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CATALYTIC CONVERSION OF COAL ENERGY TO HYDROGEN

QUARTERLY TECHNICAL PROGRESS REPORT FOR THE PERIOD 1 JANUARY — 31 MARCH 1977

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1. INTRODUCTION

Fundamentally, the production and extraction of synthetic fuels and other important chemicals from coal involves increasing the hydrogen to carbon ratio in the coal. The original source of the hydrogen to accomplish this must be water and the methodology of extracting the hydrogen from water is the key to much of the synthetic fuels technology currently being developed. The cost of producing either coal-derived liquids or high BTU gas is highly dependent on the cost of producing the required hydrogen so that processing schemes which more economically utilize the energy of lower grade fuels such as coal itself or residual coal char to separate hydrogen from water can have a major impact on the costs of producing synthetic fuels. Preliminary research conducted over the last few years at TRW Systems indicates that significant improvements in the production of hydrogen and probably methane may be achieved through the use of alkali-based catalyst systems for coal gasification reactions. Newly identified catalyst systems and concepts for utilizing them have several properties which could lead to more technically and economically feasible processes for deriving hydrogen and other synthetic fuels from coal.

Recently ERDA initiated a program at TRW to investigate the potential and feasibility of using alkali-based catalyst systems for promoting coal gasification reactions. This report covers work performed on this program from January 1, 1976 to March 31, 1977 under ERDA Contract No. E(49-18 2206, and documents all findings, experimental results and conclusions obtained for this period.

2. OBJECTIVE AND SCOPE OF WORK

The overall objective of this program is to develop a preliminary assessment of the potential of a hydrogen and/or methane generation process based upon reactions involving char, steam, lime and alkali metal salt additives. Early literature reports, as well as more recent investigations, of several researchers have shown that the production of synthesis gases rich in hydrogen from coal-char-steam reactions can be very significantly catalyzed through the use of alkali and/or alkaline earth metal compounds. It appears possible from this work that commercial hydrogen and/or methane generation rates can be obtained at temperatures below 750°C. Currently, large scale production of these gases by other means is not as economical as desired. With sharp increases projected in the demand for hydrogen and methane as both synthetic fuels and chemicals, it is thought that a process based on catalyzed char-steam reactions may represent an attractive alternative for their production. Small scale laboratory studies consisting of both fixed-bed and fluid-bed experiments need to be carried out to characterize catalyst performance in these reactions and to establish reaction conditions under which optimal performance may be obtained. Information obtained from these experiments will be used to support a preliminary engineering study of the technical and economic feasibility of a coal gasification process based upon optimized catalyst system(s).

The technical effort to accomplish these project objectives has been divided into five work areas or tasks each with their own specific objectives. These project tasks are listed below together with a brief statement of their objectives.

Task I - Fixed-Bed Reactor Experimentation

The objective of this task is to determine the effectiveness of selected alkali metal catalyst systems for promoting hydrogen and other product gases from the char-lime-steam reaction using a small laboratory scale fixed-bed tube reactor. A second task objective is to identify and define steam reaction and lime (carbon dioxide acceptor) regeneration conditions in which optimal char conversion rates and catalyst performance with recycling are obtained.

Task II - Fluid-Bed Reactor Tests

Task II's objective is to evaluate the effectiveness and recyclabilities of the best catalyst systems identified in Task I using a lab scale fluid-bed reactor under conditions which more closely approximate anticipated operation in a commercial process. Data generated in these studies will be used to perform an economic analysis of conceptualized commercial systems.

Task III - Catalyst-Acceptor Physical-Chemical Properties

The objective of this task is to determine how alkali catalyst functions during gasification and lime (carbon dioxide acceptor) regeneration, and to identify the mechanisms associated with their deactivation and stabilization. A second objective of this task is to assess the coal-char-sulfur retention characteristics of an acceptor-catalyst system during char gasification and acceptor regeneration. Understanding gained in this task will hopefully be useful in improving catalyst effectiveness during gasification and performance with recycle.

