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DEVELOPMENT OF BEACON TECHNOLOGY

Final Report. Volume I for April 1980—April 1983

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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
Morgantown Energy Technology Center
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ABSTRACT

The BEACON process is based on the catalytic deposition of a highly reactive carbon from low heating value gases, primarily by the carbon monoxide disproportionation reaction. This carbon is subsequently reacted with steam to produce predominantly methane or hydrogen, depending on the catalyst formulation and operating conditions. Commercial application envisions an air-blown coal gasification combined-cycle power plant with a coproduct of either methane or hydrogen. Significant cost reductions are anticipated relative to corresponding oxygen-blown coal gasification systems. Excellent fluid bed catalysts have been developed which have retained initial activity for over 400 hours of steady state operation. This stability was demonstrated in a tandem reactor system which provides for semi-continuous catalyst circulation between the carbon deposition and steam gasification fluid bed reactors.

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1. INTRODUCTION

This document summarizes the development of the BEACON technology, associated systems concepts and experimental data and results obtained from April 1980 through May 1983. During this period the program has been supported by a cooperative agreement (DE-FC-21-80MC14400) among the U. S. Department of Energy, TRW, Inc., and the Standard Oil Company of Ohio (SOHIO). The Department of Energy assigned the technical monitoring responsibility to the Morgantown Energy Technology Center.

A summary of the information, experimental data and results presented in this final report of work completed through May 1983 can be found in Section 2.

In Section 3, a brief history is presented of the BEACON program from its inception at TRW in 1975. This is followed by a section on the technical background of the BEACON program. A description of the system concepts and unique BEACON chemistry is presented which shows why the BEACON systems producing combined cycle electric power and chemical products (methane or hydrogen) have a major thermodynamic advantage over competitive systems producing the same products. The state of development of the program is traced from small, laboratory scale, fixed bed reactor experiments to larger bench-scale, batch, fluid bed reactor studies and eventually to semi-continuous, two reactor, fluid bed, bench-scale systems.

In Section 4, the catalyst developments achieved in the program are described. Conventional supported catalysts and unsupported carbonaceous catalysts have been developed for the preparation of SNG or hydrogen from low heating value fuel gases.

The BEACON program has employed four bench-scale test units to reach its present state of development. The design of each of these units and descriptions of their feed, product and analytical sections as well as the

experimental results obtained are presented in Section 5.

The program has had a continuous engineering analysis task as a means of helping to define the most attractive opportunities for confirmation by the experimental program. In Section 6 a summary of these activities is presented along with several preferred designs for different BEACON process options.

2. SUMMARY

BEACON is an acronym for Btu Extraction And Concentration. The process is based on the catalytic deposition of a highly reactive carbon (C*) from low heating value gases (LBG = low Btu gas), primarily by the carbon monoxide disproportionation reaction:

This deposited carbon is highly reactive with steam. Depending on catalyst formulation and operating conditions, the synthesis gas produced in the steaming reaction can be rich in either methane or hydrogen:

In a system application, the carbon deposition and steaming reactions occur in two separate fluid bed reactors. Carbon-rich catalyst is continuously removed from the deposition reactor and circulated to the steaming reactor. Carbon-lean catalyst is returned from the steaming to the deposition reactor, completing the flow loop. In this manner, energy is extracted from low heating value gases, concentrated in the form of carbon, and subsequently reacted with steam to form predominantly methane or hydrogen, as desired.

The carbon deposition reaction is highly exothermic, but essentially all of this heat of reaction is retained in the depleted LBG exiting the carbon deposition reactor. This hot gas can be utilized for combined cycle power generation, resulting in a highly energy efficient and cost effective air-gasification combined-cycle power plant which co-produces either substitute natural gas (SNG) or hydrogen. The BEACON process is unique in its ability to produce SNG or H₂ from LBG in a practical and energy efficient system.

2.1 CATALYST DEVELOPMENT AND TESTING

The bulk of the effort in this development program has been in formulating, testing and evaluating catalysts suitable for the desired reactions and for operation in a fluid bed reactor system. Two general types of catalysts have been developed. The first is a conventional supported catalyst and the second is an unsupported carbonaceous material with active metal(s) intimately dispersed in the carbon. The latter has particularly favorable fluidization properties.

Catalysts were screened initially in laboratory microreactors at atmospheric pressure. Global rates of reactions were determined and preferred operating conditions established. Two unsupported carbon catalysts showed excellent retention of catalyst activity through 40 cycles of carbon deposition and steaming. The carbon deposition temperature was 400-450°C and steaming was performed at 600°C. The preferred catalyst, designated K-1, had a higher rate of carbon deposition and was selected for further testing.

Extensive parametric tests of operating variables were made with the K-1 catalyst at pressures up to 205 psia in a new 4 inch diameter fluid bed reactor system. This was followed by cyclic operation at 115 psia pressure with carbon deposition at 450°C and steam gasification of the deposited carbon at 650°C. Over 30 cycles of operation, there was no significant change in reaction rates and near equilibrium steam utilization throughout the test. The methane yield declined, however, and this was traced to contamination of the catalyst.

The excellent fluidization and pneumatic transport properties of the K-1 catalyst made it possible to fabricate and further test this catalyst in a two reactor fluid bed system with semi-continuous circulation of catalyst between reactors. Carbon is deposited from LBG in a 6-inch diameter reactor and the deposited carbon is steam gasified in a parallel 3-inch diameter reactor. Catalyst is transferred between reactors in a 3/8-inch diameter transfer line. Figure 2-1 shows that the K-1 catalyst

Figure 2-1. Long-Term Performance of K-1 BEACON Solids Under Simultaneous Carbon Deposition and Steaming Operation at 100 Psig (Tandem Reactor Testing)

retained its activity for over 400 hours of steady state operation at 115 psia pressure. With carbon deposition at 430°C, near equilibrium conversion of fuel components ($\text{CO} + \text{H}_2$) was achieved. Steam gasification temperature was 600-620°C and steam utilization was excellent. The near equilibrium amount of methane in the product gas (20% on a dry basis) represents about 60% of the stoichiometric maximum possible methane formation. At commercial operating pressures of about 300 psia, 80-85% of the stoichiometric methane would be produced from the steam gasification reactor. A "polishing" methanation step over the BEACON catalyst at a lower temperature or over a conventional fixed bed methanation catalyst would be required in a commercial application to complete the conversion of residual CO and H_2 to CH_4 .

Laboratory scale experiments have shown that the BEACON catalysts could be modified to inhibit methane formation and enhance the hydrogen yield during the steam gasification of deposited carbon. Twenty catalysts were screened in atmospheric pressure tests. Two preferred catalysts showed good stability and selectivity through 50 cycles of carbon deposition at 450°C and steaming at 600 to 620°C. The effect of pressure up to 115 psia was studied in a bench scale fluid bed reactor, with steam gasification at 600°C. One catalyst showed a clear superiority in selectivity for hydrogen. The preferred operating pressure appears to be in the range of 65-90 psia. This catalyst will be further tested for long term stability in the tandem reactor unit.

2.2 ENGINEERING EVALUATIONS

In order to evaluate the commercial potential of the BEACON process, several conceptual process designs were prepared. Major equipment was sized, capital and operating costs estimated, and the economics evaluated relative to competitive processes. In a coal-gasification combined-cycle power plant application, the cost of power could be reduced by about 15% relative to a similar oxygen-blown coal gasification system. This is primarily due to the energy storage capability of the BEACON carbon catalyst, which permits the air-blown coal gasification unit to remain

fully loaded even with up to 30% daily variations in power demand. The coproduct SNG could be used by a utility to provide seasonal load following capability when used as fuel for peaking gas turbines.

When applied to an industrial application for the production of hydrogen and cogenerated electric power, the system would be at least cost competitive with conventional steam reforming of natural gas to produce hydrogen. This conclusion is sensitive to values assigned to natural gas, cogenerated electric power, and the LBG feed gas, as discussed in the report. For example, if natural gas values reach $\$6.00/10^6$ Btu (after deregulation), the cost of hydrogen would be $\$10.70/10^6$ Btu via steam reforming (basis a 10% rate of return on a 100% equity investment). Assuming this value for H_2 , cogenerated power at the early 1983 average industrial sector purchased cost of 5.0 cents per kilowatt hour, and coal gasification LBG cost of $\$5.00/10^6$ Btu, a BEACON-cogenerated power plant investment would yield a 17% rate of return.

Other sources of LBG feed gas were considered for application of the BEACON hydrogen process. The EXXON Flexicoking process generates LBG by air gasification of petroleum coke. Certain types of direct combustion oil shale retorts also generate large volumes of LBG. Analysis of both of these feed gas sources indicates they could be marginally attractive under limited conditions. The primary disadvantage of these sources is that they are only available at atmospheric pressure. This appreciably increases the capital cost of the BEACON system and the cost of compressing the product hydrogen.

2.3 FUTURE DEVELOPMENTS

The catalytic stability of the K-1 methane catalyst has been demonstrated by over 400 hours of steady state operation in the tandem reactor system. Work is in progress to obtain similar stability test results on the preferred hydrogen catalyst. Evaluation of several gas/solid separation techniques that may be applicable to the unsupported BEACON catalyst is also planned. At this point, the BEACON process would

be ready for testing in a larger two reactor integrated unit that incorporates heat transfer tubes and gas/solid separation equipment. This unit would be designed to obtain the additional engineering information which is essential for the design of a first-of-a-kind Demonstration Plant. Long term physical stability of the catalyst under simulated-commercial operating conditions would also be evaluated. Plans for building and operating such an integrated test unit have been deferred pending future developments in two critical areas.

The first and foremost reason for delaying further R&D efforts is due to the lack of commercial availability of an efficient pressurized (20-30 atmospheres) air-blown coal gasification system whose costs are reasonably well defined. Most work on coal gasification in the past few years has concentrated on oxygen-blown systems due to the broader applicability of the synthesis gas product. However, air-blown versions of the BGC/Lurgi slagging fixed-bed gasifier, the Westinghouse or IGT fluid-bed gasifier, or the Shell Oil Company entrained flow slagging gasifier would all provide excellent fits with the BEACON process. Commercial availability of such pressurized air-blown gasifiers would provide a good basis for renewed interest in completing the BEACON development program.

The second factor which causes some hesitancy in expending further development money at this time is the uncertainty in market conditions. Recent declines in the cost of oil imports, ample supplies of oil and gas, and uncertainties regarding the timing and effects of natural gas deregulation, all have contributed to a de-emphasis of the development of the coal gasification alternative. This, in turn, affects the development of dependent technologies such as BEACON. In the long term, the availability of huge domestic reserves of coal make it a certainty to partially replace oil and gas whose domestic reserves are more limited. The relative insecurity of imported oil and gas will also contribute to a growing reliance on coal. However, the uncertain timing of this displacement by coal suggests a prudent delay in moving forward with development of the BEACON process.

It is appropriate at this time to recognize two fundamental qualities of the BEACON catalysts, i.e. they are carbon-tolerant catalysts with excellent fluidization properties. TRW and SOHIO, with DoE support, are presently working on other applications of these catalysts which can uniquely benefit from these qualities.

3. BEACON PROGRAM - HISTORY AND TECHNICAL BACKGROUND

3.1 PROGRAM HISTORY

The BEACON program began in 1975 as an internal research and development (IR&D) program at TRW. In this program it was established that carbon could be deposited on a catalyst at attractive rates from low heating value fuel gas, and that this carbonaceous material reacted catalytically and rapidly with hydrogen to produce methane. The TRW studies investigated the influence of temperature and pressure on carbon deposition and methanation reaction rates and began to look at the possibilities of fluid bed reactors. Physical and chemical properties of the intermediate carbon material were investigated and engineering analyses of initial conceptual designs were performed.

In July 1978 the Standard Oil Company of Ohio became associated with TRW for the purpose of further development of the BEACON process. SOHIO's activities in the program included development of a supported catalyst for achieving the BEACON chemistry and contributions to fluidization reactor engineering, engineering analysis and bench-scale testing.

The U.S. Department of Energy awarded a contract in August 1979 to TRW and SOHIO (DE-AC-01-79ET10032) for "BEACON Reactor Design Modeling and Cold Flow Testing." The prime objective of this contract was to develop models for several types of catalytic reactor systems that may be employed in carrying out the BEACON reactions. Cold flow equipment was built and candidate catalysts tested to determine some of their fluid mechanical properties. This program was completed in October 1980. Knowledge of the fluidization characteristics of the BEACON carbon was expanded by the cold flow testing and a computer program was developed which was a good model of a bubbling bed reactor.

By 1980 a substantial data base on the chemistry of the two BEACON reactions had been accumulated, some results had been obtained from a batch fluid bed reactor and engineering analyses of some conceptual designs appeared attractive. In April 1980 a cooperative agreement

(DE-FC21-80MC14400) among DOE, TRW and SOHIO was concluded and experimental work initiated.

In this cooperative program it had been planned to use the steam-iron process as a source of hydrogen for preparing SNG. Since development of the steam-iron process did not proceed as rapidly as expected the emphasis shifted to reacting the BEACON carbon with steam rather than hydrogen, to produce methane. A major catalyst breakthrough made the steam-carbon reaction feasible at low temperatures. Preferred supported and unsupported catalysts for manufacturing SNG were developed using steam. The unsupported catalysts were evaluated in a batch 4-inch diameter fluid bed reactor, and supported catalysts tested in 1.5 and 3-inch diameter batch units.

In the spring of 1982 some experiments in the 4 inch batch reactor indicated a catalyst system possibility for suppressing methane and forming hydrogen. Preferred catalysts for hydrogen manufacturing were developed using additional funds made available by the cooperating parties.

With further understanding of the fluidization of the unsupported carbonaceous catalyst a tandem reactor system incorporating carbon deposition and steaming reactors was designed and built. This permitted a continuous steady state operation of both the carbon deposition and steaming reactors with carbon and catalyst circulated between the reactors. One batch of the catalyst for SNG maintained a steady activity for over 700 hours.

Other program activities have included lost work analysis, conceptual designs, heat and material balances, cost estimates and economic analysis.

3.2 TECHNICAL BACKGROUND

3.2.1 System Concepts and Chemistry

In this section the BEACON technology will be described in terms of the overall systems concepts for producing, on a cogeneration basis, energy

products (electric power and steam) and chemical products (methane or hydrogen). The chemistry involved and its unique aspects will be described. Finally, attention will be turned to the major thermodynamic leverage that is derivable through the BEACON process approaches and the unique chemistry.

3.2.1.1 What is BEACON?

BEACON stands for Btu Extraction And Concentration. Effectively what is done is to very efficiently extract a part of the energy from low heating value fuel gases in the form of a solid, carbonaceous, pollution free, storable material. This material then is upgraded to high value methane or hydrogen through rapid, modest temperature, reaction with steam. Nearly all of the exothermic heat of reaction associated with the formation of the solid carbonaceous material remains as sensible heat in the now depleted producer gas and this hot depleted gas becomes an excellent working fluid for combined cycle power generation and/or steam production. The high temperature energy available from the hot depleted fuel gas also is used in part to drive the endothermic reaction of steam with the solid carbonaceous intermediate material to produce product methane or hydrogen.

The overall system in terms of feedstocks and products is illustrated in Figure 3-1. Low heating value gas whose major constituent is nitrogen provides the feedstock or starting point for the BEACON systems. The combustible or energy containing portions of these low grade fuel gases are carbon monoxide, hydrogen, methane, and other hydrocarbons, which are generally present in a total concentration of 40% or less. Effectively, the BEACON process converts a part (~50%) of the energy content of the feedstock into chemical products (CH_4 or H_2) and the remainder into energy products (steam and electric power) at high overall efficiency. Through the use of the solid intermediate carbonaceous material there is separation of the chemical products, methane or hydrogen, from the nitrogen diluent present in the low heating value fuel gases. Thus, the BEACON process uniquely provides an approach to upgrading low heating value gases to CH_4 or H_2 and eliminates the need for oxygen blown, medium heating value synthesis gas as the feedstock for methane or hydrogen production from coal.

FEEDSTOCKS

- COAL DERIVED PRODUCER GAS
- FLEXICOKER OFF-GAS
- SHALE RETORT GAS
- "IN SITU" PRODUCER GAS
- BLAST FURNACE GAS

Figure 3-1. BEACON is a Co-generation Process

3.2.1.2 What is the BEACON Chemistry?

As illustrated in Figure 3-2 the BEACON process involves circulating a very easily fluidizable, solid carbonaceous material containing a catalyst between two fluid bed reactors.

In one reactor the solid material contacts the low heating value fuel gas feedstock resulting in the rapid deposition of very reactive carbonaceous material by reactions of the type:

Thus, in this reactor the incoming carbonaceous material and catalyst are enriched in carbon content through the deposition process and the low heating value fuel gas is depleted in energy content by an amount which is nearly equal to the heating value of the deposited carbon. The fuel gas is brought into the fluid bed carbon deposition reactor at near ambient temperature and the depleted fuel gas exits the reactor at 450°C to 550°C. Thus, most of the exothermic heat associated with carbon deposition is taken up in the depleted fuel gas as sensible heat in the nitrogen diluent, available for steam or power generation.

The carbon rich, solid, carbonaceous material and associated catalyst produced in the deposition reactor is separated from depleted fuel gas and circulated to a second reactor where the material is contacted with steam. In this reactor the steam-carbon reaction is very rapid at temperatures as low as 550°C or some 300°C below the temperature at which coals or chars will react effectively with steam. Depending on operating conditions (pressure, temperature and steam utilization) and catalyst type either of the following overall reactions may predominate:

or

Figure 3-2. BEACON Process Configuration

If the objective is to produce hydrogen rather than methane then it is desired to form as little CH_4 as possible in the steaming reaction. Higher temperatures, lower pressure and lower steam utilization all serve to suppress methane formation, but do so at an economic penalty. In this program a catalyst has been discovered which appears to very effectively suppress methane formation while still maintaining excellent steam utilization. It now appears possible to produce a 97% hydrogen product and still obtain near equilibrium steam utilizations of 60-75%.

Heat must be supplied for the steam-carbon reactions described above. However, since the reaction temperature is modest (550-650°C) this heat can readily be supplied (indirectly) from the hot, depleted, and fully combusted fuel gas. Thus, a part of the residual energy content of the depleted fuel gas is used to drive the steam-carbon reactions. This endothermic heat of reaction of course adds to the final total heating value of product methane or hydrogen at 100% efficiency. That is to say the higher heating value of the product methane or hydrogen exceeds the heating value of the reactant carbon by an amount equal to the endothermic heat of reaction.

To complete the solids circulation loop, carbon lean solids from the steaming reactor are returned to the carbon deposition reactor for carbon enrichment. For example, the carbon lean solids may contain 50-60% carbon and the carbon rich solids may contain 80-90% carbon.

In carbon deposition, Reaction 3 represents a recent addition to the technology base. It now has been shown that carbon can be deposited from fuel gases whose heating value is derived mainly from very low concentrations of hydrocarbons and that the carbon so deposited on selected catalysts is as active for steam reaction as carbon which is deposited from carbon monoxide. This discovery becomes important when looking at the possible application of producing hydrogen from shale retort gases via the BEACON technology since the major portion of the heating value of shale retort gases comes from low concentrations of hydrocarbons rather than carbon monoxide and hydrogen.

3.2.1.3 What Are the Major Technical Advantages of BEACON?

In the BEACON technology there are three key areas of technical advantage:

1. A novel chemistry which results in very fast reactions at moderate temperatures.
2. An ability through modifications of operating conditions and catalysts to produce either methane or hydrogen as a product.
3. An intermediate carbonaceous material and associated catalyst which has excellent fluid mechanical properties.

In both the carbon deposition and steaming reactions, utilizing the catalysts developed, near equilibrium compositions are obtained with gas-solid contact times that are well within the range that is commercially reasonable. Carbon deposition is rapid above 450°C and the steam-carbon reaction becomes effective above 550°C.

Very recently a catalyst has been discovered that inhibits methane formation and promotes hydrogen formation without significantly decreasing the overall global rate of the steam-carbon reaction.

The fluid mechanical properties of unsupported carbonaceous material are very different from other solid powders. Of great importance is the fact that this material fluidizes very well at commercially reasonable gas velocities.

3.2.1.4 Why Are We Interested in Hydrogen as a Product?

The market for hydrogen is projected to grow dramatically in the next twenty years. At the present time hydrogen is worth almost twice as much as methane on a Btu basis and is expected to maintain its margin relative to methane in the future. Our new BEACON technology for producing hydrogen

is the only one we know of that can use low pressure, low Btu gases as feedstocks. We project that this new process can produce hydrogen for oil refineries, tar sands and shale oil processing, and coal liquefaction plants more economically than conventional processes. Hydrogen may also be utilized as feed gas to new fuel cells now under development. We have also found that low Btu gases such as those produced in oil shale retorts can be used as feed gas to the BEACON hydrogen process. This is significantly different from the original process concept because the active carbonaceous intermediate is derived predominantly from light hydrocarbon gases rather than from carbon monoxide disproportionation.

3.2.2 Thermodynamic Leverage of the System Concepts

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

The first form of analysis is called "Model System Studies." There are simplified process heat, material and utility balances for competitive cases in which a simple model feedstock composition is selected and the competitive cases are rigorously treated in an identical manner with respect to efficiency calculations. The advantage of this approach is that it is possible rapidly to see what aspects of a particular case are important in determining the overall system efficiency, and the relative efficiency of one process concept (or case) versus another.

In the second type of evaluation a thermodynamic "lost work" analysis is performed around each of the model systems by constructing a theoretical, reversible, process model that starts with the same feedstock and ends up with the same products as the model system cases. In the reversible process we calculate the maximum (reversible) work associated with each unit operation and compare it to the actual work determined in the model system study. The difference between the reversible work and the work calculated for the model system is the so-called "lost work" which is an

accurate measure of the degree of inefficiency (or efficiency) of a particular process flow sheet.

3.2.2.1 Model System Studies

Figure 3-3 presents a simple model system for a process competitive to BEACON for producing combined cycle power and synthetic natural gas from a clean, synthesis gas fuel. For simplicity the synthesis gas fuel is defined as consisting of equal moles of carbon monoxide and hydrogen. The steam systems for power generation and shift-methanation are integrated. That is the exothermic shift-methanation system produces both process steam and steam which is used for power generation. The high temperature combined shift and methanation process (RMP Process) was chosen as being representative of the best evolving competitive SNG technology.

Figure 3-4 presents a block diagram of the BEACON model system producing combined cycle power and SNG. In this system a simplified BEACON feed gas is used consisting of equal moles of carbon monoxide and hydrogen diluted to produce low Btu gas volumetric heating value levels with nitrogen. Identical feedstock molar inputs of carbon monoxide and hydrogen are used in the BEACON (Figure 3-4) and conventional (Figure 3-3) cases and the total hourly higher heating value of the feedstock fed to each process is, of course, also identical (15.66×10^9 Btu/hr). Both the conventional and BEACON systems have been constrained to produce the same quantities of methane (20,000 moles/hr, 7.66×10^9 Btu/hr HHV). Therefore, the total hourly input heating value is the same in both cases and the total hourly methane output is the same, leaving the net power generated in each case to be the floating variable which measures the comparative overall efficiency in each system.

Identical gas turbine/compressor/generator systems and efficiencies are used in the two cases with a turbine inlet temperature of 1970°F assumed. The HRSG systems are assumed capable of converting the sensible heat remaining in the turbine exhaust gases to electric power at 25% overall efficiency, a number which is consistent with several detailed studies of the power recovery from HRSG systems. Part of the HRSG heat available

CONVENTIONAL MODEL SYSTEM (SYNTHESIS GAS FEED)

Figure 3-3.

TOTAL FUEL FED HHV	15.66 x 10 ⁹ BTU/HR
TOTAL CH ₄ PRODUCED	20,000 MOLES/HR
TOTAL POWER PRODUCED	829 MW

BEACON STEAM-CARBON MODEL SYSTEM (PRODUCER GAS FEED)

Figure 3-4.

in the BEACON case is used to raise process steam for the carbon-steam reaction, and the remainder is converted to electric power at 25% efficiency.

Excess, exothermic heat of reaction available at high temperature is assumed to be convertible to electric power at 35% overall efficiency. In the conventional system the high-temperature shift-methanation process produces 1.21×10^9 Btu/hr of excess heat which is convertible to superheated steam and then to electric power. In the BEACON carbon deposition reactor a small amount of the exothermic heat is taken out as superheated steam (0.176×10^9 Btu/hr) and converted to electric power at 35% efficiency. The remainder of the exothermic heat of carbon deposition remains as sensible heat in the working fluid of the gas turbine system. In the BEACON case, the steam-carbon reaction is endothermic overall and hence no net power is produced in this part of the system. Rather, heat must be imported from the combined cycle burner and as stated previously from the HRSG system.

In the BEACON system (Figure 3-4) we see that we pull 40,000 moles/hr of carbon (HHV - 6.77×10^9 Btu/hr) and 1.621×10^9 Btu/hr of heat out of the incoming fuel gas to the combined cycle system to make the 20,000 moles per hour of CH_4 (HHV = 7.66×10^9). Hence the overall efficiency of the methane production is 7.66×10^9 divided by 6.77×10^9 plus 1.621×10^9 or 91.3%. In the conventional system, (Figure 3-3) 9.78×10^9 Btu/hr of synthesis gas feedstock produces 7.66×10^9 Btu/hr of methane plus 1.21×10^9 Btu/hr of high level heat available for power generation. Hence, the overall efficiency of methane production in the conventional case is $7.66 + 1.21$ divided by 9.78 , or 90.7%. Thus, the efficiency of methane production in the two cases is essentially identical.

Although methane production in the two cases has about the same efficiency, on the power generation side there are dramatic differences. The BEACON system produces 262 more MW than the conventional system or 31.6% more power. The reasons for this major improvement in power production and hence in overall efficiency in the BEACON case relative to the conventional case begins to become apparent from the model system block flow

diagrams. In the conventional system 434,800 moles of air are compressed for 458,800 moles of hot combustion gases entering the turbine or a ratio of 0.947 moles of air compressed per mole of combustion gas. In the BEACON system only 285,352 moles of air are compressed for 549,352 moles of combustion product entering the turbine at the same temperature or a ratio of .519 moles of air compressed per mole of combustion gas. Each mole of air which is compressed consumes 1.38 KW-hrs of power so that the predominant difference in power production in the two systems boils down to the differences in power required to compress combustion air.

The question now comes down to why there should be so much more air compressed in the conventional system than in the BEACON system? In the conventional system a fuel is fed to the burner in which all of the energy content of the fuel is derived from the heat of combustion of the carbon monoxide and hydrogen and none of the energy content is yet in the form of sensible heat. Thus in the burner all of the chemical energy of the fuel is converted to sensible heat and in order to do this and still meet the system constraint of a 1970°F entrance temperature at the turbine, the product gases must be diluted with a great deal of compressed excess air in order to hold the final temperature at 1970°F.

In the BEACON system over 40% of its total heating value is initially extracted from the fuel gas in the form of solid carbonaceous material which is subsequently converted to methane product at very high efficiency. In addition, a significant amount of the remaining heating value of the fuel is converted to sensible heat during carbon extraction, prior to entering the burner, and hence without compression of air. This can readily be understood when we recognize that the deposition of one mole of carbon from two moles of carbon monoxide also produces one mole of carbon dioxide and a large amount of heat. In effect what has been done is deposit one mole of carbon from carbon monoxide and burn one mole of carbon monoxide to carbon dioxide without ever compressing any air. The nitrogen diluent present in the low heating value fuel serves to take up the great majority of the heat of reaction during carbon deposition. Thus, in the BEACON case a very lean fuel in which much of the heating value is already present as sensible heat enters the burner. Hence, relatively little air must be compressed to burn the remaining carbon monoxide and

hydrogen and to dilute the total combustion products to a turbine inlet temperature of 1970°F. In the limit, if there were no equilibrium constraints, all of the heating value of the depleted gas after carbon deposition would be in the form of sensible heat in the hot nitrogen plus carbon dioxide plus water vapor.

Thus, through the mechanism of extracting energy from a low heating value feedstock in the form of a solid carbonaceous material, we convert the remaining energy in the feedstock to a form where it can be more efficiently converted to electric power in the combined cycle system. This energy extraction and concentration in the form of carbon provides the basis for the unique thermodynamic synergism of the BEACON combined cycle power system.

Figure 3-5 shows the same BEACON model system as Figure 3-4 except in this case hydrogen and combined cycle power are produced rather than methane and combined cycle power. A comparison of these two model systems yields some interesting results.

1. In the hydrogen system more chemical product (hydrogen) and less power is produced than the methane system. This is because the $\text{H}_2\text{O}-\text{C}$ to H_2 reaction is more endothermic than the $\text{H}_2\text{O}-\text{C}$ to CH_4 system. Hence more heat must be transferred to the steam-carbon reaction when hydrogen is made thus resulting in less heat available for power generation and more production of chemical product (H_2).
2. The overall efficiency for hydrogen production is 9.83 divided by $6.77 + 1.551 + 2.618$ or 89.9% which is slightly lower than the 91.3% for the methane system.
3. In the hydrogen system the amount of air which must be compressed per mole of combustion product into the turbine is 180,451 divided by 444,451 or .406 moles/mole compared to .519 moles/mole for the BEACON methane system (Figure 3-4). Hence the gas turbine system in the hydrogen process is even more efficient than the turbine system in the methane process. The reason for this is that in the hydrogen system more heat is removed from the burner to drive the $\text{H}_2\text{O}-\text{C}$ to H_2 reaction than is required to drive the $\text{H}_2\text{O}-\text{C}$ to CH_4 reaction. Hence, less air must be compressed in the hydrogen case to meet the 1970°F system constraint on the turbine inlet temperature.

BEACON STEAM - CARBON TO HYDROGEN MODEL SYSTEM

Figure 3-5.

4. If the total energy required to produce hydrogen is separated ($6.77 \times 10^9 + 1.551 \times 10^9 + 2.618 \times 10^9 = 10.939 \times 10^9$) from the total input energy in Figure 3-5, there remains $15.66 \times 10^9 - 10.939 \times 10^9 = 4.721 \times 10^9$ Btu/hr. This must be the total input energy used to produce power. Therefore in the hydrogen case the efficiency of converting input heating value to power, exclusive of hydrogen production, is $838,000 \times 3414$ divided by $4,721 \times 10^9 = 60.6\%$. In the methane case (Figure 3-4) this number is 51.2%. The reason the power efficiency is so high in the hydrogen case is due to the fact that there is less air compression per mole of combustion product and also due to the fact that almost all of the heat available in the HRSG system is used to make hydrogen rather than to generate electric power at a very low 25% efficiency. Thus nearly all of the power in this case is generated in the extremely efficient gas turbine system.
5. In summary the BEACON combined cycle-hydrogen system has an even higher efficiency than the BEACON combined cycle-methane system, and from a thermodynamic viewpoint should be the system of choice. However, it must be recognized that economic as well as thermodynamic considerations are involved and the choice of one system over another will depend on many different factors.

3.2.2.2 Lost Work Analysis

In this section, the thermodynamic efficiency of the BEACON combined cycle-methane system (Figure 3-4) is compared with the thermodynamic efficiency of the competing system providing combined cycle power and SNG (Figure 3-3). The feed to the BEACON process is producer gas (64,000 moles per hour of CO, 64,000 moles per hour of H₂, and 200,000 moles per hour of N₂, at a total pressure of 17 atm). The conventional competitive process uses a synthesis gas feed (64,000 moles per hour of H₂, and 64,000 moles per hour of CO, at 17 atm pressure). Both processes produce the same amount of methane (20,000 moles per hour).

As noted in the model system discussion above, the BEACON process produces more electricity than its competitor. This results mainly from BEACON's higher inherent efficiency, but also in a minor part because BEACON makes use of the extra compression energy which is present in the low-Btu feed gas.

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

The essential thermodynamic features of the BEACON process and of the conventional competitor process are shown in Figures 3-6 and 3-7, respectively. Reactors are shown as rectangles with material flow from left to right. Heavy vertical arrows represent energy outputs. The vertical arrow above each rectangle indicates the energy that could be obtained by a Carnot engine processing the heat of reaction. The vertical arrows above the flow streams indicate energy which would be available from isothermal room temperature expansion of the material flowing between reactors, and energy which would be available from ideal heat engines which would change the gas temperatures as required while exchanging heat with the surroundings at ambient temperature. Each specie in a flow stream is considered to be removed from one reactor or put into another reactor through a semi-permeable membrane at its equilibrium partial pressure. Between reactors, each specie is cooled by a reversible heat pump to room temperature, compressed or expanded as needed isothermally and reversibly at room temperature, then heated to reaction temperature by another reversible heat pump. The net energy available from the expansion of all the species in a flow stream is shown issuing from a turbine (shown as a trapezoid), and the net energy from all of the heat engines required to bring each specie

BEACON STEAM-CARBON MODEL SYSTEM (PRODUCER GAS FEED)

Figure 3-6. Essential Thermodynamic Features

CONVENTIONAL MODEL SYSTEM (SYNTHESIS GAS FEED)

Figure 3-7. Essential Thermodynamic Features

in a flow stream down to room temperature and then back to reaction temperature is indicated by an arrow issuing from a rectangle. It should be pointed out that the reversible expansion process could also be carried out adiabatically. In such a case, the split between expansion energy and the heat engine energy would be different, but the sum would be the same.

Each part of the conceptual processes shown in Figures 3-6 and 3-7 operates reversibly; hence, a negative sign for the expansion energy indicates that more energy is required for compression than is obtained by expansion. Similarly, a negative sign for the energy from the ideal heat engines indicates a net flow of energy into the system. The energy values are given in millions of Btus per hour. The values in italicized numbers are for the reversible process. The sum of all of these values is the maximum possible useful energy which could be obtained from the system. The values in bold numbers represent the actual energy inputs and outputs of the model system. The sum of these values represents the actual energy output from the model processes.

3.2.2.3 Thermodynamic Model of the BEACON Process

In the conceptual reversible BEACON process, the entering producer gas is expanded to the equilibrium partial pressures that would occur in the carburizer and then heated to the temperature of the carburizer. The carburization reaction is exothermic and in the reversible process the reaction produces a net energy output. In the real process, the heat of reaction irreversibly supplies the heat needed to bring the reactants up to temperature, and the small amount which is left over is used to generate electricity (63 million Btus per hour).

Two streams leave the carburizer reactor; one contains carbon which goes to the steamer, the other contains carbon-depleted gases which go to the combustor. In the reversible process, the gases are first expanded to the very low equilibrium partial pressures which they would have in the combustor and are then heated to combustion temperature. Air must also be brought into the combustor in excess of that which is required for stoichiometric conversion in order to keep the temperature down to an acceptable

level, and flow work is required to move the air into the combustor. As the combustion proceeds, the heat of reaction is turned into useful energy by a Carnot efficiency engine. In the actual process, of course, the heat of reaction is used irreversibly for heating the input gas up to reaction temperature. For the actual process, the overall operation of compressing the feed gases, heating them, and then reacting them occurs with a net loss of energy: 1415 million Btus per hour.

In the reversible process, the exhaust gases from the combustor are cooled to room temperature and dropped in pressure through an expander to atmospheric pressure. In the model process, an adiabatic turbine expands the gases until their temperature drops to approximately 1000°F, and 25% of the residual enthalpy is removed by a heat recovery steam generator. The total amount of energy available from this combined cycle expansion step is 5164 million Btus per hour, approximately 20% less than the value for the reversible process.

Carbon from the carburizer enters the steamer where it reacts with water. In the reversible process, the water is heated at room temperature from a liquid to a vapor, and the vapor is then compressed to its partial pressure in the steamer reactor, and is heated to the temperature of the steamer reactor. The steaming reaction is mildly endothermic. In the reversible process, the heat of reaction is supplied by a reversible heat pump; thus, an energy input is necessary at this point.

Two streams leave the steamer reactor; one is by-product CO_2 at 70°F and one atmosphere, the other is CH_4 at one atmosphere and 70°F. The equilibrium partial pressure of the methane in the steamer is less than one atmosphere, and hence the gas must be compressed to atmospheric pressure. Some energy is recovered by cooling the methane and the carbon dioxide to room temperature. In the actual process, some of the heat from the combustion of the carbon-depleted gases is used to preheat the input to the steamer and to supply the endothermic heat of reaction, and no useful energy is obtained.

3.2.2.4 Parallel Systems for Combined Cycle Power and SNG

In the competing conventional system with combined cycle power generation and a parallel stream for methane production, the incoming synthesis gas is split into two streams; 24,000 moles per hour of CO and 24,000 moles per hour of H_2 are sent to the combustor. In the reversible process, the gases are expanded and then heated to the equilibrium partial pressures and temperature that would occur in the combustor. Excess air is also compressed and heated in the reversible process to its equilibrium partial pressures and temperature in the combustor. Useful work is obtained from the heat of reaction through a Carnot efficiency heat engine. In the real process, the heat of reaction in the combustor raises the temperature of the inlet gases to the combustion temperature. The overall energy requirement for the real combustion process is 2155 million Btus per hour.

In the conceptual reversible process, the exhaust gases are cooled by a reversible heat engine and then expanded to atmospheric pressure. The actual process uses an adiabatic expansion followed by partial recovery of the enthalpy in the heat recovery steam generator producing 4619 million Btus per hour. This is about 15% less energy than is produced in the reversible process.

The larger part of the synthesis gas, 40,000 moles per hour of CO and 40,000 moles per hour of H_2 are put through a conventional shift methanation process to produce CH_4 and by-product CO_2 at the same conditions as were assumed for the BEACON process. The overall energy which could be obtained from such a process, if it were operated reversibly with heat exchanged to the surroundings at room temperature, is 1458 million Btus per hour. This is the difference between the free energy of the incoming stream and the free energy of the exiting streams. The actual amount of energy which is obtained is calculated by assuming that the heat rejected in the process can be converted to electricity at 35% overall efficiency. This gives 433 million Btus per hour, which is about 30% of the maximum amount which could be obtained from a reversible process.

3.2.2.5 Comparison of Processes

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

The nearly 20% relative increase in the efficiency of the BEACON process over its competitor results chiefly from a 10% relative increase in the power delivered to the combined-cycle generating system, and from a 30% relative decrease in the power required to compress air for combustion.

The total reversible energy available is greater for the BEACON process than for its competition (7363 million Btus/hr vs 6938 million Btus/hr). Most of this is real (364 million Btus/hr) and results from the pressurized nitrogen in the feed to the BEACON process. The remainder is simply the cumulative error in the thermodynamic calculations.

The combustion of conventional fuels is a highly irreversible process and results in a large amount of lost work. If, instead of combustion, the same fuel could be processed in a reversible fuel cell, two to three times as much electrical energy could be produced. The extra steps involved in the BEACON process operate at conditions close to equilibrium, and hence do not introduce a large amount of lost work. The difference shows up in the amount of electricity which is available when both systems, the BEACON process system and the competing conventional process, are used to make the same amount of methane from feed gases with the same heating values.

3.2.3 Status of Development

It is important to recognize that over the past eight years several thousand material balanced tests have been performed involving either carbon deposition or steam-carbon reactions. The fluid mechanical properties of the intermediate carbonaceous materials and associated

catalysts have been studied extensively and these systems have been found to behave in an unusual and highly desirable fashion in a fluid bed reactor. Many different catalyst combinations have been screened and catalyst systems have been identified that are stable and highly active for many cycles of carbon deposition and steaming. Very recently catalyst systems which have good activity and are selective for producing hydrogen from the steam-carbon reaction while inhibiting methane formation have been identified.

Under the current program the BEACON chemistry has been tested in small, fixed bed laboratory reactors and larger fluid bed, batch reactors up to 4" in diameter. Excellent material balances and reproducibility have been obtained in most experiments. Recently a continuous bench-scale reactor system has been constructed which permits running carbon deposition and steaming reactions simultaneously and circulating carbon rich and carbon lean solids between the reactors.

4. CATALYST DEVELOPMENT

4.1 DEVELOPMENT OF SUPPORTED CATALYSTS

The goal of this work was to discover a physically stable and chemically active supported catalyst for converting a low Btu gas to SNG or H_2 . Early investigations explored fixed bed catalysts with only limited success. The technical investigation then turned to the development of supported fluid bed catalysts. This added another dimension, namely, the requirements of maintaining a good fluidization regime appropriate to the probable process conditions.

4.1.1 Variation of the Support

The first experiments involved the addition of the active catalyst on the surface of hard catalyst supports having good attrition resistance but with no internal porosity. Ceramic microballoons and Alundum support were investigated. After a few cycles the active catalysts were completely separated from these supports by the carbon deposition and removal. Figure 4-1 shows a scanning electron microscope photograph (SEM) of these catalyst particles. Some still have catalyst and carbon on the surface while other are completely free of these components.

It was concluded that if the active catalyst did not work on the external surface of the catalyst support it should be dispersed into a porous support so that the active carbon could be deposited in the pores. This direction meant that the catalyst support must have a significant pore volume, adequate physical strength during carbon deposition and removal in the pores and the active catalyst must exhibit good reaction rates in this configuration.

A variety of commercially available supports were subjected to pre-treatment variations, and different active catalysts and methods of

Figure 4-1. Scanning Electron Microscope (SEM) Photograph Showing Catalyst and Carbon Removal After Several Cycles (Catalyst Deposited on Support Surfaces)

incorporating these catalysts into the pores of the support were investigated. This was successfully achieved as shown in Figure 4-2. Figure 4-2a shows fresh catalyst before processing and Figure 4-2b shows the same catalyst after carbon deposition. No evidence for carbon on the outside surface of the catalyst particle is seen.

A catalyst system employing a support labeled C77 was found to be attractive for further investigation with candidate active catalysts. This investigation is discussed in the next section.

4.1.2 Interaction of the Active Catalysts With the Support

Three candidate active catalysts were investigated with the C77 support and it was found that they interacted differently with the support. Particularly the mobility of the catalyst was a critical problem to be overcome. Combinations of catalyst support processing, methods of adding the active catalyst to the support and post addition processing were investigated.

4-2a.

4-2b.

Figure 4-2. SEM Photographs of Catalysts With Active Ingredient Deposited in the Pores of the Support. a) As Prepared and b) After Carbon Deposition.

The three catalysts were designated K-1, K-2 and K-4. The relative reactivity of these three on the C77 support is shown in Table 4-1. K-1 and K-2 are more reactive than K-4, however the mobility of K-1 could not be controlled and a way to deposit it in the pore was not found. For these reasons the first choice of a supported catalyst for the conversion of low Btu gas to SNG was the K-2 catalyst on the C77 support.

4.1.3 Testing and Evaluation of Preferred Supported Catalyst for SNG

As discussed in Section 3 above two routes were investigated for the preparation of SNG using BEACON chemistry. In one case the BEACON carbon was reacted with hydrogen to produce methane and the second route involved reacting the carbon with steam. The preferred route for the preparation of SNG is the steaming of the carbon and this can be achieved through the use of the K-2 C77 catalyst system. Early in the program the main emphasis was on the preparation of SNG through the hydrogenation of the BEACON carbon. This called for a different active catalyst, identified as K-4, but using the same C77 catalyst support system.

Table 4-1. Comparison of Reaction Rates
for Three C77 Catalysts

Catalyst Composition	Reaction	Temp. °C	g.C/g. Active Cat./Hr	Typical % CH ₄ Levels in Tailgas
K-4 C77	Carburetion	450	0.55	--
	Methanation	550	0.25	33
K-2 C77	Carburetion	450	0.75	--
	Methanation	550	0.28	26
K-1 C77	Carburetion	450	0.84	--
	Methanation	550	0.26	26

4.1.3.1 SNG By Hydrogenation

In the early stages of the program the development of the C77 type of catalyst support was coupled with procedures for incorporating the K-4 active catalyst into the pores of the support. This candidate catalyst system was subjected to 40 cycles of carbon deposition and hydrogenation to produce SNG. These 40 cycles demonstrated that this K-4 C77 system was a dimensionally stable and chemically active BEACON catalyst. The catalyst did not exhibit any significant physical degradation during the course of the 40 cycles and the activity of the catalyst did not decline. Throughout the 40 cycles the carbon removal rate remained in the range of 0.250-0.275 grams of carbon removed per hour per gram of active catalyst.

During the course of these 40 cycles samples were taken for surface area, pore volume and active surface area determinations. These increased with the increase in the number of cycles. These results indicated that the active catalyst probably became more evenly distributed in the pores and that with increasing cycles the catalyst remained inside the pores and was not carried out by the carbon. This hypothesis explains the simultaneous increase in surface area, pore volume and active surface area.

