	0.74	0.55	3.07
			T	14.80	3.86	0.14	1.85	0.12	0.0	0.06	0.0	0.04	
550	Single	0.0280 g H ₂ O Added	F	5.24	2.87	0.0	2.31	0.92	1.17	0.56	0.59	0.45	8.25
			T	19.14	3.90	2.43	3.89	0.0	0.0	0.0	0.0	0.0	
3-13 #1-500	Staged	--	F	5.65	3.22	0.0	2.59	1.03	1.30	0.66	0.70	0.53	3.47
			T	9.52	6.78	0.30	0.86	0.0	0.0	0.0	0.0	0.0	
#2-500	Staged	Feed: 514 cc/min	F	5.95	3.18	0.0	2.60	1.02	1.29	0.64	0.68	0.51	3.55
			T	10.57	6.20	0.30	0.84	0.0	0.0	0.05	0.0	0.01	
#1-500	Staged	--	F	5.26	3.24	0.0	2.62	1.04	1.27	0.58	0.51	0.38	2.64
			T	13.48	4.21	0.11	1.10	0	0	0	0	0	

F = Feed

T = Tailgas

*Balance is N₂

3.2 EFFECT OF CARBON LOADING ON SUPPORTED CATALYST PHYSICAL PROPERTIES

3.2.1 Experimental Objectives and Description

Recent work has shown that the volume of catalyst bed increased depending on the carbon loading level of the supported catalysts. It was desired to confirm this finding, expand to higher levels the range of carbon loading studied and investigate the change in size of the individual particles more closely.

All of the experiments discussed in this section were performed in a 1" diameter quartz fluid bed reactor. The catalysts were C77-K2 type modified upon occasion as described below.

In the first series of experiments a standard C77-K2 catalyst was sieved and the -75, +53 micron fraction (-200, +270 mesh) was tagged with Element A and the -106, +75 micron fraction (-140, +200 mesh) fraction was tagged with Element B. The fractions were combined and the catalyst was exposed to carbon deposition and steaming through 11 cycles.

The catalyst for the second experiments was prepared as above except no Element A tagging of a sieve fraction was used. The same fraction was tagged with Element B as before. The catalyst was cycled until the volume leveled off when the carbon loading was approximately 20%. The carbon loading level then was raised to 35%. After the catalyst volume leveled off again the carbon loading was increased to approximately 50%. When the volume of catalyst stopped increasing carbon was removed stepwise to about 1%.

In the third group of experiments a standard C77-K2 catalyst was cycled four times with approximately 20% carbon as the highest carbon loading level. The large particles (>75 microns) were removed and the remaining catalyst was cycled two more times at approximately the same carbon loading level. The carbon loading level then was increased to approximately 35% and cycled two more times at this carbon loading.

For the fourth series of experiments the catalyst and the procedure were similar to the third experiment except that the large particles

(>75 microns) were removed after one carbon deposition to 33% loading level. Before the remaining catalyst was put back into the reactor the -75, +53 micron fraction (-200, +270 mesh) was treated with potassium carbonate. This modified catalyst then was cycled three more times.

During the course of the above experiments samples were collected at various times for Scanning Electron Microscope photographs, carbon content, particle size and elemental analysis.

3.2.2 Discussion of Experimental Results

In the first experiments, using the tagged C77-K2 catalyst, it was expected that the volume increase would level off after about 4 or 5 cycles which is what had occurred in a previous experiment. However the volume continued to increase even after 11 cycles. Since the objective was to examine the catalyst after the volume leveled off the experiment was terminated. The plot of volume vs cycle number is shown in Figure 3-6. For the earlier cycles there is only a small difference in volume between the catalyst after being steamed or after carbon deposition, but later cycles show quite a significant fluctuation. The final sample was submitted for sieve analysis and these results along with the original catalyst before deposition are given in Table 3-6. As expected the weight percent of the larger particles increased while the less than 45 micron fraction decreased relative to the starting catalysts. There is no obvious reason for this weight percent increase of the larger particles other than the possibility that Element B, used to tag the catalyst, might have been the cause.

In view of this conclusion a catalyst without Element B was used in the next series of experiments. In the early cycles there was no difference in volume after deposition of carbon to around 20 weight percent. Even removal of the carbon to 10% by steaming did not change the volume.

For the next few cycles the carbon loading was increased to around 35% and removed by steaming to the 20-25% range. Under these conditions the volume immediately increased but after a few cycles the system adjusted

Figure 3-6. Volume Change of Labeled C77-K2 Catalyst (Labeled With Elements A and B)

Table 3-6. Particle Size Distribution (Eleven Cycle Series)

After Cycle No		0	11
% C Loading		0	12.4
Volume Change (cc)		-	34 → 77
Mesh Micron		Weight %	
		<u>Initial</u>	<u>Final</u>
140	106	6.86	11.57
200	75	11.20	19.88
270	53	28.18	19.89
325	45	12.37	20.06
Pan	<45	41.39	28.6
Total		100.00	100.00

to the new carbon loading and the volume stopped increasing. Next a few cycles were conducted where the carbon deposition was continued up to 50% by weight and steaming removed the carbon down to around 35% by weight. A plot of volume vs cycle number for this second series of experiments is shown in Figure 3-7.

After selected cycles sieve analysis was performed. After Cycle 12 carbon was removed in steps from 38% down to 1.4% and sieve analysis performed after each carbon removal. All of these results are presented in Table 3-7.

The same kind of changes occurred in this experiment as did in the first experimental series. The weight percent of the fines decreases and that of the large particles increases as the volume of the catalyst sample increases. As the carbon loading level was increased the weight percent of the larger particles also increased. When the carbon was removed step-wise the weight percent also decreased except when the catalyst reached the 1.4% carbon loading level the weight percent of the large particles still was very high. Since the particles are almost carbon free it would be expected

Figure 3-7. Volume Change of Labeled C77-K2 Catalyst (Labeled With Element A Only)

Table 3-7. Particle Size Distribution
(Twelve Cycle Series)

3-19	After Cycle No.		0	4½	8½	11½	12				
	% C Loading		0	18.7	35.4	47.4	38.0	27.8	18.8	14.8	1.4
	Volume Change* (cc)		0	+18	+33	+17.5	-1.5	-5	-4	-	-
	Mesh	Micron	Weight %								
	140	106	6.86	7.35	39.63	66.09	39.45	36.21	30.87	23.80	30.07
	200	75	11.20	14.68	24.17	11.90	24.04	20.72	21.47	20.68	19.68
	270	53	28.18	23.84	20.84	6.38	15.20	14.76	14.17	17.24	14.48
	325	45	12.37	26.31	9.39	5.39	7.62	12.76	10.18	14.72	17.69
	Pan	<45	41.39	27.81	15.97	10.24	14.69	15.55	23.30	23.54	18.08
	Total		100.00	99.99	100.00	100.00	100.00	100.00	100.00	99.98	100.00

*Change from previous sample, + increase, - decrease.

that they would have a weight percent similar to the starting catalyst. The results would indicate that the particle size increase is irreversible under the conditions used.

Table 3-8 shows the carbon contents of various fractions of two samples obtained during the second series of experiments. Sample No. 9958-18-25 was taken after the run where 19% carbon was deposited and the volume of the catalyst was about 50 cc. Sample No. 9958-18-56 was taken after carbon deposition to approximately 35 wt percent of carbon and the volume of the catalyst was around 85 cc. In Table 3-8 the delta percent carbon refers to the change in the carbon content of this sample to the previous sample. Sample No. 9958-18-25 is compared with the unused catalyst which contains no carbon. The Sample No. 9958-18-56 then is compared with No. 9958-18-25 as far as the delta percent carbon is concerned. Table 3-8 shows that from the beginning the larger particles are loaded to a higher percent carbon than the smaller particles. Interestingly at the next increase of average carbon loading again the large particles increased their percent carbon level while the small particles hardly changed their carbon content. At some level, perhaps around 35% carbon content, the interior pores of the catalyst support are filled and the carbon now is deposited on the outside of the particles. This experimental series indicates that the large particles are the major contributors to uptake and release of carbon.