Task IV - Catalyzed Steam-Oxygen-Char Reaction Studies

Task IV's objective is to assess the capability of stabilized alkali catalyst systems for promoting the steam-char and char-oxygen-steam reactions. More specifically, the objective of this task is to determine the temperature and contacting conditions under which selected catalyst systems remain active and stable for the gasification of chars with varying ash contents. Small fixed-bed reactors similar to the systems used in Task I will be used for most of the studies. Confirmatory tests of the catalyst performance characteristics for an optimized catalyst system will be performed using a small, atmospheric fluid-bed reactor.

Task V - Engineering Studies

There are four major objectives of the Engineering Studies task. These are: 1) to provide preliminary design bases for investigating the economic viability of a commercial process design, 2) to provide guidelines and priorities for laboratory research by identifying process features which significantly impact scale-up, capital investment requirements and operating costs, 3) to provide a progressively upgraded conceptual commercial design, for assessing technology requirements in terms of industry practice, for comparison with other synthetic fuel processes and for projection of process commercialization capital requirements and operating costs, and 4) to develop conceptual designs related to variations and/or extended applications of the process (e.g., the general steam-carbon reaction) preliminary assessment of commercial potential.

3. SUMMARY OF PROGRESS

An overall project schedule is presented in Figure 3-1 and accomplishments made during this reporting period are summarized below. Some schedule slippage for three of the project tasks has been incurred. It is anticipated that this slippage will extend completion of the technical effort of the program beyond the 31st of July, the originally scheduled project completion date, to the 30th of September. The reason for the slippage indicated in Tasks III and IV was an overly optimistic estimate made early at the start of the program of the time required to perform some of the planned experimentation. Schedule slippage which occurred for the fluid-bed experimentation task is due to delays encountered in delivery of pieces of equipment for construction of the elevated pressure reactor and completion of necessary laboratory modifications for accommodating the reactor system.

Accomplishments made during the reporting period are summarized by task below:

Task I - Fixed-Bed Reactor Experimentation

Task I was completed during this reporting period. During this period the effectiveness of calcium fluoride, sodium dihydrogen phosphate, and calcium phosphate in extending alkali catalyst lifetime or recyclabilities were determined. In addition the effect of solution impregnation on catalyst performance for the char-lime-steam reaction was also determined.

Task II - Fluid-Bed Reactor Studies

During this reporting period the majority of the atmospheric pressure fluid-bed experiments to determine catalyst performance have been completed. The data from these experiments were also reduced and analyzed. Additionally most of the components for the elevated pressure fluid-bed reactor were received and the assembly of the laboratory reactor starter. Finally, several experiments have been conducted to observe the behavior of the