4.1.3.2 SNG by Steaming

Three catalyst systems, designated K-1, K-2 and K-4, were evaluated with the C77 catalyst support. The first investigations of these catalyst systems were conducted in atmospheric pressure laboratory test units. The temperature range investigated was 550-750°C. In this temperature range the K-4 C77 system became inactive after only a short period of time. Both the K-1 and K-2 catalyst systems were active throughout the selected temperature range. The reaction rate as evidenced by the grams of carbon removed per hour per gram of active catalyst increased in both cases with increasing temperature. The K-2 catalyst did exhibit a superior rate over the K-1 catalyst material throughout the temperature range studied and therefore was selected for the additional testing. Further testing of this K-2 C77 catalyst through multiple cycles was performed in the bench-scale equipment and is reported in Section 5.

4.1.4 Sulfur Resistance of the K-2 C77 Catalyst

The resistance of the K-2 C77 catalyst to sulfur poisoning was investigated. Figure 4-3 is the plot of carbon deposition vs cycle number when the deposition feed gas contained 12 ppm of COS. The carbon deposition rate started to decline immediately and reached a very low level by the tenth cycle. Figure 4-4 shows the steaming rates over ten cycles using carbon which had been deposited with 12 ppm COS in the feed gas. These rates were affected less than the deposition rates but they did decline continuously.

A similar test sequence was conducted with feed gas for the deposition step containing 4 ppm of COS instead 12 ppm. Figure 4-5 shows the change of deposition rates with cycling to 20 cycles. The rates do not decrease as soon nor do they fall as much as with the 12 ppm of COS shown in Figure 4-3. Figure 4-6 plots the steaming rates vs cycle number using a carbon obtained from a deposition with the feed gas containing 4 ppm of COS. For the first 13 cycles the steaming rates were about the same as for the base case without COS (Cycles 1 and 2). Starting with Cycle 14 the rates began to drop to a lower level. During the experiment using 4 ppm COS in the feed gas the feed gas and the tail gas samples were analyzed for sulfur during both steaming and carbon deposition. No sulfur was found above the detection limit of 1 ppm in the tail gas samples. It was concluded that the K2 C77 catalyst loses some of its activity after prolonged exposure to 4 ppm COS. It is possible that with feed gases containing 1 ppm or less of COS the K2 C77 catalyst would maintain its activity.

4.1.5 The Effect of Carbon Loading Level on K-2 C77 Catalyst

A set of experiments was carried out to investigate the effect of carbon loading on carbon deposition rates and catalyst integrity. The carbon deposition rate was constant and independent of carbon loading up to 50% by weight, the limit of the investigation. To evaluate catalyst integrity carbon was deposited on the catalyst up to 40% by weight, then gasified off with steam and the recovered catalyst given an attrition test. No significant break up of the catalyst was observed even with 40% carbon loading.

Figure 4-3. Deposition Rates With Feed Gas Containing 12 ppm of COS

Figure 4-4. Steaming Rate After Deposition With COS at 12 ppm in Deposition Feed

Figure 4-5. Deposition Rates With Feed Gas Containing 4 ppm of COS

Figure 4-6. Steaming Rates After Deposition With COS at 4 ppm

In another set of experiments the phenomenon of volume expansion of the catalyst was investigated. In these experiments a batch of K-2 C77 catalyst was subjected to 12 cycles of carbon deposition and steaming. In the first 4 cycles the carbon loading was kept at about 20% by weight maximum. In the 5th through the 8th cycles the carbon loading was increased to around 35%, and for the 9th through the 12th cycles the carbon loading was increased further to approximately 50% by weight. Periodically the volume changes of the catalyst bed were measured and the catalyst was subjected to a sieve analysis. Small samples of each sieve fraction were taken for the determination of carbon content and then all of the samples remixed and the experiments continued.

The changes in catalyst volume with an increase in carbon loading are shown in Figure 4-7. The sieve analyses and the carbon contents of sieve fractions are presented in Table 4-2. As shown in Figure 4-7 the catalyst volume increases with increasing carbon content in the range 20% to 50% by weight of carbon. At each carbon loading the volume stays reasonably constant. Another result of higher carbon loading is the increase in weight percent of larger particle sizes at the expense of the smaller sizes as shown in Table 4-2. This change in particle size distribution could account for the volume expansion. The data in Table 4-2 also show the reverse occurs to some extent as the carbon content is steamed off. The weight percent of the larger particle sizes decreases and that of the smaller sizes increased. The volume reversibility is not complete as shown in Figure 4-8. Here the weight percent particles greater than 106 microns does decrease as the carbon is steamed off from 47.4% to 1.4%, but the weight percent does not return to the original value.

The larger particles contained much more carbon than the average of the catalyst bed with the smaller particles contained much less carbon. Changing the average carbon loading level primarily affected the large particles with the carbon content of the small particles being affected less. Figure 4-9 shows the carbon loading levels of the various particles sizes at different average carbon contents. For instance when the catalyst bed average was 47.4% carbon loading to 106 micron particles showed 100% carbon loading while 25 micron particles shows only 40% carbon loading.

Figure 4-7. Volume Changes of K-2 C77 Catalyst With Increasing Carbon Loadings

Table 4-2. Sieve Analyses and Sieve Fraction Carbon Contents for
Different Carbon Loadings of a K-2 C77 Catalyst

After Cycle No.		0	4-1/2	8-1/2	11-1/2	← 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	19.63	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	13.69	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.

Figure 4-8. Weight Percent Particles Greater Than 106 Microns As Function of Carbon Content on Catalyst

Figure 4-9. Percent Carbon Loadings on Sieved Fractions

These experiments indicate that for the production of SNG the K2 C77 catalyst should not have carbon loadings above 20% unless space is provided in the reactor for volume expansion. The particle size distribution is an important factor in the operation of the catalyst.

Later in the program promoters to reduce volume expansion were investigated. They were selected from a group of materials designated as Class II and particularly two candidates from this class designated IIA and IIB were tested. They were both used at a concentration designated as Level 5. Both of these promoters when added to the K-2 C77 catalyst lowered the volume increase significantly at both a 20% and a 30% carbon loading level. A batch of K-2 C77 catalyst with Class IIB promoter at Level 5 concentration was prepared and subjected to 5 cycles of carbon deposition and steaming. After the final steaming the catalyst contained 7.5% carbon. Particle size distributions were compared among the catalyst before reaction, after the 5 cycles and the catalyst support only. These distributions are shown in Figure 4-10. As shown in Figure 4-10 there is very little difference in the particle size distribution among the three samples tested.

The expansion of catalyst volume with use could be explained if the carbon deposit grew outside of the catalyst particle. Sieve analyses of catalysts after various treatments are shown in Table 4-3. Notice that many more large particles are found in the used catalysts than in the freshly prepared K-2 C77, and the particles do not shrink back to the original size following gasification.

4.1.6 Structural Stability of K-2 C77 Catalyst

Theoretical objections have been presented against the use of supported catalysts in well fluidized beds for deposition of carbon from gas streams. The objections are based on the theory of the distribution of the particle residence times which predicts that some of the particles remain in the bed for long periods of time. If the deposition rate remains substantially independent of carbon loading, the particle ultimately will become loaded to the point of destruction and the excessive fines made in this way would be lost from the system.

Figure 4-10. Particle Size Distribution Before/After Carbon Loading of K-2 C77 Catalyst Promoted With the Class IIB Material.

Table 4-3. Particle Size Distributions (Percent) of a K-2 C77 Catalyst After Various Processing Steps

Sample Source	Freshly Reduced	After Carbon Loading	After Steam Gasification
Sieve Designation (U.S. Series Standard)			
+ 100	0.2	1.5	0.4
100 x 140	2.0	4.9	7.6
140 x 200	10.1	14.8	17.7
200 x 270	20.0	30.9	38.0
270 x 325	14.2	14.2	11.6
325 x Pan	44.5	33.7	24.9

The K-2 C77 catalyst, when operated in batch fluidized beds, has not shown any significant change in activity with increased carbon loading. Further there has not been any significant amount of catalyst break up even when the catalyst has been overloaded with carbon deposit to simulate above average residence times. The K-2 C77 catalyst does not appear to generate fines due to variation of residence times for different particles.

4.1.7 Testing and Evaluation of Supported Catalyst for Hydrogen Production

4.1.7.1 Promotion of C77 Catalysts for Hydrogen Production

A series of experiments was performed using promoters for the purpose of increasing the hydrogen production through reducing methane formation during steaming. K-1 C77 and K-2 C77 catalysts were used with three types of promoters. These promoters were designated Class I, II and III. In all cases standard catalyst preparation procedures were followed with the promoters being added to the active catalyst ingredients. With the K-1 C77 catalyst the Class I promoter was added at two levels designated Levels 1 and 2. With the K-2 C77 catalyst the Class I promoter was added at two levels designated Levels 1 and 2. With the K-2 C77 catalyst the Class I promoter was added in the amounts designated Levels 2 and 3.

Two promoters of Class II designated IIA and IIB were tested with the K-2 C77 catalyst. The Class IIA material was tested at a concentration Level 4 and the Class IIB material at a concentration Level 5.

The Class III material was tested with K-2 C77 catalyst for its ability to suppress methane formation.

Promotion of K-1 C77 catalyst with the Class I promoter at Levels 1 and 2 did not work when the steaming temperature was 550°C. When the promoter concentration was at Level 3 the activity of K-2 C77 catalyst lasted a little bit longer at 550°C but without much improvement in methane suppression. However at 650°C neither the K-1 C77 catalyst nor the K-2 C77 promoted with Class I material at Level 2 showed any sign of decline of activity. The methane suppression was only marginal with the promoted K-2 C77 catalyst, but it was very good with the promoted K-1 C77 catalyst.

Class II materials are good promoters for increasing steaming rates but are useless as methane suppressors.

The best results in this series were obtained with K-2 C77 catalyst promoted by Class III material. The rates were good and the methane suppression was excellent. As an added advantage the steaming was carried out at 550°C which is 100°C lower than the temperature needed for operating K-1 C77 catalyst promoted with a Class I promoter. Good steaming rates were obtained in both the first and second cycles.

A second series of experiments involving promoters utilized three groups of materials. The first group consisted of catalysts promoted to suppress methane formation during steaming. Two types of promoters were investigated; a further investigation of the Class III promoter and a new Class IV promoter. The second group of catalysts were promoted for the purpose of reducing volume expansion which has been a problem with the C77 catalyst during fluidization. The third catalyst group contained promoters from the previous two groups for the purpose of suppressing methane formation and reducing volume expansion.

The two promoters, Class III and IV, used for methane suppression were added to a batch of catalyst support after which the active catalyst was added to the support containing the promoter. From there on the standard catalyst preparation was followed. The Class III catalyst was prepared to yield a Level 5 concentration of the active ingredient and another batch was prepared to have a Level 6 active promoter concentration. The Class IV compound was formed in situ on the catalyst support and the active catalyst was then added to the support containing the promoter after which the standard catalyst preparation procedure was followed.

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

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

In the previous series of experiments the Class III promoter was shown to be very effective in suppressing methane formation during steaming. It was desired to recheck this result and to see how effective this promoter would be at a lower concentration (Level 6). These results along with those obtained in evaluating the Class IV promoter and the combination Class IIB/Class III promoter are presented in Table 4-4.

Table 4-4 shows the results obtained with the lower concentration of the Class III promoter (Batch 148). The promoter was efficient even at this lower concentration and the methane concentration generally is zero after the first cycle. The rates were somewhat lower but this probably is due to poor fluidization in the small laboratory reactor. The next

Table 4-4. Effect of Promoters on Methane Suppression During Steaming. Catalyst: K-2 C77

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

catalyst in Table 4-4 (Batch 153) is a repeat of the catalyst investigated in the first series of experiments. As with that preparation no methane was observed after the first cycle.

The Class IV promoter was unsuccessful as it completely inhibited the carbon deposition.

When Class IIA and Class IIB promoters were used with the K-2 C77 catalyst the volume increased only moderately. Without a promoter the volume expanded after the first deposition and kept on increasing until it leveled off after 15-1/2 cycles. Even after increasing the carbon loading level to 30% the catalyst volume did not expand further when the Class II promoters were used.

A catalyst which was promoted with a proven methane suppression component and with an effective volume expansion reducer was tested. Table 4-4 shows that this catalyst (Batch 145) failed as a methane suppressor although the rates were satisfactory. The 3.2% and 4.3% methane levels are higher than with the unpromoted K-2 C77 catalyst. It appears that the promoters are working against each other.

Several additional Class III compounds were tested using a K-2 C77 catalyst. With steaming at 550°C all of the compounds showed good reaction rates and excellent methane suppression over several cycles.

A Class III promoted K-2 C77 material is the preferred supported catalyst for the production of hydrogen according to the BEACON technology. No large cycle studies have been conducted with this catalyst but the unpromoted K-2 C77 catalyst has been studied extensively and its chemical activity and physical stability were demonstrated over 40 cycles.

4.1.8 Supported Catalyst for Converting Paraho Oil Shale Retort Off-Gas to Hydrogen

The hydrotreating of shale oil is an indicated step preceding the refining of the material. Therefore the use of the BEACON technology to convert the shale oil retort off-gas to hydrogen appeared to be an

attractive possibility. 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. Therefore the experimental program had to address the question of decomposing the hydrocarbons as well as converting the carbon monoxide and hydrogen to carbon. 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 feed gas to the heat content of the hydrogen produced is less than 3. This was taken as an objective for the experimental program.

The experiments were carried out in one inch quartz fluid bed reactors. In some tests just one reactor was used and in others two one-inch reactors were connected in series. In the latter case the tail gas of the first reactor was fed to the second reactor.

In the first 4 experiments in the series connected reactors, it was expected that carbon would be deposited at 450°C in the first reactor from carbon monoxide and olefins, and at 550°C in the second reactor from methane and other saturated hydrocarbons. In the experiments most of the hydrocarbons with a carbon content greater than one were removed but methane and especially carbon monoxide were increased over the feed gas. Actually in the second reactor there was hardly any carbon deposition. The main reaction taking place in the second reactor was the reduction of CO_2 with hydrogen which had been formed from the higher hydrocarbons to produce carbon monoxide and water. Further experiments showed the advantage of removing carbon dioxide so that there would be good carbon deposition in the second reactor.

After seeing the advantages of removing carbon dioxide from the feed, experiments were carried out in a single reactor at a higher deposition temperature of 550°C. However a large portion of the deposited carbon could not be gasified with steam at 550°C. In view of this result the deposition temperature was lowered to 500°C and in these runs it was possible to remove consistently all of the deposited carbon with steam at 550°C.

With this background, a group of experiments was undertaken using a simulated Paraho shale oil retort off-gas as feed to the first reactor. The composition of the off-gas is given in Table 4-5. In these experiments both the carbon dioxide and the moisture were removed before feeding to the reactors. This group of experiments investigated temperature variations in the two reactors and feed gas flow rates.

The best results obtained did have a Btu ratio of feed gas introduced to hydrogen produced of less than three, in fact ratios of 2.62-2.64. These ratios were achieved with temperatures in both reactors of 500°C or temperature in the first reactor 500°C and in the second reactor of 600°C. In both cases a lower feed gas feed rate was used. Higher feed rates led to higher Btu ratios. Good results required removal of the carbon dioxide from the feed gas.

Both K-1 and K-2 versions of the C77 catalyst were investigated in these series of experiments. A Btu ratio of less than 3 only was

Table 4-5. Composition of Paraho Shale Oil Retort Off-Gas

Components	Volume %
Hydrogen	5.5
Nitrogen	61.2
Oxygen	0
CO	2.9
CO ₂	24.3
Methane	2.4
Ethylene	0.7
Ethane	0.6
Propane and Propylene	0.6
Butanes	0.6
C ₅ ⁺	0.3
H ₂ S	0.3
NH ₃	0.6
	100% on Dry Basis
H ₂ O	17.5% (By Volume)

obtained with the K-2 C77 catalyst. It appears that both catalysts show similar trends for carbon monoxide conversion but that the K-2 catalyst is a better material for cracking the hydrocarbons.

The feasibility of using a K-2 C77 catalyst for converting the off-gas from a Paraho shale oil retort to hydrogen has been demonstrated on a laboratory scale.

4.2 DEVELOPMENT OF UNSUPPORTED CATALYSTS

This development effort involved the screening of catalytically active, unsupported, high carbon solids with the objective of identifying promising candidate unsupported catalysts for production of SNG and for production of hydrogen from steam gasification of BEACON carbon at moderate pressure and temperature conditions. The objective and criterion of success was that a primary and a backup candidate catalyst will be identified for each of the two processes, SNG and hydrogen, which demonstrated good enough performance at laboratory scale to merit further development at an advanced scale (bench scale testing). The performance requirements for success were high fuel utilization (CO and H₂ extraction from low Btu gas), near equilibrium steam utilization in the 550° to 650°C temperature range, and catalyst stability through several deposition/steaming cycles. The cost effective approach of performing the majority of the screening tests at ambient pressure was taken. Fixed beds of BEACON solids in the one to two gram range were used. A few carbon deposition tests were performed at higher than ambient pressures.

The development efforts met with success in both SNG and hydrogen production areas. Primary and backup candidate catalysts were identified for SNG and for hydrogen production which met the performance requirements listed above. In the SNG process, methane yield and steam utilization were virtually at equilibrium and the catalyst showed no deterioration during 40 cycles of operation. In the hydrogen process, selectivity was very high (near complete suppression of methane), operation was close to equilibrium, and catalyst stability through 50 deposition/steaming cycles was excellent.

The original chemistry of the BEACON process involved the catalytic deposition of carbon from a gas stream containing carbon monoxide and then exposing the carbon to a hydrogen stream at moderate temperatures and pressures to produce methane. The requirement for hydrogen was eliminated when it was discovered that BEACON carbon could be converted directly to methane through steam gasification at the same moderate temperatures and pressures. This discovery represented a breakthrough in the economics of the BEACON process; a costly reactant, hydrogen, was replaced by a relatively inexpensive one, steam.

The early steam methanation tests were conducted with BEACON solids based on the "baseline catalyst," K-0, used in the original BEACON process (hydrogen methanation). The results were promising but performance was inadequate. The "baseline" BEACON solids were very active in carbon deposition but required higher than 750°C steam methanation* temperatures for acceptable rates and catalyst stability. Data generated under reaction conditions which led to steam utilization values appreciably below those predicted for equilibrium operation (e.g., inadequate reaction temperatures (<750°C) or very high steam feed rates) revealed exhaustion of the gasification reaction much before all the carbon had been consumed. This apparent catalyst deactivation was attributed to the side reaction of steam with the catalyst causing its oxidation and its subsequent deactivation; Figure 4-11 illustrates the point. At steam utilizations of 50% or higher, 815°C and 765°C curves, the "baseline" BEACON carbon gasified at constant rate to completion. Under conditions where the steam utilization rate dropped to 32% (e.g., 711°C steaming) the catalyst was virtually deactivated while 40% of the carbon was still unreacted. A number of additional tests verified the requirement of high temperature steaming, 750°C-850°C range, as the only means of avoiding catalyst deactivation. This temperature range was considered unacceptable because of the high heat input requirements (endothermicity) of the steaming operation at that

* Steam methanation is the steam gasification of BEACON carbon to methane, carbon oxides and hydrogen; the CO and H₂ are converted to methane in a polishing methanation stage at lower temperatures; carbon dioxide and steam are removed from the product gas.

Figure 4-11. Effect of Temperature on Steam Gasification of "Baseline" BEACON Carbon

temperature range. Therefore, modifications to the "baseline catalyst" were sought which would reduce or eliminate the aforementioned drawbacks of the "baseline catalyst." The criterion of success was defined as a catalyst which would promote carbon deposition as efficiently as the "baseline catalyst" but also promote the steam gasification of the resulting carbon at temperatures below 650°C without activity deterioration for at least 50 deposition/steaming cycles.

A brief screening matrix involving the deposition and steaming of modified "baseline" BEACON solids revealed that steam gasification below 650°C was an attainable goal. Figure 4-12 compares temperature scanning data generated with "baseline" BEACON solids and with BEACON solids based on modifications to the "baseline catalyst," designated heretofore as K-1, K-2, and K-3 type BEACON solids. It is apparent that the modified solids represented a major improvement in steam methanation performance using temperature as the yardstick. For example, the K-1 based carbon exhibited appreciable gasification rates* in the 500°C to 550°C range or some 250°C below that required by the baseline catalyst. Such a large drop in steaming temperature meant that BEACON carbon could be conceivably gasified under conditions requiring the addition of very little heat. Indeed, if near-equilibrium steaming operation can be performed at about 550°C and 200 psig pressure the dry product gas will consist principally of methane and carbon dioxide, the heat input requirement would be near zero, and BEACON carbon would be converted to methane in a single step.

The data presented in Figure 4-12, augmented by additional runs to verify the depicted results, led to the conclusion that further catalyst development testing should be restricted to K-1 and K-2 based BEACON solids. An ambient pressure test matrix was initiated with the objective of selecting one of these two catalysts as the primary candidate for scale-up testing. Short-term testing (one to ten carbon deposition-steaming cycles) was used to determine the effect of operating parameters and of

* Gasification rate is expressed in milliliters of product gas generated per minute.

Figure 4-12. Steam-Carbon Temperature Scanning Experiments With "Baseline" and Modified BEACON Catalysts

solids composition (including the use of promoters) on carbon deposition and steaming performance. Multi-cycle testing was used to determine catalyst stability. The effect of steam partial pressure on methanation performance was examined at bench-scale (Section 5 of this report) because of better equipment suitability; however, the effect of carbon deposition pressure on subsequent steaming performance was examined at this scale.

4.2.1 Experimental Apparatus and Procedures

Figure 4-13 contains a photograph and a schematic drawing of the apparatus used in laboratory-scale, ambient pressure testing of BEACON solids. The apparatus consisted of a feed manifold, a microreactor, a product conditioning system, and the appropriate instrumentation for monitoring reactant and product flowrates and composition. The feed manifold was used to blend the simulated low Btu gas used for carbon deposition; a microboiler fed by a syringe-pump was used to produce a constant flow of feed steam to the reactor during the steaming cycle. The reactor itself consisted of a U-shaped quartz tube equipped with a shielded thermocouple for temperature measurement and control. A proportionally controlled electric furnace was used to heat the reactor tube. Product gases generated during a reaction were cooled by means of an ice bath chilled condenser and fed to a programmed gas chromatograph and an automatic recording gas volume flowmeter. The gas chromatograph was calibrated for measuring hydrogen, methane, carbon monoxide, carbon dioxide and nitrogen. Columns and programmed switching valves used in the chromatograph permitted a complete analysis of product gas composition to be made every ten minutes. For experiments where more frequent analyses were required, a syringe sampling port which had been plumbed into the product gas line was used. The apparatus was capable of operating at near ambient pressure and up to temperatures of 900°C. Checkout of the reactor system indicated carbon mass balances of $\pm 4\%$ could be reproducibly achieved.

The reactors were operated in batch mode with respect to solids but continuous, steady state mode with respect to feed gases. A charge of 0.5 to 2.0 grams of carburized catalyst was used in the U-tube reactor tests. During carbon deposition/steaming multi-cycle testing, carbon was steam-gasified to the desired level and carburized back to the original weight;

Figure 4-13. Packed Bed Carbon-Steam Reactor - Syringe Fed Versions

the process was repeated until the desired number of cycles was accomplished. The rates of carbon deposition or gasification were determined from the differences in carbon content of the feed and product gas streams as a function of time (gas analysis data were available in 10 minute intervals through the automatic sampling gas chromatograph). The accuracy of the carbon balances was checked by weighing the reactors (solids) at the end of each operation. Hydrogen and oxygen elemental balances were also computed during the run in order to determine the quality of data being generated (accuracy of measurements). A computer program was used for detailed mass balances on each operation (carbon deposition or steaming) and for data tabulation and storage. An example of the type of data generated during each test is presented in Appendix A of this report.

At least two U-tube reactors were being operated simultaneously during this development phase of the BEACON process and because of substantial automation two of them could be run by a single operator. These apparatuses were used to determine the short term performance of K-1 and K-2 based BEACON solids, to investigate the effect of promoters and of deposition temperature on steam methanation rates, and to perform multi-cycle testing for catalyst stability determination.

4.2.2 Steaming Performance Comparisons of K-1 and K-2 Catalysts (Parametric Data)

Thermodynamics predicts that steam partial pressure and temperature have an appreciable effect on steam utilization* and on methane yield** in the steam gasification of graphite. Also, the gasification rate data generated during the screening tests suggested that parameters which influenced steam utilization are those most likely to influence methane production through their effect on rate and product gas composition. These were temperature, steam feedrate per unit weight of carbon in the reactor, and type and composition of catalyst; pressure was not screened. Thus, the short term parametric testing centered around these parameters with major emphasis on temperature.

* Steam utilization is defined as the fraction or percent of feed steam used during gasification.

** Methane yield is defined as the concentration of methane in the product gas or as the mole fraction of methane produced per carbon gasified.

Figures 4-14 and 4-15 present typical rate data obtained from steam gasification of K-1 and K-2 based BEACON solids at several temperatures. Each test started with approximately one gram sample of K-1 or K-2 BEACON carbon. The samples were purged with nitrogen until reaction temperature

Figure 4-14. Steam Gasification Rates as a Function of Temperature at Ambient Pressure (K-1 Type BEACON Solids)

Figure 4-15. Steam Methanation Rates as a Function of Temperature at Ambient Pressure (K-2 Type BEACON Solids)

was reached and then the feed stream was switched to pure steam at a rate of 20.8 STD milliliters per minute (one gram per hour). The tests were run at one atmosphere pressure and at the temperature shown on the individual curves. Excellent carbon, hydrogen, and oxygen material balances were obtained in all cases.

Gasification proceeded at measurable rates until all or nearly all of the carbon was gasified. At the high temperatures (640°-650°C) gasification proceeded at constant rate until more than 80% of the carbon was gasified. At the intermediate (575°-600°C) and lower temperatures (525°-550°C) gasification rate remained virtually constant until carbon consumption exceeded the 70 and 50% levels, respectively. Thus, the data indicated that under the conditions of the experiments depicted in Figures 4-14 and 4-15 the overall gasification reaction was steam limited until most of the carbon was consumed; i.e., the gasification reaction was zero order with respect to the quantity of carbon in the reactor during the period of "constant rate" gasification. Changes in the geometry or size of the carbon bed did not affect the gasification rate or the composition of product gas when the reaction temperature and steam partial pressure remained constant. However, when the steam feedrate was increased, the gasification rate increased virtually proportionally without discernible change in composition. The data in Table 4-6 illustrate this point.

Table 4-6. Effect of Steam Feedrate-to-Carbon Charge Ratio on Steam Gasification Rate (Ambient Pressure, 600°C)

Type of Solids	Carbon Charge, Grams	Steam Feedrate Grams/Hour	Gasif. Rate Grams C/Hour
K-1	1	0.97	0.30
K-1	1	1.7	0.50
K-1	1	2.9	0.72

The above observations implied that during the "constant rate" portion of steam gasification the reaction(s) was controlled by equilibrium. The data in Figure 4-16 verify the validity of this assumption for the 650°C steam gasification of K-1 based carbon to methane. The agreement between the experimentally obtained composition and that predicted by thermodynamics is excellent. A more extensive and more detailed comparison between experiment and thermodynamics is presented in Tables 4-9 through 4-11 where data covering a broad range of temperatures are summarized. (Very similar results were obtained and identical conclusions were reached with K-2 BEACON solids.)

The results summarized in Tables 4-7 through 4-9 are typical of the type and quality of data generated in dozens of runs, short and long-term testing, performed during the catalyst development effort; the entries in the tables are self explanatory. It is noted that the carbon balance was excellent in all three runs. The small fluctuations in compositional entries were partially due to the $\pm 5^\circ$ fluctuations in reactor temperature and partially due to normal measurement errors. This was especially true of the water component which was not measured directly but computed from the difference between the steam fed and the steam decomposed (used in gasification) as determined from the dry product gas flowrate and composition. Table 4-7 summarizes the 650°C data; the agreement between experimental and predicted values is almost exact in this case, and it was so in all cases where steaming was performed at 600°C or higher and where the steam feed rate in grams per hour was up to twice the grams of carbon in the reactor bed at the start of the run (steam feedrate-to-carbon charge weight ratio). Table 4-8 summarizes the 575°C data. In this case, the approach to equilibrium is within 6% with respect to steam utilization and within 25% with respect to methane (or about 20°C approach to equilibrium). Table 4-9 presents the 525°C steam gasification data of K-1 based solids. In this case, the experimental results were appreciably different than those predicted by thermodynamics for the steam gasification of graphite to methane but nearly identical to predicted data for the steam gasification of graphite to hydrogen assuming complete suppression of methane. That is,

Figure 4-16. Product Gas Composition as a Function of the Percent Carbon Gasified (Type K-1 Solids) - Comparison to Thermodynamically Predicted Values

Table 4-7. Typical Data Set and Carbon Mass Balance for Packed-Bed Carbon-Steam Reaction (Type K-1 Carbon, 650°C)

Reaction Time, Min.	Dry Product Gas Volume, CC (STP)	Product Composition, Mol %					Grams Carbon Gasified (Cumulative)	Percent Carbon Gasified	Percent Steam Utilization
		H ₂	CO	CH ₄	CO ₂	H ₂ O			
10	251	43.3	24.5	5.0	13.7	13.4	0.067	7.2	79.7
30	752	43.9	24.1	4.9	13.8	13.3	0.200	21.5	79.8
50	1,254	44.1	23.8	4.9	13.9	13.3	0.332	35.7	79.9
70	1,755	44.3	23.5	4.9	14.2	13.2	0.464	49.9	80.1
90	2,257	45.1	22.0	4.8	15.3	12.8	0.594	63.9	80.8
110	2,758	45.9	20.5	4.8	16.6	12.3	0.722	77.7	81.7
130	3,220	43.0	15.3	3.5	16.7	21.6	0.837	90.0	69.5
150	3,458	34.9	4.9	0.4	14.8	44.9	0.887	95.4	43.9
Thermodynamically Predicted*									
Composition & Steam Utiliz.:		43.3	21.9	4.6	15.3	14.9			78.0

Carbon Balance for Entire Run:

$$\text{Carbon Balance} = \frac{\text{Ungasified Carbon} + \text{Carbon in Product Gases}}{\text{Carbon Charged}} \times 100 = 98.8\%$$

* Graphite-steam equilibrium

Table 4-8. Typical Data Set and Carbon Mass Balance for Packed-Bed Carbon-Steam Reaction (Type K-1 Carbon, 575°C)

Reaction Time, Min.	Dry Product Gas Volume, CC (STP)	Product Composition, Mol %					Grams Carbon Gasified (Cumulative)	Percent Carbon Gasified	Percent Steam Utilization
		H ₂	CO	CH ₄	CO ₂	H ₂ O			
10	106	17.4	4.3	1.7	10.5	55.8	0.020	2.3	29.2
30	475	37.6	8.1	6.6	20.2	27.5	0.114	12.9	64.4
50	845	37.8	7.9	6.5	19.7	28.1	0.206	23.3	63.6
70	1,241	37.8	7.7	6.4	19.6	28.3	0.305	34.4	63.3
90	1,610	38.6	7.7	5.8	19.8	28.0	0.395	44.6	63.5
110	1,967	39.2	7.6	5.2	20.2	27.8	0.485	54.7	63.7
130	2,310	40.0	7.2	5.0	20.2	28.0	0.560	63.2	63.5
150	2,640	36.4	6.0	3.5	18.0	36.1	0.639	72.1	54.2
170*	2,956	38.7	4.4	1.9	18.4	36.5	0.706	79.7	53.4
<u>Thermodynamically Predicted Composition & Steam Utiliz:</u>		35.4	9.6	8.3	21.3	25.4			67.3

Carbon Balance for Entire Run:

$$\text{Carbon Balance} = \frac{\text{Ungasified Carbon} + \text{Carbon in Product Gas}}{\text{Carbon Charged}} = \frac{0.0719 + 0.805}{.8856} \times 100 = 99\%$$

* Reaction continued to extinction (230 min. total reaction time)

** Graphite-steam reaction

Table 4-9. Typical Data Set and Carbon Mass Balance for Packed-Bed Carbon-Steam Reaction (Type K-1 Carbon, 525°C)

Reaction Time, Min.	Dry Product Gas Volume, CC (STP)	Product Composition, Mol %					Grams Carbon Gasified (Cumulative)	Percent Carbon Gasified	Percent Steam Utilization
		H ₂	CO	CH ₄	CO ₂	H ₂ O			
10	132	32.4	3.8	2.3	16.7	44.4	.029	3.3	45.5
30	422	35.3	3.6	2.5	17.8	40.4	.090	10.2	49.6
50	713	35.4	3.5	2.5	17.8	40.4	.148	16.8	49.2
70	977	35.7	3.6	2.8	18.0	40.3	.207	23.5	50.2
100	1,373	36.0	3.5	2.8	18.0	40.3	.295	33.5	50.1
130	1,795	36.2	3.4	2.0	18.0	40.4	.384	43.6	49.7
160	2,191	33.8	3.0	1.6	16.8	44.7	.454	51.5	45.2
190	2,547	31.6	2.2	1.2	14.0	54.0	.524	59.5	36.1
220*	2,904	34.7	2.4	1.1	16.9	44.8	.596	67.6	44.9

Thermodynamically Predicted**
Compositions & Steam Utiliz.:

• Normal Equilibrium	28.1	4.6	11.4	23.2	32.6	61.0
• Suppressed CH ₄ Equil.	39.0	4.0	0	17.5	39.6	49.6

Carbon Balance for Entire Run:

$$\text{Carbon Balance} = \frac{\text{Ungasified Carbon} + \text{Carbon in Product Gases}}{\text{Carbon Charged}} = \frac{0.0852 + .796}{.881} \times 100 = 100.0\%$$

* Reaction continued to extinction (330 min. total reaction time).

** Graphite-steam reaction

steam gasification was still equilibrium controlled during the "constant rate" portion of the run but the methanation reaction, the conversion of product hydrogen and carbon oxides to methane, was kinetically rather than equilibrium controlled at these test conditions. The importance of this observation is that the same catalyst can promote the production of either SNG or hydrogen selectively from the same feedstock by small changes in operating conditions; there is, however, a penalty in steam utilization in using this catalyst for hydrogen production.*

The above results were augmented with a dozen or more steaming runs performed with both K-1 and K-2 solids. The objective was to bracket gasification performance as a function of temperature for each solid and to use the data as one of the criteria in the ranking of the two catalysts. Performance was measured against rate values predicted by thermodynamics. The data** are summarized in Figure 4-17. The solid curve traces the expected gasification rate of BEACON carbon as a function of temperature assuming that equilibrium conditions prevailed and that the free energy of BEACON carbon is the same or very close to that of graphite. The filled and open circles represent the experimentally obtained steam gasification rates of K-1 and K-2 solids, respectively. At a given temperature, these rates remained constant until 50 to 80% of the carbon charge was gasified. (The higher the temperature, the higher the percent carbon gasified at constant rate, everything else being equal; refer to Figures 4-14 and 4-15 for examples.) The following conclusions were drawn from these results:

- There was no discernible difference in steam gasification rate, steam utilization, or product gas composition between K-1 and K-2 based BEACON solids in the operating ranges covered by these tests.
- Gasification rate to SNG took place at equilibrium controlled rates at 625°C or higher reaction temperatures and within 10% of such rates in the 575°-625°C range. Below 575°C steam utilization and methane yield were significantly below the corresponding equilibrium values.

* A modified form of this catalyst proved to be a more efficient promoter of hydrogen production from BEACON carbon.

** Rates only; the product composition data were similar to that presented in Tables 4-7 through 4-9.

* FOR GRAPHITE-STEAM REACTION

Figure 4-17. Steam Gasification Performance of K-1 and K-2 Catalysts as a Function of Temperature

Specific gasification rates,* expressed in grams carbon gasified per hour per gram carbon in the reactor, were also derived from the testing described above; the rates are presented as a function of temperature in Figure 4-18. These rates are applicable to the ambient pressure steaming of both K-1 and K-2 based BEACON solids. Above 625° or 630°C the rates follow the temperature dependence of the overall equilibrium constant for the steam gasification of graphite. At the lower temperatures the dependence was larger (19 vs 7 kilocalories per mole carbon gasified). At temperatures below 500°C these solids did not steam gasify to methane at measurable rates.

The curves in Figure 4-18 are valid design curves for an ambient pressure steam gasification reactor for either K-1 or K-2 based BEACON solids.

4.2.3 Carbon Deposition Performance Comparisons of K-1 and K-2 Catalysts (Effect of Promoters)

Temperature, pressure, residence time, and use of promoters were the variables examined for their influence on the performance of K-1 and K-2 catalysts in the carbon deposition operation of the BEACON Process (SNG production). Fuel utilization (CO conversion), the fraction of CO converted which deposited as carbon (selectivity), the specific deposition rate, and the activity of deposited carbon in steam gasification were the quantities evaluated; the corresponding thermodynamically predicted values, as well as comparison of the relative performance of the two catalysts were used as yardsticks.

Carbon was deposited from a mixture of 85 mole percent carbon monoxide and 15 mole percent hydrogen; this mixture was used as the carburetion feed gas in almost all laboratory scale testing.** Boat type reactors (for large

* The specific rates were derived by dividing the rate values given in Figure 4-17 by the minimum weight of carbon in the reactor which supported such rate; e.g., at 650°C, the 0.4 grams per hour rate could be supported until the weight of carbon in the reactor was reduced to 0.2 grams, therefore, the specific rate was computed to be $0.4 \div 0.20 = 2.0$ grams per hour per gram of carbon in the reactor.

** A lower Btu gas, closer related to low Btu gas derived from air blown coal gasifiers, was used at bench scale testing. The higher Btu gas was more appropriate for ambient pressure screening tests.

Figure 4-18. Gasification Rate Dependence on Temperature (K-1 or K-2 BEACON Solids)

batches) or U-tube type reactors (for small batches) were used for the deposition operation. Weight gains achieved during the reaction period were used to determine the average carbon deposition rate. Feed and product gas flowrates and compositions were used to determine instantaneous deposition rates and the chemistry of the operation. In almost all cases, the carbon deposition rate remained constant for the duration of the run. Deposition temperature was varied between 380°C and 650°C and gas residence time was varied between one and ten seconds. Ambient and 200 psig deposition pressures were used and a dozen promoters were screened during these tests.

Contrary to the results of the steaming tests, which led to the conclusion that K-1 and K-2 performance was nearly identical, the deposition data revealed appreciable differences in activity between the two catalysts. The K-1 catalyst met all the criteria for success: high fuel utilization (CO conversion close to the theoretical value); high selectivity of converted fuel to carbon; high specific rate (high carbon deposition rate per unit weight of catalyst); low temperature operation to minimize methane formation; active carbon product which can gasify at near theoretical rates; and no adverse deposition pressure effect on carbon activity. The K-2 catalyst fell short on fuel utilization and on specific deposition rates, but met all other criteria.

Table 4-10 summarizes the ambient pressure carbon deposition performance data generated in the temperature range that yielded highly active carbons. (Carbons were also deposited at 550°C and 650°C but were substantially less active in steam gasification and are discussed separately below.) The data show that at 380°C the gap in performance between the two catalysts is large, about 6-to-1 in terms of fuel utilization in favor of K-1, but it narrows appreciably at 450°C.* The K-1 catalyst is also about 20% more efficient in selectivity. Thus, at 450°C - which is

* In fact, the gap narrows even more at higher temperatures because the K-1 promoted rates reached their maximum values at about 450°C while the K-2 rate increased until about 500°C; however, the higher temperature deposited carbons were less active than desired for SNG production.

Table 4-10. Typical Carbon Deposition Performance Data on K-1 and K-2 Catalysts at Low Temperatures and Ambient Pressure

Type of Solids	CO Conversion (Mole %)		CO Selectivity To Carbon (Mole C/Mole CO Conversion)	Maximum Specific Rate Achieved Gr C/Hr/Gr M
	<u>380°C</u>	<u>450°C</u>	<u>380-450°C</u>	<u>450°C</u>
K-1	85±5	90±5	0.45±.05	3
K-2	15±5	50±10	0.40±.05	3
Theoretical*	99.9	100	0.56	11

* Thermodynamically predicted values assuming equilibrium deposition of graphite from a mixture of CO and H₂ feed in the 85:15 mole ratio.

near the best overall operating temperature for carbon deposition when both rates and carbon activity are considered, the specific rates of the two catalysts differ by a factor of about 2.7. It is believed that with better contact, less bypass, between catalyst and fed gas the K-1 promoted carbon deposition rate in the 400°-450°C would have approached by 85 to 90% the theoretical value versus the 75% approach attained in these tests. Gas residence time in the 2 to 10 second range used in these tests had no material effect on rates.

A number of elements known to influence coal gasification chemistry were incorporated into K-1 and K-2 catalysts in order to investigate their influence on the activity of these catalysts and especially to improve the performance of K-2 as a promoter of the carbon monoxide disproportionation reaction. Several batches of promoted and unpromoted catalysts were prepared using similar procedures and then carburized in a horizontal, boat type, batch reactor. Catalyst test specimens were carburized at atmospheric pressure using the 85:15 mole percent CO:H₂ gas mixture. Weight gains achieved in a 22 hour reaction period were recorded and used to compute average carbon deposition rates. These average deposition rates served as one of the means for comparing the relative promotional properties of the various additives and the proximity to theoretical (thermodynamically predicted) rates. The promoters (additives) were Group I, II, and III elements and are designated here as P1 through P12 additives.

The carbon deposition rates observed with the promoted and unpromoted catalysts are presented in Table 4-11 together with the thermodynamically expected deposition rates for the conditions used in these tests. The data indicate that Group I promoters, in general, can improve carbon deposition rates though the degree of enhancement appears to depend on the catalyst. The greatest improvement in carburization rate was obtained with the P2 promoted K-2 catalyst at 380°C -- nearly seven times the rate for the unpromoted K-2 catalyst at 380°C. However, it should be noted that the carburization rate for the unpromoted K-2 catalyst at 380°C was only about one-seventh the rate for the unpromoted K-1 catalyst at the same temperature, and the effect of the P2 additive was to make the performance of the promoted K-2 catalyst equal to that of the unpromoted K-1 catalyst at this

Table 4-11. Carbon Deposition Performance Comparison of Promoted and Unpromoted K-1 and K-2 Catalysts

Catalyst		Specific Carbon Deposition Rate* (450°C) (g carbon/hr/g catalyst metal)		Specific Carbon Deposition Rate* (380°C) (g carbon/hr/g catalyst metal)	
		K2	K1	K2	K1
Thermodynamically Predicted**		1.1	1.2	1.0	1.1
Unpromoted Catalyst		0.47	0.70	0.10	0.67
Promoter					
4-48 Group I Promoters	P1	-	-	0.36	0.54
	P2	-	-	0.66	0.82
	P3	-	-	0.20	0.82
	P4	-	-	0.25	-
	P5	-	-	0.02	-
	P1-P2-P3	-	-	0.22	-
Group II Promoters	P6	0.46	-	0.12	-
	P7	0.41	-	0.14	-
	P8	0.39	-	0.09	-
	P9	0.39	-	0.18	-
Group III Promoters	P12	0.33	-	0.13	-

* Average values computed for 22 hour reaction period.

** Predicted from thermodynamics for the conditions used in these tests.

temperature. The degree of rate enhancement for the Group I promoted K-1 catalyst at 380°C was considerably less. The Group II and Group III additives were much less effective carburization promoters. For the 450°C carburization reaction, Group II and Group III additives may have slightly depressed the carbon deposition rate. Although Group I additives tended to promote carburization, deposition rates for these promoted catalysts did not closely approach equilibrium-controlled rates. Gas bypassing of the catalyst in the horizontal, boat type, batch reactor is believed to be the major reason for that.

A number of the Group I promoted K-1 carbons were subjected to steam gasification testing for evaluation of potential beneficial effects of the additives on this operation. The results are summarized in Figure 4-19; the answer is negative.* If there was an effect, the "promoters" reduced slightly the efficiency of the unpromoted catalyst at every temperature. (Most likely, the observed differences are due to variances in catalyst preparation procedures and in test conditions than to the presence of the additive.)

As a general observation, the additives did not sufficiently improve either carbon deposition or steaming to counteract potential stability problems (leaching out and loss of additive) and cost. Thus, additional testing with them was discontinued. However, if K-2 were to be the ultimate selection as the BEACON catalyst, promotion with P2 additive may be reconsidered especially if carbon deposition rates deteriorate with cycling at pressure.