In the next experimental series it was desired to see what happens if the large particles are removed during the course of the experiment. Table 3-9 shows the particle size distribution of the catalyst samples obtained during the experiment. After 4 cycles the catalyst particles enlarged to accommodate an approximately 20% carbon loading level. The volume of the catalyst bed increased and so did the weight percent of the large particles. At this point the larger particles (>106 microns) were removed and the catalyst was cycled at the same carbon loading level. There was no change in the catalyst bed volume and there was hardly any change in the weight percent of the large particles. However, when the carbon loading level was further increased the volume and the weight percent of the large particles increased significantly.

Table 3-8. Carbon Contents of Various Fractions

Sample No. 9958-18-25 (18.7% C Loading, Average)

<u>Mesh</u>	<u>Micron</u>	<u>% C</u>	<u>Wt. of Support + C</u>	<u>Wt. of Support</u>	<u>Wt. of C</u>	<u>% C Loading</u>	<u>Δ % C</u>
140	106	24.44	0.2239	0.1692	0.0547	32.3	+24.44
200	75	19.22	0.4472	0.3612	0.0860	23.8	+19.22
270	53	17.24	0.7236	0.6011	0.1252	20.8	+17.24
325	45	17.27	0.8012	0.6628	0.1384	20.9	+17.27
Pan	<45	14.89	0.8472	0.7211	0.1261	17.5	+14.89
Total		17.41	3.0458	2.5154	0.5304	21.1	

Sample No. 9958-18-56 (34.5% C Loading, Average)

140	106	42.90	0.9557	0.5457	0.4100	75.1	+18.46
200	75	32.78	0.7796	0.5240	0.2556	48.8	+13.56
270	53	25.41	0.6723	0.5015	0.1708	34.1	+ 8.17
325	45	17.42	0.3028	0.2501	0.0527	21.1	+ 0.15
Pan	45	18.30	0.5151	0.4308	0.0943	22.4	+ 3.41
Total		30.5	3.2255	2.2421	0.9834	43.9	

Sample No. 9958-18-75 (47.4% C Loading, Average)

140	106	49.74	2.0159	1.0132	1.0027	99.0	+ 6.84
200	75	43.19	0.3629	0.2069	0.1560	75.4	+10.41
270	53	37.05	0.1947	0.1226	0.0721	57.7	+11.64
325	45	32.31	0.1644	0.1113	0.0531	47.7	+14.89
Pan	45	28.91	0.3122	0.2219	0.0903	40.7	+10.61
Total		45.05	3.0501	1.6759	1.3742	82.0	

Table 3-8. Carbon Contents of Various Fractions (Continued)

Sample No. 9958-18-79 (38.0% C Loading, Average)

Mesh	Micron	% C	Wt. of Support + C	Wt. of Support	Wt. of C	% C Loading	$\Delta\%$ C
140	106	41.68	1.1873	0.6924	0.4949	71.5	- 8.06
200	75	30.78	0.7236	0.5009	0.2227	44.5	-12.41
270	53	22.28	0.4575	0.3556	0.1019	28.7	-14.77
325	45	18.51	0.2295	0.1870	0.0425	22.7	-13.80
Pan	<45	15.74	0.4120	0.3472	0.0648	18.7	-13.17
Total		30.8	3.0099	2.0831	0.9268	44.5	

Sample No. 9958-18-83 (27.8% C Loading, Average)

140	106	35.26	1.0844	0.7020	0.3824	54.5	- 6.42
200	75	38.06	0.6204	0.4463	0.1741	34.0	- 2.72
270	53	24.84	0.4420	0.3322	0.1098	33.1	+ 2.56
325	45	20.40	0.3820	0.3041	0.0779	25.6	+ 1.89
Pan	<45	17.17	0.4658	0.3858	0.0800	20.7	+ 1.43
Total		27.52	2.9946	2.1704	0.8242	38.0	

Sample No. 9958-18-87 (18.8% C Loading, Average)

140	106	22.83	0.9188	0.7090	0.2098	29.6	-12.43
200	75	17.48	0.6388	.5271	0.1117	21.2	-10.58
270	53	13.82	0.4218	0.3635	0.0583	16.0	-11.02
325	45	12.25	0.3031	0.2660	0.0371	13.9	- 8.15
Pan	<45	10.40	0.6935	0.6214	0.0721	11.6	- 6.77
Total		16.43	2.9760	2.4870	0.4890	19.7	

Table 3-8. Carbon Contents of Various Fractions (Continued)

Sample No. 9958-18-95A (14.8% C Loading, Average)

<u>Mesh</u>	<u>Micron</u>	<u>% C</u>	<u>Wt. of Support + C</u>	<u>Wt. of Support</u>	<u>Wt. of C</u>	<u>% C Loading</u>	<u>Δ% C</u>
140	106	17.63	0.7722	0.6361	0.1361	21.40	- 5.20
200	75	14.27	0.6709	0.5752	0.0957	16.6	- 3.21
270	53	10.79	0.5593	0.4990	0.0603	12.1	- 3.03
325	45	9.34	0.4775	0.4329	0.0446	10.3	- 2.91
Pan	<45	7.69	0.7638	0.7051	0.0587	8.3	- 2.71
Total		12.2	3.2437	2.8483	0.3954	13.9	

Sample No. 9958-18-99 (1.4% C Loading, Average)

140	106	4.83	0.4905	0.4668	0.0237	5.1	-12.80
200	75	4.54	0.3210	0.3064	0.0146	4.8	- 9.73
270	53	4.56	0.2362	0.2254	0.0108	4.8	- 6.23
325	45	4.29	0.2886	0.2762	0.0124	4.5	- 5.05
Pan	<45	3.55	0.2949	0.2844	0.0105	3.7	- 4.14
Total		4.41	1.6312	1.5592	0.0720	4.6	

Table 3-9. Particle Size Distribution

Cycled C77-K2 Catalyst (Third Experimental Series)

After Cycle No.	0	4	After 140 Mesh Removed*	6	8
Highest % C Seen by Cat.	0	~20	~20	~20	~35
% C Loading	0	11.0	~11.0	9.3	10.4
Volume Change (cc)	-	20 → 33	-	0	23 → 26
Mesh	Micron	Weight %			
140	106	6.86	10.87	0	2.80
200	75	11.20	37.24	41.78	38.48
270	53	18.18	19.84	22.28	16.36
325	45	12.37	17.12	19.21	19.47
Pan	<45	41.39	14.91	16.73	22.92
Total		100.00	99.99	99.99	100.03
				100.03	100.00

* The particle size distribution was calculated.

In the fourth series of experiments it was desired to try to promote the increase of large particles. After one deposition there was an increase in the weight percent of the large particles as shown in Table 3-10. After this deposition the particles >106 microns were removed and the -75, +53 micron fraction (-200, +270 mesh) was treated with potassium carbonate and the catalyst was cycled three more times without raising the carbon loading level. In the previous experiments there have been no significant change in catalyst volume when it was cycled at the same carbon level. However, when the catalyst was treated with alkali, a tremendous increase in volume took place and the large particles were replaced from the smaller fractions.