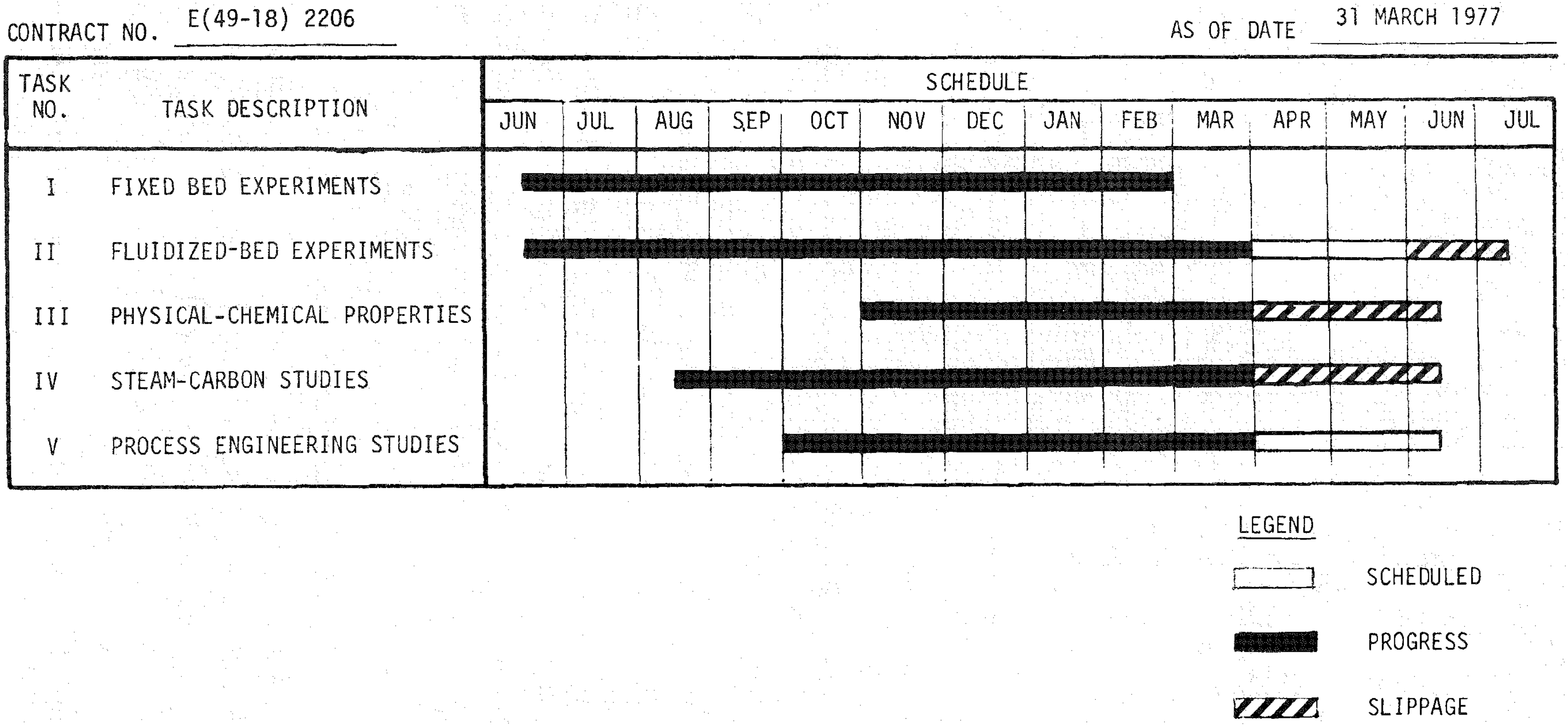


Figure 3-1. Project Schedule

acceptor material and to resolve certain difficulties concerning the performance of these materials.

Task III - Catalyst-Acceptor Physical-Chemical Properties

Significant experimental accomplishments made under this task during the reporting period included: determining of the char-sulfur retention properties of acceptor-catalyst systems, completing optical, scanning electron microscope, and X-Ray diffraction analysis of deactivated catalyst systems in reaction ash residues, and measuring the relative carbon dioxide absorption properties of chemically pure lime and a re-calcined natural dolomite.

Task IV - Catalyzed Steam-Oxygen-Char Reaction Studies

Principal accomplishments made under this task during the reporting period include completing experiments to measure the effect that catalyst concentration had on the rate and product composition of the char-steam reaction, and determining the recyclability performance of five catalyst systems for the char-steam reaction, using the fixed-bed reactor.

Task V - Engineering Studies

Under the engineering studies task, a block diagram of the conceptualized catalytic gasification process was prepared and a process design basis developed. A preliminary process flow diagram was completed and material and energy balances around lack of the process unit operations made. Identification and sizing of the major prices of process equipment was initiated.

4. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

4.1 TASK I - FIXED-BED REACTOR EXPERIMENTATION

The objective of this task is to assess the relative performance of selected materials for catalyzing the char-steam reaction, and to identify reaction and process conditions that affect catalyst performance. Catalyst performance characteristics which are of key importance in determining the technical and economic feasibility of catalytic gasification process are catalyst effectiveness and recyclability or life. Both performance characteristics can greatly influence process plant design and projected operating costs. Since only an evaluation of the relative performance of various catalyst materials is sought initially, catalyst activity screening and reaction parameter effect studies can be rapidly and cost effectively investigated using a small fixed-bed reactor system. Results obtained under this task are intended to be used to reduce the number of systems and parameters that have to be examined using a fluid-bed reactor for more quantitative and extrapolative data for engineering use.