As indicated earlier, the effect of carbon deposition temperature on the steam reactivity of the resulting solids was investigated with K-1 based carbons prepared at 380°C, 450°C, 550°C and 650°C and steamed at 550°C and ambient pressure. The effect on rates is shown in Figure 4-20. (The 380°C points were virtually identical to the 450°C data and are not shown separately.) The carbon deposition temperature effect at the higher temperatures (550°C and 650°C) was severe. Carbon grown on K-1 at 450°C can be gasified at more than twice the rate of carbon grown on the same

* Low temperature steaming was selected for these tests in order to accentuate the effect of the additives.

Figure 4-19. Gasification Performance of Promoted and Unpromoted K-1 Based BEACON Carbons

Figure 4-20. Deposition Temperature Effect on Carbon Gasification Rates at 550°C

catalyst at either 550° or 650°C. Suprisingly, no discernible difference in gasification rate was observed between the 550°C and 650°C grown carbons. At these low gasification rates, steam utilization was also low (approximately 30%) therefore methane was completely suppressed during the steaming of the 550° and 650°C carbons.

The effect of carbon deposition pressure on steam reactivity of K-1 and K-2 BEACON solids was also examined at this scale. The negative effect of elevated deposition temperatures on the activity of the resulting carbon raised concerns about similar effects from elevated carbon deposition pressures, but this concern proved to be unfounded. To assess the carburization pressure effect on steaming activity carbon was grown at 5 and 200 psig (1.3 and 14.6 atmospheres) pressure and 450°C on K-1 and K-2 catalysts and subsequently steamed at ambient pressure and 525°C. The results are summarized in Figure 4-21. Unlike the results obtained for the carbon deposition effect, deposition pressure appears to have little or no effect on carbon-steam reactivity. The 10% increase in the K-2 high pressure carbon gasification rate was due to the higher steaming temperature (540° vs 525°C) inadvertently used to steam this carbon and not to deposition pressure. The effect observed with K-1 solids was virtually zero.

4.2.4 Catalyst Performance Stability in Multi-Cycle Testing

Performance stability of the K-1 and K-2 catalysts in carbon deposition and steaming operations of the BEACON process for production of SNG was examined through multi-cycle testing of these catalysts at ambient pressure. The plan was to perform 50 cycles on each catalyst, but testing was discontinued at the end of 43 cycles for K-1 and 40 cycles for K-2 when a statistical trend analysis of the 40 cycle data revealed no apparent trend of catalytic activity deterioration.

Samples of unpromoted K-1 and K-2 based BEACON catalysts were reacted in separate but similar quartz U-tube microreactors.* The test conditions are shown in Table 4-12. Two gram samples of carburized catalysts were reacted with steam at 600°C. The steam feed rates were low enough that

* These reactors were described in Section 4.2.1.

Figure 4-21. Effect of Carburetion Pressure on Steam Reactivity of BEACON Carbon

Table 4-12. Nominal Reaction Conditions for Multi-cycle Performance Experiments

	Gasification		Recarburation	
	Reactor No. 1 (K-1)	Reactor No. 2 (K-2)	Reactor No. 1 (K-1)	Reactor No. 2 (K-2)
Pressure	Atmospheric		Atmospheric	
Temperature, °C	600		400	450
Feed Gas Composition, Mole %	H ₂ O 100%		CO 85% H ₂ 15%	
Gas Feed Rate, Moles/Hour	0.13	0.16	0.05	0.06-0.07

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

The K-1 and K-2 catalysts were then recarburation in the same U-tube microreactors using an 85:15 mole percent CO:H₂ gas mixture. Somewhat different recarburation conditions had to be used for the two catalysts because of the substantially higher CO disproportionation activity of the K-1 catalyst. The K-1 catalyst could be recarburation at an acceptable

rate at 400°C, but the less active K-2 catalyst had to be recarburized at 450°C. Recarburization was continued until the amount of carbon deposited equaled that which had been gasified in the previous steam gasification half cycle. The actual weight of carbon deposited was checked at the end of the recarburization period by weighing the microreactor tube containing the recarburized catalyst. For each recarburization half cycle, values were determined for the carbon deposition rate, CO conversion, and CO selectivity to carbon. The carbon deposition rate was determined from carbon-catalyst weight measurements made before and after recarburization. CO conversion and CO selectivity to carbon were determined from feed and exit gas composition and flow rate measurements.

The gasification performance data for the K-1 and K-2 solids are summarized in Figures 4-22 and 4-23, respectively. These figures include gasification rates, steam utilization and dry product gas composition data as a function of cycle number for the two catalysts. These data are compared to the corresponding thermodynamically predicted values (dashed lines) for the experimental conditions used in these tests.

As can be seen from the plotted gasification performance data the activity of both catalysts remained high and constant throughout the 43 and 40-cycles. The K-1 catalyst promoted an average global gasification rate of 0.78 grams of carbon per hour (versus a theoretical value of 0.86) and an average steam utilization rate of 71% (equal to the theoretical value). Also, product gas composition was very close to that predicted by thermodynamics. Gasification efficiency and stability were excellent with this catalyst.

The K-2 promoted average rate was 0.67 grams per hour (versus 1.04 grams per hour for equilibrium controlled gasification) and the average steam utilization was 56% (versus the 71% theoretical value). Methane yield was, also, below that predicted by thermodynamics. Even though performance was appreciably below that predicted by thermodynamics for the

Figure 4-22. Steam Gasification Performance of Multi-cycle K-1 Catalyst

Figure 4-23. Steam Gasification Performance of Multi-cycle K-2 Catalyst

conditions of this test, catalytic activity was still significant and very stable.*

The carbon deposition performance data for the K-1 and K-2 BEACON catalysts are summarized in Figures 4-24 and 4-25, respectively, in terms of carbon monoxide conversion, specific deposition rate, and selectivity;

Figure 4-24. Carburation Performance of Multi-cycled K-1 Catalyst

* The inferior performance of K-2 catalyst versus that of K-1 was significantly more pronounced during these tests than during the parametric tests described in Section 4.4.2. It is conceivable that the K-2 steaming temperature was overestimated by thermocouple misplacement, but it would require about a 50°C error.

Figure 4-25. Carburization Performance of Multi-cycled K-2 Catalyst

the experimental results are also compared to the corresponding thermodynamically predicted values (assuming equilibrium controlled rates). Catalyst stability was excellent in both cases. However, the K-1 catalyst exhibited significantly higher activity than the K-2 catalyst as evidenced by the closer approaches to equilibrium-limited CO conversion and carbon deposition rate values. This occurred in spite of the fact that the K-1 catalyst was carburized at 400°C while the K-2 catalyst was carburized at 450°C. The superior performance of K-1 was also noted during parametric testing (Section 4.4.3); it was concluded then, on evaluation of the available data, that promotion of the CO disproportionation reaction was slower on K-2 than on K-1. However, P2 appears to be a viable carbon deposition promoter.

4.2.5 Performance Summary and Ranking of the K-1 and K-2 Unsupported Catalysts for SNG Production

The laboratory-scale, principally ambient pressure experimentation with unsupported, high carbon catalysts, which aimed at the identification of at least one promising unsupported catalyst system meriting scale-up, led to the following findings:

- K-1 and K-2 unsupported catalysts represented a breakthrough improvement in performance in steam gasification of BEACON carbon to SNG over that obtained with K-0 based solids (the original BEACON "baseline catalyst"). A 150° to 200°C reduction in gasification temperature for similar performance (gasification rate and methane yield) became possible through the substitution of K-1 or K-2 catalyst for K-0.
- At ambient pressure,* K-1 and K-2 catalysts promoted the steam gasification of BEACON carbon to SNG with nearly equal efficiency; if there was a slight edge, it went to K-1. At steam feed rates of one to two grams per hour per gram of carbon charge in the reactor (at the start of the test), near equilibrium operation was achieved at gasification temperatures above 575°C.
- The maximum steam gasification rates at or near equilibrium steam utilization with either K-1 or K-2 carbons at 600°C and 650°C were estimated to be:

$$R_g (600^\circ\text{C}) = 1.2 \text{ grams carbon gasified/hour/gram C in reactor**}$$

$$R_g (650^\circ\text{C}) = 2.0 \text{ grams carbon gasified/hour/gram C in reactor**}$$

These maximum batch rates are equivalent to the expected gasification rates from a continuous, steady solids flow, ambient pressure reactor system; therefore, these rate expressions may be used for the design of such system.

- K-1 was a 2 to 3 times more efficient carbon deposition promoter than K-2 when the measuring stick was the specific deposition rate or CO utilization. Promoted K-2 with Group I additives, especially P-2, approached the efficiency of the unpromoted K-1. (The P-2 additive had no measurable effect on the catalytic activity of K-1 for either carbon deposition or steaming.)

* The only steam gasification pressure used at laboratory scale.

** Rates normalized to the total solids in the reactor (carbon + catalyst) will be 20 to 30% lower. For additional specific rate value (maximum equilibrium controlled rates for the batch reactors used in these tests) refer to Figure 4-17, Section 4.3.2 of this report.

- Maximum carbon deposition rates obtained at 450°C with unpromoted K-1 and K-2 catalysts were:

$$R_{CD} \text{ (K-1, 450°C)} = \frac{8 \text{ grams C deposited/hour/gram active catalyst}}{\text{active catalyst}}$$

$$R_{CD} \text{ (K-2, 450°C)} = \frac{3 \text{ grams C deposited/hour/gram active catalyst}}{\text{active catalyst}}$$

About 90% of the feed CO was utilized with approximately 45% of the converted CO going to carbon when the reaction was promoted by K-1 (i.e., approximately 40% of the feed CO was deposited as carbon); about 20% of the feed CO was deposited as carbon when the reaction was promoted by K-2 catalyst.

(Strictly, the above rates are applicable to the 85 CO:15H₂ mole ratio feed gas; but there is evidence that they apply to lower Btu feed gas also, provided the moles of CO fed per unit time are the same.)

- Carbon deposition temperatures in the 550°C to 650°C range yielded significantly less active carbon for gasification to SNG than deposition temperatures in the 380°-450°C range. Carbon deposition pressure up to 200 psi, had no discernible effect on the steaming behavior of the product carbon.
- Multi-carbon deposition/steaming cycle testing (40 and 43 cycles) revealed excellent stability of catalytic activity for either K-1 and K-2 solids in both the deposition or gasification reactions.

The above findings suggested that both catalysts merit scale-up testing, at least for a performance scan at higher steam gasification pressures. However, through ambient pressure testing, K-1 ranked as the primary catalyst for SNG production with K-2 ranked only as the backup.

4.2.6 Development of Unsupported Catalysts for Hydrogen Production

The success of the BEACON SNG development effort led to the decision to investigate the possibility of expanding BEACON technology into the production of hydrogen. A seven month laboratory scale effort resulted in the identification of two candidate catalysts both of which, at ambient pressure, promoted hydrogen production with high selectivity at near equilibrium steam utilization (hydrogen-to-methane mole ratios in the product

gas ranged between 30 and 100, depending on the catalyst and on operating conditions). Performance at pressure is discussed in Section 5.4.

The initial approach taken was to consider using the same or slightly modified catalysts that were used in SNG production but to improve their selectivity toward hydrogen production (versus methane) by altering the gasification conditions; both thermodynamic and kinetic approaches were considered. However, early into the investigation it was decided that catalyst modification rather than major alteration of gasification conditions was the most efficient path to hydrogen selectivity.

4.2.6.1 Thermodynamic and Kinetic Approaches to Hydrogen Selectivity

Selective hydrogen production from the steam gasification of BEACON carbons requires the suppression of methane and higher hydrocarbons. The principal reactions involved in BEACON carbon-steam gasification include:

For enhanced hydrogen production, Reactions (2) and (4) must be suppressed while Reactions (3) and (5) should be accelerated and forced to the right. Several thermodynamic and kinetic potential approaches for accomplishing the above are listed in Table 4-13.

*C = catalytically active BEACON carbon

Table 4-13. Thermodynamic and Kinetic Approaches for Selective Hydrogen Production (Methane Suppression)

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

The temperature-pressure flexibility afforded by thermodynamics is depicted in Figure 4-26. The equilibrium data show that hydrogen production is favored by high temperature and low pressure gasification. However, in order to obtain acceptable hydrogen-to-methane mole ratios of 30 or higher ($\leq 2\%$ v/v methane in the dry gasification product gas) for ambient pressure gasification, reaction temperatures in excess of 800°C are required according to these data. Much higher temperatures than 800°C are required to attain a H_2/CH_4 mole ratio of even 10 at ten atmosphere pressures. Poor process thermal efficiencies prohibit the use of such high temperatures for the hydrogen production process.

Gasification with excess steam was also examined. It produced the required hydrogen selectivity, at least at ambient pressure, but the penalty in low steam utilization was too high to render such a process viable (again a case of poor thermal efficiency). The pertinent data are plotted in Figure 4-27. Several one-gram samples of K-1 based BEACON carbon were gasified with steam feedrates which varied from one to eight grams per hour. Even though the plot in Figure 4-27 shows that methane suppression began as soon as steam utilization dropped only a few percentage points, it took steam utilization values below 40% or, another way of looking at it, it took 2.5 times the theoretical steam feedrate to gasify the carbon with adequate methane suppression.

Figure 4-26. Equilibrium H₂ and CH₄ Yields for Graphite - Steam Gasification

*The values in parentheses represent the % of steam feed utilized during gasification (the theoretical value is 71%)

Figure 4-27. Correlation of Methane Yield with Excess Steam

The lower temperature and/or lower residence time approaches reduced methane yield and increased hydrogen production but again at unacceptably low steam utilizations (20-40% levels).

The observations presented above suggested that the most viable approach to hydrogen selectivity was the reduction of catalytic activity toward methanation through the direct influence on catalytic sites. The paths selected for evaluation were high temperature exposure and catalyst doping with various additives selected on the basis of known influence on the gasification reactions of coal or carbon. Testing was performed in the apparatuses and in accordance with the procedures presented in Section 4.2.1 of this report. The results are summarized in the next three sections.

4.2.6.2 Selection of Candidate Unsupported Hydrogen Production Catalysts

The screening experimentation for selective hydrogen catalysts was significantly enhanced by information derived from bench-scale testing of unsupported SNG catalysts. During the 30-cycle batch testing of the unsupported K-1 catalyst at 100 psig pressure the BEACON solids were inadvertently subjected to higher than intended temperatures for short periods of time (transients) during both the carbon deposition and steaming operations (half-cycles). The apparent effect of these temperature excursions on catalyst performance at 100 psig was minimal (small reduction in methane yield) but samples drawn from the bench-scale reactor and steamed at laboratory scale exhibited almost complete suppression of methane at ambient pressure. Chemical characterization of these samples revealed contamination of the catalyst. These observations led to the conclusion that either the increased temperature, or the contaminant elements, or both could be the means to development of an efficient hydrogen catalyst.

4.2.6.3 Thermally Treated Unsupported Catalysts

The temperature approach was examined first. The effect of high carbon deposition temperatures (550°C to 650°C) on steam gasification rates and product composition at 550°C and ambient pressure was discussed

in Section 4.4.3 of this report. It was indicated then that methane was almost completely suppressed under those conditions but that steam utilization (gasification rate) was also severely suppressed from both the theoretical value and from utilization values obtained with BEACON carbon deposited at lower temperatures (450°C or lower). Table 4-14 presents more extensive data on the effect of carbon deposition temperature on steam gasification of both K-1 and K-2 based BEACON carbons at ambient pressure. In this case, gasification was performed at 600°C (vs 550°C earlier) thus, the rates were higher and methane suppression was less. The conclusion, however, is the same: methane suppression was accompanied by a too severe reduction in thermal efficiency (steam utilization) and in gasification rate. Therefore, increase of BEACON carbon deposition temperature to effect hydrogen selectivity is not very practical.

Increased steaming temperatures did not prove to be the reason for the methane suppression observed with the 30-cycle bench scale sample or to be a valid path to development of a hydrogen production catalyst. This approach was examined with K-1 solids at laboratory scale. A sample from the catalyst loaded to the bench scale unit for the 30-cycle testing was first subjected through 5-cycles of normal temperature carbon deposition (450°C) and high temperature steaming (750°C) at atmospheric pressure to simulate abnormal thermal exposures at bench scale; then it was run through a normal temperature steaming cycle at 640°C. The data are shown in Table 4-15. It is apparent that the 750°C steaming cycles (thermal soak) did not adversely affect the ability of the catalyst to form methane at 640°C. Indeed, at 640°C the steam gasification product composition and steam utilization very closely approached equilibrium. Thus, abnormal thermal exposure did not appear to be the cause of the change in catalyst methanation activity.

4.2.6.4 Compositionally Modified BEACON Catalysts

The catalyst "doping" approach to hydrogen selectivity (and potential reason for the methane suppression observed with the bench scale catalyst) was tested by the performance of a carbon deposition-steaming cycle with a K-1 catalyst modified by the addition of the major contaminant found in the 4-inch reactor sample after 30-cycles of bench scale testing. The results are summarized in Table 4-16, first row, and are compared to the

Table 4-14. Effect of Carbon Deposition Temperature on Methane Suppression

A. K-1 Based BEACON Solids

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

B. K-2 Based BEACON Solids

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

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

Table 4-15. Effect of "Thermal Soak" on Methanation Activity of K-1 BEACON Catalyst*

Steam Gasification Product Gas Composition, Mole % Dry								
	750°C Steaming Cycles**					750°C	640°C	640°C
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Equilibrium Composition	Steaming	Equilibrium Composition
CH ₄	2.4	2.1	1.9	1.9	2.2	1.8	6.4	5.9
H ₂	47.4	46.3	46.8	46.8	46.5	50.3	50.4	50.9
CO	41.0	43.4	44.5	43.8	44.3	41.9	23.8	23.8
CO ₂	9.1	7.6	6.5	7.3	7.3	6.0	20.2	19.4
N ₂	0.1	0.1	0.2	0.2	0.2	-	0.3	0
% Steam Utiliz.	85	91	90	83	91	90.7	76	77

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

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

Table 4-16. Steam Gasification of Modified K-1 BEACON Carbon (640°C, 1 atm)

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

product gas composition and steam utilization of "unmodified" K-1 catalyst and to the same quantities predicted by thermodynamics. The data in Table 4-16 show that the "modified" catalyst suppressed methane formation severely.

Comparison of the data in Tables 4-14 and 4-15 led to the tentative conclusions that the "in situ" compositional modification of the K-1 catalyst during the 30-cycle test was the primary cause for the change in its activity toward methane formation at low pressures. Furthermore, the data in Table 4-16 revealed that methane suppression occurred at a small penalty in steam utilization; that is, the "modified" K-1 catalyst appeared to be a very promising catalyst for hydrogen production by selective steam gasification of BEACON solids, if its activity proved to be stable. Later testing revealed that this particular "modified" K-1 catalyst was not very stable, but others of similar composition proved very promising.

The evidence presented above led to the conclusion that a modified form of the K-1, or possibly K-2, SNG catalyst could be an efficient hydrogen promoter. Thus, based on the information presented above, the experience gained in the development of the K-1 solids as a BEACON SNG catalyst, and open literature data on synthesis gas processing (e.g., Fischer-Tropsch synthesis) the fractional factorial test matrix presented in Table 4-17 was formulated. The screening matrix was based on five

Table 4-17. Hydrogen Production Catalyst Development Test Matrix (Laboratory-Scale Testing)

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

- Nominal test conditions: Deposition - Ambient pressure, 450°C
Steaming - Ambient pressure, 600°C
Quantity of solids cycled between 1.0g + 0.2g + 1.0 grams

composition variables (including the base component K-1) and four concentration levels, five methods of preparation variables, and three methods of pretreatment; at least two of the most promising catalysts will be subjected to two additional variables at bench scale: steam feedrate and pressure. Twenty catalysts were prepared to cover the composition variables and levels and the various methods of preparation; seven of these catalysts were also "pretreated" prior to testing, generating another ten samples for testing. These thirty samples permitted the scanning of all the variables at one to four levels at a minimum number of tests.

Emphasis was placed on modifying the most active of the BEACON SNG catalysts, K-1,* and on Additive F which the testing described above revealed to be an effective methane suppressant. Additives K-2, X, and Y were selected either because they were present as contaminants in the bench scale, 30-cycle sample which exhibited methane suppression tendencies, or because the open literature suggested them to be methane suppressants. The methods of preparation were selected because of their expected influence on the degree of mixing of the catalyst components and on "crystal" size. The pretreatment techniques were selected principally for their potential effect on catalytic sites (valence, defects, elemental arrangement). Most tests were planned at low levels of additive under the assumption that methane suppression sensitivity to parametric changes will be highest at low concentrations of additive. The data presented in Tables 4-15 and 4-16, above, were generated with Catalysts No. 1 and No. 3, respectively.

Each catalyst was subjected to a minimum of two carbon deposition (450°C) - steaming (600-650°C) cycles during the screening tests. In each cycle, carbon was gasified until steam utilization (gasification rate) dropped below 40%; that is, virtually all the active carbon was gasified in each cycle. This "deep" cycling aimed at quickly identifying catalyst activity deterioration and the buildup of inactive or less active carbon (to be labeled here as "residue"). The criteria for success during the ambient pressure screening tests were: near equilibrium steam utilization

*The K-1 catalyst exhibited the best performance in SNG testing, including the highest BEACON carbon gasification rate.

(gasification rate) at 600° to 650°C temperature range, greater than 80% methane suppression, and at least 50-cycle stability with or without catalyst regeneration. Regeneration, if needed, was to involve a simple procedure such as gasification of the inactive carbon at a few degrees higher steaming temperature. Every catalyst that met or approached this criteria was subjected to additional deposition-steaming cycles to identify potential changes in performance (trends). The two most promising catalysts were subjected to 50-cycle stability testing* and to pressure testing at bench scale. Barring performance failure, the best of these two catalysts will be subjected to a minimum of 250 hours simultaneous deposition-steaming testing in the quasi-steady state, fluid bed Tandem Reactor System during the next phase of the BEACON program.

Catalysts No. 6 and No. 11 were the only catalysts that met all the criteria of success listed above. Catalyst No. 5 could be a third candidate if an efficient regeneration technique is developed. The other 17 catalysts failed principally for one or more of the following three reasons: a) they did not suppress methane to an acceptable level, b) they suppressed methane but at low steam utilization (low gasification rate), and c) they accumulated "inactive" carbon residue, i.e., they failed the stability test.

All of the catalysts tested were unsupported BEACON type catalyst, i.e., they were high carbon content BEACON solids. They were prepared in small quantities specifically for this screening. The successful preparations, Catalysts Nos. 6 and 11, were duplicated in order to verify reproducibility of catalyst preparation. Also, most of the carbon deposition/steaming tests were performed in duplicate for at least the first two cycles to increase the level of confidence in the evaluation.

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

The carbon deposition and steaming runs were performed in the ambient pressure U-type reactors* at 450°C and 600°C to 650°C, respectively.

Catalysts No. 1 and No. 2 were unmodified K-1 type SNG catalysts which differed only in method of preparation. Catalyst No. 1 was prepared by the same technique as the SNG catalysts described in Section 4.2.1; Catalyst No. 2 was prepared by the most commonly used technique in the preparation of the candidate hydrogen catalysts ("Method B"). Neither of these catalysts suppressed methane, but both were excellent SNG catalysts of identical efficiency; thus, "Method B" of preparing BEACON catalysts had no influence on catalyst selectivity toward hydrogen.

Catalysts No. 3 through No. 6 furnished data on the effectiveness of Additive F and on the effect of its concentration on methane suppression; the effect of catalyst pretreatment was also examined with this group of catalysts. All of them exhibited good methane suppression (high hydrogen selectivity) at near equilibrium steam utilization but except for Catalyst No. 6 failed the stability test. Stability in catalytic activity decreased with increasing level of Additive F; Figure 4-28 illustrates the point (stability is measured in terms of the relative quantity of inactive carbon build-up on the catalyst, "residue"). The data show that Catalyst No 3 lasted 6 cycles before the build-up in inactive carbon reached an unacceptable level; Catalyst No. 4 lasted 14 cycles and catalyst No. 5 lasted twenty. Table 4-18 presents the data generated with Catalyst No. 5 (K-1 + 20% Additive F, Type B catalyst) in more detail in order to illustrate the limited attempts made to identify an efficient regeneration technique for these catalysts.** The data show very good methane suppression and good agreement of experimental data (product gas composition and steam utilization)

* Refer to Section 4.4.1 for apparatus and procedure descriptions.

** High temperature steaming was only partially successful as a regeneration technique; however additional regeneration testing was not pursued because candidate hydrogen catalysts were identified which did not require regeneration.

AMBIENT PRESSURE, 450°C/600°C
TYPE B, MODIFIED K-1 CATALYSTS

Figure 4-28. Effect of Additive F on K-1 Catalyst Stability

Table 4-18. Stability Testing of Catalyst No. 5 (K-1 + 20 Wt % Additive F, Type B) - Ambient Pressure Steaming*

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

* Between steamings carbon was deposited at 45°C.

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

with the "zero methane equilibrium" data.* The data also show that the "residue" remained tolerable through 15 cycles but by the 20th cycle approximately 90% of the deposited carbon could not be steam gasified at acceptable steam utilization rates at the 600 to 650°C temperature range. The catalyst was regenerated by steam gasification of the residue at 750°C, but after an additional four cycles in the 600-650°C range the residue increased to 0.9 grams again (it was up to 0.5 grams after two cycles).

Details on the performance of Catalyst No. 6 are presented in the next section where the 50 cycle data from the most promising candidate hydrogen catalysts are reported.

Catalyst pretreatment had no discernible effect on the performance of any of the catalysts in this group.

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

Catalyst Nos. 8, 12 and 14 and Catalyst Nos. 9 and 13 yielded almost identical data to Catalyst No. 5 and Catalyst No. 6, respectively, strongly suggesting that the methods of catalyst preparation, except for method of preparation C, had no effect on BEACON carbon gasification.

Catalyst No. 10 failed the stability criterion but it is believed that the failure was due to faulty preparation procedure which yielded a very unhomogeneous catalyst.

* The first and second columns of Table 4-20 list the expected product gas compositions and steam utilizations under equilibrium conditions when: a) methane is permitted to form, and b) methane is not allowed to form (complete suppression or "zero" methane equilibrium); these compositions were computed from thermochemical data.

Catalyst No. 11, which is very similar to No. 10, was the second catalyst that met all the criteria of success for a promising hydrogen production promoter. Details on the performance of this catalyst are presented in the next section (50 cycle data).

Data generated with Catalyst No. 15 (Table 4-19) revealed that the incorporation of Additive K-2 into the K-1 SNG catalyst had no apparent effect on hydrogen selectivity (methane suppression). However, Catalyst No. 15 appears to be a very good methanation catalyst. Even after subjecting the catalyst to 800°C temperature for over one hour (Cycle 3), there was no hint of methane suppression. There was a 20% drop in product gas methane concentration between the first and second cycles at 600°C, but then methane stabilized at a very high value. In fact, above 600°C steam gasification yielded equilibrium product compositions (compare first six columns of Table 4-19 to the last three). Similar results were obtained with Catalyst No. 16.

Additive Y, Catalyst Nos. 17, 18, 19 and 20, suppressed methane when added to K-1, but it also reduced the carbon deposition rate by an order of magnitude from that obtained with the unmodified K-1 catalyst or with K-1 catalysts "doped" with K-2 or F additives. Tests with this group of catalysts were discontinued before much cycling was done because of the extreme difficulty encountered in carburization.

In general, the physical properties of the above catalysts were very similar. The only exception was a 30% higher bulk density exhibited by the samples "doped" with Additive X and prepared by "Method B."

The fundamental reason for the differences in reactivity and selectivity observed among the catalysts in Table 4-17 could not be delineated from the testing performed. A fundamental investigation into the mechanism of the observed selectivity was out of the scope of this program.

Table 4-19. Effect of K-2 Additive on Methane Suppression (Type B, K-1 Catalyst)*

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

* Between steamings carbon was deposited at 450°C.

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

4.2.6.5 Multi-Cycle Data on Promising Candidate Catalysts

The testing described in the previous section identified two catalyst compositions which appeared to be strong candidates to meet the stability criterion for catalytic activity described earlier; they were Catalysts Nos. 6 and 11 in Table 4-17.

The catalyst stability tests consisted of carbon deposition/steaming cycles. The aim for each candidate catalyst was to demonstrate stable, virtually constant catalytic activity for at least 50 cycles, preferably without the need for regeneration. At least 80% methane suppression and near equilibrium steam utilization were required. Carbon deposition was effected at 450°C and steaming at 600°C-620°C under ambient pressure. Deposition was stopped when the BEACON solids weight (principally carbon) reached approximately one gram and steaming was discontinued when steam utilization dropped below 50%. The solids weight which remained in the reactor after steaming was stopped was labeled the "residue"; it consisted of the inorganic portion of the catalyst and of carbon which would not steam gasify at practical steam utilization rates at the particular steaming temperature (mostly 600°C).

Catalysts Nos. 6 and 11 met the 50 cycle stability requirement without the need for regeneration. The results are summarized in Figures 4-29 and 4-30 and in Tables 4-20 and 4-21.

Figure 4-29 shows the degree of methane suppression (comparison of the equilibrium value to methane concentration obtained in each of the 50 cycles), the percent steam utilization obtained versus predicted, and the build up of "residue" solids as a function of cycle number for Catalyst No. 6. The data show very good stability in catalyst performance through 50 carbon deposition/steaming cycles. Methane concentration in the product gas, top section in Figure 4-29, remained constant at 1.5 ± 0.5 % v/v* after the first steaming (versus 8.8% v/v predicted by thermodynamics); this is an average 83% methane suppression. Steam utilization, middle section in Figure 4-29, was also constant throughout the 50 cycles and very close to

* Methane concentration was about 2% at the start of steaming but as carbon was being consumed it dropped to about 1% without a measurable drop in steam utilization.

* The temperature was raised to 620°C near the end of the run

** Steamed at 650°C

Figure 4-29. Performance Stability Data on Catalyst No. 6 (50-Cycle Steaming Data at 600°C and Ambient Pressure)

○ 600°C steaming; △ 620°C steaming; * 620°C at end of run only

Figure 4-30. Performance Stability Data on Catalyst No. 11 (50-Cycle Steaming Data at 600°C and Ambient Pressure)

Table 4-20. Stability of Product Gas Composition With Catalyst No. 6
(50 Cycles at Ambient Pressure)

Specie	Composition Predicted By Thermodynamics (600°C)		Product Gas Composition, % v/v, Versus Cycle No. Steaming at 600°C, Ambient Pressure						
	Normal	Zero Methane	Cycle 1	Cycle 5	Cycle 10	Cycle 20	Cycle 30	Cycle 40	Cycle 50*
CH ₄	8.8	0	4	2	2	2	1.5	1.5	1.5
H ₂	49.3	61.3	56	59	59	59	59	59	59
CO	16.7	16.1	17	16	16	16	16	16	16
CO ₂	25.2	22.6	23	23	23	23	23	23	23
% Steam Utilization	71	66	66	66	65	65	65	65	65
Residue (Grams)	-	-	0.17	0.23	0.27	0.24	0.20	0.40	0.42

* During a last cycle (Cycle 51), the temperature was raised to 650°C and the residue decreased to 0.20 grams.

Table 4-21. Stability of Product Gas Composition With Catalyst No. 11
(50 Cycles at Ambient Pressure)

Specie	Composition Predicted (By Thermodynamics (600°C))		Product Gas Composition, % v/v, Versus Cycle No. Steaming at 600°C, Ambient Pressure						
	Normal	Zero Methane	Cycle 1	Cycle 2	Cycle 10	Cycle 20	Cycle 30	Cycle 40	Cycle 50 (620°C)
CH ₄	8.8	0	7	1.5	<1	<1	<1	<1	<1
H ₂	49.3	61.3	52	59	60	60	60	60	60
CO	16.7	16.1	16	16	17	17	16	17	19
CO ₂	25.2	22.6	25	23	22	22	23	22	20
% Steam Utilization	71	66	69	65	66	66	65	65	70
Residue (Grams)	-	-	~0.10	0.13	0.34	0.46	.52	0.44*	0.32

* Temperature increased to 620°C at end of run.

the equilibrium predicted value of 66%; the $\pm 1\%$ unit fluctuation was probably due to $\pm 5^\circ\text{C}$ temperature variance than to activity variance. The bottom section of Figure 4-29 shows that the "residue" remained constant in a range of 0.25 ± 0.05 grams through the first 30 cycles and then increased to a new range of 0.35 ± 0.05 during the remaining 20 cycles. At the end of Cycle 39 the temperature was raised to 620°C and the "residue" weight dropped to 0.25 grams; also, a 51st cycle was performed with the temperature raised to 650°C at the end of steaming and the "residue" dropped to 0.2 grams. In both these cases the temperature was raised to verify that the residual carbon could be steamed virtually completely at slightly higher temperatures; i.e., the "residue" did not consist of "dead" carbon.*

Table 4-20 presents data on the stability of product gas composition during the 50 cycle testing with Catalyst No. 6. According to these data not only the product gas composition was constant throughout the 50 cycles but the agreement with the thermodynamically predicted composition for suppressed methane equilibrium was excellent. It should be noted that the methane-to-hydrogen ratio was increased from 5.6 (normal equilibrium) to >30 by the selectivity of Catalyst No. 6.

Figure 4-30 and Table 4-21 summarize the 50 cycle data generated with Catalyst No. 11. Very good performance stability was obtained with this catalyst, also. Actually, this catalyst exhibited slightly higher selectivity (>50 hydrogen-to-methane ratio) than Catalyst No. 6, but it also yielded higher "residue." In order to keep the "residue" below 0.5 grams the last 5 cycles were steamed at 620°C . It may be that this catalyst will perform better at 620°C than at 600°C in the ambient pressure production of hydrogen.**

Based on the above data both these catalysts merit further development.

* It is conceivable that this extra residue built-up was due to apparatus deficiencies, e.g., carbon packing during deposition, rather than 20°C deterioration in catalytic activity.

** It is conceivable that carbon deposition in a fixed bed gives rise to "packed carbon" which causes the observed increase in "residue" formation and that the apparent 20°C reduction in activity is not real (see footnote on Catalyst No. 6, also).

4.2.6.6 Performance Summary and Ranking of Selected Unsupported Catalysts for Scale-Up Testing

The laboratory scale effort for the identification of candidate catalysts for the selective production of hydrogen from the steam gasification of BEACON carbon led to the following findings:

- K-1 based SNG catalysts modified by appropriate additives can be converted into selective hydrogen production catalysts.
- Additive F was found to be the most effective promoter of hydrogen selectivity (methane suppression).
- Additive F concentration was the parameter of most significance to the stability of catalytic activity.
- Additive X did not promote hydrogen selectivity when used alone with K-1 but it was synergistic with F when used together.
- K-2 additive had no effect on the selectivity of K-1.
- Y additive suppressed methane formation in K-1 catalyst but it also suppressed the carbon deposition rate during carburization to impractical values.
- The method of catalyst preparation had a very minor effect on hydrogen selectivity provided the catalyst was subjected to at least 400°C during the decomposition or oxidation step.
- Two catalysts were identified as meriting development at bench-scale: K-1 SNG catalyst promoted with 10% by wt F additive (Catalyst No. 6) and K-1 promoted with 10% by wt F + 5% by wt X additives (Catalyst No. 11). These catalysts suppressed methane by more than 80% giving rise to a hydrogen-to-methane mole ratio in the product gas in excess of 30 at near equilibrium steam utilization rates.
- The maximum gasification rates obtained at 600°C and ambient pressure were about the same as those obtained with the K-1 and K-2 SNG catalysts; that is, approximately 1.2 grams carbon gasified per hour per gram carbon in the reactor.
- Both Catalyst Nos. 6 and 11 met the requirement of stable performance through 50 cycles of carbon deposition and steaming at near equilibrium steam utilization.

- Catalyst No. 11 exhibited a little higher selectivity than Catalyst No. 6 but it also seemed to require about 20°C higher steaming temperature than No. 6 in order to keep inactive carbon from building up in the reactor.
- Ranking of these two catalysts at this scale of development is difficult. Catalyst No. 11 may have an edge over No. 6 because of its higher selectivity.

5. BENCH-SCALE TESTING

Four bench-scale units were built and operated during this program. For testing and evaluating supported catalysts a 1-1/2 inch diameter and a 3-inch diameter unit were used. Unsupported catalysts were tested in a 4-inch diameter, high pressure batch reactor and later studied in a Tandem Reactor System where both BEACON reactions are operated at the same time. This system also had the capability of transferring catalyst solids from one reactor to the other.

5.1 BENCH-SCALE TESTING OF SUPPORTED CATALYSTS

A system was designed into which different reactors could be installed. Three such reactors were built and tested: 1) 1-1/2 inch diameter unit without a stirrer, 2) 1-1/2 inch diameter unit with stirrer, and 3) a 3-inch diameter unit without stirring. The best results were obtained with the 1-1/2 inch diameter unit with a stirrer. The same unit without the stirrer did not operate satisfactorily. The 3-inch diameter reactor operated reasonably well but the data were not as smooth and reproducible as that obtained with the 1-1/2 inch diameter unit with a stirrer.

5.1.1 Equipment

Figure 5-1 shows a schematic of the BEACON bench-scale test system for testing supported catalysts. The gas feed section can produce a feed containing nitrogen, hydrogen, carbon monoxide, carbon dioxide and methane. A separate nitrogen line for reactor purge was provided and another nitrogen line was used to fluidize the sand bath which heated the reactors. A bypass line allowed bypassing feed gas around the reactor for the determination of gas flow rate and composition.

The water feed section pumped water from one of two reservoirs through a vaporizer and a heated line into the reactor. Provision for nitrogen feed into the water feed was included.

Figure 5-1. BEACON Bench-Scale Test System for Supported Catalysts

The reactor section in Figure 5-1 is shown as a block. Either a 1-1/2" diameter unit, with or without stirrer, or a 3" diameter reactor could fit into this block interchangeably.

The reactor effluent passed through a cold water condenser and then a Dry Test Meter (DTM) gas volume totallizing meter. The effluent was sampled continuously by a Carle-111H gas chromatographic unit (GC) and vented outside the building.

Figure 5-2 shows a diagram of the 1-1/2" reactor. At the bottom of the reactor the feed gas is distributed by a sintered ceramic disk made by Ferro, Inc. The reaction section of the reactor is 21" tall and the sand bath covers 17" of this distance. The stirrer shown in Figure 5-2 has five paddle sets. Of these, four are in the 17" heated section. The stirrer shaft is sealed by a double mechanical seal with graphite packing and the shroud over the inner seal is pressurized with nitrogen to prevent loss from the reactor. This nitrogen purge does result in a dilution of the effluent, usually to about 20%. The total volume of the reactor is 1250 cc. When the stirrer was not used a central thermocouple well held thermocouples at 1", 13", 23" and 30" above the disk of the reactor. The reactor temperature for the unstirred configuration was taken as the temperature recorded on the thermocouple 1" above the disk. When stirrers were used the sand bath temperature was taken as the reaction temperature. The bath and the 1" central thermocouple usually were within $\pm 30^{\circ}\text{C}$.

Figure 5-3 is a diagram of the 3" reactor showing thermocouple positions. The 3" section of this reactor is 49" tall and the reactor is heated by three resistance wire heaters of 1,000 watts each. The two lower heaters (zones 1 and 2) each heated 17" of the reactor and the upper heater (zone 3) heated the top 34" which included the expansion section of the reactor. The reaction temperature was taken as that shown by the central thermocouple 2" above the distribution disk.

5.1.2 Procedures

Operation of this BEACON bench-scale system was organized by "runs." A run involved charging the catalyst, activating at elevated temperature,

Figure 5-2. BEACON 1.5-Inch Reactor With Stirrer

- ◇ = ZONE HEATER CONTROL POINTS
 1, 2, 3, 4, 5 = CENTRAL WELL TC's
 6, 7, 8, 14 = INTERNAL TC's, 1 IN. THRU WALL
 9, 10, 12 = SKIN TC's

Figure 5-3. The BEACON 3-Inch Reactor
Showing Thermocouple Positions

followed by (usually alternating) cycles of carbon deposition and steaming. Two batches of K-2 C77 catalyst were made.

1. Batch 9313 - 15/16 was made in June 1981.
2. Batch 9997 - 22/1 was made in September 1982.

The feed gas rates were set by rotameters in the gas feed section. The total flow rates and gas compositions were checked by bypassing the reactor and going directly to the DTM and GC. The water feed was set by the pump control and checked and monitored by the fall in the water feed reservoir. A cycle is started when the reactor temperature and pressure is lined out by cutting off the purge gas and admitting the feed gas to the reactor. During a cycle data were taken on the system temperatures and pressures, exit gas composition and flow rate, and account was kept of the carbon laydown or uptake by the difference in the carbon content of the feed and exit streams.

5.1.3 Results

The principal engineering result of this work was that two of the three reactor designs studied gave satisfactory performance without bed sintering problems. The 1-1/2" diameter unit with a stirrer also suppresses fluidization problems. The 3" diameter reactor did not exhibit any sintering but did emphasize fluidization problems. While the work emphasized the demonstration of continuous operation over multiple cycles, some parametric variations studies were performed. A summary of these results follows.

Tables 5-1 through 5-8 show conditions for the major runs exemplifying the operation of the 1-1/2" and 3" reactors. Time average conditions over the run are reported. The deposition and gasification rates are expressed in grams of carbon per gram of active catalyst per hour. For deposition average rates are given but for gasification the rate generally declined with time. Therefore the average rate is largely a function of how long the cycle was extended and as a result either the maximum rate alone or both the maximum and average rates for steaming are given. The gas feed

Table 5-1. Run M Conditions and Results (1.5-Inch Reactor Without Stirrer)

Deposition	1	2	3I	II	III	4	5	6	7	8	9	10
Duration, Min.	345	242	88	99	286	594	352	374	330	352	374	385
Temperature, °C	401	443	413	411	415	410	460	452	453	449	449	451
Pressure, Psig	10	10	10	10	10	10	10	10	10	10	10	10
Catalyst Mass, gm	175	175	175	175	175	175	175	175	175	175	175	175
Gas-In, Std cc/Min	1279	1279	1264	1350	1319	1302	1303	1344	1336	1333	1331	1305
% H ₂	5.45	5.36	2.54	3.45	6.02	5.30	5.50	5.89	5.61	5.77	5.61	6.32
% N ₂	70.75	69.8	70.8	20.2	69.3	69.5	69.8	69.5	69.6	69.0	69.6	69.0
% CO	23.79	24.9	25.6	25.3	25.8	25.2	24.7	24.9	24.8	25.3	24.8	24.7
Rate, g-C/g-Active Catalyst-Hr	0.14	.16	.08	.18	.10	.067	.12	.12	.13	.12	.11	.12

Steaming	1	2	3	4	5	6	7	8	9
Duration, Min.	143	242	550	453	440	506	616	616	509
Temperature, °C	555	560	559	559	549	549	547	542	543
Pressure, Psig	10	10	10	10	10	10	10	10	10
N ₂ In, Std cc/Min	716	736	708	736	739	736	739	730	730
H ₂ O In, Std cc/Min	398	307	353	374	368	368	368	370	368
Rate, Average	.19	.16	.11	.10	.10	.086	.069	.072	.083
Rate, Maximum g-C/g-Active Catalyst-Hr	.20	.19	.13	.12	.12	.12	.11	.12	.12

Table 5-2. Runs N and P Conditions and Results (1.5-Inch Reactor Without Stirrer)

Deposition	N1	N2	N3	N4	N5	P1	P2
Duration, Min	374	132	154	88	77	176	114
Temperature, °C	452	455	493	517	468	459	436
Pressure, Psig	10	10	10	10	10	10	10
Catalyst Mass, gm	175	175	175	175	175	82	82
Gas In, Std cc/Min	1331	1380	1416	1609	1655	1349	1357
% H ₂	5.56	9.1	12.9	14.4	13.6	10.8	10.5
% N ₂	69.9	50.8	29.2	27.9	27.8	29.5	29.6
% CO	24.6	40.1	58.0	57.7	58.4	59.6	59.9
Rate, Average g·C/g·Active Catalyst-Hr	.16	.28	.23	.47	.48	.72	.70
Steaming	N1	N2	N3	N4	N5	P1	P2
Duration, Min	99	165	176	220	286	118	242
Temperature, °C	544	545	516	508	515	490	518
Pressure, Psig	10	10	10	10	10	10	10
Gas In, Std cc/Min	396	368	468	461	0	376	374
Water In, Std cc/Min	724	730	383	922	942	688	665
Rate, Average	.20	.26	.12	.18	.076	.36	.34
Rate, Maximum g·C/g·Active Catalyst-Hr	.28	.27	.14	.18	.45	.42	

Table 5-3. Run Q* Conditions and Results (1.5-Inch Reactor)

Deposition	1	2	3	4	5	6	7	8	9	10
Duration, Min	132	77	64	55	66	55	77	57	66	44
Temperature, °C	409	400	404	400	404	450	454	450	454	450
Pressure, Psig	10	10	10	10	10	1	1	2	2	2
Catalyst Mass, gm	82	82	82	82	82	82	82	82	82	82
Gas In, Std cc/Min	1287	1416	1444	1392	1388	1339	1315	1359	1290	1362
% H ₂	10.4	11.1	10.9	10.9	11.1	13.2	14.4	13.6	13.3	14.0
% N ₂	30.3	30.3	29.7	28.6	29.1	27.8	28.3	28.7	28.7	28.1
% CO	59.2	58.6	59.4	60.5	59.5	58.8	57.4	57.6	58.0	57.9
Rate, Average g-C/g-Active Catalyst-Hr	0.65	.82	.65	.85	.79	.81	.71	.78	.72	.95

Steaming	1	2	3	4	5	6	7	8	9
Duration, Min	297	121	91	103	106	93	118	148	132
Temperature, °C	576	570	570	570	572	550	550	550	550
Pressure, Psig	10	10	10	10	10	2	2	1	2
Gas In, Std cc/Min	378	378	419	379	403	353	373	358	361
Water In, Std cc/Min	681	899	808	1027	697	703	724	718	724
Rate, Average	.42	.83	.63	.57	.41	.42	.39	.40	.40
Rate, Maximum g-C/g-Active Catalyst-Hr	.57	.88	.73	.59	.62	.49	.43	.48	.46

* Stirrer used.