Table 3-10. Particle Size Distribution

Cycled C77-K2 Catalyst (Fourth Experimental Series)

After Cycle No.	1/2	After 140 Mesh* Removed, K_2CO_3 trt.	3-1/2	Δ
% C Loading	32.7	~32.7	29.3	-
Volume Change (cc)	33 $\rightarrow$ 69	-	49 $\rightarrow$ 73	
Mesh	Micron	Weight Percent		
140	106	10.84	0	9.73 +9.73
200	75	20.63	23.14	29.23 +6.09
270	53	25.25	28.32	21.92 -6.40
325	45	16.86	18.91	15.62 -3.29
Pan	<45	26.42	29.63	23.47 -6.16
Total		100.00	100.00	99.97

* The particle size distribution was calculated on in this case.

Some conclusions from these four sets of experiments are:

- The volume expansion is due to an increase in the number and size of the larger catalyst particles.
- The growth of the particles is irreversible under the conditions used.
- The larger particles have higher carbon levels than the overall average of the bed.
- It was found that after removing the large particles hardly any small particles grew to replace them if the catalyst is exposed to the same carbon loading level as before.

3.3 EFFECT OF PROCESS VARIATIONS ON CATALYST ACTIVITY AND PROPERTIES

3.3.1 Experimental Objectives and Description

Three series of experimental tests are reported in this section. The first series was designed to investigate the influence of some process variations on the formation of lumps of catalysts during deposition and gasification. The second set of experiments was initiated to deliberately build a quantity of C77-K2 material with a high carbon loading and then to divide the sample into various particle size fractions and look for variations in chemistry. Some previous experiments had indicated that agglomeration and the formation of lumps might be due to a high degree of carbon overloading compared to the more fluid portions of the catalyst sample. A third set of experiments was designed to determine if a C77-K1 catalyst exhibited similar tendencies to form lumps compared with C77-K2 catalyst. In this series an experiment, also was performed to determine if the rate of deposition could influence the magnitude of the lump formation.

The 1-1/2 inch diameter stainless steel laboratory reactor was used to perform the tests described and discussed in this section. The apparatus was described in a previous report* and the same configuration was used except that no thermocouple in the center of the reactor was employed. All gasifications were conducted at 600°C using 100% steam and the depositions were run at 450°C.

The first series of experiments employed a single charge (32.53 g) of a C77-K2 catalyst prepared in the SOHIO pilot plant. This material was subjected to three cycles of deposition and gasification. The experimental conditions and results are compiled in Table 3-11.

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

Table 3-11. Deposition/Gasification of a C77-K2 Catalyst

Type of Run	1 D	2 G	3 D	4 G	5 D	6 G
Character of Catalyst						
Before Run	Powder	-80 Mesh Powder	-80 Mesh Powder	-80 Mesh Powder	-	-80 Mesh Powder
After Run	Agglomerated	Some Lumps	Agglomerated	Not Determined	Some Small Lumps	Large Lumps
Wt. of Catalyst Charge(g)	32.53	35.88	29.97	37.95	-	39.01
Feed Rate ml/min, STP	660	216	3800	397	3800	328
Test Duration (Hrs)	3	3.75	2.5	2.7	4.2	4
Deposition/Gasification Rate g-C/g Active Catalyst/Hr	0.59	-0.62	0.73	-1.0	0.39	-0.85
Carbon Content, %						
Before Run	0	21.3	2.7	25.4	-	26.5
After Run	21.3	2.7	25.4	-	26.5	6.4
Vol. of Catalyst, ml						
Before Run	50	84	66	113	-	146
After Run	-	66	113	-	146	112
Feed Gas Composition, %						
CO	46		45		45	
H ₂ O	5	100	4	100	5	100
N ₂	49		51		50	

D = Deposition
G = Gasification

NOTE: In Run 5 the feed gas was cooled and the bed temperature was only 355°C.

For the second set of experiments a similar sample of C77-K2 catalyst was subjected to carbon deposition. The deposition was continued until a high carbon loading of 50.6% carbon was achieved. Half of this 50% carbon material was gasified with steam and the other half was subjected to sieve analysis. Three of the cuts from the sieve analysis were large enough that steam gasification was feasible. These cuts were -140 +200 mesh fraction, 200 +270 mesh fraction and the pan fraction. The temperatures of deposition and gasification were the same as given in the first series of experiments namely 450°C and 600°C respectively.

The third set of experiments was designed to determine if a C77-K1 catalyst gave similar results to a C77-K2 catalyst as far as the formation of lumps was concerned. A further question was addressed in the experiments; namely whether slowing the rate of deposition would reduce the magnitude of the lump formation.

3.3.2 Discussion of Experimental Results

As discussed above the test information for the first set of runs is given in Table 3-11. In deposition of carbon a change of the feed rate over about a six fold range did not eliminate agglomeration. The increase of feed rate did increase the deposition rate by a little over 30%. Since flowrate alone did not stop catalyst agglomeration another approach was taken. In early runs feed to the reactor had been preheated to bath temperature. One thought was that this action could cause excess activity at the entrance of the catalyst bed. Accordingly a water jacket was built around the feed tube and the feed was cooled during the next deposition (Run 5). The result was a very low conversion rate which was probably caused by the low bed temperature.

The product from gasification Run 6 was subjected to a sieve analysis and additional determinations were made on the various fractions. These data are presented in Table 3-12. The bulk density of the fraction show an increase with a decrease in particle size. Conversely the carbon content and surface area decrease with particle size.

Table 3-12. Analytical Inspection of a Used C77-K2 Catalyst

Fraction	A	B	C	D	E	F
Sieve Cut	+100	+140	+200	+270	+325	PAN
Amount of Cut (Wt. %)	0.4	7.6	17.7	38.0	11.5	24.9
Bulk Density (g/cc)	--	.236	.276	.271	.299	.425
Carbon Content, %	--	8.8	7.7	7.9	6.3	4.8
BET Surface Area (m ² /g)	--	53	52	50	50	43

The second set of experiments involved a C77-K2 catalyst with high carbon loading (50.6% carbon). Half of the sample was gasified as produced and the other half subjected to a sieve analysis. In the case of the material gasified as produced a gasification rate of 2.19 grams of carbon removed per gram of active catalyst per hour was obtained. After the same material was subjected to a sieve analysis, three fractions were large enough to run comparable gasification tests. The -140 +200 mesh fraction had a gasification of 5.7 grams of carbon removed per gram of active catalyst per hour, more than twice as fast as the rate from the material as produced. The same results was obtained with the -200 +270 mesh fraction. The gasification rate for the smallest particle size material, the pan fraction, was lower than the other two fractions but higher than that obtained for the total material. The pan fraction gasification rate was 3.5 grams of carbon removed per gram of active catalyst per hour. The carbon content of the original material varied from 67.3% for the +100 mesh fraction down to 43.2% for the fraction remaining in the pan. Similarly the carbon contents were reduced after gasification. The carbon content of the -100 +140 mesh fraction had been reduced to 29.7% after gasification and that of the pan fraction, to 13.6%.

The third series of experiments was designed to determine whether a C77-K1 catalyst would resist a lump formation compared to a C77-K2 catalyst. Generally speaking the answer is that both types of catalysts showed the similar tendencies except for one particular situation. When the rate of deposition was reduced for a C77-K1 catalyst, agglomeration did not occur.

Another possible reason for the presence of agglomeration in the catalysts discussed and reported here in Section 3.3 can be poor fluidization in the 1-1/2 inch stainless steel reactor. Agglomeration was not experienced as much in the one inch quartz reactor used in the experiments report in Sections 3.1 and 3.2 of this report. Occasionally visual examination of the bed was possible with the quartz reactor and changes including taping of the reactor could be employed to improve fluidization.