4.1.1 Work Accomplishments

During this reporting period the fixed-bed reactor experimentation task has been completed. In the studies completed this quarter, the effectiveness of calcium fluoride, sodium dihydrogen phosphate, and calcium phosphate in extending alkali catalyst lifetimes or recyclabilities has been determined. In addition the effect of solution impregnation on catalyst performance for the char-lime-steam reaction was also determined. Presented below in the remainder of this section are more detail descriptions of the experiments performed, and the observation and results obtained from them.

4.1.1.1 Effectiveness of Fluorspar and Phosphate Salts as Alkali Catalyst Stabilizers

It was observed in earlier experiments and reported in a previous report[1] that fluorspar (CaF_2) was able to significantly extend the useful lifetime or recyclability of potassium carbonate and sodium borate catalysts in the char-lime-steam reaction. The degree of improvement in catalyst recyclability appeared to depend on the particular catalyst and whether a high temperature (950°C) acceptor regeneration treatment of reaction residues was a part of the reaction cycle. It was desirable to determine whether the addition of fluorspar could extend the recyclability of sodium carbonate catalyst and whether other salts, such as phosphates, could function as catalyst stabilizers. It was thought that the stabilizing action of fluorspar may be due to the ability of the salt to alter the rate and/or the product species formed in a deactivating reaction involving alkali catalyst and char ash constituents such as silica and alumina. Fluorspar is known to catalyze the formation of calcium trisilicate from the reaction between CaO and SiO_2,[2] and thus could be functioning to promote this reaction during char gasification and acceptor regeneration rather than the reaction between alkali catalyst and char ash components. Since phosphate salts are also capable of forming stable aluminosilicate glasses, they were selected to be screened as catalyst stabilizers. The phosphate salts selected for evaluation were calcium phosphate and sodium dihydrogen phosphate since they are the most abundant and inexpensive phosphate salts available.

The experimental procedure used to evaluate the effectiveness of fluorspar and phosphate salts as catalyst stabilizers was the same as that employed in earlier catalyst performance screening tests. Reaction mixtures consisting of COED char, lime, catalyst and stabilizer were prepared by dry blending the materials and reacting them with steam in the fixed-bed reactor for one hour. A reaction temperature of 650°C was used for all of the experiments with a fixed steam flow rate of 0.33 mole per minute. After reaction with steam, reaction residues still in the reaction vessel were placed in a preheated 500°C furnace for a period of 1/2 hour to burn off any unreacted carbon. Fresh char equal to the quantity present in the original mixture was dry blended with ash residue and the reconstitued mixture re-reacted with steam. The reaction cycle was repeated until catalytic char gasification was no longer observed. Reaction product gas volume and composition were measured as a function of time in order to determine char gasification extent and rate. Observed differences in product evolution rate with recycle could thus be interpreted as changes in catalyst performance. A more comprehensive description of the fixed-bed reactor, sample preparation and product evolution measurement techniques can be found in the previous project technical report.[1]

The results obtained from the stabilizer experiments are reported in Table A-1 in the Appendix. Presented in the table are the product evolution rate observed for each reaction cycle as well as the catalyst usage ratios derived from the experiments. Also reported are catalyst : silica mole ratios for each of the deactivated reaction residues. These ratios were calculated from the quantity of catalyst initially charged and the amount of ash added by the char with each reaction cycle. The ash content of COED char as well as the elemental constituents of the ash were determined and reported previously.

The effects of stabilizer addition on catalyst usage and catalyst : silica ratio are summarized in Table 4-1. As can be seen from these results, the presence of fluorspar and phosphate salts can significantly improve catalyst recyclability. For K_2CO_3, Na_2CO_3, and $Na_2B_4O_7$, the addition of 5% fluorspar is able to increase the usage ratio for these catalysts by approximately 110%, 60%, and 50%, respectively. The improvements observed in catalyst usage are also reflected in the lower catalyst : silica mole ratios obtained for fluorspar amended catalysts. These figures show that if silica contained in char ash is a deactivating agent, fluorspar addition is able to, substantially and favorably, alter the apparent empirical formula of the product compound. For K_2CO_3, $Na_2B_4O_7$ and Na_2CO_3 catalysts, fluorspar addition is observed to lower the molecular ratio of catalyst : silica in the presumed product compound by 52%, 37%, and 35%, respecitvely. The improvement in alkali catalyst recyclability achieved with phosphate salt addition is also substantial though the degree is dependent on the particular salt used. Addition of 5% and 10% calcium phosphate to reaction mixtures containing potassium carbonate resulted in modest 16% and 26% increases in catalyst usage over the unamended catalyst while addition of 10% sodium phosphate approximately doubled catalyst usage. It is interesting to note that for those cases where catalyst usage was doubled through the addition of CaF_2 or NaH_2PO_4, the mole ratio of catalyst : silica in the deactivated ash residue is approximately constant and equal to 0.2 suggesting the