Table 5-4. Run E Conditions and Results (3-Inch Reactor)

Deposition	1	2	3	4	5	6	7	8	9	10
Duration, Min	135	50	60	60	90	170	114	115	90	140
Temperature, °C	450	450	449		457	376	453	468	431	459
Pressure, Psig	0	0	0		0	0	0	0	0	0
Catalyst Mass, gm	475	→								
Gas In, Std cc/Min	7760	7731	7684		7845	7942	7858	7873	7873	7845
% H ₂	13.3	14.0	13.8		13.3	13.7	13.2	13.8	13.8	13.8
% N ₂	28.4	29.0	27.6		28.1	27.9	28.2	27.8	27.8	27.8
% CO	58.3	57.0	58.6		58.6	58.5	58.7	58.5	58.5	58.5
Rate, Average g·C/g·Active Cat.-Hr	.89	.70	.68		.53	.23	.44	.35	.36	.25
Steaming	1	2	3	4	5	6	7	8	9	10
Duration, Min	90	98	100	88	100	123	100	80	130	120
Temperature, °C	535	543	535	542	542	505	530	545	474	500
Pressure, Psig	0	0	0	0	0	0	0	0	0	0
Gas In, Std cc/Min	2804	2856	2785	2851	2874	2835	2813	2955	2955	2955
Water In, Std cc/Min	4233	4055	4212	5588	4140	4026	3943	4129	4337	4005
Rate, Maximum g·C/g·Active Cat.-Hr	.51	.47	.38	.50	.48	.43	.47	.47	.54	.45

Table 5-5. Run F Conditions and Results (3-Inch Reactor)

Deposition	1	2	3	4	5	6	7	8	9	10
Duration, Min	106	90	98	135	100	110	90	80	120	110
Temperature, °C	446	469	501	458	452	459	457	472	461	471
Pressure, Psig	0	0	0	0	0	0	0	0	0	0
Catalyst Mass, gm	510	→								
Gas In, Std cc/Min	7957	8100	7844	7759	7844	7872	7844	8127	7844	7844
% H ₂	13.3	13.6	13.8	13.3	13.3	13.3	13.3	13.6	14.1	13.3
% N ₂	27.6	27.7	27.7	27.3	27.3	27.3	27.2	27.9	27.6	27.3
% CO	59.0	58.7	58.5	59.4	59.4	59.4	59.4	58.5	58.3	59.6
Rate, Average g·C/g·Active Cat.-Hr	.52	.41	.45	.42	.41	.40	.41	.47	.34	.06

Steaming	1	2	3	4	5	6	7	8	9	10
Duration, Min.	60	100	150	100	110	120	120	110	110	50
Temperature, °C	530	530	532	531	538	539	545	539	542	540
Pressure, Psig	0	0	0	0	0	0	0	0	0	0
Gas In, Std cc/Min	2860	3144	3100	3100	2830	2830	2830	2830	2830	2830
Water In, Std cc/Min	4241	4280	4333	4360	4350	4300	4207	4600	4500	4500
Rate, Maximum g·C/g·Active Cat.-Hr	.52	.54	.43	.50	.43	.46	.46	.44	.55	.46

Table 5-6. Run G Conditions and Results (3-Inch Reactor)

Deposition	1	2	3	4	5	6	7	8	9	10
Duration, Min	60	90	70	60	60	20	40	60	60	60
Temperature, °C	429	461	413	461	478	440	426	426	479	456
Pressure, Psig	0	0	0	0	0	0	0	0	0	0
Catalyst, gm	510									
Gas In, Std cc/Min	3115	12600	7815	3002	14987	3313	3172	3058	13875	6275
% H ₂	13.4	19.3	13.3	12.2	14.1	13.4	12.7	12.8	19.8	9.7
% N ₂	26.5	27.7	27.3	27.0	28.6	26.5	28.0	26.8	28.1	26.9
% CO	60.1	53.0	59.4	60.8	57.4	60.1	59.3	60.4	52.2	34.7
Rate, Average g·C/g·Active Cat.-Hr	.23	.12	.27	.26	1.02	.24	.21	.23	.42	.21

Steaming	1	2	3	4	5	6	7	8	9
Duration, Min	80	120	80	80	100	90	70	225	170
Temperature, °C	540	512	500	531	542	509	485	545	542
Pressure, Psig	0	0	0	0	0	0	0	0	0
Gas In, Std cc/Min	2830	2662	2830	3200	2900	2800	2830	2860	2860
Water In, Std cc/Min	5254	4020	4380	4210	4110	1135	4030	2880	2980
Rate, Maximum g·C/g·Active Cat.-Hr	.44	.36	.36	.26	.27	-	.36	.22	.40

Table 5-7. Range of Conditions and Results (1-1/2 Inch and 3-Inch Bench-Scale Reactors)

Run	M	N	P	Qa ²	Qb ²	E	F	G
Reactor Diameter, Inch	1.5	1.5	1.5	1.5	1.5	3	3	3
Catalyst, gm	175	175	82	82	82	475	510	510
<u>Depositions</u>								
Temperature, °C	443-460 ¹	452-517	436-459	400-409	450-454	431-459 ³	446-471 ⁵	413-479
Pressure, Psig	10	10	10	10	1-2	0	0	0
Velocity, afps	.09-.10	.10-.13	.10-.102	.09-.10	.15-.16	.24-.26	.25-.27	.10-.49
C-Fed.*	.39-.41	.40-1.14	1.9-2.0	2.0-2.2	2.0	2.0-2.1	1.9-20	.77-3.0
SDR,* Average	.11-.16	.16-.48	.70-.72	.65-.85	.71-.95	.25-.89	.34-.52	.12-1.0
% CO Use	63-95	58-95	75-86	81-95	84-89	36-90	42-63	34-74
<u>Steamings</u>								
Temperature, °C	542-560	508-545	490-518	570-576	550	500-545 ⁴	530-545	485-545
Pressure, Psig	10	10	10	10	1-2	0	0	0
Velocity, afps	.062-.064	.078-.113	.03	.09-.123	.14	.23-.25	.25-.26	.23-.29
H ₂ O Fed,*	.56-.73	1.3-1.7	2.6-2.7	2.7-4.0	2.8	2.7-2.9	2.7-2.3	2.4-3.3
SUR,* Maximum	.11-.20	.14-.28	.42-.45	.57-.88	.43-.50	.43-.551	.43-.55	.22-.44
% H ₂ O Use	26-49	12-39	29-32	39-66	41-51	36-46	38-47	24-41

* Units - g·C/g·Active Cat.-Hr.

¹ Excluding Cycles 1, 3 and 4.

² Qa = Cycles 1-5, Qb = Cycles 6-10.

³ Excluding Cycles 4 and 6.

⁴ Excluding Cycles 4 and 9.

⁵ Excluding Cycles 3 and 10.

and water feed rates are given in standard cubic centimeters per minute. The performance of the 1-1/2" unit without stirring was the objective of Runs M, N and P, that of the 1-1/2" unit with a stirrer of Run Q and that of the 3" unit of Runs E, F and G.

Table 5-7 summarizes the ranges of conditions and responses for all of these runs. Run Q was separated into parts "a" "b," which differed markedly in temperature, pressure and velocity. Velocity is in actual feet per second (afps) at the reaction conditions. Specific deposition rate (SDR) and specific uptake rate (SUR) are given in grams of carbon per gram of active catalyst per hour.

Excluding Cycles 1, 3 and 4, which were run at lower temperatures, the other M cycles were reasonably smooth and gave generally reproducible performances. However, on opening the reactor at the end of the run, the catalyst bed seemed to be an agglomerated sintered mass together with a central "rat hole."

Run N was done with varying gas velocities, gas compositions and temperatures to see if some mode of operation might avoid the sintering. Such was not the case.

Run P used a much smaller catalyst mass with most of the other conditions remaining generally the same. Quite good rates were obtained in comparison with runs M and N. However, a problem with a seal in the reactor cut the run short after two cycles. When the reactor was opened no bed sintering had occurred during these two cycles.

Run Q was performed with a stirrer installed and the main result was that bed sintering was eliminated. In addition the operation was steady with time during a cycle and when the operating conditions were the same, results were reproducible from cycle to cycle. These improved operating characteristics afforded higher confidence in the data obtained from the unit. The results are more likely to relate to fundamental process variables-temperature, pressure, velocity, gas composition and bed height.

With the introduction of the stirrer in the 1.5" unit and the use of a smaller catalyst bed, good average specific deposition rates were obtained and the percentage of carbon monoxide usage was attractive. In the steaming step, thermodynamic constraints suggest the maximum water conversions possible for particular conditions of temperature, pressure and steam/nitrogen ratio. Table 5-8 shows this comparison. It shows that for the higher specific uptake rates the experimental conversion is from 78% to 96% of the theoretical thermodynamic conversion.

In the 3" reactor, Run E showed a progressive drop in deposition rates from cycle to cycle. Run F, a repeat of Run E, showed quite steady rates from cycle to cycle except for a disturbingly low rate in F10E. The steaming rates for both Runs E and F were reasonably consistent and reproducible. In Run G the temperature and gas feed rates of the deposition cycles were varied and yielded expected variations in the specific deposition rate. In the steaming cycles of Run G, variations of temperature, steam feed rate and gas feed rate were introduced to detect their influence on the specific uptake rate of carbon.

5.1.4 Conclusions

1. Design modifications of the 1-1/2" reactor which allowed good operating characteristics were: a) alonizing
b) a centered ceramic distributor disk, and c) a low RPM stirrer.
2. The ceramic disk had a limited operating life of around 200 hours.
3. The advantage of the stirrer is that a wider range of gas velocity can be used to yield steady rates.
4. Operation of the 1-1/2" reactor at "standard" conditions (2 ft bed height, 0.15 fps velocity) give reaction rates lower than the laboratory 1" unit on a grams of carbon deposited per gram of active catalyst per hour basis. This probably is due to the laboratory unit using a lower bed height.
5. The 3" reactor did not show the bed sintering problems found in the 1-1/2" reactor without a stirrer.

Table 5-8. Comparison of Equilibrium Steam Conversion
and Observed Steam Conversion

Cycle	Pressure	Temperature	% H ₂ O Fed	% H ₂ O Use	Equilibrium % H ₂ O Use
M1S	10	555	36	62	67*
2	10	560	33	65	68*
3	10	562	32	52	68*
4	10	560	34	46	68
5	10	550	33	46	67
6	10	548	33	46	67
7	10	544	33	41	66
8	10	542	34	47	66
9	10	542	34	47	66
N1S	10	543	65	51	63*
2	10	544	66	49	63*
3	10				
4	10	508	67	40	59
5	10				
P1S	10	492	65	43	57
2	10	518	64	40	60
Q1S	10	577	64	56	65*
2	10	570	71	66	64*
3	10	570	65	61	65*
4	10	570	73	38	64
5	10	573	63	60	66*
6	10	550	67	49	63
7	2	550	66	38	66
8	2	550	67	51	66
9	2	550	67	45	66

* Cycles with maximum SUR's.

6. The 3" reactor showed some irregularity of performance suggestive of fluidizing problems. It showed this to a substantially greater extent than the 1-1/2" reactor with a stirrer.
7. Comparison of the laboratory 1" reactor showed that the 3" unit could substantially outperform the laboratory unit. Gas solid contacting problems are inferred in the 1" laboratory reactor from this comparison

5.2 BATCH REACTOR TESTING OF UNSUPPORTED HIGH CARBON BEACON SNG SOLIDS

A 4" fluidized bed reactor system was constructed for the evaluation of the major unit operations of the BEACON process under pressure and fluidized bed conditions. Testing was performed with K-1 and K-2 type BEACON solids; K-1 was identified during laboratory scale testing as the best unsupported promoter of SNG production from the steam gasification of BEACON carbon and K-2 as a promising backup catalyst. The reactor system was operated in batch mode with respect to solids and in continuous mode with respect to gas feed.

The objective of this testing was to determine steaming performance of BEACON carbon at pressure (up to 200 psig) in single and two stage operation and to evaluate the effect of pressure on rates and on the physical characteristics of the solids in multi-cycle operation. The 4-inch reactor data was used to design a tandem reactor system with solids transfer for the simultaneous testing of the BEACON unit operations (deposition and steaming), to select the best catalyst for long-term stability testing in the tandem system, and to formulate the appropriate conceptual process design scheme for engineering evaluation of the BEACON SNG process. All of these objectives were met.

5.2.1 Apparatus and Procedures

The 4-inch reactor apparatus was designed and constructed to meet the following requirements:

- To accommodate a charge of up to 2 kilograms of catalyst solids which upon fluidization could expand up to four times their volume at rest.

- To accommodate superficial gas velocities of at least one foot per second (based on the properties of air at ambient temperature and pressure).
- To operate with H₂ or carburetion gases at temperatures up to 800°C and pressures up to 200 psig.
- To be capable of supplying N₂ and H₂ to the reactor in the quantities required to accommodate the one foot per second superficial gas velocity in the reactor at the highest operating pressure (200 psig) and lowest operating temperature (400°C); CO, CO₂, and CH₄ at half the above rate.
- To be capable of preheating gases to maximum reaction temperature.
- To be capable of supplying heat to the reactor at a rate of at least 7,000 Btu per hour per foot of reactor for endothermic reactions.
- To be capable of retaining all the solids to submicron size within the system (greater than 90% retention within the reactor during each test).
- To be appropriately trapped for collection of condensable vapors.
- To be adequately controlled for steady feed of gases and for constant reactor temperature and pressure.
- To be appropriately instrumented for continuous or frequent (better than every 10 minutes) monitoring and recording of gas feed and effluent rates and composition, reactor temperatures and pressures, and reactor pressure drop.

The resulting apparatus (system) consisted of a 4-inch diameter fluid bed reactor, its feed supply and product collection units, and of the appropriate data acquisition and process control system. The reactor assembly was attached to a steel framework ("the stand"); the control panel and the computerized process control and data acquisition system were housed inside an office trailer ("the trailer"). Figure 5-4 presents a photo showing the stand and trailer and Figure 5-5 is a closeup photo of the installed reactor. A photo of the reactor shell is shown in Figure 5-6 and the control panel and computer system in Figure 5-7. Details of the system are presented in Figure 5-8, Process Flow Diagram, and Figure 5-9, Piping and Instrumentation Diagram.

Figure 5-4. Fluid Bed Reactor Stand and Instrumentation Trailer

Figure 5-5. Close-Up Photo of Reactor and Superheaters

Figure 5-6. Photo of 4-Inch Reactor Shell

Figure 5-7. Control Panel and Computer System of 4-Inch Reactor System

FLOW RATES, GASES IN ACFM AT METER

STREAM	1	2	3	4	5	6	10	12	REACTION
CARBON DEPOSITION	—	.07 to 2.0	—	.04 to 1.1	.02 to .54	—	.09 to 2.5	.06 to 3.1	752 to 1022 752 to 1202
METHANE PRODUCTION	.1 to 2.1	.05 to .90	—	—	—	—	0 to .48	.04 to 1.0	17,215 215

REACTION T, °F P, PSIA

Figure 5-8. Process Flow Diagram for 4-Inch Fluid Bed Reactor System

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Figure 5-9. Piping and Instrumentation Diagram

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Figure 5-8 shows the major elements of the apparatus which consisted of a feed gas and steam manifold, a gas heater-steam superheater unit, electrically heated and air cooled reactor, a solids-gas separator unit (cyclone and filter), a gas cooler and water condenser, a water trap, and a vent. The apparatus was instrumented with approximately seventy sensors for continuous monitoring of temperature, pressure, gas feed rate and composition, product flowrate and composition, and pressure drop in the reactor. Gas flowrate and system pressure were under automatic control with the aid of a Digital Equipment Corporation microprocessor; part of data acquisition and reduction was also performed automatically by the same microprocessor.

The gas manifold was capable of blending and feeding to the reactor up to five component gas mixtures plus steam. The component gases were supplied from bottled gas in large size cylinders or from trailers. Water vapor was supplied from a 34 KW steam generator (boiler) capable of delivering 90 pounds per hour steam at a maximum pressure of 225 psig. Component gas flowrates were measured by orifice meters. Viatran transducers were used to sense the DP across the orifices and to convert it to a voltage signal for transmittal to the microprocessor and to the control panel. Pneumatically controlled valves were used for flow control. Temperature and pressure measurements were made on the downstream side of the orifice meters. The blended gas mixture was also measured by an orifice meter and its composition was determined by an on line chromatograph. The gas manifold was capable of delivering carburetion or methanation feed gas mixtures which could accommodate the maximum design superficial gas velocities in the reactor of one foot per second. The entire feed system was constructed of 316 stainless steel piping and fittings.

The blended gas mixture, except for CO, was preheated (superheated in the case of steam) to reaction temperature by two suitcase type electric heaters (13 KW total rating) prior to entering the reactor. Carbon monoxide was fed to the remaining gas mixture downstream of the preheaters, at the bottom of the reactor, in order to avoid its disproportionation in the coiled gas line within the heaters and the potential plugging of this line.

The hot feed gas entered the reactor through a specially designed three-way valve located underneath the cone at the bottom of the reactor (the P&ID drawing in Figure 5-9 depicts the piping in more detail than Figure 5-8). The same valve served as support to the solids when at rest; it also served as a means of sampling the solids during testing and emptying the reactor at the conclusion of a test. The solids were fluidized by the feed gas using the appropriate linear gas velocity for the size and density of the solids in the reactor and for the reaction conditions (desired temperature, pressure, gas composition, residence time, and extent of reaction). The solids were fed through the 2-inch port on the upper left portion of the reactor at the start of the test. The reactor was 4-inch ID, 12 feet long, Incoloy 800H equipped with conical bottom of the same alloy for gas distribution, with two 2-inch ports for solids loading and gas exit, and with a 4-inch blind flange at the top for the introduction and support of temperature and DP sensor wells. The number of DP and thermocouple probes in the reactor during a given test depended to some degree on the nature of the test. There were less probes in the reactor during carbon deposition than during methanation in order to minimize the potential of carbon bridging across the reactor. Probes were located in a manner which permitted both radial and axial temperature measurements. (No radial temperature differential was observed in any of the tests.) The reactor was heated by 19-inch high temperature cable heaters divided into eleven separately controlled heating zones; the total power rating of the reactor heaters was 30.3 KW. Cooling of the reactor was accomplished by compressed air fed between reactor wall and its insulation through eight 1/2-inch air distributor rings; air supply was controlled manually by needle valves. The reactor was insulated with 4-inch thick insulation block.

In early testing, entrained solids in the product gas stream were separated and retained by cyclone and filter units connected in series outside the reactor vessel. Because of high solids entrainment rates at reactor superficial gas velocities in excess of 0.3 feet per second, an attempt was made to continuously return the cyclone separated solids to the reactor by means of a solids return loop connecting the bottom of

cyclone to the bottom of the reactor (a sort of external dip leg); the experiment failed. The external filter was then placed in the reactor by attaching it to the top flange of the reactor. This arrangement solved the problem of solids entrainment at superficial gas velocities up to 0.5 fps. At higher velocities the filter tended to plug and required frequent back-flushing which was a nuisance to the operation and introduced undesirable transients to the data. The majority of testing was therefore performed at the lower gas velocities.*

A water jacketed gas cooler was used to condense water vapor in the product stream. A 2-gallon liquids trap was used for collection of the condensed water. The "dry" product gas was released to the atmosphere through a pressure control valve to the vent stack.

Temperature throughout the system was monitored by 45 thermocouples (the location of the thermocouples in the reactor and on its walls are indicated in the P&ID). Eight DP probes monitored the pressure drop across the system with six of them being located inside the reactor to determine pressure drop as a function of bed length. System pressure was monitored by pressure sensors at three locations (feed manifold, top of reactor, gas product line). Feed and effluent gases were monitored by orifice meters and controlled by computer. Feed and product gas compositions were monitored by a Carle chromatograph with automatic sampling valve every 8.5 minutes and by three Beckman NDIR continuous analyzers (CO , CH_4 , CO_2). Solids samples were withdrawn at the completion of several of the tests for characterization. These samples were subjected to some or all of the following determinations: carbon, hydrogen and metal content; bulk density; and SEM examination. Most of these examinations were performed in-house. Figure 5-9, the P&ID of the system, gives additional details on the location of the various instrument and sampling probes.

The control and data acquisition sensors fed their signals to the control panel and the microcomputer located in the office trailer adjacent

* Installation of expanders to the reactor vessel and longer surface area filters improved greatly the performance of internal reactor filters in the Tandem System (Section 5.3 of this report).

to the apparatus stand. The majority of the signals were recorded and processed automatically by the Data Acquisition and Process Control System. This system was a PDP-11/03 DECLAB microprocessor based digital computer system. The system consisted of a microprocessor with 32 K word (16 bit word) memory, a 50 μ sec A/D converter multiplexed into 16 channels, two 16 bit parallel digital input/output ports, a programmable real time clock, a dual floppy disk drive system, and a 30 character per second typewriter. The 12 bit A/D converter operated at a rate of 20,000 channels/second. Additional analog input capability was provided by the installation of a 60-channel Doric Digitrend 220 data logger. The programmable real time clock was used to keep track of the schedule of the computer operation. The dual floppy disk drive system had an average access time of 483 μ sec at a transfer rate of one word per 35 μ sec. Thus, it required approximately 4 seconds to completely read a disk. The capacity of a single disk was 125 K words and the disk was divided into 480 blocks with 256 words per block.

The Data Acquisition and Process Control System performed the following functions:

- Continuous monitoring of plant conditions through temperature, pressure, flow and gas analysis sensors. The first three were measured every 0.5 seconds but the GC analysis every 8.5 minutes; all sensors were recorded every 8 minutes. (Many of the sensors were also recorded continuously on strip chart recorders.)
- Automatic control of system pressure through feedback loops.
- The issuing of on-line reports on request on reactor temperatures, pressures, gas flowrates, GC analyses, flow and mass balance.
- Data reduction upon completion of test (data averaging, mass balances, rate data, data summarizing, organization and tabulation).

The 4-inch apparatus was used in parametric investigations of single and two stage steaming of BEACON solids and in carbon deposition-steaming multi-cycle testing. Approximately 40 kilograms, two batches, of K-1 based carbon and 20 kilograms, single batch, of K-2 based carbon were prepared.

In the single stage steam tests, or the first stage of two stage steaming, a sample of the K-1 or K-2 based BEACON carbon, nominally 2 kilograms, was loaded into the reactor, the reactor was pressurized with N_2 gas to reaction pressure and heated up to the desired reaction temperature under fluid bed conditions in nitrogen flow. Nitrogen was replaced by steam at "zero reaction time" (start of test). Steam feed flow, reactor pressure, and reactor temperature were continuously monitored and maintained constant throughout the run. Reaction temperature was monitored by eight thermocouples located in a thermowell in the center of the reactor; the thermocouples were spaced at varying distances along the reactor length varying from 6 inches (near the bottom) to 2 feet (near the top). The dry product gas flowrate was monitored by the computer every 0.5 seconds and its average value was recorded every 8 minutes; the computer reading (orifice meter measurement) was checked frequently against dry gas meter readings. The water vapor in the product gas was condensed and measured as liquid water. The dry gas composition was determined chromatographically every 8 minutes (minimum analysis time); in addition, the CO , CO_2 , and methane components of the product gas were continuously monitored by Beckman NDIR analyzers. The NDIR analyzers served as verifiers for the gas chromatograms and as a means of continuous tracing of any transients in reactor performance. Virtually all first stage gasification tests were carried out to complete exhaustion (less than 10% steam utilization). The reactor was then purged with nitrogen, cooled, depressurized and the residual solids recovered and analyzed.

The output of the steam gasification tests consisted of the following performance yardsticks: a) global carbon gasification rate in kilograms per hour, which could be converted to specific rate based on the initial charge of solids to the reactor or on the quantity of solids (or any component of the solids, e.g., carbon) present in the reactor at any time during the test; b) steam utilization rate as a fraction of steam feed; and c) product gas composition. Carbon gasification rates were computed from the carbon species in the product gas; the integrated value of gasified carbon was checked against the value of missing carbon determined from solids balance performed at the end of each test (carbon solids

loaded minus carbon solids recovered). Steam utilization rates were computed independently from: 1) the hydrogen in the product stream, 2) the oxygen in the product stream, and 3) the steam feedrate and liquid water recovery rate from the product stream (a sight glass reading taken every 15 minutes).

In the second stage tests the cooled product gas of the first stage (simulated from bottled gases) was used as the feed gas to the reactor containing BEACON carbon; both unreacted and partially steamed (first stage "exhausted") BEACON solids were used in this operation. Conceptually, the 600-700°C product gas of the first stage was cooled by 100-200°C and fed to a bed of BEACON solids where the fuel components of the feed gas were catalytically converted to methane (because of more favorable thermodynamics). The objective of the second stage steaming tests was to determine the viability and performance efficiency of this concept.

The operational procedure for second stage steaming was similar to that for the first stage described above. However, the solids in the second stage were not consumed; they served only as the catalyst and therefore were not replaced after each test as was the case with first stage testing. The other difference was that instead of pure steam, the feed consisted of steam, CO, H₂, CO₂, and CH₄ (simulated first stage product gas). Flowrates, compositions, temperature and pressure were monitored and recorded. The performance yardstick in these tests was the extent of conversion of feed CO and H₂ to methane. Conversions were computed from feed and effluent flowrates and compositions.

In multi-cycle testing a single sample from the same large batch of K-1 based solids used in steaming parametric tests was recycled during 30 carbon deposition and steaming cycles. The steaming procedure was identical to that described for single stage steaming. Upon completion of the steaming operation steam was substituted by nitrogen and the temperature was dropped to 450°C. Simulated low Btu gas was then fed to the reactor to start carbon deposition. The nominal carburization feed gas composition was 30% CO, 15% H₂, 5% CO₂, 50% N₂. Carbon deposition continued until the carbon deposited equalled the quantity of carbon consumed in the steaming operation. The reactor was then purged with nitrogen gas, the temperature

raised to the steaming temperature and the cycle was repeated. Testing was conducted in two shifts. The reactor was depressurized and cooled overnight, but the solids remained under a nitrogen blanket during idle periods. Periodically, solids samples were withdrawn from the reactor for chemical and physical characterization and for activity monitoring at laboratory scale (ambient pressure); the activity test results were compared to those of the starting solids (initial reactor charge).

5.2.2 Single-Stage Steaming Results

Table 5-9 summarizes the parametric testing performed on first stage steaming of K-1 based BEACON carbon. The parameters examined for effect on gasification performance were temperature, steam feedrate-to-carbon solids charge ratio, steam partial pressure, reactor total pressure, residence time, gas velocity, and solids carbon content. The objectives of each test are indicated in the last column of Table 5-9. The values of the parameters listed are nominal but do not deviate appreciably from those actually used. Within the ranges investigated the only parameters exhibiting discernible effects were temperature and the H_2O/C ratio.

Figures 5-10 and 5-11 illustrate typical raw product gas composition and flowrate data generated at two levels of global gasification rate (tests K1-2 and K1-10, respectively). In both these tests, as it was the case for the entire matrix of the K-1 tests including the ambient pressure laboratory scale runs, gasification rate and product gas composition remained virtually constant until most of the carbon in the reactor was gasified. This permitted the generation of quasi steady state data with respect to solids even without continuous feed and withdrawal of solids.

A complete summary of the data on the parametric effects on gasification of K-1 based BEACON carbon is presented in Tables 5-10 and 5-11. Table 5-10 summarizes principally the parametric effects on rates and Table 5-11 the effects on composition.

The first column in Table 5-10 lists the test numbers and the next five columns present the reaction temperature, steam partial pressure, steam feedrate-to-solids charge ratio (pounds of steam fed per hour-to-pounds of BEACON solids charged to the reactor at the start of the test),

Table 5-9. Parametric Test Matrix on Steam Gasification of K-1 Based BEACON Carbon

Exp. No.	Temp. °C	Pressure P _T PSIA	P _{H₂O} PSIA	Steam Feed Lbs/Hr	BEACON Solids Charge Lbs	$\frac{H_2O^{(1)}}{C^*}$	Reactor Gas		Effects Examined
							Velocity u, FPS	Resid. Time θ, Seconds	
K1-1	550-650	215	118	5.4	4.4	1.2	.12-.14	~18	System and Catalyst Activity Check
K1-2	600	215	118	5.4	4.4	1.2	.13	~18	Temperature
K1-3	650	215	118	5.4	4.4	1.2	.14	~19	
K1-4	600	215	215	13.2	4.4	3.0	.18	~16	(H ₂ O/C) + P _{H₂O}
K1-5	650	215	215	13.2	4.4	3.0	.20	~17	(H ₂ O/C) + P _{H₂O}
K1-6	650	215	215	19.8	3.3	6.0	.30	~15	(H ₂ O/C) + u
K1-7	650	215	215	13.2	2.2	6.0	.20	~ 8	θ + u
K1-8	600	215	118	6.6	2.2	3.0	.18	~ 8	P _{H₂O} + θ
K1-9	600	118	118	13.2	4.4	3.0	.36	~ 8	P _T + u
K1-10	650	215	215	13.2	4.4	3.0	.20	~17	Carbon Content
K1-11	600	215	215	13.2	4.4	3.0	.18	~18	
K1-12	650	215	215	26.4	4.4	6.0	.40	~ 8	Gas Velocity
K1-13	550	215	215	13.2	4.4	3.0	.17	~20	Temperature

K1-9A and 12B Repeat and reproducibility checks

(1) Steam mass flowrate - to - solids charge ratio; C* represents high carbon content BEACON solids

Figure 5-10. Typical Intermediate Temperature K-1 Based Carbon Gasification Test (First Stage)

Figure 5-11. Typical High Temperature (Short Duration)
K-1 Based Carbon Gasification Test (First Stage)

Table 5-10. Parametric Effects on Gasification of K-1 Based BEACON Carbon

Test No.	Temp. °C	P _{H₂O} ⁽¹⁾ (Psia)	H ₂ O ⁽²⁾ C*	u Fps	θ Sec	Gasification Rate ⁽³⁾	Steam Utilization (%) Exper.	Equil. ⁽⁴⁾	CH ₄ Concentration (% v/v) Exper.	Equil. ⁽⁴⁾
1. Temp. Effect										
K1-2	600	118	1.2	.13	18	.32	50	59	17	24.5
K1-3	650	118	1.2	.14	16	.41	63	63	17.8	19.7
K1-13	550	205	3.0	.17	20	.15	15	55	0.5	33.1
K1-4	600	205	3.0	.18	16	.50	40	57.5	13	28.4
K1-5	650	205	3.0	.20	17	.74	50	61.1	19.9	23.1
2. H₂O/C Effect										
K1-3	650	118	1.2	.14	17	.41	63	63	17.8	19.7
K1-5	↓	205	3.0	.20	17	.74	50	61.1	19.9	23.1
K1-6	↓	↓	6.0	.30	15	1.49	55	↓	16.1	↓
K1-7	↓	↓	6.0	.20	8	1.48	52.7	↓	17.8	↓
3. Pressure Effects										
K1-4	600	205	3.0	.18	16	.50	40	57.5	13	28.4
K1-9	↓	118 ⁽¹⁾	↓	.36	8	.51	31.9	59.1	11	24.7
K1-8	↓	118	↓	.18	8	.50	40	59.1	11	24.7

(1) Total pressure was 205 psia (nominal) for all tests except K1-9 which was performed at 118 psia.

(2) Steam feedrate-to-solids charge ratio (lbs per hour per lb solids charged to the reactor at the start of the test).

(3) Lbs carbon gasified per hour per lb solids charged to the reactor at the start of the test.

(4) Computed from graphite-steam reaction equilibria.

Table 5-11. Parametric Effects on Gasification of K-1 Based BEACON Carbon
(Product Gas Composition)

Test No.	P_{H_2O} Psia	Temp. °C	$\frac{H_2O}{C^*}$	Product Gas Composition ⁽¹⁾ , % V/V Dry Basis				Gasif. Rate ⁽²⁾
				CH ₄	CO	CO ₂	H ₂	
K1-2	118	600	1.2	17 (24.5)	5 (7.7)	37 (36.3)	41 (31.5)	0.3
K1-4	205	600	3.0	13 (28.4)	4 (6.2)	37 (38.7)	44 (26.6)	0.5
K1-11	205	600	3.0	13 (28.4)	3 (6.2)	37 (38.7)	47 (26.6)	0.5
K1-3	118	650	1.2	18 (19.7)	6 (12.5)	37 (31.6)	39 (36.2)	0.4
K1-5	205	650	3.0	20 (23.1)	6 (10.7)	36 (34.0)	38 (32.2)	0.7
K1-10	205	670	3.0	21 (21.3)	7 (12.8)	36 (31.9)	36 (34.0)	1.1
K1-6	205	650	6.0	16 (23.1)	7 (10.7)	34 (34.0)	42 (32.2)	1.5
K1-12	185	650	6.0	18 (22.3)	3 (11.1)	39 (33.4)	40 (32.2)	1.4
K1-12B	185	650	6.0	18 (22.3)	4 (11.1)	38 (33.4)	40 (32.2)	1.5

⁽¹⁾ Values in parentheses represent equilibrium concentrations based on the graphite-steam reaction.

⁽²⁾ Lbs carbon gasified per hour per lb solids charged to the reactor at the start of the test.

superficial gas velocity in the reactor in feet per second,* and approximate gas residence time in seconds (the exact value of this parameter depends on bed expansion which was not precisely determined). All tests except K1-9 were performed at 205 psia (nominal) reactor pressure. In the cases where steam partial pressure differed from 205 psia, the balance used was nitrogen. In Test K1-9 the total pressure used was 118 psia. Column 7 lists the measured gasification rate normalized to the weight of solids charged to the reactor at the start of the test. Column 8 lists the experimentally obtained steam utilization rate (as percent of steam feed) and Column 9 lists the same quantity calculated from graphite-steam equilibria. Column 10 shows the experimentally obtained methane concentration in the dry product gas and Column 11 shows the same quantity computed from graphite-steam equilibria. (Table 5-11 compares the complete product gas compositions.)

The data in Table 5-10 are grouped in terms of the effect studied. The first group examines the effect of temperature at two H_2O/C and two steam partial pressure values.** In both cases the effect of temperature is appreciable. The data indicate that in the 550-650°C range carbon gasification rate, steam utilization rate, and methane partial pressure in the product gas all increase with increasing temperature. Thermodynamics dictate that methane yield increases with decreasing temperature, but the lower than equilibrium steam utilization rates at temperatures below 650°C render attainment of equilibrium methane concentrations impossible in single stage gasification. These data therefore appear to indicate that with K-1 based BEACON solids it may be desirable to perform steam gasification in two stages with the first stage operated at conditions that maximize the gasification and steam utilization rates (at or near 650°C) and the second stage operated at conditions that maximize fuel (CO and H_2) conversion to methane (550°C or lower temperature). A polishing methanator could be an alternative to second stage steaming.

* Based on steam feedrate; the actual velocity was higher due to the increase in the number of moles as a result of the reaction.

** Test K1-1 was a temperature scan test in the 550-560°C range for establishing the capability of the system to supply the heat needed for the gasification reactions; the data revealed that there was adequate heat transfer capability to perform the planned tests.

The second group of data examines the effect of H_2O/C ratio on gasification and steam utilization rates. This effect was examined for H_2O/C ratios from 1.2 to 6 at $650^\circ C$. In this range and at this temperature, the gasification rate appears to increase in proportion to the increase in the ratio. Since the same increase in gasification rate was obtained by increasing the steam feedrate as by decreasing the quantity of solids charged to the reactor by a corresponding amount (see Table 5-9, tests K1-6, 7, and 12), the observed effect cannot be due to gas velocity (mass transfer and mixing effects). It was concluded therefore that the gasification rate was limited by steam feed and that at higher H_2O/C ratios the rate will be still higher than the maximum of 1.5 lbs of carbon per hour per pound of solids charged shown in these tables. Indeed, the gross gasification rate normalized to steam feed depended only on temperature for all tests included in the K-1 matrix (Table 5-9). For $650^\circ C$ and 205 psia steam partial pressure, the pounds (or kilograms) of carbon gasified per hour per pound (kilogram) of steam fed was $0.30 \pm .02$; the corresponding rate based on equilibrium steam utilization is 0.35 pounds per hour per pound. This is a very good approach to equilibrium (a fact verified by the compositional data in Table 5-11). The corresponding values for $600^\circ C$ gasification were 0.20 ± 0.04 lbs per hour per lb versus 0.33 for equilibrium steam utilization; the deviation from equilibrium was appreciable in this case and it was also manifested in the compositional data (Table 5-11).

The last group of data in Table 5-10 examines the effect of reactor pressure and steam partial pressure on gasification rate at $600^\circ C$. At constant H_2O/C ratio there was no discernible effect of pressure on gasification rate. This observation is consistent with thermodynamic predictions for this pressure range (100 to 200 psig) provided the steam feed-to-BEACON solids ratio is kept constant.

Table 5-11 summarizes the effects of temperature and H_2O/C ratio on product gas composition; gasification rate is also included in the last column. The values in parentheses refer to calculated compositions from thermodynamic data for steam-graphite equilibria. The data reveal that at 1.2 and 3.0 H_2O/C ratios methane production increases with temperature; this is probably because at temperatures below $650^\circ C$ steam utilization drops off and the excess water in the product gas suppresses methane

production. At 650°C and at H₂O/C ratios of three or less, methane production was near its thermodynamically predicted value; at a H₂O/C ratio of 6, methane production was 20 to 30% below its equilibrium value probably because of mechanical interference (e.g., gas bypassing, solids entrainment) rather than kinetic limitations.

Maximum gasification rates*, expressed in weight of carbon gasified per hour per unit weight of solids in the reactor, were also estimated from these data. Their values were as follows:

$$R_g (600^\circ\text{C}, 205 \text{ psia}) = 1.4 \pm 0.2 \text{ lbs carbon gasified per hour per lb solids** in reactor.}$$

$$R_g (650^\circ\text{C}, 205 \text{ psia}) = 2.8 \pm 0.2 \text{ lbs carbon gasified per hour per lb solids** in reactor.}$$

These rates were approximately twice as high as the corresponding ambient pressure rates (Section 4.2.1.5). The reason for the enhanced efficiency was attributed to the fact that the maximum gasification rates at 205 psia were attained at a steam feed-to-BEACON solids ratio of about 10 versus a ratio of 5 for maximum rates at ambient pressure. In general, the pressure data verified the conclusions drawn at laboratory scale. These data also suggested that process efficiency improves with scale up (rates estimated at low scale may be too conservative); in this case, the scale up was one thousand-to-one and it appears that the maximum gasification rates were underestimated by a factor of two.

Test K1-9A and K1-12B (Table 5-9) were performed to verify the reproducibility of the data. The agreement with results obtained during Tests K1-9 and K1-12, respectively, was excellent. Data comparisons between K1-12 and K1-12B are presented in Table 5-11; comparisons between K1-9 and K1-9A were similar.

* This rate differs from that listed in Tables 5-10 and 5-11 in that it is normalized to the quantity of BEACON solids in the reactor at the point of the start of drop off in steam utilization rather than being normalized to the weight of solids in the reactor at the start of steaming. These maximum specific rates should be nearly equal to the steady state gasification rates obtainable from a steady flow reactor operated at the same temperatures and pressures and not limited by either steam or carbon.

** The rate values were $2 \pm .3$ and $4 \pm .3$ lbs/hr/lb, respectively, when normalized to carbon only rather than total BEACON solids in the reactor.

The performance of K-2 based BEACON solids, the back up catalyst, in steaming and deposition at elevated pressure was also examined during this parametric testing. Steaming tests were performed in the 4-inch fluid bed reactor at 100 psig reactor pressure (105 psig steam partial pressure). Typical results on steaming of K-2 carbon at 600°C and 650°C and a steam feed rate-to-solids ratio of 3 are summarized in Table 5-12, which includes the corresponding equilibrium values in parentheses. These data show that a reactor temperature of 650°C was required for near equilibrium steaming; steam utilization was also higher at the higher temperature. Thus, just as in the case of K1-based BEACON carbon, a second lower temperature gasification stage where the fuel (CO and H₂) in the product gas from the first stage is converted to methane, was suggested by the data.

The maximum specific gasification rate at 650°C (Test K2-1) was estimated at 2.2 lbs carbon gasified per hour per lb solids in the reactor (or 3.2 lbs per hour per lb carbon in the reactor rather than total solids). This rate is about 20% lower than that obtained with K-1 solids but still a practical steaming rate. A maximum steaming rate for 600°C was not computed due to uncertainty in the quantity of solids in the reactor during the two 600°C tests performed (uncertainties on solids entrainment beyond the reaction zone). Typical steam utilization values were 58% and 54% at 650 and 600°C respectively.

Table 5-12. K-2 Based BEACON Steaming at Elevated Pressure
7.8 atm (100 psig), Feed 90% H₂O/10% N₂
Linear Gas Velocity = 6.1 cm/sec (0.2 ft/sec)

Test No.	Temp. (°C)		Product Gas Composition (% v/v, Dry, N ₂ -Free)				Steam Utilization %
			CH ₄	H ₂	CO ₂	CO	
K2-1	650	Measured	13.7	44.9	29.7	11.6	58
		Equilibrium	(17.8)	(38.3)	(30.2)	(13.6)	(64)
K2-2	600	Measured	13.4	48.7	34.3	3.6	54
		Equilibrium	(23.3)	(32.9)	(35.7)	(8.1)	(60)

Carbon deposition tests on K-2 solids performed at 450°C and 100 psig with a nominal feed gas composition of 30% CO, 15% H₂, 5% CO₂, and 50% N₂ revealed CO conversion in excess of 90% at deposition rates of 1 to 2 lbs of carbon deposited per hour per lb metal in the catalyst. The deposition rates and CO conversions were stable through four deposition-steaming cycles with no discernible trend toward activity deterioration. Maximum deposition rates were not determined because of solids entrainment complications at higher gas velocities. However, the quoted data show that carbon deposition on K-2 solids at elevated pressures is at least as efficient as deposition at ambient pressure (Section 4.4.3 of this report). Also, the carbon deposited at 100 psig was equally as reactive in steaming as carbon deposited at ambient pressure.

Carbon deposition data on K1-based BEACON solids will be discussed in Section 5.2.4 (Multi-Cycle Testing of K-1 Solids).