4. BENCH-SCALE TESTING (4-INCH AND TANDEM REACTORS) [TRW]

The bench-scale effort on unsupported catalysts, at TRW, during the March-June quarter concentrated into two areas: a) the completion of batch testing in the 4-inch reactor, and b) the construction of the Tandem Reactor Unit which will permit the transfer of solids during testing (quasi-continuous, long term testing apparatus). The specific accomplishments include the following:

- Performed second stage steaming tests. It was successfully demonstrated that methane yield from the steam gasification of BEACON carbon is appreciably enhanced if the gasification product gas is brought into contact with K-1 based BEACON solids (e.g. feed solids to the first stage) in the 500-550°C temperature range prior to cooling and steam recovery. Better than 85% conversion efficiency of fuel to methane was achieved. The K-1 based solids promoted near equilibrium operation for the second stage except when contaminated by other metals.
- Examined the effect of Additive F on the selectivity of K-1 based BEACON solids toward the promotion of methane production. The effect was examined as a function of pressure; it was revealed that at the concentration level tested Additive F had a pronounced effect on methane selectivity at near ambient pressures but virtually no effect at 100 psig.
- Completed approximately 80% of construction and instrumentation of a bench scale Tandem Reactor Unit which will permit the transfer of solids between the carbon deposition and steam gasification reactors. Solids will be transferred in the fluidized state by means of changing pressure drops between the deposition and steaming reactors ("huff-puff" concept). Once the transfer concept is proven valid (unit shakedown), the apparatus will be used to test the long term physical and chemical stability of the BEACON catalyst, selected from batch reactor testing, prior to process scale-up. If successful, the "huff-puff" concept represents a very efficient means of performing long term testing involving hundreds of carbon deposition/steaming cycles. The Tandem Reactor Unit will be used for the testing of both methane and hydrogen production promoters.
- An ability to influence K-1 catalyst selectivity toward methane or hydrogen was achieved.

Details of each of these accomplishments are presented in the ensuing paragraphs.

4.1 SECOND STAGE STEAMING TESTS

Steam gasification tests performed to date with K-1 based BEACON solids indicated that equilibrium conversions to methane can be obtained at nearly twice the rate assumed in conceptual BEACON process designs. These high rates were achieved when steaming of the BEACON carbon was conducted at or near 650°C. (Somewhat lower rates were obtained with K-2 based solids.) This observation led to the concept of two-stage steam gasification of BEACON carbon to methane. In the first stage BEACON carbon is gasified at about 650°C to take advantage of high rates (3 tons/hour/ton solids inventory) and high steam utilization (61% at 650°C vs 51% at 500°C). In the second stage the product gas from the first stage is enriched in methane by cooling to 500°C taking advantage of the dictates of thermodynamics which at the lower temperature permit additional conversion of CO and H₂ to methane. In proof-of-principle tests performed last year (January-March 1981 quarterly report) it was shown that second stage steaming for methane enrichment is feasible. Equilibrium conversions of CO and H₂ to methane were obtained at practical rates (approximately 12 seconds residence time) when freshly prepared K-1 based BEACON solids catalyzed the reaction. The test simulated countercurrent two-stage steaming operation.

The successful completion of the 30-cycle testing with K-1 based solids (carbon deposition at 450°C/steaming at 650°C) led to the conclusion that these solids represent the principal candidate for use in BEACON Process scale-up (the 30-cycle test data were presented in the previous quarterly report). Thus, it became desirable to verify the proof-of-principle results obtained last year on methane enrichment with the K-1 solids used in the 30-cycle testing. Tests were performed with a) uncycled but "aged" K-1 based solids (prepared approximately one year ago and stored in ambient air environment) from the same batch that the cycled solids were derived, and b) contaminated cycled solids. The data are summarized in Table 4-1 and they are compared to data obtained with freshly carburized K-1 solids and to the second stage product gas composition predicted by equilibrium for the same feed gas.

Table 4-1. Methane Enrichment on K-1 Based BEACON Solids
(2nd Stage Steaming at 200 Psig and 500°C)*

SPECIE	FEED GAS MOLES	PRODUCT GAS, MOLES		RECYCLED & CONTAMIN. SOLIDS	EQUILIBRIUM PREDICTED COMP., MOLES
		FRESH SOLIDS	AGED SOLIDS		
CH ₄	10.9	14.8	14.3	12.2	14.9
CO	3.1	0.5	0.2	2.1	0.6
H ₂	21.6	8.7	8.5	17.5	8.0
CO ₂	20.8	19.5	19.5	20.5	19.2
H ₂ O	43.4	48.5	48.4	44.9	49.0
N ₂	<u>0.2</u>	<u>0.2</u>	<u>0.2</u>	<u>0.2</u>	<u>0.2</u>
	100.	92.2	91.1	97.4	91.9

• METHANE YIELD (% OF MAX. POSSIBLE): $\frac{14.8}{14.8 + 1/4 (8.7 + 0.5)} = 86.5\%$

* TESTS PERFORMED IN THE 4-INCH BENCH SCALE REACTOR

The "feed gas" column represents typical product gas composition obtained from first stage steam gasification of K-1 based carbon. The next three columns present the product gas composition obtained experimentally when 100 moles of the above feed gas was contacted (in fluidized bed) with (a) freshly carburized K-1 based BEACON solids, (b) K-1 based solids stored in air for approximately one year ("aged" solids), and (c) recycled contaminated K-1 solids. The last column shows the expected moles of product gas if the feed gas in column 2 had reached equilibrium at the indicated temperature and pressure (prediction based on thermochemical data). The experimental data were generated at 200 psig, 500°C and approximately 12 seconds gas residence time in the 4-inch batch reactor.

The data in Table 4-1 reveals the following:

- Methane enrichment in second stage steaming is catalyzed very efficiently by K-1 based BEACON solids. Conversions are virtually identical to those predicted by equilibrium.
- Aging and prolonged exposure to air does not appear to affect the activity of K-1 based solids in the promotion of the CO and H₂ conversion to methane.
- Contamination of K-1 based solids (contaminant/K-1 ratio of approximately 0.25) affects appreciably their ability to promote methane enrichment.

The "methane yield" obtained in these tests, defined as the ratio of the moles of CH₄ in the product gas to the maximum moles of methane possible if all of CO + H₂ was converted to methane by any means or under any conditions, renders two-stage steaming a promising alternative to single stage steaming plus bulk methanation.

4.2 EFFECT OF CONTAMINANT ON SELECTIVITY OF K-1 SOLIDS

During the 30-cycle testing of K-1 BEACON solids inadvertent and appreciable contamination of these solids occurred with elements "leached" from the reactor walls. The contaminants had no discernible effect on the steam gasification rate or even the composition of the product gas at 650°C and 100 psig, but steam gasification at ambient pressure at laboratory scale revealed appreciable suppression of methane in the product gas. The major

contaminant was identified as Additive F, and it was speculated that Additive F must have an effect on the promotion of the methanation reaction and that this effect is influenced by pressure. A series of tests was performed in the 4-inch reactor to investigate the latter using the "contaminated" 30-cycle material as the catalyst. Additional testing will be performed in the future to verify that the effect is due to Additive F and not to some other "contaminant."

The results of these tests are summarized in Table 4-2. The data depicts the product gas composition and percent steam utilization obtained during the steam gasification of several batches of Additive F contaminated K-1 solids. All of these batches were derived from the 30-cycle solids (The contaminant/K-1 ratio was ≈ 0.4). The tests were performed at 650°C except one which inadvertently was performed at 700°C. The data in the second column were generated at laboratory scale (1 to 2 gram samples); the rest of the data were generated in the 4-inch reactor (1-2 kilogram batches). The values in parenthesis represent thermodynamic predictions for methane concentration in product gas and steam utilization assuming steam-graphite equilibrium at the indicated conditions.

The data seems to indicate that there is a pressure effect on the suppression of methane by Additive F contamination of the K-1 catalyst. The trend is apparent in every component of the product gas, although the unusually high delta in methane concentration between 84 to 115 psia is suspect. However, even though individual values may be in error, the trend appears to be real. Additional testing will be performed at a later date to quantify the pressure effect on K-1 catalyst selectivity. The ability to influence K-1 catalyst selectivity toward methane or hydrogen represents a major accomplishment in the development of the BEACON technology.

4.3 TANDEM REACTOR CONSTRUCTION

Approximately half of the bench scale team's effort during the quarter was expended in the procurement, construction, and instrumentation of the Tandem Reactor Unit. The apparatus will be used to generate the missing

Table 4-2. Pressure Effect on Methane Suppression*

(Equilibrium Values in Parenthesis)

SPECIES	LAB SCALE DATA 15 PSIA, 650°C	4-INCH REACTOR DATA			
		23 PSIA 650°C	47 PSIA 700°C	84 PSIA 650 C	115 PSIA 650 C
CH ₄	<1 (5.3)	1.0 (6.6)	2.7 (7.9)	2.1 (15.0)	10.6 (18.4)
CO	24.1 (25.7)	17?	30.6	27.4	16.9
CO ₂	17.0 (18.0)	21	13.6	14.9	25.6
H ₂	55.4 (51.0)	61	53.1	55.5	46.7
STEAM UTILIZ. %	75 (75)	75	82	70	65

*K-1 based BEACON solids contaminated with Additive F (the solids had been previously subjected to 30 carbon deposition/steaming cycles in the 4-inch reactor).

data needed for BEACON Process scale up to the predemonstration unit (Integrated Test Facility). Specifically, the Tandem Reactor Unit will be used to evaluate the long-term performance of candidate BEACON catalysts, previously selected on the basis of batch testing, under quasi-continuous solids transfer between the deposition and steaming reactors. In the future (1983), the unit is expected to be used for the evaluation of hydrogen production promoters derived from BEACON solids technology.

The design of the Tandem Reactor Unit was based on rate data generated during batch reactor testing and on cold flow data generated in the Tandem Cold Flow unit described in the January-March 1982 quarterly report. The cold flow unit tests verified that BEACON solids can be transferred in the fluidized state between reactors in a tandem system by the "huff-puff" technique. Pressure drops between reactors of 1 to 4 psi proved adequate to transfer the required solids in 20 seconds or less. Figure 4-1 presents typical design curves generated in the cold flow proof-of-principle testing. Also, cold flow testing indicated that sloping transfer lines would be preferable to horizontal lines.

The available information led to the following design requirements for the reactor system:

<u>Parameters</u>	<u>Deposition Reactor</u>	<u>Steaming Reactor</u>
Temperature	400-600°C	500-750°C
Pressure	1-7 Atm	1-7 Atm
Gas Velocity	10-45 cm/sec	10-45 cm/sec
Feed Gas Composition:		
• Steam	0	50-100%
• Nitrogen	20-65%	0-50%
• Hydrogen	5-40%	0
• Carbon Monoxide	20-50%	0
• Carbon Dioxide	0-10%	0

It also was required that the minimum reactor diameter for proper fluidization be 3-inches and that the materials of construction of the system would not leach out metals into the BEACON catalyst that exceeded 20 percent of its weight after 300 hours of operation.

Figure 4-1. Transfer of Fluidized BEACON Solids in 3-Inch Cold Flow Tandem Unit (Sloping Transfer Lines)

The above requirements and the requirement that the apparatus will accommodate the quasi-continuous transfer of solids between the deposition and steaming reactors led to the system depicted in Figure 4-2. The Tandem Reactor Apparatus consists of the following sections: gas feed system, steam boiler, carbon deposition reactor, steam gasification reactor, product gas cleanup train, reactor pressure control and product gas metering system, solids transfer system, and data acquisition system. Brief descriptions of each are presented in the following paragraphs.

- Gas Feed System

The gas feed system is constructed of 316 stainless steel tube, fittings and valves (1/4 to 1/2-inch tube size). Provisions have been made to feed as many as five reactive gases to the deposition reactor and steam and/or nitrogen to the gasification reactor. Feed gas flow rates are controlled by pressure regulators and needle valves. The feed gas flow rates are determined by measuring the pressure drops across calibrated orifices. Dry feed gas compositions are also measured using a gas chromatograph.

The gasification reactor feed steam is superheated using two tube furnace heaters which heat feed gas coils. Each superheater is controlled by gas exit temperature. Override control is based on furnace heated zone temperature (override set point should be 1550°F or less).

- Steam Boiler

The steam boiler is a 34kW electric unit which can provide up to 90 lbs per hour of steam at 220 psig. Power to the boiler is controlled by a pressure switch in the boiler package.

- Carbon Deposition Reactor

The deposition reactor consists of a 10-1/2 foot long reaction section which is flanged and bolted to a five foot long disengagement section having a one foot long transition cone. The reaction and disengagement sections are 6" and 12" SCH 40 pipe, respectively. The reactor bottom is fitted with a cone gas distributor. A "shoulder" has been machined into the inside surface of the cone to provide a seat for a plate type gas distributor if needed. The reactor was constructed with type 316 stainless steel; its inside surfaces have been aluminized by Alon Processing, Inc., Tarentum, PA. The reactor is designed to meet the maximum operating condition of 100 psig at 1200°F. The reactor is equipped with an internal cyclone at the top of the de-entrainment section with a dip-leg for recycling solids to the reaction zone.

Figure 4-2. Tandem Reactor System

There are twelve heating zones in the reaction section of the deposition reactor, two on the cone and ten on the 10-1/2 foot 6-inch diameter section. Each zone is heated with two 500 watt heaters which are controlled using West proportional band temperature controllers with high limit alarm output capability. There are two heaters per controller. Temperature sensors (Type K thermocouples) located in the middle of each zone measure the reactor internal temperature at a point within 1/2-inch from the reactor wall. Three external thermocouples measure the external reactor wall temperature. The de-entrainment section is not heated (heaters will be added to this section if it proves necessary to avoid moisture condensation). Beaded heaters are used to heat the 1/2-inch line between the reactor and filter, as well as the filter housing itself. Variacs are used to control the outputs from these heaters. Temperatures of the line and filter housing are measured with Type K thermocouples.

The reactor is insulated with two layers of one inch thick ceramic fiber blanket insulation which is lagged and painted for weather protection.

- Steam Gasification Reactor

The gasification reactor consists of a 10-1/2 foot long reaction section which is flanged and bolted to a five foot long disengagement section having a one foot long transition section. The reaction and disengagement sections are 3-inch and 6-inch SCH 40 pipe, respectively. The inlet to the reactor consists of a one inch tube through which feed gases enter via a cone-shaped gas distributor. A "shoulder" has been machined into the inside surface of the cone to provide a seat for a gas distribution plate, if necessary. All material is Type 316 stainless steel, the inside surfaces of which have been aluminized. The design conditions are 90 psig at 1400°F for the flange and 100 psig at 1400°F for the reactor.

Two three-zone 8.5 KW tube furnaces are used to heat the cone and lower 2/3 of the 3-inch diameter reaction section, while 7 pairs of 500 watt heaters are used to heat the upper 1/3. The tube furnaces are controlled using a 6 zone temperature controller having proportional and override shut-off control. The temperatures in each of the 6 zones are measured using internal thermocouples. Another internal thermocouple is located between the two tube furnaces and is not used for control. The furnace override temperatures are sensed by thermocouples which are inserted in the bodics of each furnace so that their tips are extended into each of the heated zones. External reactor temperatures in the middle of each furnace are also recorded. The 500 watt heaters are controlled using seven West proportional band controllers.