5.2.3 Two-Stage Steaming Results

As reported in the previous section, single-stage steam gasification tests showed that in order to obtain high K1 or K2 based carbon gasification and steam utilization rates, reaction temperatures in the range of 600 to 650°C were required. However, at these temperatures methane yield is not favored thermodynamically. Therefore, it was concluded that in order to maximize methane yield and gasification rate a second reaction stage operating at a lower temperature (500-550°C) may be desired. Under this scheme, the product gases from the first stage are passed over BEACON solids at a lower temperature where the CO and H₂ components of the gas are converted to additional methane. The BEACON solids can be either high carbon content material contacted prior to steaming (countercurrent process) or low carbon content material contacted after the high temperature first stage steaming (co-current process). The terms "countercurrent" and "co-current" refer to the relationship between the BEACON solids and the gas flow in a conceptual process design rather than to the experiment configuration in the bench-scale reactor.

A test matrix was designed to investigate the feasibility of using a two stage steam gasification process operating in either the counter-current or co-current mode. The matrix is presented in Table 5-13. The assumption was made that the first stage will be operated at 650°C and 205 psia and that its performance will be identical to that obtained in the 4-inch reactor single stage tests at 650°C; thus the feed gas composition used in the second stage gasification tests (except test K1-18) simulated the average product gas composition from tests K1-3, 5, 6, 7, 10 and 12. Test K1-18 was performed with feed gas simulating first stage product gas generated under equilibrium conditions (steam-graphite reaction) at 700°C.

The first test, K1-14, examined the catalytic activity of the reactor walls by feeding a simulated first stage product gas mixture to the empty reactor at 550°C and 200 psig. The data in Table 5-14 show that reaction with the reactor walls was insignificant at the conditions of the test. The remaining tests were performed with BEACON solids in the reactor in the temperature range of 400 to 550°C, at 200 psig pressure, and at a superficial gas velocity of 0.17 feet per second. Temperature was the principal operating parameter varied during these tests. The solids charge was nominally 4 lbs for the countercurrent tests (K1-15 through K1-18) and 2 lbs for the co-current tests (K1-19 through K1-24). High carbon (unsteamed) solids were used for the countercurrent tests and partially carbon-depleted (steamed) solids were used for the co-current tests. A smaller charge of the low-carbon was used because of their higher catalyst content. The results of the countercurrent and co-current tests are presented in separate sections below.

5.2.3.1 Countercurrent Steam Gasification Results (Second Stage)

The test results of countercurrent steam gasification of K1-based BEACON carbon are summarized in Table 5-15 and 5-16 (Tests K1-15A,* K1-15B,* K1-16 and K1-18). Test K1-17 was not completed because of low activity,

* Test K1-15A was intended to be performed at 550°C but temperature control equipment problems forced the lower operating temperature and the larger than normal temperature range in the reaction zone. (The deviations in the average operating temperature represent the maximum variation in temperature along the reaction axis.) Test K1-15B was intended to be a 525°C run instead of $528 \pm 11^\circ\text{C}$ obtained during the test. The temperature control problems were solved later.

Table 5-13. Test Matrix for Second Stage Steaming of K1-Based
BEACON Carbon at 200 Psig

TEST NO.	TEMPERATURE* °C	GAS FEED* SCFM	SOLIDS CHARGE* LBS	GAS VELOCITY IN REACTOR*	EFFECTS EXAMINED
K1-14	550	5	0	0.17 fps	Catalytic Activity of Reactor Walls **
K1-15	550	5	4	0.17 fps	Temperature ** (Countercurrent)
K1-16	500	5	4	0.17 fps	
K1-17	450	5	4	0.17 fps	
K1-18	500	5	4	0.17 fps	Feed Gas Composition *** (Countercurrent)
K1-19	550	5	2	0.17 fps	Temperature** (Co-Current)
K1-20	525	5	2	0.17 fps	
K1-21	500	5	2	0.17 fps	
K1-22	475	5	2	0.17 fps	
K1-23	450	5	2	0.17 fps	
K1-24	400	5	2	0.17 fps	

*Nominal values.

**These tests were performed with feed gas composition which simulated 650° C first stage product gas generated during steam gasification of K1-based carbon in the 4-inch reactor.

***This test was performed with K1-based simulated product gas assumed to have been generated from equilibrium carbon-steam gasification at 700° C.

Table 5-14. Second Stage Steam Gasification Test
Results (Empty Reactor Test K1-14)

REACTION TIME, MIN.	TEMP °C	PRESSURE PSIA	FEED GAS, SCFM						TOTAL FEED SCFM
			CO ₂	CO	H ₂	CH ₄	H ₂ O	N ₂	
8	558	218	1.106	0.169	1.173	0.578	2.032	0.291	5.349
17	552	217	1.125	0.173	1.191	0.594	2.068	0.012	5.163
25	548	217	1.139	0.169	1.181	0.589	2.068	0.008	5.154
34	547	217	1.156	0.172	1.192	0.590	2.066	0.006	5.182
51	541	217	1.142	0.169	1.195	0.596	2.091	0.006	5.199
59	539	218	1.128	0.173	1.186	0.593	2.069	0.071	5.220
			PRODUCT GAS, SCFM						TOTAL PRODUCT SCFM
			CO ₂	CO	H ₂	CH ₄	H ₂ O	N ₂	
			1.050	0.118	0.917	0.567	2.253	0.291	5.196
			1.201	0.163	1.084	0.619	2.026	0.012	5.105
			1.091	0.132	1.978	0.532	2.293	0.008	5.034
			1.126	0.168	1.123	0.636	2.086	0.006	5.145
			1.095	0.148	0.983	0.566	2.284	0.006	5.082
			1.073	0.153	1.041	0.600	2.200	0.071	5.138

although it is possible that this test was discontinued prematurely. Results are presented in terms of 100 moles of first stage product gas which serves as second stage feed gas, Column 2 of Tables 5-15 and 5-16. Column 3 presents the moles of second stage product generated from 100 moles of feed, and Column 4 gives the volumetric composition of the product gas. The next two columns give the moles of product gas and its composition assuming that the 100 moles of feed were allowed to convert to the product gas under equilibrium conditions at the indicated temperature and pressure. For Tests K1-15A, K1-15B and K1-16, these equilibrium values were computed from thermochemical data under the assumption that the carbon in the reactor does not react with the feed gas. (Thermodynamically a small amount of carbon gasification by these feed gases in the 500-550°C range is possible, but it was not observed during these tests; so it was not allowed to take place in the thermochemical computations either.) By contrast, thermodynamic equilibrium predicts the formation rather than gasification of carbon under the conditions of Test K1-18 (simulated product gas from 700°C steam-graphite reaction); in this case (Table 5-16B), carbon was allowed to form in the computed equilibrium values because it represents an appreciable fraction of the product carbon species (fortunately, none was formed in Test K1-18).

It is evident that maximum feed conversions were obtained in Tests K1-15A, K1-15B and K1-16 since the product gas compositions are virtually identical to those predicted assuming equilibrium conditions. It is conceivable that high second stage efficiency could have been achieved at much lower residence times (smaller reactor vessels) than those used in these tests. Future testing should involve higher feed gas rates and/or smaller catalyst beds to examine the effect of gas residence time.

The last column in Tables 5-15 and 5-16 shows the methanation efficiency obtained in the first and second stage tests combined. Methanation efficiency is defined as the ratio of moles of methane produced in the two stages to the moles of methane that could be produced if all of the unreacted CO and H₂ fuel in the second stage reactor effluent were to be converted to methane under any operating conditions or by whatever means (e.g., polishing methanator at lower temperature). It is noted that methanation efficiency as high as 86% is achievable when two stage steaming is used.

Table 5-15. Countercurrent Steam Gasification - Second Stage Test Results (K1-15)
High Carbon (Steamed) K1-Based BEACON Solids

(a) Test K1-15A - Steady State Data at $536 \pm 14^\circ\text{C}$, 203 PSIG

	FEED GAS MOLES	PRODUCT GAS				
		OBTAINED EXPERIMENTALLY MOLES	V/V%	PREDICTED FROM EQUILIBRIUM* MOLES	V/V%	
CH ₄	10.5	13.5	14.4	13.8	14.8	METHANATION EFFICIENCY** (BOTH STAGES):
CO	3.1	0.6	0.6	1.0	1.1	
H ₂	21.4	11.9	12.7	10.3	11.0	OBTAINED FULL CONVERSION = $\frac{13.5}{13.5 + 12.5/4} = 81\%$
CO ₂	20.5	20.0	21.3	19.3	20.6	
H ₂ O	43.4	46.9	49.9	47.9	51.3	
N ₂	1.1	1.1	1.2	1.1	1.2	
	100	94.0	100	93.4	100	

(b) Test K1-15B - Steady State Data at $528 \pm 11^\circ\text{C}$, 203 PSIG

	FEED GAS MOLES	OBTAINED EXPERIMENTALLY MOLES	V/V%	PREDICTED FROM EQUILIBRIUM* MOLES	V/V%	
CH ₄	11.0	14.9	16.1	14.8	16.0	OBTAINED FULL CONVERSION = $\frac{14.9}{14.9 + 10/4} = 86\%$
CO	3.2	0.6	0.6	0.9	1.0	
H ₂	22.0	9.4	10.2	9.2	9.9	
CO ₂	21.1	19.1	20.7	19.6	21.2	
H ₂ O	42.6	48.3	52.3	47.8	51.7	
N ₂	0.1	0.1	0.1	0.1	0.1	
	100	92.4	100	92.4	100	

* Does not allow reaction with carbon.

** The ratio of methane produced to methane expected if all fuel (CO + H₂) was consumed:

$$\frac{(\text{CH}_4)_{\text{obtained}}}{[(\text{CH}_4)_{\text{obtained}} + (\text{H}_2 + \text{CO})/4]}$$

Table 5-16. Countercurrent Steam Gasification - Second Stage Test Results (K1-16 and K1-18)
High Carbon (Steamed) K1-Based BEACON Solids

(a) Test K1-16 - Steady State Data at $504 \pm 3^\circ\text{C}$, 202 PSIG

	FEED GAS MOLES	PRODUCT GAS		PREDICTED FROM EQUILIBRIUM*	V/V%
		OBTAINED EXPERIMENTALLY MOLES	V/V%		
CH ₄	10.9	14.8	16.1	14.9	16.2
CO	3.1	0.5	0.5	0.6	0.7
H ₂	21.6	8.7	9.4	8.0	8.7
CO ₂	20.8	19.5	21.1	19.2	20.9
H ₂ O	43.4	48.5	52.6	49.0	53.3
N ₂	0.2	0.2	0.2	0.2	0.2
	100	92.2	100	91.9	100

METHANATION EFFICIENCY**
(BOTH STAGES):

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{14.8}{14.8 + 9.2/4} = 86.5\%$$

(b) Test K1-18 - 500°C with the Feed Gas Being the Product Gas of 700°C Steam Gasification

	FEED GAS MOLES	PRODUCT GAS		PREDICTED FROM EQUILIBRIUM*	V/V%
		OBTAINED EXPERIMENTALLY MOLES	V/V%		
CH ₄	13.3	19.1	21.9	17.6	20.7
CO	11.6	1.9	2.2	0.7	0.8
H ₂	26.0	12.9	14.8	6.7	7.9
CO ₂	20.5	21.5	24.7	20.6	24.3
H ₂ O	28.5	31.6	36.3	39.2	46.2
N ₂	0.1	0.1	0.1	0.1	0.1
			100		100
C	0	0		6.5	
	100	87.1		91.4	

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{19.1}{19.1 + 14.8/4} = 84\%$$

* Does not allow reaction with carbon.

** The ratio of methane produced to methane expected if all fuel (CO + H₂) was consumed:

$$\frac{(\text{CH}_4)_{\text{obtained}}}{[(\text{CH}_4)_{\text{obtained}} + (\text{H}_2 + \text{CO})/4]}$$

Test K1-18 was run to determine second stage performance when the first stage is operated at a higher temperature. The advantages of operating the first stage at 700°C versus 650°C are a higher gasification rate and better steam utilization; the disadvantage is the higher heat input requirement. Test data are presented in Table 5-16(b). It is noted that Test K1-18 did not perform according to equilibrium predictions. Thermochemistry predicts the deposition of 6.5 moles of carbon per 100 moles of feed; the experimental data revealed that carbon was not deposited but instead more methane was produced than expected from thermodynamics. Below are listed the over-all reactions predicted by equilibrium and the ones indicated by the experimental results:

Equilibrium Reactions

Experimental Reactions

These reactions indicate that K1-based BEACON solids promote the reactions to hydrogen and methane rather than the CO reduction to carbon. Since methane and hydrogen are the desirable products of this process, this promotional selectivity of K1-based solids is very important.

5.2.3.2 Co-current Steam Gasification Results (Second Stage)

Tests K1-19 through K1-24 were performed to investigate the co-current two stage process option. The results of these tests are presented in Tables 5-17 through 5-19. The second stage feed gas composition, which was the same for each test, simulated the product gas obtained from steam gasification of K1-based BEACON carbon at 650°C. The second stage operating temperatures ranged from 550°C for Test K1-19 to 403°C for Test K1-24. All tests were performed at 200 psig. The solids utilized during these tests consisted of steamed K1-based solids recovered from previous single stage steaming operations.

Table 5-17. Co-Current Steam Gasification - Second Stage Test Results (K1-19 and K1-20)
Low Carbon (Steamed) K1-Based BEACON Solids

TEST K1-19 - STEADY STATE DATA AT 551 ± 4°C, 200 PSIG

	FEED GAS MOLES	PRODUCT GAS			
		OBTAINED EXPERIMENTALLY		PREDICTED FROM EQUILIBRIUM*	
		MOLES	V/V%	MOLES	V/V%
CH ₄	10.3	13.2	13.9	13.3	14.2
CO	3.0	1.5	1.6	1.2	1.3
H ₂	21.8	13.1	13.8	11.5	12.2
CO ₂	19.7	19.0	20.0	18.4	19.6
H ₂ O	42.5	45.4	47.8	46.8	49.8
N ₂	2.7	2.7	2.9	2.7	2.9
	100	94.9	100	93.9	100

METHANATION EFFICIENCY**
(BOTH STAGES):

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{13.2}{13.2 + 14.6/4} = 78.3\%$$

TEST K1-20 - STEADY STATE DATA AT 524 ± 8 °C, 200 PSIG

	FEED GAS MOLES	MOLES	V/V%	MOLES	V/V%
CH ₄	10.3	12.5	12.9	13.9	15.0
CO	3.0	1.6	1.7	0.8	0.9
H ₂	21.7	16.3	16.9	9.4	10.1
CO ₂	19.8	20.1	20.8	18.3	19.8
H ₂ O	42.5	43.4	44.9	47.6	51.3
N ₂	2.7	2.7	2.8	2.7	2.9
	100	96.6	100	92.7	100

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{12.5}{12.5 + 17.9/4} = 73.6\%$$

* Does not allow reaction with carbon.

** The ratio of methane produced to methane expected if all fuel (CO + H₂) was consumed:

$$\frac{(\text{CH}_4)_{\text{obtained}}}{[(\text{CH}_4)_{\text{obtained}} + (\text{H}_2 + \text{CO})/4]}$$

Table 5-18. Co-Current Steam Gasification - Second Stage Test Results (K1-21 and K1-22)
Low Carbon (Steamed) K1-Based BEACON Solids

TEST K1-21 - STEADY STATE DATA AT 501 ± 4°C, 200 PSIG

	FEED GAS MOLES	PRODUCT GAS			
		OBTAINED EXPERIMENTALLY		PREDICTED FROM EQUILIBRIUM*	
		MOLES	V/V%	MOLES	V/V%
CH ₄	10.4	12.7	13.2	15.0	16.5
CO	3.1	1.4	1.5	0.6	0.6
H ₂	23.3	16.9	17.6	7.5	8.3
CO ₂	20.4	20.4	21.3	18.3	20.2
H ₂ O	40.2	42.0	43.7	46.8	51.5
N ₂	2.6	2.5	2.7	2.6	2.9
	100	96.0	100	90.8	100

TEST K1-22 - STEADY STATE DATA AT 480 ± 5°C, 200 PSIG

CH ₄	10.5	13.6	14.4	15.4	17.1
CO	3.1	1.1	1.2	0.4	0.4
H ₂	22.9	13.8	14.6	6.0	6.6
CO ₂	20.2	19.7	20.9	18.0	20.0
H ₂ O	40.8	43.7	46.3	47.9	53.1
N ₂	2.5	2.5	2.6	2.5	2.8
	100	94.4	100	90.2	100

METHANATION EFFICIENCY**
(BOTH STAGES):

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{12.7}{12.7 + 18.3/4} = 73.5\%$$

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{13.6}{13.6 + 14.9/4} = 78.5\%$$

* Does not allow reaction with carbon.

** The ratio of methane produced to methane expected if all fuel (CO + H₂) was consumed:

$$\frac{(\text{CH}_4)_{\text{obtained}}}{[(\text{CH}_4)_{\text{obtained}} + (\text{H}_2 + \text{CO})/4]}$$

Table 5-19. Co-Current Steam Gasification - Second Stage Test Results (K1-23 and K1-24)
Low Carbon (Steamed) K1-Based BEACON Solids

TEST K1-23 - STEADY STATE DATA AT $455 \pm 5^\circ\text{C}$, 200 PSIG

		PRODUCT GAS			
	FEED GAS MOLES	OBTAINED EXPERIMENTALLY		PREDICTED FROM EQUILIBRIUM*	
		MOLES	V/V%	MOLES	V/V%
CH ₄	10.7	13.1	13.8	16.1	18.1
CO	3.1	1.2	1.3	0.2	0.2
H ₂	23.4	15.7	16.5	4.7	5.3
CO ₂	20.7	20.1	21.1	18.2	20.4
H ₂ O	39.5	42.5	44.6	47.4	53.1
N ₂	<u>2.6</u>	<u>2.6</u>	<u>2.7</u>	<u>2.6</u>	<u>2.9</u>
	100	95.2	100	89.2	100

METHANATION EFFICIENCY**
(BOTH STAGES):

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{13.1}{13.1 + 16.9/4} = 75.6\%$$

TEST K1-24 - STEADY STATE DATA AT $403 \pm 3^\circ\text{C}$, 200 PSIG

CH ₄	10.7	11.4	11.5	16.1	18.1
CO	3.1	1.3	1.3	0.1	0.1
H ₂	21.2	21.2	21.4	2.7	3.0
CO ₂	20.5	22.0	22.2	18.1	20.3
H ₂ O	41.1	39.8	40.2	48.8	54.7
N ₂	<u>3.4</u>	<u>3.4</u>	<u>3.4</u>	<u>3.4</u>	<u>3.8</u>
	100	99.1	100	89.2	100

$$\frac{\text{OBTAINED}}{\text{FULL CONVERSION}} = \frac{11.4}{11.4 + 22.5/4} = 67.0\%$$

* Does not allow reaction with carbon.

** The ratio of methane produced to methane expected if all fuel (CO + H₂) was consumed:

$$\frac{(\text{CH}_4)_{\text{obtained}}}{[(\text{CH}_4)_{\text{obtained}} + (\text{H}_2 + \text{CO})/4]}.$$

The data in Tables 5-17 through 5-19 indicate that near-equilibrium methane yield can be obtained at a temperature of 550°C. At this temperature the overall fuel conversion (methanation) efficiency was 78.3%. Between 550 and 450°C the conversion efficiency remained essentially constant but the methane yield did not approach the equilibrium value. Below 450°C the conversion efficiency as well as equilibrium approach dropped appreciably.

A comparison of the data from the countercurrent and co-current tests reveals that the countercurrent mode of operation produced a higher methane yield with higher fuel conversion efficiency at a lower operating temperature (500°C vs 550°C). The reason for the observed higher efficiency in the countercurrent mode is not readily apparent especially since the quantity of catalyst in the reactor on a carbon-free basis during co-current testing was appreciably larger than during countercurrent testing. However, since the larger catalyst content required a smaller total solids charge to the reactor, the co-current tests were performed at approximately half the gas residence time (twice the space velocity) of the countercurrent tests; the lower gas residence time may have been the reason for the reduced efficiency.

The data in Tables 5-17 and 5-18 indicate that the co-current mode of operation is feasible when the second stage is operated in the 475 to 550°C temperature range at 200 psig even though it may be slightly less efficient than the countercurrent mode.

5.2.4 Multi-Cycle Testing of K-1 Solids

The primary catalyst for SNG production, K-1 based BEACON solids, was subjected to 30 carbon deposition/steaming cycles at 100 psig and at 450°C and 650°C, respectively. One objective of this test was to determine the effect of pressure on catalyst performance and on fluidization properties of the solids after repeated cycles of carbon deposition and steaming. The tests were performed in the 4-inch diameter, 12 feet high reactor which was of adequate size to minimize apparatus related effects. The results were used in making the final selection of the catalyst for use in BEACON SNG scale up and as a major input to the design of a continuous solids feed and

withdrawal apparatus for long term physical and chemical activity testing of BEACON solids.. It was decided to cycle only the K-1 BEACON solids; if they failed the test, K-2 based solids would be the backup candidate. The 30 cycle testing was successfully completed with the K-1 BEACON solids.

A 1542-gram batch was used as the starting material for multicycle testing. Prior to bench scale testing, these solids were subjected to laboratory scale screening tests for catalytic activity. The tests showed good approach to equilibrium for the deposition and steaming reactions with no apparent deterioration in catalytic activity during the 10 cycles performed. The nominal test conditions selected for multicycle testing are summarized in Table 5-20. The test procedures used are delineated in Section 5.2.1, last paragraph. The results obtained are summarized in Figures 5-12 and Table 5-21.

Figure 5-12 presents the steam utilization and carbon gasification rates as a function of cycle number. Two conclusions can be drawn from these data concerning gasification performance:

- Steam gasification of K-1 based BEACON carbon took place virtually at equilibrium steam utilization (gasification rate).
- There was no discernible effect of cycling on either steaming or deposition efficiency.

Table 5-20. Nominal Multi-Cycle Test Conditions

Reactor Pressure:	115 PSIA
Reactor Temperature:	
● Carbon Deposition	450°C
● Carbon Steaming	650°C
Linear Gas Velocity:	10 cm/sec (0.3fps)
Feed Gas Composition (mol%):	
● Carbon Deposition	30% CO 15% H ₂ 5% CO ₂ 50% N ₂
● Carbon Steaming	90% Steam 10% N ₂

*EQUILIBRIUM PREDICTED VALUES FOR GRAPHITE-STEAM REACTION AT 100 PSIG AND 650°C

Figure 5-12. Steam Gasification of K-1 BEACON Solids (100 psig, 650°C)

Table 5-21. Steam Gasification of K-1 Based BEACON Solids at 100 Psig and 650°C

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

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

Furthermore, physical examination of the solids at the end of 30 cycles did not reveal measurable changes on the physical characteristics of the solids due to cycling: bulk density remained the same, fluidization behavior was virtually identical to that of the uncycled solids. SEM photographs revealed similar filamental particles to those of the starting solids.

The data in Figure 5-12 show appreciable scatter, but the scatter does not appear to be masking deterioration of catalytic activity.

The data scatter was due to "normal" experimental error in the control and measurement of operating parameters and to error due to "system upsets"; the data have been grouped accordingly in Figure 5-12. The circles represent the data within the expected deviation about the mean, which in the case of steam utilization is virtually identical to the equilibrium line. The mean deviation is less than 10% and can be easily justified by an error analysis of the measurement (e.g., a $\pm 5^\circ\text{C}$ variation in reaction temperature caused a variation of ± 2 percentage points in steam utilization). The Xs represent data generated under operational upsets where an appreciable fraction of the solids were outside the reaction zone. The majority of these upsets occurred between cycles 15 and 25 when problems were experienced with the automatic flow control of the feed gases. Electronic noise resulted in very large

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

The product gas composition data presented in Table 5-21[†] lead to the same conclusions concerning performance stability of the K-1 solids as those listed above based on the rate data in Figure 5-12. In this case there was a drop in methane concentration in the product gas from approximately 16% by volume to about 11% between cycles 1 and 3 and then it remained constant at $10.5 \pm 1\%$ in the remaining 27 cycles. This rather abrupt drop in methane concentration, and the corresponding small changes in the remaining components, was later traced to catalyst contamination. The recognition that methane suppression could be effected through modification of the composition of K-1 BEACON solids and the catalyst development effort detailed in Section 4.5 led to the identification of two very promising catalysts for the production of hydrogen from BEACON carbon.

The small reduction in methane yield observed during steaming at 100 psig in the 4-inch reactor became almost complete suppression of methane when these solids were steamed at ambient pressure. During the 30 carbon deposition/steaming cycles performed at 100 psig pressure in the 4-inch fluidized bed reactor, samples of solids were withdrawn at frequent intervals for characterization testing. These samples were subjected to

* The source of electronic noise was traced later to defective data logger channels.

[†] Data are presented for every 5th cycle except for cycle 20; because of system upsets between the 15th and 24th cycles, the compositional data were neither steady nor reliable (see discussion of this problem in the previous paragraph).

chemical and physical analyses and to activity tests at laboratory scale to verify catalyst performance in the 4-inch reactor. The laboratory scale tests were performed in a U-tube microreactor (1 to 2 gram beds) at ambient pressure. It was during these tests that the virtually complete suppression of methane was observed even though steam utilization and gasification rates were those indicated for near equilibrium operation.

The laboratory-scale data are summarized in Table 5-22. The first column shows the dry product gas composition obtained from steaming a sample of the K1-based BEACON solids before they were subjected to the 30 cycle testing in the 4-inch reactor. The measured composition was virtually identical to that expected from equilibrium operation (predictable from thermodynamic data).^{*} The first solids sample drawn from the 4-inch reactor for performance verification testing at laboratory scale was after 11 cycles were completed. The sample was steamed at laboratory scale at 600°C and 650°C; it showed very good steam utilization but almost complete absence of methane in the product gas. Steaming performance was virtually that predicted by thermodynamics for equilibrium steam gasification of graphite assuming complete suppression of methane (see Section 4.5.2.2, also). Samples drawn after 14, 18, 22, 26, and 30 cycles and steamed at laboratory scale furnished identical results to those described for the cycle 11 sample, i.e., high gasification rate but low methane yield.

The rather quick contamination of the catalyst was believed to be due to exposure of the reactor walls to high temperature carburization gas during shakedown and the first deposition-steaming cycle. These high temperature excursions during early testing created a question as to whether methane suppression was due to thermal effects or to chemical contaminants on K-1 BEACON solids. The catalyst development testings described in Section 4.5.2 eliminated temperature as the direct cause for methane suppression.

^{*} This fresh sample was cycled at laboratory scale in glass equipment for 10 cycles prior to using this batch of solids as the starting material for the 30 cycle testing in the 4-inch reactor. There was no change in either product gas composition or steam utilization during the laboratory scale cycling.

On the basis of both laboratory scale and bench scale data, the K-1 BEACON solids were selected for long term testing in the Tandem Reactor System.

Table 5-22. Laboratory-Scale Steam Gasification of K-1 Based BEACON Solids Carburized During Cycling in the 4-Inch Reactor

Product Gas Composition, Mole Percent Dry						
	Fresh Sample 600°C**	After 11 Cycles* 600°C** 650°C**		After 14 Cycles* 600°C** 650°C**		After 18 Cycles* 650°C**
CH ₄	9	<1	<1	<1	<1	<1
CO	16	14	23	10	18	18
CO ₂	29	25	20	27	22	23
H ₂	46	59	56	63	59	59
		After 22 Cycles* 600°C** 650°C**		After 26 Cycles* 600°C**	After 30 Cycles* 600°C**	
CH ₄		<1	<1	<1	<1	
CO		12	20	14	16	
CO ₂		27	21	27	25	
H ₂		61	59	59	58	

* At 100 psig pressure in the 4-inch reactor

** Laboratory steam gasification temperature

5.3 TANDEM REACTOR TESTING OF UNSUPPORTED BEACON SNG SOLIDS

The batch reactor data on SNG and hydrogen production from BEACON carbon described in the previous sections led to the selection of a primary and a back-up catalyst for each process for use in scale-up testing. This was the principal objective of the bench scale program. A second objective was the design, construction and testing of a scaleable reactor system which would permit the continuous, or near continuous, feed and withdrawal of solids from both the carbon deposition and steaming reactors of the BEACON process. The aim was to develop a reactor system which would permit the simultaneous, steady state operation of carbon deposition and steaming through continuous or frequent solids transfer between these units. Such a system was necessary as a precursor to scale-up reactor designs and as an efficient (cost effective) means of conducting long-term performance stability testing of BEACON solids at bench scale. This objective was met through the use of a "huff-puff" type tandem reactor system. In addition, the successful operation of this unit permitted the accumulation of over 600 hours of simultaneous carbon deposition-steaming time on K-1 based BEACON solids in SNG production. Catalyst performance was excellent with no indication of degradation in catalytic activity.

The tandem reactor system is a two reactor apparatus based on a variable differential pressure transfer line ("huff-puff") concept for the transfer of solids between BEACON carbon deposition and carbon gasification reactors instead of the lock-hopper type of solids feed and withdrawal system normally used in these type operations. The "huff-puff" transfer system does not require gas/solids separation prior to transfer, and therefore it is simpler than a lock-hopper type system for fluidized bed operations. Adaptation of the "huff-puff" concept in BEACON processing was considered possible because of the unique properties of BEACON solids-gas mixtures which give rise to stable fluid beds.

In the tandem concept the two reactors are connected with a fluid bed transfer line located below the top of the beds. Transfer is accomplished by establishing a small differential pressure between the two reactors at the frequency required. Solids are transferred back and forth by changing

the sign of the differential pressure. Less than 5% of the bed is transferred each time. Monitoring and control of the quantity of solids transfer can be accomplished by bed level or pressure monitors and by pressure or flow control valves. The two reactors can be operated at different operating conditions, except pressure, as needed to optimize deposition or gasification; pressure must be nearly equal in the reactors. The two additional requirements are that the relative size of the two reactors be such that the quantities of carbon deposited and gasified per unit time are equal and that both reactors operate under fluidized bed conditions.

5.3.1 Cold Flow Proof-of-Concept Testing

Proof-of-principle verification of the tandem reactor concept was first conducted in a cold flow unit constructed for this purpose. A schematic of the unit is shown in Figure 5-13 and a photograph of the constructed test facility in Figure 5-14. A more detailed engineering sketch of the unit is shown in Figure 5-15. The apparatus was constructed mostly with clear polycarbonate (Lexan) tube for visual observation of quality of fluidization and transfer behavior. It consisted of a gas delivery and metering system, a fluidization and solids transfer unit, and a solids recovery section. The system was capable of withstanding one atmosphere operating pressure above ambient (15 psig).

Nitrogen gas was used as the fluidization medium for the BEACON carbon. A two-stage regulator (Matheson) staged the high pressure gas from the nitrogen storage trailer down to a nominal working pressure of 120 psig. The gas was then split to two identical sets of gas metering equipment. Each fluidization vessel had individual gas metering equipment which consisted of a low pressure regulating valve (Belfram), a high accuracy test gauge (Ashcroft), a sonic nozzle (Lee), and a shutoff valve (Nupro). The low pressure regulating valve provided a stable discharge pressure (0-100 psig) to the sonic nozzle. In each case, the pressure gauge and sonic nozzle provided gas flow rates with accuracies of $\pm 1.0\%$. Gas flow rate (linear gas velocity in the fluidization vessel) was one of the parameters examined for its effect on the transfer of solids between vessels.

Figure 5-13. Cold Flow Tandem Reactor Schematic

Figure 5-14. Cold Flow Tandem Reactor Test Facility

Figure 5-15. Engineering Sketch of Cold Flow Tandem Unit

Based on the anticipated minimum size of the hot flow apparatus (tandem reactors), the cold flow fluidization vessels were constructed of 7.6 centimeter (3-inch) diameter pipe, 3 meter (10 feet) long. The geometry (slope and size) of the transfer tubes was another of the variables investigated during cold flow testing. Solids bed height and pressure differential between reactors prior to transfer were two additional variables examined for their effect on transfer. Solids entrained in the effluent gas from the fluidization vessels were separated and collected by cyclone and filter units connected in series.

Fluidization quality and solids transfer performance (efficiency) were monitored visually and through differential pressure measurements across each fluidization vessel and between the two vessels. The differential pressure measurements were verified by solids weight determinations.

The cold flow tests verified that BEACON solids could be transferred in the fluidized state between reactors in a tandem system by the "huff-puff" technique. The transfer could be conducted either in continuous or pulsed mode with no problem. Sloping transfer lines appeared to be preferable to horizontal lines. Gas velocity, in the range between minimum fluidization and entrainment of BEACON solids, did not affect solids transfer performance. Pressure drops between reactors of 1 to 4 psi proved adequate to transfer the required solids in 20 seconds or less. Figure 5-16 presents typical design curves generated during the cold flow proof-of-concept testing. These data were used in the design of the corresponding hot unit.

5.3.2 Tandem Reactor Apparatus and Procedures

The design of the tandem reactor system was based on rate data generated during batch reactor testing and on the cold flow information described in the previous section. These data led to the following design requirements for the reactor system:

Figure 5-16. Transfer of Fluidized BEACON Solids in 3-Inch Cold Flow Tandem Unit (Sloping Transfer Lines)

<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	10-85%	0-50%
● Hydrogen	5-30%	0
● Carbon Monoxide	10-50%	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 be compatible with the reactions and operating conditions.

The above requirements and the requirement that the apparatus needed to accommodate the quasi-continuous transfer of solids between the deposition and steam reactors led to the system depicted schematically in Figure 5-17. Detailed description of the apparatus and its component parts, including photographs of completed sections, are presented in Appendix B of this report. Figure 5-18 shows the reactor section of the apparatus completely installed and instrumented and Figure 5-19 the apparatus control panel; the Piping and Instrumentation Diagram is presented in Figure 5-20.

Briefly, the tandem system consisted 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. The deposition reactor had a 6-inch inside diameter and the gasifier a 3-inch inside diameter (the difference in reactor size was dictated by the difference in deposition and gasification rates at the desired operating ranges). Both reactors were constructed from 316 stainless steel parts and were surface aluminized by the Alon Process to prevent catalyst contamination from the reactor walls (especially through carburization of the deposition reactor walls).

Figure 5-17. Schematic Diagram of Tandem Reactor System

Figure 5-18. Tandem Reactors and Stand

Figure 5-19. Tandem Reactor Apparatus Control Panel
(Computer not shown)

Figure 5-20. Piping and Instrumentation Diagram, For Tandem Reactor System

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The "Alonization Process" was supposed to produce a continuous protective coating of aluminum-steel alloy on the reactor surfaces and solids transfer lines, but both visual observation and SEM photographs of sections cut from the dip-legs and transfer lines indicated defects in several places. Visual inspection revealed "rusty" spots on the surfaces; SEM photographs revealed hairline but deep cracks on the protective layer. The Alon Company representative inspected the reactor parts and concluded that the "rusted" spots were due to loose granules of steel and that after brushing them off, indicated there was nothing to worry about. This contention appeared to be justified by short-term carburization (12 and 24 hours) performance tests on the empty carbon deposition reactor (see data in next section). These tests showed insignificant carbon deposition on the reactor walls, especially the test performed subsequent to brushing the reactor; however, tests performed on specimens cut from transfer line tubing showed appreciable carburization potential.

Even though during the approximately 600 hours of carbon deposition-steaming operation catalyst contamination from reactor elements was minimal, the above experience with Alonization of 316 stainless steel suggests that such coating does not always guarantee protection against carburization. It is believed that a very clean surface is required prior to Alonization for successful coating; however, a ceramic lined reactor may be better for carbon deposition.

Upon completion of construction, the apparatus was subjected to a thorough shakedown where it was verified that it met the prescribed design requirements. The reactors were then loaded with the selected K-1 based BEACON solids, samples of which were pretested at laboratory scale, for the start of long-term, simultaneous carbon deposition-steaming testings. Approximately 6 kilograms of K-1 BEACON solids, prepared at ambient pressure in another unit, were loaded to the deposition reactor and about 1.5 kilograms to the steaming reactor. The reactors were brought to the desired temperature and pressure under nitrogen and then were switched to the corresponding reactive gases. The nominal carburization reactor feed gas composition was 10% CO, 5% H₂, 2% CO₂, and 83% nitrogen by volume.

Carbon monoxide was varied at times in order to fine tune the balance between the carbon deposition rate and the steaming rate (hydrogen was also changed in order to keep the CO/H_2 mole ratio at about 2). The feed to the steamer was 100% steam but in the reaction zone it was diluted by approximately 20% v/v nitrogen gas used to maintain the DP legs and solids transfer lines free of solids (purge gas). The nominal gas velocity in the deposition unit was 15 centimeters per second (0.5 fps) at 430°C and 7.8 atmospheres (100 psig); the corresponding nominal values for the steamer were 6 centimeters per second (0.2 fps) at 600°C or 620°C and 7.8 atmospheres (100 psig). During a brief parametric scan at the conclusion of the long-term testing both temperature and pressure were varied beyond the above values. The carburization gas was fed to the reactor slightly below reaction temperature (carbon deposition is exothermic) and the steam to the gasifier slightly above gasification temperature (endothermic reaction). The temperatures in the reactor (reaction zone) were kept constant, but the product gases were cooled immediately upon leaving the reactor (at least by 150°C before reaching the corresponding expander sections). Figure 5-21 illustrates typical temperature profiles obtained during deposition and steaming of K-1 BEACON carbon in the tandem system.

Carbon deposition and steaming took place simultaneously and at equal rates. Typical rates were approximately 400 grams carbon deposited or steamed per hour; thus, the net solids transfer from the deposition reactor to the gasifier was about 400 grams per hour. Nominally, transfers were conducted about once an hour; approximately 700 grams were transferred from the carburizer to the gasifier and about 300 grams in the opposite direction. These quantities represented about 10% of the total solids in the system so that the disturbance of steady state was minor (the transfer was noticeable for one gas chromatogram of the product gas of the gasifier but had no effect on the product gas of the carburizer). Solids were transferred from the bottom of the reaction zone of one reactor to the top of the reaction zone of the other reactor; occasionally, the direction was reversed. The two-directional transfer operation took about three minutes, including the time (about one minute) required for system equilibration between the single transfers.

Figure 5-21. Typical Temperature Profiles During Deposition and Steaming of K-1 Carbon in Tandem Reactor System

About every 50 hours of operation, samples of solids were withdrawn from each of the two reactors for characterization. About every 100 hours the solids were removed from the reactors, weighed, inspected, sampled, and reloaded for further processing; the data were used principally for verification of mass balances computed from feed and product gas flow rates and compositions. At the same time, the reactor walls were inspected for deposits or other changes. Care was taken not to contaminate the solids during these transfers and inspections; also, exposure to air was minimized.*

The data collected included the following: feed and effluent flow rate and composition; reactor temperatures and pressures; reactor gas velocities; pressure drop at several reactor bed levels (bed density and quality of fluidization); solids transfer rate; extent of solids entrainment in the product gas; changes in solids composition and physical properties as a function of processing time.

Most of the data was generated in two-shift operation but in order to verify system operability in around-the-clock operation, a 72 hour continuous run was performed prior to completion of the long-term testing.

5.3.3 Tandem System Results

System shakedown was almost uneventful. The most serious mechanical problem was the defective Alon coating of the deposition reactor which, through "empty" reactor carburization tests, proved to be inconsequential. The "empty" reactor tests (no solids present in the reactor) consisted of a 24 hour and a 12 hour exposure of the reactor walls to a high CO content carburizing gas mixture at carbon deposition conditions. The tests were performed at 100 psig and 450°C with a feed gas containing 33% carbon monoxide, 17% hydrogen and 50% nitrogen by volume. In the 24 hour test, the average carbon deposition rate was approximately 2.5 grams carbon per hour (less than 500 ppm CO₂ in the reactor effluent gas). The reactor was brushed well and the 12 hour test was performed. The carbon deposition

*Laboratory scale data indicated that ambient air exposure does not affect the reactivity of these solids (at least in BEACON related reactions).

rate was 11 grams in 12 hours or less than 1 gram per hour and the CO₂ concentration in the effluent was less than 150 ppm. These low deposition rates indicated that the catalytic activity of the reactor walls would not affect performance measurements or catalyst composition (catalyst contamination by metals leached from reactor walls) to a significant measure.

The only operational problem of any significance encountered during shutdown or testing was the poor performance of the internal reactor cyclones.* The problem was solved by the replacement of the cyclones with stainless steel filters.

Testing started with proof-of-concept demonstration and the determination of operability ranges for the apparatus and was completed with a long-term stability test on K-1 solids under simultaneous carbon deposition and steaming operations. The principal aspect of the tandem reactor concept requiring successful demonstration was solids transfer in the fluidized state; the other aspect demonstrated was reactor bed fluidization and the ability to monitor changes in bed weight through differential pressure measurements. In catalyst stability verification testing, methane yield and steam utilization were the yardsticks in steaming and fuel utilization was the measure of activity in carbon deposition.

The solids transfer system and its monitoring and recording instrumentation were tested successfully under nominal operating conditions (450°C, 100 psig deposition reactor and 600°C, 100 psig steam gasification reactor conditions); the system performed well from the start. Initial tests were conducted with nitrogen feeds at nominal reaction temperatures and pressures. BEACON solids were transferred back and forth between the deposition and gasification reactors by both manual and automatic manipulation of the transfer valves with no apparent problems. The transfer of solids was tracked well by changes in reactor bed differential pressures. Transfer system performance was subsequently verified with reactive gas.

*The inadequacy of the cyclones is believed to be due to inadequate reactor length; BEACON solids-gas separation techniques will be investigated during the next phase of BEACON development.

The system operated trouble free through hundreds of transfers during the long-term testing of BEACON solids. Upon completion of testing the transfer lines and valves were visually inspected for evidence of carbon deposits; none was found.

Figure 5-22 depicts a typical solids transfer cycle during tandem testing of the carbon deposition and steaming operations of the BEACON process (the curves are actual recorder traces). At the "start" of the transfer cycle, carbon lean solids were transferred from the bottom of the gasifier (right trace in Figure 5-22) to the top of the deposition reactor. In this case, approximately 150 grams of the lean solids were transferred from the gasifier to the deposition unit in about 20 seconds (each inch of horizontal scale represents 2.7 inches of water pressure drop which corresponds to 1300 grams of solids in the deposition reactor - 6 inches ID - and 325 grams of solids in the steamer - 3 inches ID); the reactors were allowed to equilibrate for about 2.5 minutes and then approximately 400 grams of high carbon solids were transferred from the deposition to the steam gasification reactor in about 30 seconds. The traces in Figure 5-22 show that the DP system tracked very well the transfer of solids between the reactors of the tandem system. The same traces tracked well carbon consumption versus reaction time in the steaming reactor and carbon deposition versus time in the deposition reactor. The amplitude and frequency of the "noise" in these traces reveal the changes in pressure drop in the fluidized bed; i.e., they show that the beds were fluidized and that the quality of fluidization was very good (uniform bed with small bubbles, if any, and no slugging).

A more direct evidence of fluidization is derived from the data in Table 5-23 which correlates the weight of solids in the bed to bed DP values. The data were generated at 600°C and 100 psig with K-1 based BEACON solids in nitrogen gas. Determinations performed at ambient pressure (not included in Table 5-23) showed that the weight of solids in the reactor bed can be computed directly and accurately from differential pressure measurements when the gas velocity in the reactor is above minimum fluidization value for the reactor solids. However, the data in Table 5-23

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

Figure 5-22. Typical Solids Transfer Operation (Tandem Reactors)

Table 5-23. Bed Weight Determination by DP Measurements

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

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

show that at 100 psig reactor pressure, the computed weight of solids was below the actual weight of solids in the reactor; also the drop was larger in the smaller reactor. However, a very reproducible "correction factor" was determined which permitted the correlation of reactor bed weight to reactor bed DP for each of the two reactors (last two columns of Table 5-23). Originally, it was believed that the discrepancy was due to wall effects, but differential pressure measurements in the reactor expander revealed that the underestimating of the solids in the reactor was due to loss of solids to the expander.* During testing with reactive gases the pressure drop in the expander was taken into consideration (also the gas velocity in the gasifier was reduced from 0.5 fps to 0.2-0.3 fps) and the correlation between computed and actual values was excellent.

Prior to K-1 performance stability testing under simultaneous carbon deposition and steaming operation (long-term testing) a number of tests with reactive gases were performed in order to bracket system operability and to correct system deficiencies, if any. Table 5-24 presents a summary of the data obtained during the first test with reactive gases in the tandem apparatus. The data show that the catalyst performed very well even though the charge of BEACON solids loaded to the tandem apparatus to start these tests were prepared more than a year previously and were stored in ambient air during the interim. Both product composition and steam utilization were close to thermodynamically predicted values; also, fuel conversion during deposition was excellent even though a high hydrogen, low CO content low Btu gas was used in this first test in order to make sure that the deposition reactor temperature could be controlled. Later tests showed that deposition temperature was no problem at appreciably higher deposition rates.