Beaded heaters are used to heat both the line between the reactor and filter and the filter housing itself. Variacs are used to control the outputs from these heaters. External wall temperatures of the line and filter housing are monitored using Type K thermocouples. The de-entrainment section will also be heated by beaded heaters.

The bottom two-thirds of the reaction section are insulated by two tube furnaces which provide reactor heat (the heating system is described in the operating procedures). The remainder of the reactor will be insulated with three layers of 1-inch thick ceramic fiber blanket insulation which is lagged and painted for weather protection.

The reactor is equipped with an internal cyclone at the top of the de-entrainment section with a dip-leg for recycling solids to the reaction zone.

- Product Gas Cleanup Train

Each reactor is equipped with a filter and condenser for removal of solids and for condensation of water vapor. The filter elements consist of sintered stainless steel covered by stainless steel wire mesh. The filtration area is two square feet (per reactor). Filter efficiency is 100% of 2 micron and larger particles and 98% for 0.5 micron to 2 micron particles. The filter temperatures will be maintained above 400°F so as to decompose any carbonyl compounds.

The condensers consist of stainless steel tubing (1/2-inch for gasification reactor, 3/4-inch for deposition reactor) with a water jacket for once-through cooling water flow. Condensed water is separated from the dry product gas in "knock-out" vessels.

- Reactor Pressure Control and Product Gas Metering System

Reactor pressure is controlled using pneumatically actuated needle valves with manually actuated metering valves ("by-pass valves") for increasing rangeability. The pneumatically actuated valves can be manually or automatically controlled. The automatic valve controller for the deposition unit is a pneumatic unit which is designed to accept a single pressure set point. The gasification reactor is equipped with an electronic process controller which accepts various setpoints that are selected by the solids transfer control system. The pressure drop between the two reactors is the controlled parameter.

Product gas metering is performed using calibrated orifices. Dry gas molecular weight is determined through gas chromatography. Dry gas meters are utilized to confirm product gas flowrates.

- Solids Transfer System

The solids transfer system is designed to automatically transfer solids between the deposition and gasification reactors in a cyclic manner. The system is controlled by programming a comparator relay and a series of timers which trigger alternate pressurization and depressurization of the gasification reactor as well as the opening and closing of the transfer valves. Once programmed, the system can operate independent of operator action. Alternatively, the transfer of solids can be performed manually if so desired for testing, or to perform corrective solids transfer operations in the case of upset conditions.

- Data Acquisition System

The data acquisition system consists of pressure, temperature, flow rate and gas composition measurement instrumentation. Pressure gauges, digital voltmeters and chart recorders will serve as visual display instrumentation. A DEC PDP-11 computer and a DORIC data logger will be used to record all process data. Computer printout of selected process information will be available in "real time" during test runs. An offline program will provide averaged data summaries and a full "dump" of all data channels after the run is concluded.

Dry product gas composition will be determined every 8.5 minutes using gas chromatographs dedicated to each reactor. A reporting integrator serving each g.c. will determine gas composition from peak areas. The composition data will be printed on the integrator strip chart and will be fed to the computer for use in process calculations. Non dispersive infrared analyzers will be used for continuous monitoring carbon monoxide, carbon dioxide and methane concentrations in the product gas.

The data will be used for "real time" evaluation of system performance thru mass balance computations.

The next seven figures present photographs of parts or sections of the Tandem Reactor Apparatus. Figures 4-3 and 4-4 show the deposition and gasification reactors, respectively; the reactors are shown equipped with pressure and temperature probe parts; the deposition reactor is depicted with its heaters installed. Figure 4-5 shows the expander sections (solids de-entrainment sections) for the two reactors (the larger expander

Figure 4-3. Carbon Deposition Reactor

Figure 4-4. Steam Gasification Reactor

Figure 4-5. Solids De-entrainment Sections for Gasification and Deposition Reactors (Reactor Expander Sections)

is for the deposition reactor). Figure 4-6 shows the two reactors installed in the four-story BEACON test stand as they were at end of the current quarter. Figure 4-7 shows the Tandem Reactor Control Panel (except for the DEC data acquisition computer). Figures 4-8 and 4-9 show the gas analysis instrumentation and temperature control system dedicated to the Tandem Reactor Apparatus.

Shakedown of the apparatus will commence during August 1982 and operation by late September or early October 1982 depending on the extent of modifications dictated by shakedown.

Figure 4-6. Tandem Reactors Installed in Test Stand

Figure 4-7. Tandem Reactor Apparatus Control Panel (DEC Computer not Shown)

Figure 4-8. Gas Analysis Instrumentation for Tardem System

Figure 4-9. Temperature Control System for Tandem Reactors

5. ENGINEERING ANALYSIS

5.1 AN INTEGRATED TEST FACILITY

An Integrated Test Facility (ITF) is needed to prove the operability of the BEACON Process. It is necessary to determine how immersed heat transfer surfaces within the fluidized bed affect fluidization behavior, channeling, the heat transfer coefficient and the physical stability of catalyst and carbon. The ITF reactors should be large enough to obtain process data for commercial scale-up and designed to evaluate either supported or unsupported catalysts.

Recall that carbon accumulates as particles pass through the carbon deposition reactor and that carbon is depleted in the steaming reactor. Because of backmixing within the steaming reactor, a fraction of particles will stay in the reactor long enough for their associated carbon to be steamed down to zero. How this will affect the fluidization behavior of the solids is not known. Very small particles formed in the steaming reactor may remain intimately mixed with the other solids, or they may segregate, or they may be rapidly entrained. Because the fluidization characteristics of BEACON materials are unique, the existing literature on entrainment and solids circulation is not very useful.

There also may be problems with the carbon deposition reactor. Some particles will remain in the reactor for a very long time and may grow so large that they could fall out of fluidization. It is possible that a gradual densification of the carbon will occur, thereby changing its fluidization and transfer characteristics. It is not anticipated that all of these problems actually will happen, and it is believed that if problems do occur, modifications to get around them are available. Partial answers will come from running the tandem reactor but the tests of important process characteristics such as heat transfer rates, solids transfer characteristics and entrainment rates will require a larger reactor than the tandem reactor. The Integrated Test Facility has been designed to provide these answers.

5.2 PRELIMINARY DESIGN OF THE ITF

A preliminary process design has been developed for a BEACON Integrated Test Facility (ITF). The ITF will contain a carbon deposition reactor and a carbon steaming reactor, with continuous catalyst circulation between reactors. The carbon steaming reactor will incorporate a small bank of immersed heat transfer tubes. The carbon deposition reactor will be compatibly sized to allow continuous circulation of carbon between reactors with no net accumulation or depletion. Both reactors will be designed to operate at pressure, and at commercially realistic superficial gas velocities. E&L Associates of Long Beach, California, an engineering and construction firm, was retained to derive a $\pm 25\%$ budget cost estimate for the ITF based on the preliminary design information.

The technical details of the preliminary design are reviewed in the following discussion.

5.2.1 Design Conditions

- Plant Feed Gas

The ITF will be operated using low-Btu feed gases with a range of CO to H₂ ratios. The heat and material balance for the preliminary design is based on a Flexi-coker offgas composition (CO/H₂ = 1.2, LHV ~ 110 Btu/Scf).

- Reactor Type

The carbon deposition and steaming reactions will be carried out in a continuous operation in fluidized bed reactors. BEACON solids will circulate continuously between the reactors.