* The expander sections of the reactors had twice the diameter of the reactor sections; thus, the measured pressure drop due to solids that had escaped into the expander was 1/4 of the DP value that would have been measured if they had remained in the reactor. Since it was assumed that all the solids were in the reactor sections, the quantity of solids computed through pressure drop measurements was underestimated. It is also noted that the fraction of solids that escaped into the expander at the conditions of these tests (0.5 fps) was larger for the smaller reactors.

Table 5-24. Carbon Deposition/Steaming Test (Run T-1) - 100 Psig, 450°/650°C

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

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

Additional tests were performed at the same gas velocity but at lower temperatures and, in some cases, lower steam partial pressures. These data are summarized in Table 5-25. Again the product gas composition reveals proximity to equilibrium composition for graphite-steam reaction with some additional $\text{CO}/\text{H}_2\text{O}$ shift to CO_2 and H_2 (compare T-4 to 620°C equilibrium in Table 5-25). However, steam utilization was appreciably below the corresponding equilibrium value; the reason for the discrepancy was attributed to steam bypassing because of reactor pressure fluctuations. These fluctuations were caused by the installation of the wrong type filter* in the expander section and by the use of too high gas velocity in the gasifier. When a coarser filter was installed and the gas velocity was reduced by about half (from 0.5 fps to 0.2-0.3 fps), steam bypassing was eliminated and steam utilization approached equilibrium (see long-term test data, below).

The same batch of K-1 BEACON solids used in the nine tests discussed in the proceeding two paragraphs were also used in long-term testing. In order to make sure that the lower steam utilization was due to mechanical problems and not to activity deterioration from long storage in ambient air, samples from these solids were subjected to ambient pressure steaming at laboratory scale at 600° and 650°C. The results are summarized in the first two columns of Table 5-26 and are compared to the composition and steam utilization predicted by thermodynamic equilibrium for steaming of graphite carbon (last two columns of Table 5-26). The data are virtually identical which indicates that aging of K-1 based BEACON solids and exposure to air have no effect on their activity in steam gasification.

The nominal conditions during the long-term testing of K-1 solids in the tandem system were 7.8 atmospheres (100 psig), 620°C, and 6 centimeters per second (0.2 fps) gas velocity for steaming and 7.8 atmospheres (100 psig), 430°C, and 15 cps (0.5 fps) for carbon deposition. Steaming was initiated at 600°C and 15 cps (0.5 fps) gas velocity but in order to

*The fluctuations in pressure were due to the installation of an inappropriate filter (too small and too fine) in the expander section; the filter operated at high and variable pressure drops which affected the pressure control of the reactor.

Table 5-25. Tandem Reactor Steam Gasification Data (600°C, 100 Psig)

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

(a) Grams/Hour/SCFM steam feed

(b) 585 ± 10°C reactor temperature

(c) 615 ± 10°C reactor temperature

Table 5-26. Activity Screening Tests of BEACON Solids for Tandem Reactor Use*

Product Gas Composition, % V/V (Dry Basis)				
Specie	K-1 Carbon		Composition Predicted By Thermo.**	
	600°C	650°C	600°C	650°C
CH ₄	8	5	8.8	5.3
H ₂	48	50	49.3	51.0
CO	17	27	16.7	25.7
CO ₂	27	18	25.2	18.0
	<u>100</u>	<u>100</u>	<u>100.</u>	<u>100.</u>
Steam Utilization	70%	78%	70.7%	78%

* Screened at ambient pressure and at 600°C and 650°C. The steam feed rate was one gram per hour per gram of carbon initially charged to the reactor; at least 80% of the carbon was gasified.

** Based on graphite-steam equilibria.

attain smoother operation these values were changed to 625°C and 6 cps (0.2 fps), respectively. More uniform temperature profile (Figure 5-21, Section 5.3.2) was attained in the reactor when the steam temperature at the bottom of the reaction zone was at 620°C than at 600°C; the gas velocity was reduced in order to minimize solids escape into the expander section (the gasifier operated well at 0.3 fps, also). The gasifier feed was 80% v/v steam and 20% v/v N₂ (the latter served as purge gas for DP legs and solids transfer lines); the nominal carburizer feed was 10% v/v CO, 5% v/v H₂, 2% v/v CO₂ with the balance being nitrogen.* A single batch of K-1 BEACON solids was subjected to approximately 600 hours of BEACON processing (simultaneous carbon deposition and steaming in separate reactors). Processing time consisted of 420 hours of steady state operation and about 180 hours of transient operation (mostly start-up and shutdown). Processing time includes about 50 hours of parametric testing used to bracket apparatus operability ranges (discussed earlier) and a 73 hour around-the-clock run performed at the last part of the long-term testing in order to demonstrate tandem apparatus operability in continuous testing service; it does not include an additional 40 hours of operation performed at the conclusion of long-term testing to investigate pressure and temperature effects on extensively cycled solids. The catalyst performance data generated during long-term testing are summarized in Figure 5-23 and in Tables 5-27 and 5-28.

The top section of Figure 5-23 summarizes the performance of the carbon deposition operation expressed in terms of "fuel" (CO + H₂) utilization. Carbon monoxide and hydrogen utilization was high (near equilibrium) and constant throughout the near 600 hours of operation (420 hours of steady state processing). The middle and bottom sections of Figure 5-23 summarize data pertaining to the performance of the steam gasification operation. During the first 50 hours of operation, prior to installation

* Initially, the carburizer feed gas composition was 30% CO, 15% H₂, 5% CO₂ and 50% nitrogen; when the gas velocity in the steam reactor was reduced by 60% (the global gasification rate was also reduced proportionately), the CO feed rate had to be reduced accordingly in order to balance the global deposition rate with the global steaming rate; the H₂ and CO₂ were reduced proportionately to CO in order to maintain the constant component ratios in the feed.

Figure 5-23. Long-Term Performance of K-1 BEACON Solids Under Simultaneous Carbon Deposition and Steaming Operation at 100 psig (Tandem Reactor Testing)

Table 5-27. Stability of Product Gas Composition in Tandem Reactors
(Steam Gasification of K-1 Solids at 600°C and 620°C, 100 Psig)

Specie	Thermod. Predicted Composition		Product Composition, % V/V Versus Hours of Operation							
	600°C	620°C	50 Hrs*	100 Hrs*	150 Hrs*	200 Hrs**	250 Hrs**	300 Hrs**	350 Hrs**	420 Hrs**
CH ₄	21	19	22	24	19	21	20	20	20	20
H ₂	35	37	36	34	41	40	40	41	40	41
CO	9	11	3	1	3	2	4	1	2	1
CO ₂	35	33	39	41	37	37	36	38	38	38
% Steam Utiliz	61	62	62	61	63	59	62	62	62	59

- Typical Feed Composition: 80% Steam - Balance Nitrogen
- Typical Gas Velocities: 0.2 FPS in Gasifier, 0.4-0.5 FPS in Deposition Reactor

* 600°C Data

** 620°C Data

Table 5-28. Stability of Product Gas Composition in Tandem Reactors
(Carbon Deposition on K-1 Solids at 430°C, 100 Psig)

Species	Thermodyn. Predicted Composition* (430°C)		Hours of Operation (Test Data)							
			50 Hrs	100 Hrs	150 Hrs	200 Hrs	250 Hrs	300 Hrs	350 Hrs	420 Hrs
A. <u>PRODUCT GAS COMPOSITION, % V/V (NITROGEN FREE)</u>										
CH ₄	10.9	6.4	10.8	10.8	4.5	12.5	10.3	11.1	12.1	8.2
H ₂	17.7	11.8	16.5	18.8	16.8	14.4	20.3	22.3	18.6	18.0
CO	2.1	2.0	12.1	10.6	14.6	15.2	12.5	5.4	4.6	13.6
CO ₂	69.3	79.8	60.6	59.8	64.1	57.9	56.9	60.9	64.7	60.2
B. <u>FEED GAS COMPOSITION, % V/V (BALANCE NITROGEN)</u>										
CO	10	10	13	10	10	10	10	10	10	10
H ₂	5	5	7	5	5	5	5	5	5	5
CO ₂	0	2	3	2	2	0	0	1	1	1
C. <u>FUEL UTILIZATION</u>										
% CO	98.9	98.7	87	90	85	89	91	95	96	88
% H ₂	82.6	84.5	69	75	60	76	67	59	65	67

* Column 1 refers to feed composition without CO₂ and Column 2 to feed composition with CO₂.

of the appropriate size reactor filter, difficulties were experienced with pressure control, as discussed earlier, which influenced steam utilization and to a lesser degree methane yield (data represented by triangles in Figure 5-24). Once the reactor pressure stability problem was solved, steam utilization and methane yield reached equilibrium values and remained virtually at equilibrium, within normal test data fluctuations, for the duration of the 420 hour steady state operation at both steaming temperatures used. Neither the deposition nor the gasification data reveal any trend of catalyst deterioration.

The stability of K-1 catalyst performance is even more evident from the data presented in Tables 5-27 and 5-28, where a set of product gas composition data (dry and nitrogen free) are presented for every 50 hours of operation. Table 5-27 summarizes steaming data which are compared to compositions predicted by thermodynamics for equilibrium operation at 600° and 620°C (columns 1 and 2). The comparison of experimental data to equilibrium reveals that some CO (and steam) have shifted to CO₂ and H₂, probably at the transition zone (hot-to-cold) of the reactor. This indicates that K-1 solids are a good water shift catalyst as well as being an excellent methanation catalyst. Table 5-28 presents similar data on the carbon deposition operation; again product gas composition stability was excellent and agreement with thermodynamically predicted values very good. Feeds of low Btu gas with and without CO₂ were used during long-term testing; the only discernible effect was that CO₂ appeared, in some cases, to reduce the methane concentration in the spent gas (predictable also by thermodynamics).

Upon completion of the long-term test, a brief temperature and pressure scan (about 40 hours total processing time) was performed on the extensively cycled solids to determine if prolonged processing had any adverse effects on steaming performance at lower pressures or at higher temperatures than those used in cycling. The data are summarized in Figures 5-24 and 5-25. It is apparent that long-term processing had no detrimental effect on the performance of K-1 solids in the parametric ranges covered by these tests; the experimental data traced closely the temperature and pressure effects predicted by thermodynamics.

Figure 5-24. Effect of Temperature on Steam Methanation Performance of Recycled K-1 BEACON Solids

Figure 5-25. Effect of Pressure on Steam-Methanation Performance of Recycled K-1 BEACON Solids

Periodically during testing and at the conclusion of tandem testing, samples of the cycled K-1 solids were submitted to chemical and physical examinations in search of possible modification due to processing. The observed changes were insignificant. Emission spectrographic analyses showed that toward the end of long-term testing a very small quantity of iron started to appear on the catalyst (probable contamination from the reactor wall where the Alon coating was defective); no other chemical changes were apparent. Physically the catalyst appeared to consist of particles of more uniform size after processing than before. SEM photographs of before and after processing samples seemed to support this conclusion; no other changes were apparent from SEM analyses. Size distribution determinations will be attempted in the future on processed K-1 samples. There was no discernible change in fluidization behavior due to processing. Also, there was no change in bulk density due to processing according to the data in Figure 5-26. One deposition reactor sample taken after 250 hours of processing showed a 50% increase in bulk density, but it is believed that the sample was nonrepresentative.*

5.4 UNSUPPORTED HYDROGEN CATALYST SCREENING TESTS AT ELEVATED PRESSURE

The catalyst development effort detailed in Section 4 led to the identification of two promising candidate unsupported catalysts for the selective production of hydrogen through the steam gasification of BEACON carbon; the catalyst development testing was performed at ambient pressure. The objective of this pressure screening test was to evaluate the performance of the two previously selected catalyst candidates in the pressure range of one to 7.8 atmospheres (0 to 100 psig) at 600°C. Performance criteria were hydrogen selectivity (degree of methane suppression) and extent of steam utilization (gasification rate). The data were used to select the

*It is conceivable that the sample contained either low carbon material or crunchy carbon that had formed on internal reactor probes or on the wall as a cake rather than fiber. A few "crunchies" were present in every unloading (normally easily crushable); they were crushed against a screen and returned to the reactors.

Figure 5-26. Solids Bulk Density Versus Hours of Operation

better of the two catalysts for performance stability testing in the tandem reactor apparatus and to identify the best pressure for such testing.*

Testing was performed in the apparatus shown in Figure 5-27. The apparatus consisted of a constant gas feed (including steam) system, an electrically heated reactor and a gas conditioning system. It was appropriately instrumented for gas flow measurements, gas composition determinations, and temperature and pressure measurements.

Bottled gases supplied the carburization feed and an Altex Model 110A solvent metering pump supplied the steam through a homemade boiler. The feed system was capable of delivering the required feed gases and steam at pressures up to 18 atmospheres (250 psig) and 650°C. The entire feed system was constructed of 316 stainless steel.

The reactor consisted of a vertically mounted 1-inch O.D. (0.87-inch ID) x 7 feet long Inconel 600 tube equipped with a preheater section filled with quartz beads and Inconel screens at each end of the reaction zone for catalyst retention. The reaction zone was set at 60 centimeters (2 feet). The reactor was heated by a 10.3 KW Lindberg Type 54372-S-V four-zone tube furnace. The vertically-mounted suitcase type furnace was equipped with 1 foot long top and bottom zones with a pair of 2 foot long center zones for a total heated length of 6 feet. Each heating zone was separately controlled by its own temperature controller. External reactor wall temperatures were measured at four locations using sheathed thermocouples strapped to the reactor. A 10 gram charge of catalyst was used in these tests. After each steaming, to approximately 4-5 grams, carbon was re-deposited at 430°C to about 10 grams total solids. At the conditions of these tests, the catalyst bed was fluidized.

The product gas was cooled by at least 200°C immediately after leaving the reaction zone, filtered through quartz wool, and dewatered by a

* Stability testing on the hydrogen catalyst will be performed in the next phase of the BEACON development program.

Figure 5-27. Elevated Pressure Batch Reactor System
(Catalyst Screening Apparatus)

condenser/liquids trap system; it was then measured, sampled, and exhausted into a hood.

Catalyst No. 6 and Catalyst No. 11 (Table 4-19, Section 4.5.2.2) were selected for the pressure screening tests. These catalysts were modified forms of K-1 SNG solids highly selective to hydrogen. They differed in the quantity and composition of modifiers and in method of preparation; however, their ambient pressure performance was similar. An "empty reactor" (no solids) carbon deposition/steaming test was performed (2 cycles) at 7.8 atmospheres (100 psig) to determine the reactivity and/or catalytic activity of the apparatus (especially reactor walls). None was detected (only traces of CO_2 were detected during carburization). Pressure screening tests were performed at 1, 4.4, 6.1, and 7.8 atmospheres (0, 50, 75, and 100 psig) and 600°C. The steaming feed was 80% v/v steam and 20% v/v N_2 and the steam feed rate-to-carbon charge (start of test) ratio was one for most tests and 1.5 for the rest.* The carburization feed was 42% v/v CO, 8% v/v H_2 , and 50% v/v nitrogen (the 84% CO-16% H_2 commercially prepared gas mixture was used in laboratory scale testing was diluted here with nitrogen). The screening data generated in these tests are summarized in Figures 5-28 and 5-29 and in Tables 5-29 and 5-30.

Figure 5-28 illustrates the effect of pressure on steam utilization and on methane concentration in the product gas during steam gasification of Catalyst No. 6 promoted BEACON solids at 600°C; the experimental data (circles in Figure 5-28) are compared to thermodynamically predicted values for the same conditions (curves in Figure 5-28). Methane suppression (deviation from the equilibrium value) was appreciable at all pressures, but suppression (hydrogen selectivity) was higher at the lower pressures. At ambient pressure the methane concentration in the product gas was only 15% of that predicted by thermodynamics for "normal" (methane is allowed to form) equilibrium; at 4.4 atmospheres (50 psig) it was 34% of equilibrium, at 6.1 atmospheres (75 psig) was 42%, and at 7.8 atmospheres

*There was no detectable effect on performance in this range of ratios (of course, the global rate increased with increasing ratio).

Figure 5-23. Effect of Pressure on Performance of Catalyst No. 6 in Hydrogen Production from BEACON Carbon

Figure 5-29. Effect of Pressure on Performance of Catalyst No. 11 in Hydrogen Production from BEACON Carbon

Table 5-29. Pressure Effect of Hydrogen Selectivity of Catalyst No. 6

A. Experimental Data (600°C)*

Specie	0 Psig		50 Psig		75 Psig		100 Psig	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
CH ₄	1.3	1.1	6.5	5.8	8.3	8.8	10.9	9.7
H ₂	60.8	60.1	55.6	56.6	54.1	53.4	51.0	53.8
CO	16.9	17.1	10.7	10.2	9.3	9.1	8.7	8.5
CO ₂	21.0	21.7	27.1	27.4	28.3	28.7	29.4	27.9
% Steam Utilization	68	69	50	51	50	50	40**	33**

B. Equilibrium Data (Predicted for Steam*Graphite Reaction at 600°C)

Specie	0 Psig		50 Psig		75 Psig		100 Psig	
	Normal	Zero Methane	Normal	Zero Methane	Normal	Zero Methane	Normal	Zero Methane
CH ₄	7.9	0	18.0	0	20.5	0	22.5	0
H ₂	50.2	61.0	39.2	63.3	36.2	63.6	33.8	63.8
CO	17.7	17.0	10.5	10.0	9.3	9.0	8.5	8.2
CO ₂	24.2	22.0	32.3	26.7	34.0	27.4	35.2	28.0
% Steam Utilization	72.0	67.5	62.6	49.6	61.1	46.8	60.1	44.2

* 80% v/v steam + 20% v/v N₂ reactor feed.

** Very approximate values due to mechanical problems with apparatus.

Table 5-30. Pressure Effect on Hydrogen Selectivity of Catalyst No. 11

A. Experimental Data (600°C)*

<u>Specie</u>	<u>0 Psig</u>		<u>50 Psig</u>		<u>75 Psig</u>		<u>100 Psig</u>	
	<u>Run 1</u>	<u>Run 2</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 1</u>	<u>Run 2</u>
CH ₄	0.7	0.5	2.1	2.0	2.0	2.0	8.2	7.8
H ₂	60.4	59.5	61.4	61.0	61.6	62.0	55.0	55.1
CO	16.7	17.1	9.7	10.5	9.6	9.1	8.7	8.6
CO ₂	22.2	22.9	26.8	26.5	26.8	26.9	28.1	28.5
% Steam Utilization	63	65	53	50	46	47	47	47

B. Equilibrium Data (Predicted for Steam*Graphite Reaction at 600°C)

<u>Specie</u>	<u>0 Psig</u>		<u>50 Psig</u>		<u>75 Psig</u>		<u>100 Psig</u>	
	<u>Normal</u>	<u>Zero Methane</u>	<u>Normal</u>	<u>Zero Methane</u>	<u>Normal</u>	<u>Zero Methane</u>	<u>Normal</u>	<u>Zero Methane</u>
CH ₄	7.9	0	18.0	0	20.5	0	22.5	0
H ₂	50.2	61.0	39.2	63.3	36.2	63.6	33.8	63.8
CO	17.7	17.0	10.5	10.0	9.3	9.0	8.5	8.2
CO ₂	24.2	22.0	32.3	26.7	34.0	27.4	35.2	28.0
% Steam Utilization	72.0	67.5	62.6	49.6	61.1	46.8	60.1	44.2

* 80% v/v steam + 20% v/v N₂ reactor feed.

(100 psig) was 46%. The experimental values of steam utilization fell in between the thermodynamically predicted values represented by curves for "normal" and "suppressed methane" (methane is not permitted to form at all) equilibria; this was in accordance with expectation since methane suppression was not complete in most tests with this catalyst.

A more detailed picture of the effect of pressure on hydrogen selectivity by Catalyst No. 6 is presented by the data in Table 5-29. Experimental data on product gas composition and steam utilization (two runs at each pressure) in part A of Table 5-29 are compared to thermodynamic data for "normal" and "suppressed" methane equilibria in part B (bottom section) of the same table. The data show very good methane suppression at ambient pressure with a hydrogen-to-methane mole ratio as high as 50 to 1 at equilibrium steam utilization, adequate selectivity at 4.4 atmospheres (50 psig) with a hydrogen-to-methane ratio of 9 at above 50% steam utilization (near equilibrium), probably marginal selectivity at 6.1 atmospheres (75 psig) with a hydrogen-to-methane ratio of about 6 and at 7.8 atmospheres (100 psig) with an even smaller ratio (not reliably defined because of instrumentation problems at the time of the 100 psig runs with Catalyst No. 6).

A 10-to-1 hydrogen-to-methane ratio would yield 90% v/v or better hydrogen product if the CO is allowed to water shift to CO_2 and H_2 on the same catalyst at a little lower temperature than used in these tests. Tandem reactor testing (Section 5.3) revealed that K-1 solids are excellent water shift reaction catalysts.

Figure 5-29 and Table 5-30 present the same type of data for Catalyst No. 11. While gasification rate performance (steam utilization) was about the same as that observed with Catalyst No. 6,* hydrogen selectivity was better with Catalyst No. 11. The hydrogen-to-methane ratios were appreciably higher with this catalyst at all pressures tested. Table 5-31 highlights the hydrogen selectivity difference between these two promising hydrogen production catalysts. Clearly Catalyst No. 11 is the winner in

* Both catalysts exhibited steam utilization rates which were nearly identical to those expected for equilibrium operation.

Table 5-31. Hydrogen Selectivity Comparisons Between Catalyst Nos. 6 and 11

Pressure (psig)	Catalyst No. 6		Catalyst No. 11	
	(1) % CH ₄ Suppressed	(2) H ₂ /CH ₄	(1) % CH ₄ Suppressed	(2) H ₂ /CH ₄
0	84.8	50/1	92.4	100/1
50	65.8	9/1	88.6	30/1
75	58.3	6/1	90.2	31/1
100	54.2	5/1	64.4	7/1

$$(1) \% \text{CH}_4 \text{ suppressed} = \left(1 - \frac{(\text{CH}_4) \text{ measured}}{(\text{CH}_4) \text{ predicted}^{(3)}} \right) \times 100$$

(2) H₂/CH₄ volume or mole ratio in product gas.

(3) Predicted by thermodynamics for "normal" (unsuppressed methane) graphite-steam equilibrium.

this comparison. It is the one recommended as the primary candidate for performance stability testing (tandem reactor apparatus) with Catalyst No. 6 as the backup.

The pressure effect data on either catalyst also suggest that 4.4 atmospheres (50 psig) pressure would be a good selection as the commercial operating pressure for these catalysts; thus, it is the recommended pressure for tandem reactor testing. A second choice would be 6.1 atmospheres (75 psig). The intermediate pressures appear to also be a good compromise based on steam utilization considerations even when equilibrium operation is assumed. At pressures above 50 psig and complete methane suppression, steam utilization drops below 50% and keeps dropping as the pressure increases (refer to Tables 5-29 and 5-30 for examples).

5.5 SUMMARY OF BENCH SCALE EFFORT (4-INCH AND TANDEM REACTORS)

Batch testing of K-1 and K-2 based BEACON solids in the 4-inch high pressure, fluidized bed reactor represented a 1,000-to-1 scale up from laboratory scale testing. In general, the data generated at bench scale verified the tentative conclusions drawn about these catalysts at laboratory scale concerning their absolute and relative performance as BEACON process catalysts. These conclusions and observations were augmented with new ones based on pressure data. The principal findings of high pressure, batch reactor testing were as follows:

- Both K-1 and K-2 based BEACON solids proved to be active SNG production catalysts. K-1 solids promoted the BEACON carbon steaming reaction with about 20% higher rate than K-2 solids and the carbon deposition reaction by an even greater delta. K-1 solids were selected as the primary catalyst with K-2 as the backup catalyst.
- Specific gasification rates, expressed in weight of carbon gasified per hour per unit weight of solids in the reactor, at 600° and 650°C were estimated to be:

$$R_g (600^{\circ}\text{C}, 205 \text{ psia}) = 1.4 \pm 0.2 \text{ lbs carbon gasified per hour per lb solids in reactor}$$

$$R_g (650^{\circ}\text{C}, 205 \text{ psia}) = 2.8 \pm 0.2 \text{ lbs carbon gasified per hour per lb solids in reactor}$$

These rates were obtained at or near equilibrium steam utilization. The rate values were 2 ± 0.3 and $4 \pm .3$ lbs/hr/lb, respectively when normalized to carbon only rather than total BEACON solids. The 14 atmosphere (205 psia) rates were approximately twice as high as the corresponding ambient pressure rates; the reason for the enhanced efficiency at higher pressure was attributed to scale up (better performance at the higher scale because of good fluidization, large beds, etc.). (These rates are higher than those used in early engineering and cost analyses of the BEACON SNG process.)

- Two stage, countercurrent steaming was suggested by the 4-inch reactor data as an option to single stage steaming with polishing methanator. The suggested operating conditions were 600°-650°C, 14 atmospheres first stage to take advantage of high steam utilization and high gasification rates and 500°C, 14 atmospheres second stage to take advantage of increase methane formation (methane is thermodynamically favored at low temperature, CO and H₂ are not); the catalyst for both stages was K-1 based BEACON Solids. Steam utilizations in excess of 60% were achieved and an overall (two stage) dry product gas composition of 34.8% v/v CH₄, 1.5% v/v CO, 18.7% v/v H₂, 45% v/v CO₂ was obtained. Higher than 86% methanation efficiency* was attained in such two stage processing (it is noted also that the CO concentration in the product gas was very low).
- Maximum carbon deposition rates were not determined at pressure but CO utilization in excess of 90% and H₂ in excess of 70% were attained at the following conditions: 430°C, 7.8 atmospheres (100 psig), 10-30% v/v CO feed, 15 centimeters per second (0.5 fps) superficial gas velocity, <10 seconds residence time, K-1 catalyst.
- Repeated carbon deposition-steaming cycles (30) with K-1 based BEACON solids verified the validity of selecting K-1 as the primary catalyst for SNG production from BEACON carbon.

A two vessel fluid bed, high pressure, bench scale reactor apparatus (Tandem Reactor System) was constructed for use in long-term performance stability testing of BEACON solids. The apparatus was based on the concept of simultaneous carbon deposition and steaming operation in separate

* Methanation efficiency is defined as the ratio of methane produced in the two stages to the methane that could be produced if all of the unreacted CO + H₂ in the second stage reactor effluent were to be converted to methane by any means at any operating conditions.

vessels with continuous or quasi continuous transfer of solids between them in the fluidized state; a 2-4 psi pressure differential between the two reactor vessels provided the driving force for the transfer. The apparatus performed very well through almost 1,000 hours of system shakedown and BEACON solids testing, including 73 hours of around-the-clock operation. The concept of transferring BEACON solids by the "huff-puff" method in fluidized state was successfully demonstrated.

The tandem reactor apparatus was used to verify performance stability of K-1 based solids in production of SNG from low Btu gas by the BEACON process. A single batch of K-1 solids was cycled for about 600 hours (420 hours at steady state operation) with no discernible degradation in either deposition or steaming performance.

The two most promising promoters of hydrogen production from BEACON carbon were subjected to a brief matrix of pressure effect testing on hydrogen selectivity and production rates. Both catalysts performed very well up to 6.1 atmospheres (75 psig). Catalyst No. 11 (a modified K-1 type BEACON catalyst) was selected as the primary catalyst for stability testing in the Tandem Reactor System.

6. BEACON APPLICATIONS, CONCEPTUAL DESIGNS AND ECONOMIC ANALYSES

This section presents the results of preliminary economic evaluations of the BEACON process based on several conceptual commercial process designs and capital and operating cost estimates. Potential industrial applications for the production of hydrogen were analyzed on the basis of three potential sources of low-Btu feed gases (LBG). Production of hydrogen by the BEACON process appears to be marginally attractive if the feed gas is derived from a Flexicoker off-gas or an oil shale retort off-gas. The BEACON hydrogen process is potentially very attractive economically based on LBG from pressurized air-blown coal gasifiers.

In utility applications, the BEACON process would produce combined-cycle electric power and coproduct SNG in a very energy efficient and cost competitive system, which includes a pressurized air-blown coal gasifier. Power costs can be further reduced by utilizing the BEACON catalysts' high carbon content as an energy storage mechanism. In a utility load following concept, the capital intensive coal gasification section of the plant can be kept fully loaded with up to 30% reduction in power demand. The associated capital cost reduction significantly lowers the cost of electric power. Co-produced SNG can be used for further system load following by utilizing the coal derived SNG in peak power turbines.

6.1 INTRODUCTION

BEACON is a technology for converting the reducing gas components (CO and H_2) of low heating value gases to an activated carbon solid intermediary that can then be separated and reacted with steam to produce hydrogen or methane. The original BEACON concept was formulated during the natural gas shortage of the late 1970's. Then researchers were pursuing methods for generating substitute natural gas (SNG) from a variety of hydrocarbon sources, most notably coal. Coal can be gasified with combinations of steam and either air or oxygen. Oxygen blown gasification of coal requires an air separation plant and produces medium heating value gas, MBG. MBG can fuel industrial furnaces, power gas turbines and, being essentially synthesis gas, can feed many chemical and fuel processes

including methanol and SNG plants. Air blown gasification eliminates the need for air separation but requires larger equipment for an equivalent coal rate to accommodate the nitrogen. The low BTU gas (LBG) produced can fuel industrial furnaces, and an integrated coal gasifier combined cycle power plant is an efficient electric power alternative. LBG, however has limited use as a chemical or fuel feedstock...except through BEACON.

The objective of the following engineering analyses has been to evaluate the technical and economic feasibility of utilizing BEACON in various applications for the production of hydrogen, SNG, and cogenerated combined cycle power (CCP). This report summarizes three hydrogen design studies and two cases producing SNG/CCP from LBG.

Economic evaluations of the BEACON process are complicated due to: 1) uncertainties regarding the cost of the LBG feed gas to the process, and 2) the coproduction of steam or electric power. Pressurized air-blown coal gasifiers are not yet commercially proven, so reliable capital and operating costs are not available on a consistent basis that could be used to set feed gas costs. The value of coproduced combined cycle electric power should, in principle, be based on an alternative value established by a competitive oxygen-blown coal gasification combined cycle power plant. Again, the problem of costing such a system on a consistent basis arose since detailed equipment lists, etc., for such a system are not available to us. For these reasons, the economic analyses on the following pages rely mostly on baseline estimates for the cost of LBG feed gas, and estimated values for cogenerated electric power, steam, and SNG. Sensitivities and parametric analysis around these baseline estimates then indicate ranges which would make a commercial project economically viable.

The three hydrogen cases were evaluated for industrial applications assuming 100% equity financing. The two cases producing SNG and cogenerated CCP were evaluated on both an equity and utility financing basis. A description of the assumptions, premises, and other bases for both the equity and utility financing analyses are described in Section 6.4.

6.2 HYDROGEN PRODUCTION

Large quantities of hydrogen are consumed in oil refineries for desulfurizing oil products and upgrading heavy oil fractions to lighter transportation fuels (motor gasoline, diesel and aircraft turbine fuels). In the future, hydrogen requirements are expected to increase substantially for heavy oil and residuals processing, tar sands and shale oil processing, and for coal liquefaction plants. This hydrogen would normally be produced by the steam reforming of natural gas. A possible alternative is via shift conversion of synthesis gas generated by oxygen-blown coal gasification.

The BEACON process can produce hydrogen from LBG sources which in some cases have a relatively low value or cost. Three such sources were evaluated: 1) LBG produced as off-gas in the EXXON Flexicoker process, 2) LBG produced in oil shale retorts, and 3) LBG from an air-blown coal gasification plant. Conceptual commercial plant descriptions, flow diagrams, material balances, and details of the capital and operating costs are presented in the following sections:

6.2.1 H_2 from Flexicoker Off-Gas

6.2.2 H_2 from Oil Shale Retort Off-Gas

6.2.3 H_2 from Coal Derived LBG

The economic analysis of these cases is given in Section 6.2.4.

6.2.1 Hydrogen from Flexicoker Off-Gas

Flexicoking is a licensed Exxon process which integrates fluid bed coking with air gasification of the coke. This process is attracting increasing attention for processing heavy oils and residues because the coke from delayed cokers has little market value. Large volumes of off-gas, however, must find a use locally as fuel to make the Flexicoker a viable process option. Depending on feedstock and severity, a 50,000 barrel/day Flexicoker unit will produce 15 to 22 million SCF/hour of LBG. The BEACON process can be used to convert this LBG to H_2 and coproduct steam.

The conceptual design for this BEACON hydrogen plant produces 76×10^6 SCFD of hydrogen with a purity of over 97% from 18×10^6 SCF/hour of Flexicoker LBG. This feed gas, after sulfur removal in a Stretford unit, was assumed to have the composition given in an Exxon R&E paper (Hydrocarbon Processing, September 1979, page 138, Table 1). The process flow diagram and material balance for this BEACON plant are given in Figure 6-1 and Table 6-1, respectively. The sweetened Flexicoker off-gas fed to the BEACON carbon deposition reactors has a heating value of 117 Btu/SCF (HHV).

Eight trains of carbon deposition and steaming reactors are required. In the carbon deposition reactors, 75% and 40% of the CO and H₂ in the feed gas, respectively, are converted over the BEACON catalyst at 842°F (450°C). In the steaming reactors, 60% of the steam fed is converted at reactor conditions of 1112°F (600°C) and 22 psia. These conversions are consistent with laboratory data. Carbon-rich solids are pneumatically transferred from the carbon deposition reactors and carbon lean solids returned from the steaming reactors. The depleted gas from the carbon deposition reactors has an LHV of 54 Btu/SCF plus its sensible heat at about 840°F.

Steam gasification of the BEACON carbon is a highly endothermic reaction. With steam at 25 psia and 750°F, an additional 263×10^6 Btu/hr must be provided in order to maintain the bed temperature in the hydrogen production reactors. This heat is provided by combusting 60% of the carbon deposition reactor off-gases with excess air so that 2000°F gas can flow through heat exchanger coils located in the fluid beds. The remaining 40% of the carbon deposition reactor off-gas is combusted in a conventional furnace to generate and superheat steam. The hot gases from the in-situ heat exchanger coils at 1350°F also are used to generate and superheat steam. Flue gases are exhausted to the atmosphere at 275°F.

Raw BEACON hydrogen is cooled to 600°F to feed two stages of parallel shift conversion reactors. CO is converted, increasing the H₂ and consequently the CO₂ content. Shift reaction effluent gases are cooled, partially by heating methanation feed gases, and compressed to 278 psia to

Figure 6-1. Flexicoker Off-Gas to Hydrogen

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Table 6-1. Flexicoker Off-Gas to Hydrogen

Material Balance

Stream No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
Gas Flow (lb moles/hr)							
H ₂ O	2431	3717	80	80	220	55	6
H ₂	6963	8595	8595	8595	8218	8218	8218
CH ₄	561	57	57	57	175	175	175
CO ₂	4766	4306	4306	22	0	0	0
CO	8178	97	97	97	0	0	0
N ₂	23831	0	0	0	0	0	0
O ₂	0	0	0	0	0	0	0
Total:	46730	16772	13135	8851	8613	8448	8399
Temperature (°F)	100	320	120	120	602	120	120
Pressure (PSIA)	25	18	278	265	264	260	2515

feed a Selexol CO₂ removal plant. The product gas from CO₂ removal is heated against the shift reactor effluent to 430°F and fed to a single methanation reactor to react residual CO down to a level of less than 10 ppm total carbon oxides. The product gas is cooled and compressed to 2515 psia. This was selected as a nominal refinery pressure requirement for purposes of cost estimating and process comparisons.

Installed equipment costs for the BEACON plant are estimated at \$83 million, as shown in Table 6-2. This does not include costs for a Stretford unit to remove sulfur from the feed gas since this desulfurization step is frequently included with Flexicoker plant designs. Nevertheless, in economic evaluations, the cost of desulfurizing the feed gas must be considered in estimating the cost of this feed gas. Other capital investment costs, operating costs, and product revenues are given in Table 6-3. These data are used in the economic evaluations of Section 6.2.4.

6.2.2 Hydrogen From Oil Shale Retort Off-Gas

Combustion gas heated shale oil retorts (e.g. Paraho) produce large quantities of LBG. Proposed plants would utilize this retort off-gas to generate steam and power. The objective of this study is to assess the incentive for incorporating BEACON technology into an oil shale facility to produce hydrogen from such retort off-gas.

The process flow scheme for a 76×10^6 SCFD hydrogen plant is shown in Figure 6-2. The associated material balance is Table 6-4. The flow scheme is similar to the Flexicoker hydrogen plant. The hydrogen recovery scheme downstream of the steaming reactor is virtually identical. The heating value of this gas, however, derives mostly from light hydrocarbons rather than CO and H₂. This LBG is also notably different from Flexicoker and coal gasification derived LBG by its high CO₂ content (23%). Laboratory data have shown that this LBG can produce reactive carbon over the BEACON catalysts primarily by hydrocarbon pyrolysis rather than CO disproportionation. Preferred conditions for these reactions, as shown in the flow

Table 6-2. Hydrogen From Flexicoker Off-Gas

Installed Equipment Costs

Items	Number	Description	Installed Cost \$10 ⁶ (1983)
CD-1	8	Carbon Deposition Reactors and Coolers	6.6
SR-1	8	Steaming Reactors & Heaters	16.9
HTS/LTS	2 each	Shift Reactors	1.3
MR-1	1	Methanator	1.0
DM	2	KO Drums	1.0
HX 1-4		Heat Exchangers & Coolers	1.6
SG 1-4		Steam Generators & Superheaters	15.9
C-1		Combustor	1.5
CY 1-4	8 each	Cyclones	3.2
GC-1	6	LP Gas Compressors	21.0
GC 2-3		Air Blowers	3.8
GC 4	3	HP Hydrogen Compressors	4.5
AGR-1	1	Selexol System	4.7
Total Installed Cost			83.0

diagram, Figure 6-2, are two stages of carbon deposition preceded by removal of most of the CO₂ in a Benfield (or equivalent) acid gas removal step.

A significant cost factor associated with this LBG is the low pressure at which it is anticipated to be available, e.g., 13 psia. While no pressure optimization studies were made for this application of the BEACON process, the design was made consistent with experimental data for BEACON reactions at 35 psia. This required compression of the inlet gas to 45 psia, with a power requirement of almost 35,000 HP.

Table 6-3. Hydrogen From Flexicoker Off-Gas

<u>I. Depreciable Capital (\$10⁶)</u>			
A.	Total Installed Cost		83.0
B.	Off-Sites		8.3
C.	Project Contingency		24.9
			<hr/> 116.2
D.	Fixit.		5.8
E.	Initial Catalysts & Chemicals		4.5
F.	Prepaid Royalties		0.5
			<hr/> 127.0
<u>II. Investment Expense (\$10⁶)</u>			
A.	Owner's Engineering	Year 1	1.75
		Year 2	1.75
B.	Start-up	Year 4	1.8
C.	Property Tax & Insurance	Year 3	1.75
		Year 4	1.75
			<hr/> 8.8
<u>III. Working Capital (10⁶)</u>			
A.	Spare Parts	Year 4	1.2
C.	Accounts Receivable	Year 5	9.9
			<hr/> 11.1
<u>IV. Land (\$10⁶)</u>			
			5.0
<u>V. Fixed Operating Costs (\$10⁶/Year)</u>			
A.	Operating Labor (3 Shifts, 17 Man-Crew)		3.0
B.	Supervision, G&A		2.4
C.	Maintenance		3.5
D.	Insurance/Property Taxes		2.3
			<hr/> 11.2
<u>VI. Variable Operating Costs (\$10⁶/Year)</u>			
B.	Steam: 10psig, 750°F, 1.773x10 ⁸ lb/year		15.5
D.	Feed Gas: 16.5 x 10 ¹² Btu/Year		16.5 x
E.	Power Import: 42.76x10 ⁶ kWh/Year		2.4
F.	Catalysts & Chemicals		1.5
H.	Raw Water		0.1
			<hr/> 19.5+16.5 x
<u>VII. Revenues (\$10⁶/Year)</u>			
A.	Hydrogen: 8.61x10 ¹² Btu/Year		8.61 y
B.	Steam: 600 psig, Sat'd, 4.77x10 ⁸ lbs/Year		4.50
	600 psig, 720°F, 3.45x10 ⁹ lbs/Year		37.05
	15 psig, 260°F, 156.3x10 ⁶ lbs/Year		1.07
			<hr/> 42.6+8.61 y

Figure 6-2. Oil Shale Retort Off-Gas to Hydrogen

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Table 6-4. Oil Shale Retort Off-Gas to Hydrogen/Steam Via BEACON

MATERIAL BALANCE

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
H ₂ O (lb mole/h)	2428	2843	3162	3188		5063	4253	3814	1459	81	81	338	54	6		12528
H ₂	2424	2424	2298	6433		7479	8289	8729	8729	8729	8729	8089	8089	8089		
CH ₄	1057	1057	3333	1454		58	58	58	58	58	58	249	249	249		
CO ₂	10397	156	316	328		3110	3920	4359	4359	4359	65					2363
CO	1277	1277	639	589		1376	566	126	126	126	126					
N ₂	26877	26877	26877	26877	51473										9712	88071
O ₂					13683										2582	9845
ethylene	309	309														
ethane	265	265	79													
propylene	131	131														
propane	130	130	26													
1-butene	129	129														
n-butane	126	126	12													
1-pentene	80	80														
n-pentane	153	153														
hexane	51	51														
Total (lb mole/h)	45834	36008	36742	38869	65156	17086	17086	17086	14731	13353	9059	8676	8392	8344	12294	112807
Temp. (°F)	100	157	932	1022	70	1112	694	488	120	120	120	723	120	120	70	1127
Pressure (PSIA)	13	38	35	35	12	35	29	23	17	278	273	267	263	2515	12	12.5

The reactors are designed for a superficial gas velocity of 1 FPS and a minimum gas residence time of 10 seconds per reactor. Eight trains of carbon deposition and steaming reactors are connected through dense phase fluid transport solids circulating loops. The in situ heat exchangers provide 18 and 12×10^6 Btu/hr to each of the first and second stage deposition reactors respectively, and 31×10^6 Btu/hr to each hydrogen reactor. In the hydrogen reactors, 60% of the steam feed is converted to yield a gas that after CO shift, CO₂ removal and methanation results in a 97% H₂, 3% CH₄ product.

Eighty four percent of the depleted gas from carbon deposition is combusted to supply the heat requirements for the reactors. The remaining 16% of the carbon deposition off-gas is combusted, blended with exhaust from the in situ reactor heat exchangers and expanded to recover power prior to the HRSG. Although 42 MW are generated, an additional 23 MW are needed to meet process requirements.

Installed equipment costs for this BEACON hydrogen plant are estimated at \$138.5 million, as shown in Table 6-5. Total capital investment costs, operating costs, and product revenues are presented in Table 6-6. These data are used for the economic evaluations given in Section 6.2.4.

6.2.3 Hydrogen From Coal Derived LBG

The following conceptual process design and economic evaluation was made to assess the incentive for developing a BEACON catalyst selective for hydrogen production (i.e., one which suppresses methane formation) at pressures on the order of 300 psia. The LBG feed gas to BEACON is assumed to come from a pressurized, entrained flow slagging type coal gasifier. The feed gas composition from such a gasifier was estimated, assuming a dry feed system such as is used in the Shell gasifier. A Westinghouse or U-Gas type fluid bed gasifier would be equally suitable, although the feed gas composition would be different. There are two major advantages of this conceptual process relative to the Flexicoker and oil shale cases. First, the feed gas is derived from coal which is abundant in the U.S. This provides complete flexibility in plant location, rather than being limited

Table 6-5. Hydrogen From Oil Shale Retort Off-Gas

Installed Equipment Costs

<u>Items</u>	<u>Number</u>	<u>Descriptions</u>	<u>Installed Cost</u> <u>\$10⁶ (1083)</u>
CD	8	2-stage Carbon Deposition Reactors & Heaters	17.5
SR	8	Steaming Reactors & Heaters	15.0
C/F		Cyclones & Particulate Separators	26.6
FH	2	Start-up Heaters	2.0
HTS/LTS	2 each	Shift Reactors	1.0
MR	1	Methanation Reactor	0.3
		Steam Generators, Superheaters, HRSG	8.2
GC 1-3		Gas Compressors & Drives	18.5
		Air compressors, Gas Expanders, Gas Turbines, Burners	27.2
AGR-1	1	Benfield Acid Gas Removal	10.2
AGR-2	1	Selexol Acid Gas Removal	5.0
		Pumps, Air Coolers, KO Drums, other	4.0
CT-1	1	Cooling Tower	<u>3.0</u>
		Total Installed cost	138.5

Table 6-6. Hydrogen From Oil Shale Retort Off-Gas

<u>I. Depreciable Capital (\$10⁶)</u>			
A.	Total Installed Cost	138.5	
B.	Off-Sites	13.9	
C.	Project Contingency	41.6	
	Plant Capital	<u>194.0</u>	
D.	Fixit	9.7	
E.	Initial Catalysts & Chemicals	4.8	
F.	Prepaid Royalties	<u>0.5</u>	
			208.5
<u>II. Investment Expense (\$10⁶)</u>			
A.	Owner's Engineering	Year 1	2.9
		Year 2	2.9
B.	Start-Up	Year 4	1.8
C.	Property Tax & Insurance	Year 3	2.9
		Year 4	<u>2.9</u>
			13.4
<u>III. Working Capital (\$10⁶)</u>			
A.	Spare Parts	Year 4	1.9
C.	Accounts Receivable	Year 5	<u>10.0</u>
			11.9
IV.	<u>Land (\$10⁶)</u>		5.0
<u>V. Fixed Operating Costs (\$10⁶/Year)</u>			
A.	Operating Labor (3 Shifts, 17 Man-Crew)	3.0	
B.	Supervision, G&A	2.4	
C.	Maintenance	5.8	
D.	Insurance/Property Taxes	<u>3.9</u>	
			15.1
<u>VI. Variable Operating Cost (\$10⁶/Year)</u>			
D.	Feed Gas: 17.63×10^{12} Btu/Year	17.63 x	
E.	Power Import: 181×10^6 kWh/Year	10.3	
F.	Catalysts & Chemicals	1.7	
H.	Raw Water	<u>0.1</u>	
			12.1+17.63 x
<u>VII. Revenue (10⁶/Year)</u>			
A.	Hydrogen: 8.65×10^{12} Btu/Year	8.65 y	
B.	Steam: 600 psig, Sat'd, 3.275×10^9 lb/hr	<u>35.2</u>	
			35.2+8.65 y

to the location of shale oil plants or Flexicoking units. This coal derived hydrogen could also be used to feed fuel cells, and location flexibility will be important for such application. Second, this system operates at a pressure consistent with that of the gasifier effluent. This reduces the BEACON plant equipment size and gas compression requirements.

The process flow diagram for a 76×10^6 SCFD hydrogen plant is shown in Figure 6-3. The corresponding steam system is shown in Figure 6-4. The associated material balance is given in Table 6-7.

The LBG feed gas is assumed to be essentially sulfur-free (<5 ppmw) from upstream processing. Conversion of this gas in the carbon deposition reactors is consistent with laboratory data at 932°F (500°C), extrapolated to a pressure of 300 psia. Sixty percent of the steam fed to the steaming reactors is converted at 1112°F (600°C). Steam conversion and product gas composition are based on laboratory data at 45 psia; catalyst development work in progress is expected to provide a basis for process optimization at higher pressures.

The depleted effluent gas from the carbon deposition reactors is split. About 53% is combusted with air to provide a 2000°F flue gas which supplies the endothermic heat requirements of the steaming reactors through heat exchange tubes immersed in the fluid bed reactors. The remaining depleted gas provides the fuel for a combined cycle power plant. The gas turbines are assumed to operate with a turbine blade inlet temperature of 1850°F. Compressed air from these gas turbine-air compressor units provides combustion air to the gas turbines and to the burners for the steaming reactor in situ heat exchangers. Compressed air is also routed to the air-blown coal gasifiers to supply their air requirements. In the economic evaluations, output credit is taken for this compressed air equivalent to 49.8 MW of power required for its compression. This assumes that full and efficient utilization of this air can be achieved in an integrated coal gasification /BEACON/ combined cycle power plant design. A total of 87.1 MW of power is produced; process power requirements are 13.7 MW, leaving a net power production of 73.4 MW for export.

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Figure 6-3. LBG to H₂/Power Via BEACON/Combined Cycle: Process Flow Diagram

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Figure 6-4. LBG to H₂/Power Via BEACON Combined Cycle - Steam System

Table 6-7. Hydrogen From Coal Derived LBG

MATERIAL BALANCE

	1	2	3	4	5	6	7	8	9	10	11	12
CH ₄ , M/HR		789	422	367							57	57
CO	11,985	2,277	1,218	1,059							1,350	503
CO ₂	2,588	7,048	3,769	3,279		5,409		10,114	10,114		3,052	3,899
H ₂	4,384	2,017	1,079	938		2,345					7,342	8,189
H ₂ O		789	422	367				4,384	4,334	12,425	4,970	4,123
O ₂					3,859	1,867	190	324	437			
N ₂	31,208	31,208	16,687	14,521	14,519	31,206	715	46,442	47,057			
Total, M/HR	50,165	44,128	23,597	20,531	18,378	40,827	905	61,264	62,042	12,425	16,771	16,771
	13	14	15	16	17	18						
CH ₄ , M/Hr	57	57	57	163	163	163						
CO	84	84	84									
CO ₂	4,318	4,318	22									
H ₂	8,608	8,608	8,608	8,268	8,268	8,268						
H ₂ O	3,704	79		128	55	5						
O ₂												
N ₂												
Total, M/Hr	16,711	13,146	8,771	8,559	8,486	8,436						

Effluent gas from the steaming reactors goes through two stages of shift conversion, CO₂ removal in a Selexol Unit, trim methanation, and compression to 2530 psia.

Installed equipment costs for this hydrogen and cogenerated power plant are estimated at \$93.9 million, as shown in Table 6-8. The power recovery part of the plant accounts for 55% of the installed cost. Total capital and operating costs and product revenues are shown in Table 6-9. These data are used in the economic evaluations discussed in Section 6.2.4.

Table 6-8. Hydrogen From Coal Derived LBG

<u>Installed Equipment Costs</u>	
	Installed Cost \$10 ⁶ (1983)
BEACON System (2 trains of Reactors) (deposition and steaming reactors, coils, cyclones, pumps, drivers, catalyst storage & conveyance, start-up heater, etc.)	24.9
Gas Cooling	1.1
Shift Conversion	5.2
Methanation	1.1
Hydrogen Compressor	6.7
Acid Gas Removal	3.6
Combustion Gas Turbine	28.4
Heat Recovery Steam Generator	9.0
Steam Turbine	12.7
Cooling Tower	<u>1.2</u>
Total Installed Cost	93.9

Table 6-9. Hydrogen From Coal Derived LBG

<u>I. Depreciable Capital (\$10⁶)</u>			
A.	Total Installed Cost		93.9
B.	Off-Sites		9.4
C.	Project Contingency		28.2
	Plant Capital		131.5
D.	Fixit		6.6
E.	Initial Catalyst & Chemicals		2.5
F.	Prepaid Royalties		<u>0.5</u>
			141.1
<u>II. Investment Expense (\$10⁶)</u>			
A.	Owner's Engineering	Year 1	1.85
		Year 2	1.85
B.	Start-Up	Year 4	2.3
C.	Property Tax and Insurance	Year 3	1.85
		Year 4	<u>1.85</u>
			10.1
<u>III. Working Capital (\$10⁶)</u>			
A.	Spare Parts	Year 4	1.3
C.	Accounts Receivable	Year 5	<u>13.3</u>
			14.6
<u>IV. Land (\$10⁶)</u>			
			5.0
<u>V. Fixed Operating Costs (\$10⁶/Year)</u>			
A.	Operating Labor (3 Shifts, 7 Man-Crew)		1.2
B.	Supervision, G&A		1.0
C.	Maintenance		3.9
D.	Insurance/Property Taxes		<u>2.6</u>
			8.7
<u>VI. Variable Operating Costs (\$10⁶/Year)</u>			
D.	Feed Gas: 15.75x10 ¹² Btu/Year		15.75 x
F.	Catalysts and Chemicals		0.6
H.	Raw Water		<u>0.2</u>
			0.8+15.75 x
<u>VII. Revenues (\$10⁶/Year)</u>			
A.	Hydrogen: 8.52 x 10 ¹² Btu/Year		8.52 y
B.	Power Export: 578.7x10 ⁶ kWh/Year		33.0
C.	Power Equivalent of Compressed Bleed Air: 392.5x10 ⁶ kWh/Year		<u>23.6</u>
			56.6+8.52 y

6.2.4 Economic Analysis of Hydrogen Cases

There is a high degree of uncertainty about the cost of LBG feed gas to the BEACON system in each of the three hydrogen cases. Therefore, the objective of these economic analyses is to indicate a range of feed gas costs which would make a BEACON hydrogen plant competitive with an alternative hydrogen plant based on conventional steam reforming of natural gas.

These industrial applications of the BEACON process are based on 100% equity financing, with a constant dollar or "real" internal rate of return (IRR) calculated by standard discounted cash flow (DCF) analysis. (See Section 6.4.1 for details). An acceptable IRR would be in the range of 10 to 15%, dependent on other risks associated with a given project. Our evaluation technique is to establish a hydrogen product value based on steam reforming of natural gas, then use this value to determine the break-even cost which could be paid for LBG to obtain a 10 or 15% IRR.

The installed capital cost for a 76 million SCFD steam-methane reforming plant, Gulf Coast construction, is about \$47.6 million. This is derived from actual costs of a recent H_2 plant installation with appropriate location and installation adjustments. Other capital and operating costs were developed on the same basis as the comparative BEACON cases, as shown in Table 6-10. From these data, the value of H_2 is determined to be \$10.70 and \$11.70 per million Btu for 10 and 15% IRR, respectively. Sensitivity of this value to potential escalation in the real (non-inflation) costs of natural gas up to 2% average annual increase (AAI) is shown in Figure 6-5. The indicated H_2 values are effective fixed values over the 20 year operating life of the plant which will provide the indicated 10% and 15% return on investment. This assumes the H_2 value stays constant in spite of escalating costs for the methane feed gas. The resulting H_2 product values were used to determine the break-even costs for LBG in the BEACON cases, using the same IRR for the BEACON cases and the comparative steam-methane reformer case.

Table 6-10. Hydrogen From Steam-Methane Reforming

<u>I. Depreciable Capital (\$10⁶)</u>			
A.	Total Installed Cost		47.6
B.	Off-Sites		4.8
C.	Project Contingency		14.3
	Plant Capital		<u>66.7</u>
D.	Fixit		3.3
E.	Initial Catalysts & Chemicals		1.9
F.	Prepaid Royalties		0
			<hr/> 71.9
<u>II. Investment Expense (\$10⁶)</u>			
A.	Owner's Engineering	Year 1	1.0
		Year 2	1.0
B.	Start-Up	Year 4	0.7
C.	Property Tax & Insurance	Year 3	1.0
		Year 4	<u>1.0</u>
			4.7
<u>III. Working Capital (\$10⁶)</u>			
A.	Spare Parts	Year 4	0.7
C.	Accounts Receivable, Net	Year 5	<u>10.1</u>
			10.8
<u>IV. Land (\$10⁶)</u>			
			5.0
<u>V. Fixed Operating Costs (\$10⁶/Year)</u>			
A.	Operating Labor (3 shifts, 6 Man-Crew)		1.1
B.	Supervision, G&A		0.9
C.	Maintenance		2.0
D.	Insurance/Property Taxes		<u>1.3</u>
			5.3
<u>VI. Variable Operating Costs (\$10⁶/Year)</u>			
B.	Steam: 50 psig, Sat'd, 29.75x10 ⁶ lb/Year		0.2
	330 psig, Sat'd, 258x10 ⁶ lb/Year		2.2
C.	Natural Gas: 11.76x10 ¹² Btu/Year		70.6
E.	Power Import: 108.9x10 ⁶ kWh/Year		6.2
F.	Catalysts and Chemicals		1.0
H.	Raw Water: 94.45x10 ⁶ Gal/Year		<u>0.04</u>
			79.8
<u>VII. Revenues (\$10⁶/Year)</u>			
A.	Hydrogen: 8.74x10 ¹² Btu/year		8.74 y
B.	Steam: 640 psig, Sat'd, 783x10 ⁶ lb/Year		<u>7.4</u>
			7.4+8.74 y

Figure 6-5. Hydrogen Value as Determined From Steam-Methane Reforming

A summary of the BEACON and steam reformer input/output streams and depreciable capital and operating costs is shown in Table 6-11. While the steam reformer costs are lower, the BEACON cases have substantial coproduct values in steam and power generation. Results of the DCF calculations are shown in Figure 6-6. These results show break-even LBG costs for a range of 10-15% IRR and H₂ product values based on \$6.00/10⁶ Btu natural gas and real increases up to 2% AAI above that gas cost. From this chart, the following break-even costs for LBG can be estimated:

<u>Source of LBG</u>	<u>Break-even Cost \$/10⁶ Btu</u>
Flexicoker Off-Gas	4.40 - 5.40
Oil Shale Retort Off-Gas	2.70 - 4.00
Coal Derived LBG (air-gasification)	6.40 - 7.40

In the Flexicoker off-gas case, the LBG break-even cost is 75-90% of the value of natural gas. For a Flexicoking facility located in a refinery or heavy oil/tar sand upgrading plant, LBG could displace natural gas as the refinery fuel. The incremental cost of installing boilers capable of using this LBG in a new refinery or tar sands plant is marginal so the value of the Flexicoker LBG in that situation would be close to natural gas costs - assuming natural gas availability at the site. Installation, however, of a Flexicoking unit in an existing refinery could result in extensive revamps of existing boilers and furnaces, additional boilers to compensate for derating, and lost production due to the impact of modifying existing facilities. For this situation, we have estimated that these costs plus efficiency losses would reduce the fuel value of Flexicoker LBG to 80-90% of the cost of natural gas. This suggests that the BEACON process might have some limited, but not widespread, application in new Flexicoker installations at existing refineries. Potential improvement in the BEACON design could be made with development of the new catalysts which suppress methane formation and permit operation at higher pressures. Feed gas compression costs would increase, but product gas compression and reactor costs and the number of parallel reactor trains would decrease. A detailed analysis of this design option has not been made.

Table 6-11. Summary of Hydrogen Cases

Case No.	1	2	3	A*
<u>Input Requirements</u>				
Feed Gas				
Source	Flexicoker	Shale Retorts	Coal Gasifiers	Natural Gas
Flow, 10^6 SCFD	425	417	456	34.4 (incl. fuel)
HHV, 10^9 Btu/day	49.7	53.4	48.1	35.6
Power, MW	5.4	23	-	13.8
Steam, 10^3 lb/hour				
Low Pressure, superheated	-	228	-	-
300 psig, sat'd	-	-	-	252
<u>Products</u>				
Hydrogen (97-98%)				
Flow, 10^6 SCFD	76.4	75.9	76.7	76.6
HHV, 10^9 Btu/day	25.9	26.2	25.9	26.5
Power, MW	-	-	73.4	-
Steam, 10^3 lb/hour				
600-640 psig, sat'd	40.1	-	-	99.3
600 psig, superheated	667	414	-	-
<u>Depreciable Capital Cost,</u>				
$\$10^6$ (1083)	127	209	141	72
<u>Operating Cost, $\\$10^6$/year**</u>	113	115	88	85

* Case A is steam-methane reforming for comparison.

** Basis natural gas at $\$6/10^6$ Btu and LBG at $\$5/10^6$ Btu (HHV).

Figure 6-6. Break-Even Cost of Feed Gas

For the oil shale retort off-gas case, an acceptable LBG cost would be 45-65% of the assumed cost of natural gas. This LBG has little direct fuel value at an oil shale processing plant because the huge volumes produced far exceed plant fuel requirements. It could be used to generate electric power for export. An analysis was made of the value of this LBG based on an efficient combined cycle power plant generating export power. This study indicated an alternate use value of this LBG as only 40% ($\$2.35/10^6 \text{ Btu}$) of the assumed cost of natural gas. Therefore, the BEACON hydrogen system could be an attractive alternative (greater than 15% IRR) to power generation as a means of utilizing the large volumes of LBG produced in some proposed oil shale projects. Examples include the Paraho combustion gas heated shale oil retorts or the off-gas from in-situ retorts.

The most interesting of the hydrogen systems is that based on LBG feed gas from a pressurized air-blown coal gasification system. The depleted gas is used to generate export power in a combined cycle system. This export power plus credit for the compressed air supplied to the gasifiers from the gas turbine system together account for approximately 35% of product revenues. Literature data plus some limited internal studies indicate that pressurized LBG could be produced for less than $\$6.00/10^6 \text{ Btu}$, perhaps in the range of $\$5.00$ - $\$5.50/10^6 \text{ Btu}$. These costs are well below the break-even value which would yield greater than 15% IRR for the BEACON plant.

A more conservative approach to an evaluation of this case would be to assign a value of $\$10.70/10^6 \text{ Btu}$ to product hydrogen. This is based on steam reforming of natural gas, with a cost $\$6.00/10^6 \text{ Btu}$, and an IRR of 10% - probably a minimum acceptable return on an industrial investment using proven technology. With this fixed value of competitive product hydrogen, the IRR of the BEACON LBG to hydrogen plus combined cycle power case was determined as a function of LBG cost and coproduct electric power value. Results shown in Figure 6-7 indicate the sensitivity to these parameters. Department of Energy statistics for February 1983 show a national average cost for purchased electricity by the industrial sector was 4.96 cents per kWh. Figure 6-7 shows that even if coal derived LBG

costs were as high as projected natural gas costs of $\$6.00/10^6$ Btu, over 12% IRR could be achieved by an industrial, equity financed, BEACON hydrogen project in which the cogenerated power displaced electric power purchased at a cost of 5 cents per kWh. With pressurized LBG at a more likely cost of $\$5.00/10^6$ Btu (constant 1983 \\$), the IRR would approach 17%.

This analysis assumes 100% equity financing of the coal gasification project; costs would be appreciably less on a utility financing basis. In some locations, it might be appropriate to consider a utility financed air-blown coal gasification combined-cycle power plant with a slip stream of the LBG used to produce H_2 via the BEACON process. The H_2 could be sold to a nearby refinery via pipeline transport. Perhaps a better alternative for future application would be to use the H_2 in utility fuel cells. If

Figure 6-7. Sensitivity of Internal Rate of Return (IRR) to Cost of LBG and Value of Coproduct Electric Power

the fuel cells are designed to handle a mixture of $H_2 + CO$, the BEACON costs for downstream shift conversion, acid gas removal and methanation would be eliminated.

The type of air-blown pressurized gasifiers suitable for this application should be considered. Published information suggests that a fluid bed gasifier of the type under development by Westinghouse and IGT (U-Gas) could be efficient and cost-effective air gasifiers. Theoretically, a pressurized, entrained flow, slagging gasifier with a dry feed system would be the most suitable and efficient unit. This is the type under development by Shell Oil Company. Its product gas contains no methane and very low levels of CO_2 . Unfortunately, all three of these developers are concentrating efforts on oxygen-blown gasification. They are all adaptable to air gasification, however, if market demand warrants such application. Another gasification system that could be considered is the Allis-Chalmer Kilngas process. This is designed for air gasification and a demonstration unit is expected to start up in 1983. This system operates at lower pressure than the others and is not expected to be as efficient or cost-effective for a BEACON application as the higher pressure fluid or entrained bed systems mentioned above.

6.3 PRODUCTION OF SNG AND COGENERATED POWER

Two cases for cogeneration of SNG and electric power are developed in this study. The first case starts with an LBG feed and analyzes the cost of power as a function of the cost of the LBG feed. The second case includes a Westinghouse type coal gasification system and adds a unique capability of the BEACON system which permits load following at a very low incremental cost.

6.3.1 SNG/Power From LBG

The BEACON/combined cycle power plant was sized to produce about 450MW electric power. The LBG feed gas composition is the same as used in the coal derived LBG to H_2 case, which is based on an assumed entrained flow, dry feed, slagging type gasifier. This could be obtained in a Shell Oil Company type gasifier if the oxidant were air rather than oxygen. A total feed gas flow of $1,750 \times 10^6$ SCFD is required, giving a net export power

production of 445 MW and coproduction of 79.3×10^6 SCFD of SNG. This LBG feed is assumed to have been desulfurized to <10 ppmw sulfur and is available at a battery limit pressure of 300 psia and temperature of 120°F.

Figure 6-8 shows the process flow diagram for this case, with the related material balance given in Table 6-12.

LBG, Stream 1, is fed to the BEACON Carbon Deposition Reactors CD-1 where 81% of the CO and 54% of the H_2 are converted. Eight reactor trains are required. The carbon deposition reactions take place in the reactors in a fluidized bed of carbon-rich solids at a temperature of 932°F (500°C). The exothermic heat of reaction is removed by HP steam generation coils, CDX-1, and MP steam reheat coils, CDX-2, immersed in the fluid bed. Solids entrained in the effluent gas from the reactor are removed in cyclones CY-1, CY-2, and filter F-2.

The hot, solids-free, partially depleted LBG from the carbon deposition reactors, Stream 2, at 932°F, 295 psia is split. Approximately 88% of the gas, Stream 3, is used to fuel a 1985°F inlet combustion gas turbine. The remaining 12% of the gas, Stream 4, is combusted to provide a 2,000°F flue gas, Stream 6, which serves as an indirect heat source (via coils immersed in the fluid bed) for the endothermic carbon steaming reactions.

Air is compressed in the combustion gas turbine axial compressor to 205 psia, 730°F. Approximately 55% of the compressed air is bled off to supply the air requirements of the coal gasification plant (not shown). An additional 6% of the compressed air is utilized to generate the 2,000°F flue gas for the steaming reactor heat input coils. The remainder of the air, along with the 1400°F oxygen containing flue gas from the steaming reactor coils, is used to generate the 1985°F combustion turbine inlet gas from the partially depleted LBG, Stream 3. Exhaust gas from the turbine, Stream 6 at 1,012°F, flows to the Heat Recovery Steam Generator (HRSG). A total of three Westinghouse W-501D Combustion Gas Turbines is required. Each unit generates 101.2 MW (net) power for a total of 303.6 MW.

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Table 6-12. LBG to SNG/Power Via BEACON/Combined Cycle

MATERIAL BALANCE TABLE

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12
CH ₄ , M/Hr		3,024	2,666	358				7,467	7,467	7,467	8,500	8,500
CO	45,925	8,726	7,694	1,032				579	579	579		
CO ₂	9,919	27,007	23,813	3,194	4,584	38,757		9,041	9,041	498	44	44
H ₂	15,801	7,729	6,815	914				3,728	3,728	3,728	175	175
H ₂ O		3,024	2,666	358	1,988	16,801	34,703	16,041	70		8	1
O ₂					1,582	11,136						
N ₂	119,589	119,589	105,445	14,144	26,451	215,186						
Total, M/Hr	192,234	169,099	149,099	20,000	34,605	281,880	34,703	36,856	20,825	12,272	8,727	8,720
Temp, °F	120	932	932	932	2,000	1,012	900	1,022	100	80	100	100
Pressure, PSIA	300	295	295	295	205	15	400	300	285	275	1,020	1,015

Each turbine feeds hot flue gas to a separate HRSG. The exiting flue gas temperature from the HRSG is 275°F. The heat recovered in each HRSG is approximately 547×10^6 Btu/hr for a total of $1,642 \times 10^6$ Btu/hr heat input to the steam system.

The carbon-rich solids from the deposition reactors are transported to the Steaming Reactors, SR-1. Eight steaming reactors are required. The carbon steaming reactions take place in the reactors in a fluidized bed of solids at 1,022°F (550°C). Carbon laid down on the solids in the deposition reactors is steamed off to form a gas containing CO, CO₂, CH₄, H₂, and unreacted steam. The effluent gas is assumed to be at equilibrium for the reactor conditions. Approximately 88% of the CH₄ in the final SNG product is produced in the steaming reactor. The steam feed to the reactor, Stream 7, is at 900°F. The heat for the endothermic steaming reactions is provided by flowing hot flue gas through coils immersed in the fluid bed. Flue gas enters the coils at 2,000°F and exits at 1400°F. The carbon-lean solids from the steaming reactors are circulated back to the deposition reactors. Solids entrained in the effluent gas from the steaming reactor are removed in cyclones CY-3, CY-4. The raw SNG, Stream 8, is then cooled in Gas Cooling Unit, CL-1, to 326°F. A total of 344×10^6 Btu/hr of heat is removed from the gas in CL-1. This heat is transferred via a number of services to the steam system. Condensate is removed from the raw SNG in KO-1 and then the gas is cooled in Air Cooler, ACL-1, and Water Cooler, WCL-1, to 100°F. Additional condensate is removed in KO-2.

Raw SNG, Stream 9, at 100°F, 285 psia, is fed to a Selexol Acid Gas Removal Unit, AGR-1, for removal of 94.5% of its CO₂ content. The Acid Gas Removal unit effluent, Stream 10, is compressed in compressor, GC-1, to 1,080 psia. It is then fed to a methanation unit where its hydrogen content is reduced to two percent by methanation of carbon monoxide and carbon dioxide. The methanation unit contains a bulk methanator, M-1, with gas recycle to limit the methanator outlet temperature to 900°F. Most of the hydrogen in the methanator feed is reacted in this unit. The hydrogen content of the SNG is then reduced to a final value of two percent in two

polishing methanators, PM-1 and PM-2, following the bulk methanator. The SNG is cooled and condensate removed. The SNG, Stream 11, is then dried in Gas Drying Unit, DR-1, to meet pipeline specifications. SNG production is 79.3×10^6 SCFD.

The plant steam system is shown in Figure 6-9. In addition to the HRSG, heat removed from the carbon deposition reactor, steaming reactor effluent gas cooling unit, and the methanator is utilized in the plant steam system. The steam system power recovery unit consists of a single three-stage turbo-generator. High pressure 1450 psig, 900°F steam is fed to the Steam Turbine, ST-1. The exhaust steam from ST-1 is reheated to 900°F and fed to the IP Steam Turbine, ST-2. Steam at 629°F, 115 psig is fed to the LP Steam Turbine, ST-3. A small amount of steam is extracted at this point for the HP BFW pump steam turbine driver, ST-4. Both ST-3 and ST-4 are condensing turbines operating at an outlet condition of 2 psia (4" Hg Abs.) and 126°F. Condensation of steam from ST-3 and ST-4 is completed in water cooled surface condenser, CN-1. Heat removed in the surface condenser, 1061×10^6 Btu/hr, is rejected to the atmosphere in a cooling tower. A total of 162.4 MW (net) of power is generated by the turbogenerator.

A total of 466 MW of power is produced by the combustion gas turbines and the steam turbines. In-plant power requirements are 21 MW. Therefore, net power available for export is 445 MW.

Installed equipment costs for this plant are \$277.2 million, as shown in Table 6-13. Of this total, 70% is required for the combined cycle power plant. Other capital investment costs, operating costs and product revenues, assuming the baseline values of \$6.00/ 10^6 Btu for SNG and 5.7¢/kWh for power, are given in Table 6-14. For this analysis, a service factor of 70% would be appropriate for a base load power plant application. A sensitivity analysis based on a 90% service factor is also presented, representative of an industrial application in which the power is used to replace purchased power for non-BEACON related production facilities. In Table 6-14, the feed gas cost and product revenue numbers in parentheses represent the 70% stream factor case.

Figure 6-9. LBG to SNG/Power Via BEACON/Combined Cycle: Steam System

Table 6-13. SNG/Power From LBG
Installed Equipment Costs

<u>Section</u>	<u>Installed Cost</u> <u>\$10⁶ (1Q83)</u>
BEACON System	34.7
Gas Cooling	18.3
Acid Gas Removal	6.4
Gas Compression	2.9
Methanation	16.9
Combined Cycyle Power Generation	<u>198.0</u>
Total Installed Cost	277.2

Results of an equity financing analysis of this BEACON case are shown in Figure 6-10, assuming baseline product values and also for a constant dollar (real) escalation in SNG value at 2% AAI (average annual increase). The sensitivity to the estimated value of export electric power (or displaced purchased power) is shown in Figure 6-11. If our estimate of the cost of LBG of \$5.50/10⁶ Btu (for a 100% equity venture) is correct, the IRR of 10.3% at a 90% service factor is only marginally attractive at best. Since current industrial purchased power costs are less than the estimated national average of 5.7¢/kWh, an equity investment in this type of plant would not be of commercial interest at this time. The basic problem for an industrial power generation facility is competition with utility power costs. Since utilities have a much more favorable financing structure (high debt, low taxes), their power generation costs are much lower than those for a private investor. In recent years, however, utilities have had

Table 6-14. SNG and Power From Low Btu Gas For Base Load Applications

I. Depreciable Capital (\$10⁶)			
A.	Total Installed Cost	277.2	
B.	Off-Sites	27.7	
C.	Project Contingency	83.2	
	Plant Capital	<u>388.1</u>	
D.	Fixit	19.4	
E.	Initial Catalysts & Chemicals	2.3	
F.	Prepaid Royalties	<u>2.0</u>	
			411.8
II. Investment Expense (\$10⁶)			
A.	Owner's Engineering		
	Year 1	5.8	
	Year 2	5.8	
B.	Start-Up	2.3	
C.	Property Tax & Insurance		
	Year 3	5.8	
	Year 4	<u>5.8</u>	
			25.5
III. Working Capital (\$10⁶)			
A.	Spare Parts		
	Year 4	3.9	
C.	Accounts Receivable		
	Year 5	<u>36.6</u>	
			40.5
IV. Land (\$10⁶)			
			5.0
V. Fixed Operating Costs (\$10⁶/Year)			
A.	Operating Labor (3 Shifts, 22 Man-Crew)	3.9	
B.	Supervision, G&A	3.1	
C.	Maintenance	11.6	
D.	Property Taxes and Insurance	<u>7.8</u>	
			26.4
VI. Variable Operating Costs (\$10⁶/Year)			
D.	Feed Gas: 60.37x10 ¹² Btu/Year	60.37 x	
	(46.95x10 ¹² Btu/Year)	(46.95 x)	
F.	Catalysts and Chemicals	0.3	
H.	Raw Water	<u>0.6</u>	
			0.9+60.37 x
			(0.9+46.95)
VII. Revenues			
C.	Power Export: 3508x10 ⁶ kWh/year	200.0	
	(2728x10 ⁶ kWh/year)	(155.5)*	
D.	SNG: 25.9x10 ¹² Btu/Year	155.4	
	(20.1x10 ¹² Btu/Year)	(120.9)	
E.	Power Equivalent of } 1523x10 ⁶ kWh/Year	86.8	
	Compressed Bleed Air } (1185x10 ⁶ kWh/Year)	<u>(67.5)</u>	
			442.2
			(343.9)

*Numbers in parentheses correspond to 70% stream factor.

Figure 6-10. IRR vs Cost of LBG

Figure 6-11. IRR vs Value of Power

difficulty in financing new power plants. One option might be a privately financed coal gasification/BEACON SNG plant with an adjacent (over-the-fence) utility company financing and operating only the power section of the integrated system.

It is clear from the above that a BEACON SNG/Power system must be considered as a utility type of plant with the primary product being power. SNG is a coproduct which can be used in peaking turbines and for off-peak sale to natural gas pipeline companies. This system should be of particular interest to the many combined gas and electric utility companies in the U.S.

When the BEACON SNG/power plant is analyzed on a utility financing basis (see Section 6.4.2 for premises and calculation), the results are more favorable, as shown in Figure 6-12. In this case, we must compare the power value against a utility's busbar cost of generation, exclusive of distribution costs. This has been estimated for a new Texaco coal gasification combined cycle power plant of 500MW capacity based on data in the May 1983 EPRI Report No. AP-3084, "Economic Assessment of the Impact of Plant Size on Coal Gasification-Combined Cycle Plants." The EPRI installed capital cost estimate (by Fluor) was escalated to 1983 dollars and other capital costs added on a consistent basis with our study (Section 6.4, Table 6-19). EPRI operating costs were also escalated to 1983 and coal costed at $\$1.50/10^6$ Btu. The resulting power cost was calculated, by the same formula as in this study, to be 4.6¢/kWh. For the same power value, at a 70% service factor in both cases, the BEACON system would be competitive at a cost of $\$5.30/10^6$ Btu for the LBG. A coal gasification plant built under a utility financing structure should be able to produce LBG at a lower cost than this, as will be indicated by the following coal to power study.

6.3.2 SNG/Power From Coal With Load Following

This conceptual process design starts from coal and also addresses the load following capabilities obtained by integrating a BEACON unit into a coal gasification combined cycle power plant. The design involves integration of a Westinghouse type air-blown coal gasifier with a combined

Figure 6-12. Value of Power vs Cost of LBG

cycle power plant and with BEACON in a manner which allows the entire plant to follow changes in power production requirements while delivering a constant amount of SNG product. A daily (24 hour) power demand cycle is assumed.

The material and energy balance for the Westinghouse gasifier was derived from a design presented in the March 1981 NASA Technical Memorandum

81687 entitled "Conceptual Design Study of a Coal Gasification Combined-Cycle Power Plant for Industrial Cogeneration."

The gasifier heat and material balance is based on feeding Ohio #9 coal. This coal has a higher heating value (HHV) = 11,590 Btu/lb (as received), and the following analysis:

	<u>Wt %</u>
C	64.8
H	4.34
O	7.79
S	2.42
N	1.30
Ash	15.73
Water	<u>3.62</u>
Total	100.00

The total prepared coal fed to the gasifier for this design is 4,392 tons per day. The gasifier operates at this constant coal feed rate as long as the electrical power demand is within the load following capability of the plant.

The cooled, dust free LBG product from the gasifier has the following composition:

	<u>MOLE %</u>
CO	25.7
CO ₂	5.2
CH ₄	2.0
H ₂	13.5
H ₂ O	0.6
H ₂ S	0.5
N ₂	<u>52.5</u>
	100.0

HHV = 146.5 Btu/Scf

The BEACON SNG and power plant design is similar to that in the previous case with appropriate modifications due to the change in LBG composition. Sulfur-free (<5 ppm H_2S) LBG reacts to deposit carbon on a catalyst in fluidized bed reactors operating at $932^{\circ}F$ ($500^{\circ}C$) and 295 psia. A CO conversion of 80 percent and a H_2 conversion of 53.3 percent is estimated based on laboratory data. The superficial gas velocity in the reactor is 1 ft/sec. Heat transfer coils immersed in the fluid bed remove the heat of reaction.

Steaming of the carbon carrying catalyst takes place in fluidized bed reactors operating at $1,022^{\circ}F$ ($550^{\circ}C$) and 295 psia. Equilibrium effluent gas composition is assumed at these conditions. Superficial gas velocity in the reactor is 1 ft/sec. The endothermic heat of reaction is supplied by passing hot flue gas at $2,000^{\circ}F$ through heat transfer coils immersed in the fluid bed.

The SNG product, containing approximately 2 percent hydrogen, is delivered to the pipeline at a pressure of 1,000 psig.

The combustion gas turbines are Westinghouse W-501D units. The temperature of the combustion gas to the first rotating row of blades of the gas turbine is $1985^{\circ}F$. The air compressor pressure ratio is 14:1.

Heat and material balances were developed for both minimum power generating capacity (without turndown of the coal gasifiers) and at maximum generating capacity. SNG is produced at a constant rate corresponding to the average carbon deposition rate. During the period of minimum power production, all of the gasifier LBG flows through the carbon deposition reactors. Carbon deposited in excess of steamer requirements is stored. During the period of maximum power generation only 10 percent of the LBG flows through the carbon deposition reactors. This is sufficient to maintain the deposition reactors in a state of minimum fluidization. In this mode, the bulk of the LBG is fed directly to the combustion turbines. Carbon is removed from storage to supplement the carbon deposited and thus maintain a constant SNG production rate.

The plant is heat and flow integrated such that it can be operated efficiently in both the minimum and maximum power production modes.

A large quantity of high pressure (1550 psig) saturated steam is generated in the gasifier heat recovery section. This steam is superheated by combustion gas turbine flue gas in the heat recovery steam generator (HRSG).

The air required for the gasifier is bled from the gas turbine unit's air compressor at 205 psia. The gasifier air is then increased to the required feed pressure of 385 psia in a booster compressor.

Coal, ground to 1/4" x 0" in size, is pressurized to approximately 320 psia in lockhoppers and transported to the gasifiers. The gasification system consists of six trains of Westinghouse fluid bed reactors and associated heat recovery and particulate removal equipment. Coal is gasified in the reactors with air and steam. Hot gas exits the reactors at 1850°F. Much of the sensible heat in the raw gas is recovered as steam in a waste heat recovery unit. The high pressure (1550 psig) saturated steam generated in the waste heat recovery convective boiler is fed into the steam headers common to the heat recovery steam generator (HRSG) block. Particulates are removed from the cooled gas exiting the waste heat recovery unit by wet scrubbing in a venturi. Cooled, solids-free raw gas, Stream 1, at 330 psia and 120°F is fed to the desulfurization unit.

The cool raw gas from the particulate removal section is desulfurized in a Selexol acid gas removal unit. H_2S is removed to <5 ppm as required by the BEACON system. The acid gas stream from Selexol is sent to a sulfur recovery unit. Sulfur is recovered in a Claus unit, and the tail gas is treated in a Beavon-Stretford unit. The sweet gas exiting from the Selexol unit is at 315 psia and 100°F.

To this point the process flow is identical for both minimum and maximum power generating modes of operation.

Minimum Power Case

The block flow drawing for the minimum power case is given in Figure 6-13. The accompanying material balance is given in Table 6-15. A steam balance for this case is summarized in Figure 6-14.

The bulk of the LBG, Stream 2, at 315 psia, 100°F is fed to the BEACON Carbon Deposition reactors. A small quantity (approximately 3%) of the LBG, Stream 3, is diverted to a combustor to generate the 2000°F flue gas required for heat input to the steaming reactors. The Carbon Deposition reactors are fluid bed units operating at 932°F. Reaction heat is removed by H.P. steam generation and steam reheat tubes immersed in the fluid beds. Three reactors, each approximately 17' ID x 37' TT, are required. The carbon rich catalyst from the deposition reactors is transported to the steaming reactors. Approximately 13.5 tons per hour of carbon (45 percent of the total deposited) is diverted to a carbon storage silo. The carbon in the silo is maintained hot and in a state of minimum fluidization. It is used to supplement the reduced amount of carbon deposited during times of maximum power generation, thus maintaining a constant SNG production level. Twelve hours of carbon storage capacity is provided.

The steaming reactors are fluid bed units operating at 1,022°F. Reaction heat is provided by passing hot flue gas through coils immersed in the fluid beds. The hot flue gas enters the coils at 2,000°F and leaves at 1,400°F. Steam feed to the reactor, Stream 8, is at 455 psia, 615°F.

The raw SNG from the steamer, Stream 9, is upgraded to pipeline specifications in an SNG purification and compression unit. This unit contains equipment for gas cooling, particulate removal, CO₂ removal (via Selexol), gas compression, and methanation. The methanator, consisting of bulk and polishing reactors, is required to remove residual carbon oxides and to reduce the hydrogen content of the SNG to approximately 2 percent. The SNG product is dried and fed to the pipeline at 1,000 psig. SNG, Stream 10, is produced at the rate of 12.8×10^6 SCFD.

Figure 6-13. Block Flow Diagram Coal to SNG/Power Via BEACON/Combined Cycle Load Following - Minimum Power Case

Table 6-15. Coal to SNG/Power Via BEACON Combined Cycle
Load Following - Minimum Power Case

MATERIAL BALANCE

Stream No.	1	2	3	4	5	6	7	8	9	10
CO, Moles/Hr	14,688	14,156	459	2,331					93	
CO ₂	2,943	2,442	86	7,137		13,307			1,455	8
CH ₄	1,140	1,093	38	2,417					1,202	1,368
H ₂	7,729	7,459	262	3,481					601	28
H ₂ O	366	49	2	1,381		10,036		5,588	2,583	
H ₂ S	269									
O ₂					33,707	17,313	7,948			
N ₂	30,067	28,999	1,021	28,599	126,801	126,923	29,898			
Total, Moles/Hr	57,202	54,198	1,907	46,546	160,508	167,579	37,846	5,588	5,934	1,404
Temperature °F	120	100	100	932	70	275	500	615	1,022	100
Pressure, PSIA	330	315	315	310	15	15	385	455	295	1,015

Figure 6-14. Steam System - Coal to SNG/Power Via BEACON/Combined Cycle Load Following - Minimum Power Case

The hot gas from the Carbon Deposition reactors, Stream 4, is processed through cyclones and a filter for particulate removal. It is then burned with air supplied by the air compressor in the gas turbine power plant to produce 1985°F combusted gas. This hot gas then drives a gas turbine (which is mechanically coupled to the air compressor and the generator) to generate electric power. The air requirements for the coal gasifier (approximately 24 percent of the total air, Stream 5, compressed) is bled from the air compressor. This air, Stream 7, at 205 psia, 730°F is cooled and then boosted in pressure to 385 psia as required by the gasifier. To maintain high efficiencies, only two of the three available gas turbines are on line during minimum power operation. A net total of 160.6 MW of power is generated by the gas turbines.

The turbine exhaust gas at 983°F contains a significant quantity of sensible heat. This heat is extracted in the heat recovery steam generator (HRSG). This unit consists of convective sections for steam superheating, steam generation, and BFW heating. The H.P. steam generated in the gasifier waste heat recovery unit is superheated in the HRSG. A turbogenerator produces 179.3 MW of electric power from steam raised in the HRSG and from process derived steam. The turbogenerator consists of a three stage steam turbine with the low pressure condensing stage operating at 4 inch Hg Abs. Flue gas, Stream 6, exits the HRSG at 275°F and is discharged to the atmosphere through a stack.

Gross power generated is 339.9 MW. Approximately 38 MW of power is required in plant. Therefore, net electric power available for sales is 301.9 MW.

Maximum Power Case

The block flow diagram for the maximum power case is given in Figure 6-15. The accompanying material balance is given in Table 6-16. A steam balance for this case is summarized in Figure 6-16.

Figure 6-15. Block Flow Diagram Coal to SNG/Power Via BEACON/Combined Cycle Load Following - Maximum Power Case

Table 6-16. Coal to SNG/Power Via BEACON/Combined Cycle Load
Following - Maximum Power Case

MATERIAL BALANCE

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12
CO, Moles/Hr	14,688	14,156	498	12,740	1,416	283					93	
CO ₂	2,943	2,442	86	2,198	244	744		17,813			1,455	8
CH ₄	1,140	1,093	38	984	109	242					1,202	1,368
H ₂	7,729	7,459	262	6,713	746	348					601	28
H ₂ O	366	49	2	44	5	137		10,036		5,588	2,583	
H ₂ S	269											
O ₂							56,359	35,461	7,948			
N ₂	30,067	28,999	1,021	26,099	2,900	2,900	212,019	212,141	29,398			
Total, Moles/Hr	57,202	54,198	1,907	48,778	5,420	4,654	268,378	275,451	37,346	5,588	5,934	1,404
Temperature, °F	120	100	100	500	500	932	70	275	500	615	1,022	100
Pressure, PSIA	330	315	315	300	300	295	15	15	385	455	295	1,015

Figure 5-16. Steam System - Coal to SNG/Power Via BEACON/Combined Cycle Load Following - Maximum Power Case

LBG, Stream 2, at 315 psia, 100°F is reheated to 500°F in the gasifier waste heat recovery unit. It should be noted that in the minimum power case, with no gas reheat required, the extra heat available in the gasifier waste heat recovery unit is used to raise 150 psig steam. The bulk of the LBG at 500°F, Stream 4, is fed directly to the gas turbine power plant. The remainder of the LBG, Stream 5, is fed to the Carbon Deposition reactors. Stream 5 is approximately 10 percent of the minimum power case flow to the Carbon Deposition reactors and is required to maintain the reactors in a state of minimum fluidization. The carbon rich catalyst from the deposition reactors is transported to the Steaming reactors along with approximately 13.5 tons per hour of carbon that is withdrawn from the carbon storage silo. Thus the total carbon flow to the Steamer is unchanged from that for the minimum power case. Steamer and SNG purification and compression unit operation remains unchanged from the minimum power case. SNG production is maintained at 12.8×10^6 SCFD.

The hot gas from the deposition reactors, Stream 6, at 932°F is filtered and then blended with LBG, Stream 4, at 500°F. The mixture is burned with air supplied by the air compressor in the gas turbine power plant to produce 1,985°F combusted gas. This hot gas drives a gas turbine (which is mechanically coupled to the air compressor and the generator) to generate electric power. The air requirements for the coal gasifier (approximately 14 percent of the total air, Stream 7, compressed) is bled from the air compressor. This air, Stream 9, at 205 psia, 730°F is cooled and then boosted in pressure to 385 psia as required by the gasifier. Three gas turbine units are required. A net total of 258.5 MW of power is generated by the gas turbines.