- Reactor Size

The gasification reactor, the smaller of the two fluidized bed reactors, has been sized to have a cross sectional area of approximately 1.0 ft². This is considered a minimum size for studying the effect of an immersed tube bundle on fluidization heat transfer and catalyst stability.

- Reactor Pressure

The nominal operating pressure for the ITF is 100 psig. This pressure level was chosen to simulate operation of the process at a pressure level reasonably close to that anticipated in commercial operation (perhaps 200-300 psig for combined cycle power production) and to keep feed gas supply costs at a reasonable level. Higher operating pressures will also be tested, but not at full operating conditions in long sustained runs. The reactors will be designed mechanically for 300 psig at process temperatures.

- Reactor Temperature

The carbon deposition reactor will be operated in the 450-550° range.

The gasification reactor will be operated in the 550-650°C range.

- Reactor Throughput

The superficial fluidized bed gas velocities in both reactors will be ~1 ft/sec. At this velocity, it is anticipated that entrainment of catalyst from the beds will be held to reasonable levels. Also, at this velocity, reactor throughputs will be economically viable on a commercial scale.

5.2.2 Mode of Operation of the ITF

Figure 5-1 is the preliminary process flow diagram for the proposed ITF that was used to obtain the cost estimate. This drawing should be referred to in the following discussion.

- Feed Gas Synthesis

A package skid-mounted gas generator will be provided by the Thermal Systems Division of Midland-Ross Corporation to generate medium Btu gas. This unit catalytically reforms propane with steam and CO₂ at low pressure (~10 psig) and elevated temperatures (~2,000°F). The unit is quite flexible in that by proper adjustment of the relative proportions of feed gas, medium Btu gas with a wide range of CO to H₂ ratios can be produced.

The medium Btu gas is compressed to process pressure. Nitrogen and methane as well as additional CO₂ are then added to the medium Btu gas in a mixing tee to produce the desired low Btu gas composition for the BEACON Process.

Figure 5-1. Process Flow Sheet for Preliminary Design of the Integrated Test Facility

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The CO₂, N₂, propane and methane required for feed gas synthesis and fuel will be stored as liquids onsite. The tankage and delivery systems required will be provided under a rental agreement with the gas suppliers.

- Carbon Deposition

The low Btu gas fed to the BEACON carbon deposition reactor reacts in a fluidized bed of catalyst at ~100 psig, 450-550°C to deposit carbon on the catalyst. The carbon deposition reaction is highly exothermic. The desired bed temperature is maintained by removing heat from the fluid bed by a high temperature organic heat transfer fluid circulating through tubes immersed in the bed. The heat transfer fluid is cooled externally by generating steam.

Carbon rich catalyst (up to 90 wt percent carbon) is continuously transferred from the deposition reactor and conveyed to the gasification reactor in a transfer line.

Entrained catalyst is returned to the carbon deposition reactor by a cyclone located in the reactor freeboard. The gas leaving the reactor is processed through an external two-stage cyclone and a hot gas filter for final particulate removal. The catalyst removed is collected in lock hoppers, and the solids-free gas is flared.

- Steaming to Produce SNG or H₂

Superheated steam is fed to the steaming reactor to gasify the carbon laid down on the circulating catalyst in the carbon deposition reactor. The gasification reactions take place in a fluidized bed of catalyst at ~100 psig, 550-650°C, to produce a raw SNG (CH₄, CO, CO₂, H₂, H₂O) stream; or a raw H₂ (H₂, CO, CO₂, H₂O, trace of CH₄) stream if a methane suppressing catalyst is used.

The steaming reactions are highly endothermic. The desired bed temperature is maintained by flowing a hot flue gas through tubes immersed in the fluid bed. In the ITF, the hot flue gas is generated in a propane combustor. As a precaution to minimize thermal stress on materials, the inlet temperature of the flue gas to the tubes is controlled at 1600°F maximum by quenching the combustor flue gas with air as required.

Carbon-lean catalyst is transferred continuously from the steamer reactor back to the carbon deposition reactor.

Entrained catalyst is returned to the steaming reactor by a cyclone located in the reactor freeboard. After leaving the reactor, the gas is processed through a two-stage cyclone and

a hot gas filter for final particulate removal. The catalyst removed is collected in lock hoppers. The solids-free gas is cooled to condense unreacted water, thereby upgrading the heating value of the gas. The gas is then combined with the carbon deposition reactor off-gas and flared.

- Product Gas Treating

Particulate-free off-gas from the steaming reactor is cooled and then flared. In a commercial unit, this gas would be purified via conventional gas processing steps such as CO₂ removal, shift conversion and fixed-bed methanation to either pipeline SNG or hydrogen. Since no new technology would be demonstrated by including these steps, they have been omitted in the interest of holding down the capital cost and operating complexity of the ITF.

- Catalyst Circulation

Catalyst will be circulated between the BEACON reactors in dense phase/dilute phase flow in transfer lines. The solids circulation rate will be controlled by varying the aeration gas to the transfer lines.

- Process Heat Integration

No attempt has been made to heat-integrate the ITF as would be done in a commercial scale unit. Process steam is generated and superheated in propane-fired heaters. Hot flue gas for heat input to the steaming reactor is produced in a propane-fired combustor. In a commercial scale unit, heat input for these services would be provided by combustion of the partially depleted low Btu off-gas from the carbon deposition reactor.

Heat integration of the ITF would add to the capital cost and complexity of the unit and reduce the flexibility of operation.

- Data Collection

The ITF will be instrumented to provide sufficient data (temperature, pressure, and gas analysis) to enable a complete heat and material balance to be performed. Additional pressure measurements will be obtained to provide a measure of the hydrodynamic performance of the reactors and transfer lines.

5.2.3 Site Specification

For the purpose of obtaining a preliminary cost estimate, TRW's Capistrano Test Site (CTS) in San Juan Capistrano was assumed to be the selected site for the BEACON ITF.

Utilities available at the site selected include plant and instrument air, electric power supply, plant fire water-system, CW circulation system and evaporation pond. In addition, there is a mechanical shop and instrumentation shop on location which is available for 24 hour-a-day operation.

No gas pipeline exists into CTS. Liquid propane would therefore be used for fueling the ITF. Propane will be trucked in as needed along with other liquified gas such as N_2 , CO_2 and CH_4 by suppliers located in the Los Angeles area (approximately one hour from the plant site).

5.2.4 Description of Major Process Elements

- Synthesis Gas Generator

The skid-mounted packaged gas generating system provided by the Midland-Ross Corporation, Thermal Systems Division will provide ~9,500 SCFH of medium Btu (~300 Btu/scf) gas. Similar size units have been placed in service at other locations. This unit should be a reliable source of constant composition feed gas for the BEACON ITF.

- Carbon Deposition Reactor

The Carbon Deposition Reactor will be constructed in three vertical sections. The bottom section of the reactor will have a 19-inch inner diameter and be 8 feet in length, and it will contain a fluidized bed of carbon-rich catalyst. This section of the reactor will have internals consisting of a feed gas distributor and also several bundles of vertical, ~7-feet long, 5/8 inch diameter, heat-exchange tubes, headered at top and bottom. A high temperature heat transfer fluid will circulate through these tubes to remove reaction heat from the fluidized bed.

A conical transition section is utilized to gradually increase the cross section from the 19-inch diameter bottom section to the 38-inch diameter of the upper section. The transition section has an included angle of 15° to prevent solids from hanging up on its walls and is approximately six feet in overall length. If the fluidized bed level is maintained completely in the lower section, the transition section will function as free-board. On the other hand, reactor residence time can be increased if desired by allowing the fluid bed to partially expand into the transition section.

The upper section of the reactor, 38 inches in diameter, is six feet in length. Gas velocity in this section will have been reduced to ~ 0.25 ft/sec greatly facilitating gravity settling of catalyst particles entrained from the fluidized bed. This section also will contain an internal cyclone for removal and return of particles to the fluid bed via a buried dipleg.

The overall height of the carbon deposition reactor is 20 feet.

The metallurgy of the reactor will be established during the final design phase for the ITF (although tentative selections were made for the preliminary cost estimate). Both hot wall and cold wall (refractory lining) options will be considered. In either case any steel surface in contact with the process environment probably will have to be coated to prevent the surface from acting as catalytic sites for the carbon deposition reaction. Flanged connections will be utilized for the top and bottom reactor heads as well as at the junction of the bottom and transition sections. This will allow access to the reactor internals.

- Gasification (Steaming) Reactor

The Steaming (carbon gasification) reactor will be constructed in three vertical sections. The bottom section of the reactor will have a 14-inch inner diameter and be eight feet in length, and it will contain a fluidized bed of carbon-lean catalyst. This section of the reactor will have internals consisting of a feed gas distributor and also several bundles of vertical (~ 7 feet long, $3/4$ inch diameter) heat transfer tubes headered at top and bottom. Hot flue gas flowing through these tubes will transfer heat to the fluid bed as required.

A conical transition section is utilized to gradually increase the reactor cross section from the 14-inch diameter bottom section to the 28-inch diameter upper section. The transition section has an included angle of 15° to prevent solids from hanging up on its walls, and it is 4 feet 5 inches in overall length. If the fluidized bed level is maintained in the lower section, the transition section will function as free-board. On the other hand, reactor residence time can be increased if desired by allowing the fluid bed to partially expand into the transition section.

The upper section of the reactor is 28-inches in diameter and 6 feet in length. Gas velocity in this section will have been reduced to ~ 0.25 ft/sec facilitating gravity settling of catalyst particles entrained from the fluidized

bed. This section also will contain an internal cyclone for removal and return of particles to the fluid bed via a buried dipleg.

The overall height of the steaming reactor is 17 feet 5 inches.

The metallurgy of the reactor will be established during the final design phase for the ITF (although tentative selections were made for the preliminary cost estimate). Both hot wall and cold wall (refractory lining) options will be considered.

Flanged connections will be utilized for the top and bottom reactor heads as well as the junction of the bottom and transition sections to allow access to the reactor internals.

- Catalyst Inventory Monitoring

The preliminary design includes facilities for monitoring the condition of catalyst within the system. Lock hoppers will be utilized to collect catalyst fines which are removed from the effluent gases by cyclones and filters. These solids will be analyzed to determine the attrition occurring in the system. Small amounts of catalyst will be withdrawn periodically from the fluid beds via a lock hopper system. This will serve to prevent any undesirable materials from accumulating in the beds to levels that effect catalyst performance. A catalyst makeup system has been provided in the design to allow periodic addition of catalyst to the reactors to replace losses due to attrition, entrainment, and sampling.

5.3 A RESEARCH PROGRAM USING THE ITF

The objective of this research is to bring the BEACON processes for making methane or hydrogen through the proof-of-concept stage. The key concepts have been developed and investigated at a laboratory or bench scale. The chemistry and fluid dynamics are both novel. Thus there is a need to test the key concepts in a facility which operates under realistic process conditions. The Integrated Test Facility (ITF) is designed to do just that.

There are four phases in the ITF research plan. The first is the selection of an Engineering and Construction (E&C) firm; the second is the Detailed Design Phase; the third is the Procurement and Construction Phase; and fourth is the Operating Phase. Time estimates for the Detailed

Phase (6 months) and for the Procurement and Construction Phase (12 months) are estimates based on the preliminary design study which was done by E&L Associates of Long Beach, California.

A brief synopsis of the major tasks involved in each of the phases is presented in the subsections which follow.

- Phase I - E&C Selection

The selection process will start with the compilation of a list of candidates which will be screened on the basis of capability, performance, accessibility and relevant experience. The candidates judged most promising will be requested to submit bids for the design and construction of the ITF. The process flow sheet and specifications described in Section 5.2 will serve as the basis for the bids.

- Phase II - Detailed Design

Five activities would be part of this detailed design phase. For the detailed design itself, TRW and SOHIO would furnish the selected E&C firm with basic process design and equipment specifications; instrument, control systems and data gathering specifications and site preparation specification. From vendor quotations a detailed cost estimate will be prepared.

Second, cold-flow testing will be performed during the six month detailed design phase. Existing cold-flow facilities are available. Testing will cover two areas:

- Fluidized behavior in the vicinity of immersed heat transfer surfaces.
- Transfer of solids between the two reactors.

Testing will be performed to verify that acceptable fluidization quality is obtained including uniformity of fluidization, absence of gas bypassing or the presence of stagnant regions of solids. These studies will be used in the design of the heat transfer surfaces and the solids circulation system of the ITF.

Third, the materials of construction of the reactors and other components of the system will be tested to see how well the materials themselves stand up and also to see if there may be any adverse reaction with catalyst material.

Fourth, no site modifications will be made during the design phase, but close coordination between the selected site

(TRW's Capistrano Test Site) and the design team will be required in order to incorporate utility connections, siting of storage tanks, cooling water connections and instrument lines into the design. Soil sample analysis for construction permits will be performed.

Fifth, engineering models for the performance of the ITF will be developed for use both in interpreting the data and predicting performance of a commercial scale unit.

- Phase III - Procurement and Construction

This approximate one year long phase would involve design modifications that may be required, procurement of equipment, site preparation and the construction of the ITF.

- Phase IV - Operation

Task IV-A - Chemical Analysis. During the operating phase, catalysts will be sampled frequently and tested for chemical and physical stability. Modifications of the catalyst systems may be necessary, and the chemical analysis testing in this task will serve as the basis for changes.

Task IV-B - Shakedown and Testing. The first activity in this task will be a careful review of operating manuals, emergency procedures, shutdown procedures and other pertinent safety considerations. The instrumentation and data gathering system will be checked out for proper operation followed by testing of individual subsystems such as the solids transfer system, reactor temperature control system, pressure regulation system, etc. Emergency procedures will be worked through in detail. Flow and mixing patterns in the reactors will be obtained from tracer testing. When it is determined that all of the parts of the ITF are working properly, then the actual operating phase will begin.

Task IV-C - Operation of the ITF. Separate sets of runs will be made to test the BEACON system performance both with methane-producing catalysts and with hydrogen-producing catalysts. The operating mode will be with continuous solids circulation between the carbon deposition reactor and the carbon steaming reactor. The effects of varying the system pressure and of changing the temperatures in either or both of the reactors as well as varying the cycling rate of solids between reactors will be evaluated. Long-term changes in the catalyst will be studied. Measurements of systems performance such as entrainment losses, heat transfer, fouling, and operational instabilities will be noted. Attempts will be made to correct any poor performance by modifying operating conditions or catalyst physical properties as necessary.

Task IV-D - Experimental Data Collection. Experimental data will be collected and evaluated in terms of process models, and will be used in engineering analysis studies to obtain a realistic evaluation of the process potential. The data will include operating efficiencies, entrainment losses, catalyst lifetimes, energy requirements, and power generation.

Task IV-E - Data Reduction. The experimental results obtained from operation of the ITF will be compared with predictions of the models developed in Phase II. A disagreement between actual performance and predicted performance will indicate the need for further studies to bring the model into agreement with actual data.

Task IV-F - Engineering Analysis. Engineering analysis will determine optimal tradeoffs of efficiency versus cost and determine the best operating conditions and system configurations both for steady state operation and for load following applications.

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DEVELOPMENT OF BEACON TECHNOLOGY

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