The turbine exhaust gas at 973°F contains a significant quantity of sensible heat. This heat is extracted in the heat recovery steam generator (HRSG). This unit consists of convective sections for steam superheating, steam generation, and BFW heating. The H.P. steam generated in the gasifier waste heat recovery unit is superheated in the HRSG. A turbogenerator produces 201.8 MW of electric power from steam raised in the

HRSO and from process derived steam. The turbogenerator consists of a three stage steam turbine with the low pressure condensing stage operating at 4 inch Hg Abs. Flue gas, Stream 8, exits the HRSO at 275°F and is discharged to the atmosphere through a stack.

Gross power generated is 460.3 MW. Approximately 38.7 MW of power is required in plant. Therefore net electric power available for sales is 421.6 MW.

System Analysis

A coal gasification combined cycle power (CG-CCP) system, designed with the BEACON reactors as described above, has two major advantages over competitive CG-CCP systems:

1. The carbon storage provides a low cost method of keeping the capital intensive coal gasification system operating at full capacity, even with power demand reduced by 30% below design.
2. The coproduced SNG, 12.8×10^6 SCFD, provides further load following capability if it is used by the utility in peaking turbines. By the 1990's, this coal derived SNG may be lower in cost than natural gas.

The SNG production can "float" on existing natural gas pipeline supply systems. With appropriate infrastructure arrangements, it can be sold to the gas company when seasonal demand is high (winter) and repurchased in the summer when needed for mid-day peak air-conditioning demands to fire peak load gas turbines.

This BEACON system will produce an average of 362 MW of power plus 12.8×10^6 SCFD of SNG from 4392 TPD of bituminous coal. Peak power capability is 422 MW. The installed capital cost for such a facility is estimated at $\$395 \times 10^6$ (1Q83\$), as shown in Table 6-17. Other capital and operating costs and product revenues, based on SNG valued at $\$6.00/10^6$ Btu,

Table 6-17. SNG/Power From Coal With Load Following
Installed Equipment Costs

	Installed Cost \$10 ⁶ (1Q83)
Coal Receiving, Preparation	26
Gasification	76
Acid Gas Removal	45
Sulfur Recovery	8
BEACON (including carbon storage)	26
Power Generation	185
Water Systems	29
	—
Total Installed Cost	395

are given in Table 6-18. On a utility financing basis, the busbar cost of power is 4.0¢/kWh assuming coal at a cost of \$1.50/10⁶ Btu. The sensitivity of power cost as function of the coal feed cost is shown in Figure 6-17.

This cost of 4.0 /kWh compares favorably with the estimate of 4.6 /kWh (See page 6-46) derived from the EPRI report, AP-3084, for a Texaco CG-CCP plant. It is recognized that installed equipment cost estimating methods may differ and that the BEACON cost is slightly sensitive to SNG coproduct values. However, the primary factor affecting these cost differences is the 90% stream factor achievable with the BEACON systems.

Another comparison with the Texaco CG-CCP design study that is appropriate is heat rate. For the BEACON case, this is complicated by the SNG coproduct. A correction for this coproduct can be made by allocating the coal feed heat value appropriately between SNG and power. Well

Table 6-18. SNG and Power From Coal For Load Following Applications

<u>I. Depreciable capital (\$10⁶)</u>			
A.	Installed Cost		395.0
B.	Off-Sites		79.0
C.	Project Contingency		118.5
	Plant Capital		<u>592.5</u>
D.	Fixit		29.6
E.	Initial Catalysts & Chemicals		1.6
F.	Prepaid Royalties		<u>2.0</u>
			625.7
<u>II. Investment Expense (\$10⁶)</u>			
A.	Owner's Engineering	Year 1	8.9
		Year 2	8.9
B.	Start-Up	Year 4	2.0
C.	Property Tax and Insurance	Year 3	8.9
		Year 4	<u>8.9</u>
			37.6
<u>III. Working Capital (\$10⁶)</u>			
A.	Spare Parts	Year 4	5.9
B.	Storable Supplies (Coal)	Year 4	8.4
C.	Accounts Receivable	Year 5	<u>18.8</u>
			33.1
<u>IV. Land</u>			
			5.0
<u>V. Fixed Operating Costs (\$10⁶/Year)</u>			
A.	Operating Labor (3 Shifts, 19 Man-Crew)		3.4
B.	Supervision, G&A		2.7
C.	Maintenance		17.8
D.	Property Taxes and Insurance		<u>11.9</u>
			35.8
<u>VI. Variable Operating Costs (\$10⁶/Year)</u>			
A.	Coal, 33.44x10 ¹² Btu/Year (4392 TPD)		50.2
F.	Catalysts and Chemicals		0.3
G.	Ash/Sludge Disposal, 300 x 10 ³ tons/year		0.7
H.	Raw Water		<u>0.7</u>
			51.9
<u>VII. Revenues (\$10⁶/Year)</u>			
C.	Export Power, 2852x10 ⁶ kWh/Year (362 MW)		2852x
D.	SNG, 4.17x10 ¹² Btu/Year (12.8x10 ⁶ SCFD)		25.0
E.	Sulfur, 33x10 ³ tons/year		<u>3.8</u>
			28.8+2852x

Figure 6-17. Value of Power vs Cost of Coal

designed and efficient coal to SNG plants are reported to have efficiencies in the range of 60-65%. Assuming 62%, the heat rate for the BEACON system is:

$$\frac{33.44 \times 10^{12} - (4.17 \times 10^{12} / 0.62)}{2852 \times 10^6} = 9370 \text{ Btu/kWh}$$

This compares very favorably with the Texaco GC-CCP 500 MW plant heat rate of 9738 Btu/kWh (EPRI, AP-3084, *ibid.*). This improved heat rate is attributed primarily to the inherent efficiency of the BEACON system, as discussed in detail on the basis of model system analyses in Section 3.2., pages 3-10 through 3-24.

In summary, the BEACON system, with intermediate carbon storage to provide load following capability, represents a very efficient coal

gasification combined - cycle power concept. Capital costs are minimized by its ability to utilize a very high stream factor on the coal gasification section in spite of wide variations in power demand.

6.4 BASIS FOR ECONOMIC EVALUATIONS

The basis for the economic evaluations discussed in Sections 6.2 and 6.3 is presented in this Section. Both equity and utility financing methods are presented. The general method of calculating capital investment and operating costs is given in Table 6-19. The rationale for most of these cost assumptions is discussed below. All dollar figures are in first quarter 1983 dollars.

Off-site (or general facilities) are estimated at 10% of the installed equipment costs in all cases except the SNG/power with load following case. This is reasonable for those cases starting with LBG and producing either hydrogen or SNG and cogenerated steam or power. Such plants would be within battery limits of associated refineries or process plants and require no feed or product storage. The last case, which includes a coal gasification plant, could be a grass-roots facility with added requirements for buildings, roads, sulfur storage, etc. Off-site costs of 20% of installed equipment costs are estimated for this case.

The same project contingency of 30% is used in all cases. No separate process contingency is added to reflect differences in the state of development between new and established, proven technologies such as steam reforming of methane. This is because the intent of these analyses is to ascertain the potential advantage of a new process once it is fully developed. It is recognized that there are greater risks and uncertainties attached to the construction of a first-of-a-kind plant, but this factor should be considered separately in the initial investment decision. The objective here is to make a realistic capital cost estimate and then take uncertainties into account by appropriate judgement in regard to an acceptable return on investment.

Table 6-19. Bases for Economic Evaluations

I. Depreciable Capital

A. Total Installed Cost (IC)	XXX
B. Off-Sites	10-20% of IC
C. Project Contingency	30% of IC
Plant Capital (PC)	XXX
D. Fixit	5% of PC
E. Initial Catalyst & Chemicals	As Appropriate
F. Prepaid Royalties	<u>As Appropriate</u>

II. Investment Expense

A. Owner's Engineering	Year 1	1.5% of PC
	Year 2	1.5% of PC
B. Start-Up	Year 4	4 Months Labor
C. Property Tax & Insurance	Year 3	1.5% of PC
	Year 4	<u>1.5% of PC</u>

III. Working Capital

A. Spare Parts	Year 4	1% of PC
B. Storable Supplies (Coal, etc.)	Year 4	2 Months
C. Accounts Receivable, Net	Year 5	<u>10% of Revenues</u>

IV. Land Year 1 \$5 Million

V. Fixed Operating Costs Per Year

A. Operating Labor (OL)	\$177,390/Operating Position
B. Supervision, G&A	80% of OL
C. Maintenance	3% of PC
D. Insurance/Property Taxes	<u>2% of PC</u>

VI. Variable Operating Costs Per Year

A. Coal	\$1.50/10 ⁶ BTU
B. Steam	See Item IX Below
C. Natural Gas (After Deregulation)	\$6.00/10 ⁶ BTU
D. Feed Gas	\$x/10 ⁶ BTU
E. Power Import	\$0.057/kWh
F. Catalysts & Chemicals	As Required
G. Ash/Sludge disposal	\$2.00/Ton (Wet Basis)
H. Raw Water	\$0.40/1000 Gal.

Table 6-19. Bases for Economic Evaluations (Continued)

VII. Revenues

A.	Hydrogen	\$y/10 ⁶ Btu
B.	Steam	See Item IX Below
C.	Power Export	\$0.057/kWh
D.	SNG	\$6.00/10 ⁶ Btu

VIII. Equity Investment Analysis

A.	Operating Life	20 Years
B.	Depreciation (100% of Depreciable Cap.)	5 years, ACRS
C.	Construction Schedule, 4 Years	10%, 20%, 35%, 35%
D.	Investment Tax Credit	10% in the Year of Expenditure
E.	Federal + State Taxes, Net	49%
F.	First year Production	50%
G.	Service Factor	90%

IX. Steam Values (\$/1000 lb)

640 psig, Saturated	9.50
600 psig, Saturated	9.44
600 psig, 720°F	10.74
330 psig, Saturated	8.65
50 psig, Saturated	7.25
15 psig, 260°F	6.85
10 psig, 750°F	8.76

An investment expense of 3% of the plant capital is assumed for Owner's Engineering based on industrial experience. This is split equally between the first two years of the construction.

The start-up costs in Table 6-19 pertain to four months of labor, although there are three components of start-up costs taken into account in these analyses. The indicated labor costs represent the need to hire and train operators about four months prior to start up, and includes the cost of supervisors and administrative personnel to support this operating staff. Other start-up costs considered separately, include "fixit" at 5% of the Plant Capital Investment and an assumed operating level of only 50% of plant capacity during the first year of operation. Both of these factors allow for repairs, modifications, and other problems incurred after the nominal "start-up" of the plant.

An additional investment expense of 3% of plant capital is allocated for property tax and insurance. This is divided equally between the last two years of construction.

Working capital includes spare parts equivalent to 1% of plant capital and two months equivalent storable supplies, both treated as expense in the last year of construction. An accounts receivable of 10% of expected annual revenues is assumed. Since this involves prior knowledge of the price of the product, in principle, computations would be iterative. The product price, however, is quite insensitive to accounts receivable. Therefore, to avoid iterative calculations, a constant hydrogen price of \$11.52/10⁶ Btu and a power price of \$0.057/kWh are assumed. This working capital is charged to the first year of operation and recovered in the last year.

A land value of \$5 million is capitalized in the first year of construction for all cases.

The operating labor is calculated based on a rate of \$15 per hour per person. Assuming a burden rate of 35%, total operating labor cost per operating position per year is \$177,390. The number of operators in each case study is based on judgement involving the complexity of the process, such as the number of trains required in each segment of each process.

The cost of coal is estimated to be \$1.50/10⁶ Btu, which is an average delivered contract price for midwest bituminous coal. The cost of natural gas is projected to be about \$6.00/10⁶ Btu after deregulation based on a Btu parity with sweet residual oil. This value is subject to much debate and speculation, but sufficient data is presented in these analyses to permit the reader to adjust the analyses according to his own perception of future natural gas prices.

The cost of purchased electric power or the value of export power can vary widely dependent on site location, fuel source, quantity purchased or produced, and peak vs average demand or production. As a baseline value in these studies, an approximate national 1982 average cost of 5.7¢/kWh was used. Industrial costs at the point of consumption are lower than this average, but there is strong political pressure to more nearly equate industrial user costs with commercial and residential costs. Use of this baseline value in the three hydrogen design cases tends to penalize the cases which purchase power, but this effect is not significant since purchased power requirements are rather small. It could be considered somewhat optimistic for the coal derived LBG case since power credit is a significant factor in that case. Uncertainties in the cost of the LBG feed gas, however, outweigh anticipated variations in the power credit. For the two SNG/power cases, utility applications are more likely because of their more favorable financing structure. The cost of cogenerated power from the BEACON system should then be compared with alternative power costs from new power plants. Presumably these would be coal fired plants, either direct fired with flue gas desulfurization or coal gasification combined-cycle plants.

The values of the several qualities of steam which appear either as input or output in the cases studied are estimated by adding to the fuel equivalent value of steam a fixed value corresponding to capital charge and operating costs. The fuel equivalent value is computed in accordance with the procedure given by W. V. L. Champagne in his article, "What's Steam Worth?" which appeared in "Hydrocarbon Processing," August 1981. This procedure essentially involves computing the heat required to raise steam to the appropriate quality from boiler feed water and then assuming that this heat is provided by burning of a fuel of known value at an estimated total thermal efficiency. Only the lower heating value of the fuel is used in these calculations.

For high pressure, high temperature steam, the fuel for raising steam is assumed to be natural gas, valued at \$6.00/10⁶ Btu HHV or \$6.66/10⁶ Btu LHV. The component of steam value corresponding to capital charge and operating costs is estimated to be about \$1.70/1000 lb. Lower values for fuel, capital charge and operating costs are assumed for raising low pressure, low temperature steam; this is based on the rationale that low grade waste heat can be used to produce low quality steam. The foregoing discussion is reflected in the steam values listed in Item IX of Table 6-19.

6.4.1 Equity Financing

A discounted cash flow (DCF) analysis is computed to yield an internal rate of return (IRR) assuming a 100% equity investment (no debt). This is the most common method used to evaluate and compare industrial investment opportunities. All DCF calculations are on a constant dollar basis (first quarter 1983 dollars). Due to the long term nature of these projects and the uncertainty of inflation rates, current dollar analyses were not felt to be warranted and could be misleading. However, if natural gas shortages develop in the time frame of potential BEACON projects, the real value of natural gas could escalate at a rate higher than the average U.S. inflation rate. The sensitivity to such a real escalation in natural gas prices was analyzed in some of the studies. A service factor of 90% was assumed in all cases, except as otherwise stated.

6.4.2 Utility Financing

The following procedure is based on the techniques presented in "Technical Assessment Guide" prepared by EPRI, July 1979, Report Number EPRI PS-1201-SR.

The levelized annual cost of electricity is the sum of levelized annual costs related to capital, fuel and operation and maintenance (O&M) costs. The cost related to capital is a function of the capital and a "fixed charge." The cost related to fuel is a function of fuel cost, a "levelized factor" and service factor. The cost related to O&M is a

function of O&M costs, "levelized factor" and service factor. The "fixed charge" and "levelized factor" can be expressed in terms of the financing parameters described below:

Project Book Life = n

Project Tax Life = m

Inflation Rate = i

Debt: Equity: Stock = $d:e:s$ ($d+e+s=1$)

Minimum Acceptable Return

on debt = r_d

on equity = r_e

on stock = r_s

Federal + State
Tax Rate = t

Investment Tax
Credit Rate = c

Property Taxes +
Insurance Rate = p

The discount rate = $r = dr_d + er_e + sr_s$

To calculate the levelized annual fixed charge (FC) we need to first determine what type of depreciation schedule we should use. Although the Accelerated Cost Recovery Schedule (ACRS) is advantageous, we have chosen in this study the sum-of-the-years digits depreciation because (1) it offers use of a simple formula whereas ACRS does not and (2) in making comparisons between different technologies, the differences are more

important than the absolute numbers. The annual fixed charge is then given by

$$FC = CRF + RD + IT + PT - ADF - ITC,$$

where CRF = capital recovery factor

$$= \left(\frac{r}{1 - (1 + r)^{-n}} \right)$$

RD = allowance for retirement dispersion

= Iowa Type S₁ (from Table on p.3-16 in EPRI Report No. PS-1201-SR)¹

IT = Levelized annual income tax

$$= \left(CRF - \frac{1}{n} \right) \left(1 - \frac{dr_d}{r} \right) \left(\frac{t}{1 - t} \right)$$

PT = p = Property Taxes, Insurance

ADF = Levelized accelerated depreciation factor

$$ADF = \left[2(CRF) \left(\frac{mr - 1 + (1 + r)^{-m}}{m(m + 1)r^2} \right) - \frac{1}{n} \right] \left[1 - \frac{tdr_d}{r} \right] \left[\frac{t}{1 - t} \right]$$

and ITC = Levelized annual investment tax credit

$$= \left(\frac{c}{1 - t} \right) \left[\left(\frac{CRF}{1 + r} \right) - \frac{tdr_d}{r} \left(\frac{CRF}{1 + r} - \frac{1}{n} \right) \right]$$

The levelized factor (LF) is given by

$$LF = (CRF) \left(\frac{k(1 - k^n)}{1 - k} \right),$$

where

$$k = \frac{1 + i}{1 + r}.$$

Since the equity financing calculations are performed under the constant dollar scenario, similar constant dollar calculations are also performed here. It should be noted that when inflation is eliminated, the discount rate r must be substituted by r^* , the discount rate under constant dollar conditions, that is,

$$r^* = \frac{1+r}{1+i} - 1 = \frac{r-i}{1+i}$$

Therefore, substituting this in the expression for LF, we find that $LF = 1$, as is to be expected.

The foregoing information is now adequate for calculating the levelized busbar cost of electricity under the constant dollar scenario, according to the following identity:

$$\begin{aligned} \text{(Annual revenue)} &= \text{(FC) (Total Capital Requirements)} \\ &+ \text{(Annual Fixed Cost)} \\ &+ \text{(Annual Variable Cost)} \\ &+ \text{(Annual Fuel Cost)} \end{aligned}$$

The financial criteria for evaluating FC are chosen from Table 5-1 in the report "Economics of the Texaco Gasification Process for Fuel Gas Production," EPRI Report Number AP-2488, July 1982. These criteria are as follows:

$$\begin{aligned} n &= 30 \\ m &= 13 \\ i &= 0.1 \\ d: e: s &= 0.5: 0.35: 0.15 \\ r_d &= 0.1225 \\ r_e &= 0.16 \\ r_s &= 0.1275 \\ t &= 0.52 \\ c &= 0.1 \\ p &= 0.03 \\ r &= 0.1364 \end{aligned}$$

Using these criteria, the constant-dollar discount rate r^* , will be 0.0331. Substituting this in the equation for fixed charge, we get:

$$FC = 0.0821$$

Here, a retirement dispersion allowance, $RD = 0.0054$ has been used. In the utility finance calculations, this annual fixed charge of 8.21% has been applied against the sum of Depreciable Capital, Investment Expense, Working Capital, and Land (Items I through IV in Table 6-19).

APPENDIX A
EXAMPLES OF LABORATORY SCALE DATA
(COMPUTER REDUCED AND TABULATED FOR EVALUATION AND STORAGE)

1. Carbon Deposition Data

Table A-1 is a summary of the raw data as generated in the laboratory ("Input Dump") during a carbon deposition run. The top row gives the run number, date and operator's name. The second row from left to right gives the reaction temperature (°C), reaction pressure (psig), ambient temperature (°C), ambient pressure (psia), starting weight of sample (grams), final weight of sample (grams, initial percent carbon in the sample (deleted), and product gas flow meter fill volume (cc).* The third row from left to right gives the feed gas flow rate (cc/min at ambient conditions) and the feed gas composition (mole percent H₂, CO₂, N₂, CH₄ and CO). The remaining rows from left to right give in tabular form the reaction time (seconds), the number of flow meter fill volumes of product gas during the indicated reaction interval (600 seconds in this case), the reaction pressure (psig), and the dry product gas composition (mole percent H₂, CO₂, N₂, CH₄ and CO).

Table A-2 presents the computer output of the performance of the carbon deposition run. In the top section of Table A-2, the columns from left to right give the reaction time in minutes, the cumulative dry product gas volume (cc at STP), the normalized dry product gas composition (mole percent H₂, CO₂, N₂, CH₄ and CO), the percent CO utilization (both instantaneous and averaged cumulative values), and the moles of CH₄ formed per mole of CO converted (both instantaneous and averaged cumulative values). At the bottom of the top section of Table A-2, the carbon balance obtained during the run is shown.**

* The product gas flow rate was measured by water displacement; the time to displace the indicated volume of water was recorded.

** The carbon balance is defined as follows:

$$\frac{\text{Carbon in Product Gases} + \text{Final Carbon Content in Solids}}{\text{Carbon Charged} + \text{Carbon in Feed Gases}} \times 100$$

Table A-1. Laboratory Scale BEACON (Carbon Deposition Data)

INPUT DUMP

K-1 13660-60-11 10/19/81 PENG

400.0000	0.0000	23.0000	14.7000	.5372	1.1172	XX.XXXX	20.6000
19.2000	13.8600	0.0000	1.7100	0.0000	84.4300		
TIME	AFMB	PREACT	H2	CO2	INERT*	CH4	CO
600	6.0000	0.0000	5.800	1.000	30.500	.060	70.400
1200	5.0000	0.0000	2.300	61.700	17.200	7.800	13.500
1800	5.0000	0.0000	1.700	68.300	4.500	9.000	9.900
2400	5.0000	0.0000	1.700	73.300	3.800	9.900	10.200
3000	5.0000	0.0000	1.700	75.100	3.700	10.200	10.200
3600	5.0000	0.0000	1.300	75.500	3.500	10.300	10.000
4200	5.0000	0.0000	1.500	72.800	3.300	10.000	10.000
4800	5.0000	0.0000	1.400	71.800	3.200	9.900	10.000
5400	5.0000	0.0000	1.100	75.300	3.200	10.200	10.400
6000	5.0000	0.0000	1.400	71.300	3.000	9.800	10.600
6600	5.0000	0.0000	1.300	74.300	3.000	10.100	11.100
7200	5.0000	0.0000	1.400	67.500	2.600	9.200	10.800
7800	5.0000	0.0000	1.400	69.600	2.600	9.500	11.500
8400	5.0000	0.0000	1.700	73.900	2.900	10.100	13.100
9000	5.0000	0.0000	1.800	72.700	2.800	9.800	13.700
9600	5.0000	0.0000	1.800	70.900	2.600	9.600	14.000
10200	5.0000	0.0000	1.800	70.900	2.600	9.600	14.000

*"Inert" gas was N₂.

Table A-2. Carbon Deposition Performance Data

RUN NO. K-1 13660-60-11
 RUN DATE 10/19/81
 RUN BY PENG

REACTN TIME MIN	CUM DRY PROD GAS VOL CC(STP)	----DRY PRODUCT COMPOSITION, MOL PCNT					INST CO CONV. PERCENT	CUM. CO CONV. PERCENT	MOL CH4/MOL CO CON.	
		H2	CO2	INERT*	CH4	CO			INST.	CUM.
10	114	5.38	.93	28.30	.06	65.33	50.21	50.21	.00	.00
20	209	2.24	60.20	16.78	7.61	13.17	91.64	70.92	.05	.03
30	304	1.82	73.13	4.82	9.64	10.60	93.27	78.37	.07	.05
40	399	1.72	74.12	3.84	10.01	10.31	93.45	82.14	.07	.05
50	494	1.68	74.43	3.67	10.11	10.11	93.58	84.43	.07	.06
60	589	1.29	75.05	3.48	10.24	9.94	93.69	85.97	.07	.06
70	684	1.54	74.59	3.38	10.25	10.25	93.49	87.05	.07	.06
80	779	1.45	74.56	3.32	10.28	10.38	93.41	87.84	.07	.06
90	874	1.10	75.15	3.19	10.18	10.38	93.41	88.46	.07	.06
100	969	1.46	74.19	3.12	10.20	11.03	93.00	88.91	.07	.06
110	1064	1.30	74.45	3.01	10.12	11.12	92.94	89.28	.07	.06
120	1159	1.53	73.77	2.84	10.05	11.80	92.50	89.55	.07	.06
130	1254	1.48	73.57	2.75	10.04	12.16	92.28	89.76	.07	.06
140	1349	1.67	72.66	2.85	9.93	12.88	91.82	89.91	.07	.06
150	1444	1.79	72.12	2.78	9.72	13.59	91.37	90.00	.07	.07
160	1539	1.82	71.69	2.63	9.71	14.16	91.01	90.07	.07	.07
170	1634	1.82	71.69	2.63	9.71	14.16	91.01	90.12	.07	.07

CARBON BALANCE = 101.95

TIME MIN	INST DRY GAS EVOL CC/MIN (STP)	--WET PRODUCT GAS COMPOSITION, MOL PERCENT					INST C DEP. RATE GM C PER HR-GM METAL	CUM C DEPOSITED GRAMS
		H2	CO2	INERT*	CH4	CO		
10	11.4	3.84	.66	20.21	.04	46.65	5.852	.0396
20	9.5	1.93	51.83	14.45	6.55	11.34	5.747	.0785
30	9.5	1.77	71.21	4.69	9.38	10.32	4.817	.1111
40	9.5	1.69	73.01	3.78	9.86	10.16	4.736	.1432
50	9.5	1.66	73.53	3.62	9.99	9.99	4.720	.1751
60	9.5	1.28	74.45	3.45	10.16	9.87	4.676	.2068
70	9.5	1.52	73.90	3.35	10.15	10.15	4.687	.2385
80	9.5	1.44	73.85	3.29	10.19	10.29	4.677	.2702
90	9.5	1.09	74.71	3.17	10.12	10.32	4.640	.3016
100	9.5	1.44	73.44	3.09	10.09	10.92	4.662	.3331
110	9.5	1.29	73.80	2.98	10.03	11.03	4.642	.3645
120	9.5	1.51	72.92	2.81	9.94	11.67	4.646	.3960
130	9.5	1.46	72.66	2.72	9.92	12.01	4.636	.4274
140	9.5	1.64	71.35	2.80	9.76	12.66	4.658	.4589
150	9.5	1.75	70.62	2.72	9.52	13.31	4.661	.4904
160	9.5	1.78	70.09	2.57	9.49	13.84	4.652	.5219
170	9.5	1.78	70.09	2.57	9.49	13.84	4.652	.5534

* "Inert" gas was N₂.

The columns in the bottom section of Table A-2 from left to right show the reaction time (minutes), the product gas evolution rate (cc/min at STP), the wet product gas composition (mole percent H₂, CO₂, N₂, CH₄, CO and H₂O), the instantaneous carbon deposition rate (grams carbons per hour per gram catalyst), and the cumulative carbon deposited (grams).

2. Carbon Steaming to SNG Data

Table A-3 is a summary of the raw data as generated in the laboratory ("Input Dump") during a steaming run. The top row gives the run number, date, and the operator's name. The second row from left to right gives the reaction temperature (°C), reaction pressure (psig), ambient temperature (°C), ambient pressure (psia), starting weight of sample (grams), final weight of sample (grams), percent carbon in the sample at the start (deleted), and product gas flow meter fill volume (cc). The third row from left to right gives the steam feed (liquid cc/hr), and nitrogen feed (cc/min at ambient conditions). The remaining rows from left to right give in tabular form the reaction time (seconds, the number of flow meter fill volumes of product gas during the indicated reaction interval (600 seconds in this case), and the dry product gas composition (mole percent H₂, CO₂, N₂, CH₄ and CO).

Table A-4 is a computer output of the performance of a steaming run. In the top section, the columns from left to right give the reaction time (minutes), the cumulative dry product gas volume (cc at STP), the normalized dry product gas composition (mole percent H₂, CO₂, N₂, CH₄ and CO), the carbon gasification rate (grams per given time interval), the percent of the carbon charge that has been gasified, the cumulative water in the product gas (grams), and the cumulative water that reacted (grams). At the bottom of the top section of Table A-4, the carbon balance obtained during the run is shown.*

In the bottom section of Table A-4, the columns from left to right show the reaction time (minutes), the percent of the carbon charge that has been

* The carbon balance is defined as follows:

$$\frac{\text{Ungasified Carbon} + \text{Carbon in Product Gases}}{\text{Carbon Charged}} \times 100$$

Table A-3. Laboratory-Scale BEACON (Carbon Steaming Data)

INPUT		DUMP					
K-1 13176-B-7		5/29/80		JOHN PAUL			
650.0000	0.0000	20.0000	14.7000	1.0105	.1035	XX.XXXX	28.3300
.9700	0.0000						
TIME	AFMB	PREACT	H2	CO2	INERT*	CH4	CO
600	9.5000	0.0000	50.500	16.000	.200	5.800	28.600
1200	9.5000	0.0000	51.500	16.200	0.000	5.850	28.600
1800	9.5000	0.0000	51.800	16.300	0.000	5.800	28.500
2400	9.5000	0.0000	51.900	16.300	0.000	5.800	28.300
3000	9.5000	0.0000	52.000	16.400	0.000	5.800	28.000
3600	9.5000	0.0000	52.000	16.700	0.000	5.700	28.000
4200	9.5000	0.0000	52.000	16.700	0.000	5.700	27.600
4800	9.5000	0.0000	52.100	17.300	0.000	5.600	26.700
5400	9.5000	0.0000	52.500	17.800	0.000	5.600	25.600
6000	9.5000	0.0000	53.000	18.600	0.000	5.600	24.500
6600	9.5000	0.0000	53.000	19.200	0.000	5.500	23.700
7200	9.5000	0.0000	53.700	19.500	0.000	5.500	23.000
7800	8.0000	0.0000	55.400	21.500	0.000	4.450	19.700
8400	4.0000	0.0000	58.100	23.700	0.000	3.350	16.000
9000	5.0000	0.0000	64.000	27.200	.500	.700	9.000
9600	2.0000	0.0000	61.000	24.000	8.800	.450	7.500

*"Inert" was N₂.

Table A-4. Carbon Steaming Performance Data

RUN NO. K-1 13176-B-7
 RUN DATE 5/29/80
 RUN BY JOHN PAJL

REACTION TIME MIN	DRY PRODUCT GAS VOL CC(STP)	DRY PRODUCT COMPOSITION MOL %	INST.C GASIFIED GRAMS	PERCENT CARBON GASIFIED	CUM.H2O IN PRODUCT GRAMS	CUM.H2O REACTED GRAMS
		H2 CO2 INERT* CH4 CO				
10	251	50.0 15.8 .2 5.7 28.3	.067	7.2	.04	.12
20	502	50.4 15.9 0.0 5.7 28.0	.067	14.4	.08	.24
30	752	50.6 15.9 0.0 5.7 27.8	.066	21.5	.12	.37
40	1003	50.7 15.9 0.0 5.7 27.7	.066	28.6	.16	.49
50	1254	50.9 16.0 0.0 5.7 27.4	.066	35.7	.20	.61
60	1505	50.8 16.3 0.0 5.6 27.3	.066	42.8	.24	.73
70	1755	51.0 16.4 0.0 5.6 27.1	.066	49.9	.27	.86
80	2006	51.2 17.0 0.0 5.5 26.3	.065	56.9	.31	.98
90	2257	51.7 17.5 0.0 5.5 25.2	.065	63.9	.35	1.10
100	2508	52.1 18.3 0.0 5.5 24.1	.064	70.8	.39	1.23
110	2758	52.3 18.9 0.0 5.4 23.4	.064	77.7	.42	1.35
120	3009	52.8 19.2 0.0 5.4 22.6	.063	84.5	.46	1.48
130	3220	54.8 21.3 0.0 4.4 19.5	.051	90.0	.51	1.59
140	3326	57.4 23.4 0.0 3.3 15.8	.024	92.6	.62	1.64
150	3458	63.1 26.8 .5 .7 8.9	.026	95.4	.72	1.71
160	3511	60.0 23.6 0.6 .4 7.4	.009	96.3	.85	1.73

CARBON BALANCE = 98.77

TIME MIN	CUM PCT C GASIFIED	AVE GAS EVL RATE CC/MIN	WET PRODUCT GAS COMPOSITION, MOL %	PCNT STEAM UTLZD	CUM. C GASIFIED GRAMS	SPECIFIC GASIF RATE MOL/MIN-MOL C
			H2 CO2 INERT* CH4 CO H2O			
10	7.2	26.9	41.8 13.2 .2 4.8 23.7 16.4	75.6	.067	.6078
20	14.4	26.9	42.2 13.2 0.0 4.8 23.4 16.3	75.7	.133	.6084
30	21.5	26.9	42.3 13.2 0.0 4.7 23.3 16.3	75.7	.200	.6091
40	28.6	26.9	42.5 13.2 0.0 4.7 23.2 16.3	75.7	.266	.6100
50	35.7	26.9	42.6 13.4 0.0 4.8 22.9 16.3	75.8	.332	.6110
60	42.8	26.9	42.6 13.5 0.0 4.7 22.9 16.2	75.9	.398	.6124
70	49.9	26.9	42.7 13.5 0.0 4.7 22.7 16.2	76.0	.464	.6141
80	56.9	26.9	43.0 14.3 0.0 4.3 22.1 16.0	76.3	.529	.6164
90	63.9	26.9	43.6 14.8 0.0 4.3 21.2 15.8	76.6	.594	.6193
100	70.8	26.9	44.0 15.4 0.0 4.7 20.3 15.5	77.1	.658	.6237
110	77.7	26.9	44.3 16.4 0.0 4.3 19.8 15.3	77.5	.722	.6309
120	84.5	26.9	44.8 16.5 0.0 4.3 19.2 15.2	77.6	.786	.6441
130	90.0	22.7	41.4 16.7 0.0 3.3 14.7 24.5	65.9	.837	.6551
140	92.6	1.3	25.3 10.3 0.0 1.5 7.0 56.0	33.2	.861	.6350
150	95.4	4.2	33.4 14.2 .3 .4 4.7 47.1	41.6	.887	.6398
160	96.3	5.7	14.2 5.4 2.0 .1 1.7 76.4	15.1	.896	.6260

*"Inert" was N₂.

gasified, the product gas evolution rate (cc/min at ambient conditions), the wet product gas composition (mole percent H_2 , CO_2 , N_2 , CH_4 , CO and H_2O), steam utilization (percent of feed), cumulative carbon gasified (grams), and the specific gasification rate (moles carbon gasified per minute per mole carbon remaining in reactor).

APPENDIX B

DESCRIPTION OF TANDEM REACTOR APPARATUS

The Tandem Reactor Apparatus discussed in Section 5.3.2 of this report consisted 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 was constructed of 316 stainless steel tube, fittings and valves (1/4 to 1/2-inch tube size). Provisions were 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 were controlled by pressure regulators and needle valves. The feed gas flow rates were determined by measuring the pressure drops across calibrated orifices. Dry feed gas compositions were also measured using a gas chromatograph.

The gasification reactor feed steam was superheated using two tube furnace heaters which heated feed gas coils. Each superheater was controlled by gas exit temperature. Override control was based on furnace heated zone temperature.

- Steam Boiler

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

- Carbon Deposition Reactor

The deposition reactor consisted of a 10-1/2 foot long reaction section which was flanged and bolted to a 5 foot long disengagement section having a 1 foot long transition cone. The reaction and disengagement sections were 6 inch and 12 inch SCH 40 pipe, respectively. The reactor bottom was fitted with a cone gas distributor. A "shoulder" was machined into the inside surface of the cone to provide a seat for a plate type gas distributor if needed; it was not used because the conical bottom proved to be an adequate distributor. The reactor was constructed with type 316 stainless steel; its inside surfaces were aluminized by Alon Processing, Inc., Tarentum, PA. The reactor was designed to meet the maximum operating condition of 100 psig at 650°C. The reactor initially was equipped

with an internal cyclone at the top of the de-entrainment section with a dip-leg of recycling solids to the reaction zone. In order to improve separation efficiency the cyclone was replaced with a filter element at the same position.

There were 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 was heated with two 500 watt heaters which were controlled using West proportional band temperature controllers with high limit alarm output capability. There were two heaters per controller. Temperature sensors (Type K thermocouples) located in the middle of each zone measured the reactor internal temperature at a point within 1/2 inch from the reactor wall. Three external thermocouples measured the external reactor wall temperature. The de-entrainment section was not heated. Beaded heaters were used to heat the 1/2 inch line between the reactor and filter, as well as the filter housing itself. Variacs were used to control the outputs from these heaters. Temperatures of the line and filter housing were measured with Type K thermocouples.

The reactor was insulated with two layers of 1 inch thick ceramic fiber blanket insulation which was lagged and painted for weather protection.

- Steam Gasification Reactor

The gasification reactor consisted of a 10-1/2 foot long reaction section which was flanged and bolted to a 5 foot long disengagement section having a 1 foot long transition section. The reaction and disengagement sections were 3 inch and 6 inch SCH 40 pipe, respectively. The inlet to the reactor consisted of a 1 inch tube through which feed gases entered via a cone-shaped gas distributor. All material was Type 316 stainless steel, the inside surfaces of which had been aluminized. The design conditions were 90 psig at 760°C for the flange and 100 psig at 760°C for the reactor.

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

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

The reactor was equipped with an internal filter at the top of the de-entrainment section.

- Water Removal from Product Gas

Each reactor was equipped with a condenser for recovery of the water vapor in the product gas. The condensers consisted 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 was separated from the dry product gas in "knock-out" vessels.

- Reactor Pressure Control and Product Gas Metering System

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

Product gas metering was performed using calibrated orifices. Dry gas molecular weight was determined through gas chromatography. Dry gas meters were utilized to confirm product gas flow rates.

- Solids Transfer System

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

- Data Acquisition System.

The data acquisition system consisted of pressure, temperature, flow rate and gas composition measurement instrumentation. Pressure gauges, digital voltmeters and chart recorders served as visual display instrumentation. A DEC PDP-11 computer and a DORIC data logger were used to record all process data. Computer printout of selected process information was available in "real time" during test runs. An off-line program provided averaged data summaries and a full "dump" of all data channels after the run was concluded. Examples of computer printouts generated during Tandem testing for both deposition and steaming operations, with pertinent explanations, are included in Appendix C of this report.

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

The data were 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 B-1 and B-2 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 B-3 shows the expander sections (solids de-entrainment sections) for the two reactors (the larger expander is for the deposition reactor). Figure B-4 shows the two reactors installed in the four-story BEACON test stand. Figure B-5 shows the Tandem Reactor Control Panel (except for the DEC data acquisition computer). Figures B-6 and B-7 show the gas analysis instrumentation and temperature control system dedicated to the Tandem Reactor Apparatus.

Figure B-1. Carbon Deposition Reactor

Figure B-2. Steam Gasification Reactor

Figure B-3. Solids De-entrainment Sections for Gasification and Deposition Reactors (Reactor Expander Sections)

Figure B-4. Tandem Reactors Installed in Test Stand

Figure B-5. Tandem Reactor Apparatus Control Panel
(DEC Computer not Shown)

Figure B-6. Gas Analysis Instrumentation for Tandem System

Figure B-7. Temperature Control System for Tandem Reactors

APPENDIX C
BEACON TANDEM REACTOR TEST FACILITY
DATA ACQUISITION SYSTEM

The BEACON tandem reactors are an experimental test facility for the evaluation of candidate BEACON catalysts. The purpose of constructing this reactor system, at the scale and configuration selected, is to obtain process engineering data for commercial viability as well as efficiently testing candidate catalysts for long-term chemical and physical stability under near commercial, steady state operating conditions.

Rigorous investigations, in bench scale facilities, normally require extensive instrumentation to provide adequate monitoring and recording of key process variables. This coupled with the large volume of data generated, which normally require repetitious calculations, indicated the need for a flexible data acquisition system. As a result the existing microprocessor based data processing system, together with the necessary peripheral equipment, was modified for use in the Tandem Reactor Test Facility.

The existing data acquisition system (DAS) consists of a PDP-11/03 DECLAB package; a microprocessor with 32K word memory, a 50 microsecond A/D converter multiplexed into 16 channels, two 16 bit parallel digital input/output ports, a programmable real-time clock, a single density dual floppy disk drive system and a 30 character per second typewriter. The modifications required for the tandem reactors were specific to process monitoring and evaluation software. Process control was deemed beyond the present scope of the Tandem Reactor System.

The basic requirements for tandem reactor data acquisition are as follows:

- Monitoring of Facility Conditions

There are multiple process sensors associated with the Tandem Reactor Facility which measure temperatures, pressures, feed and product flows. The data is obtained on a continuous basis in essentially duplicate fashion for each reactor.

To provide the necessary information for subsequent performance evaluation, the computer calculates several key process conditions using available subroutines to the main BEACON program. Of paramount importance is the calculation of all feed gas streams. To accomplish this the computer senses all necessary input signals associated with a given feed stream and performs flow/orifice calculations. The necessary input signals for calculation of volumetric flow rates are the differential pressure across a flatplate orifice, orifice absolute pressure and temperature, orifice coefficient, and molecular weight. The dependent and independent variables are applied to the standard orifice equation to obtain volumetric flow.

Although the capability also exists to determine the total product flow using similar logic as described above, it has become more reliable to compute the total volumetric product flow using a constant displacement dry gas meter. The dry gas meter (DGM) is independent of molecular weight and provides an improved "average" reading of total product flow during a performance block.

- Gas Chromatograph Data Analysis

The product gas is analyzed by a Carl Process Gas Chromatograph and the concentration in mole fractions is converted to percent concentration (using peak area) by a Hewlett Packard reporting integrator. A single dedicated chromatograph is used to analyze the outlet gas streams of each reactor. Each GC collects data over a ten minute period for five mutually exclusive windows. Using total product flow and the results of the GC analysis, individual product flow rates can be computed.

- Performance Data Summary

Upon completion of collecting all pertinent process and product gas data, chemical engineering computations are performed to yield near real time mass balance and chemical rate data. These results, printed in ten minute intervals, provide the basis for real time process evaluation. A typical example of on-line performance calculations is shown in Figure C-1.

OPTION:

GASIFICATION REACTOR PERFORMANCE

TIME : 17:30:21 TO 17:40:21

	H2O	H2	CO2	N2	CH4	CO	TOTAL
	SCFM/ %	SCFM/ %	SCFM/ %	SCFM/ %	SCFM/ %	SCFM/ %	SCFM
IN	1.08/			0.00/ 0.0			
OUT		0.33/ 26.6	0.29/ 23.8	0.41/ 33.9*	0.15/ 12.0	0.02/ 1.4	1.20

GASIFICATION RATE	0.46	SCFM	FEED PRESSURE	113.4	PSIA
GASIFICATION RATE	6.54	GMS/MIN	REACTOR PRESSURE	99.6	PSIG
TOTAL C GASIFIED	65.4	GRAMS	PRODUCT PRESSURE	116.6	PSIA
PROD H2:O RATIO	1.0 : 1		LINEAR VELOCITY	0.195	FPS
% H2O UTILIZATION: USING O =	55.5 %		REACT TEMP(7 AVG)	621.1	DEG.C
% H2O UTILIZATION: USING H2 =	57.2 %				

*Purge Nitrogen

DEPOSITION REACTOR PERFORMANCE

TIME : 17:30:21 TO 17:40:21

	H2	CO2	N2	CH4	CO	TOTAL
	SCFM / %	SCFM / %	SCFM / %	SCFM / %	SCFM / %	SCFM
FEED	0.462/ 4.4	0.155/ 1.5	8.055/ 76.7	0.0 / 0.0	0.967/ 9.2	10.497
PROD	0.187/ 2.0	0.555/ 5.9	8.394/ 88.8	0.091/ 1.0	0.058/ 0.6	9.285

	C (SCFM)	O (SCFM)	H2(SCFM)	N2(SCFM)	PRES(Psia)
FEED	1.122	1.277	0.462	8.913	125.37
PROD	0.704	1.168	0.369	8.394	112.61

LINEAR GAS VELOCITY	0.28	FT/SEC	CARBON DEPOSITED	0.42	SCFM
REACTOR PRESSURE	95.1	PSIG	DEPOSITION RATE	6.01	GM/MIN
REACTOR TEMPERATURE	454.4	DEG.C(9 TEMP)	TOTAL DEPOSITION	60.1	GRAMS

Figure C-1. On-line Performance Data Summary for BEACON Tandem Reactor System