Table 4-1. Effect of Stabilizer Addition on Catalyst Usage and the Catalyst-Silica Ratio

Catalyst System	Mole Weight Catalyst	Cat/Si Ratio[a]	Useage Ratio[b]
5% K_2CO_3	138	0.399	19
5% K_2CO_3 + 5% CaF_2	138	0.191	40
5% K_2CO_3 + 5% $Ca_3(PO_4)_2$	138	0.351	22
5% K_2CO_3 + 10% $Ca_3(PO_4)_2$	138	0.318	24
5% K_2CO_3 + 10% NaH_2PO_4	138	0.203	37
5% Na_2CO_3	106	0.325	30
5% Na_2CO_3 + 5% CaF_2	106	0.211	47
5% $Na_2B_4O_7$	201	0.457	11
5% $Na_2B_4O_7$ + 5% CaF_2	201	0.289	18
5% NaF	42	0.547	46

[a] Ratio of number of moles catalyst used to mole SiO_2 in deactivated reaction mixture.

[b] Weight char catalytically gasified per unit weight alkali catalyst employed.

possibility that very similar catalyst deactivation pathways are being followed in these cases.

4.1.1.2 Effect of Solution Impregnation on Catalyst Performance

It was decided to determine whether application of catalyst to reaction mixtures by solution impregnation rather than simple dry admixturing resulted in any improvements in catalyst performance for the char-lime-steam reaction. In particular, an evaluation of the effect of solution impregnation on catalyst recyclability and activity was sought. Reaction test mixtures consisting of COED char, lime and either sodium carbonate or potassium carbonate catalyst were used so that comparisons with catalyst performance obtained with dry blended catalyst could be made. Reaction test mixtures were prepared by first dry blending the powders as is normally done for dry catalyst application, then adding sufficient deionized water to thoroughly soak the powder mixtures. The wetted samples were allowed to stand in a reaction vessel for one to two hours and then dried for sixteen hours in a 105°C oven. Dried test mixtures were then reacted with steam under conditions used in normal catalyst screening experiments, i.e., 650°C steam reaction temperature, 0.33 mole per minute steam flow rate, and one-hour reaction period. Product evolution rate and composition were measuared during gasification in the manner described previously.[1] When reaction with steam was completed, the reacted samples were transferred from the fixed reactor system and placed in a preheated 500°C muffle furnace for thirty mintues to burn off any unreacted char in the sample. Upon completion of the burn off treatment, fresh char equal to the amount in the initially prepared sample was added. The mixture was then dry blended, wetted and handled in the same manner as before. Reaction residues were put through seven of these preparation/reaction cycles.

Results of these recycle experiments are summarized in Table 4-2. Also included in the table for comparison are results obtained for the dry admixed catalysts. As can be seen from the results presented, dispersion of catalyst in mixtures by solution is not without some effect on catalyst

Table 4-2. Comparative Catalyst Performance Results for Dry and Solution Dispersed Catalyst Systems

System			Catalyst Dispersion	Product Evolution Rate[a]										Useage Ratio[b]	C/S Ratio[c]
				Reaction Cycle											
Char	Acceptor	Catalyst		1	2	3	4	5	6	7	8	9	10		
19% COED	76% CaO	5% K_2CO_3	Dry	2.87	3.00	3.13	2.47	1.47	0.44	0.33				19	0.399
19% COED	76% CaO	5% K_2CO_3	Wet	2.87	2.97	2.63	2.63	1.77	1.87	1.63				>26	<0.29
19% COED	76% CaO	5% Na_2CO_3	Dry	2.75	3.20	3.22	3.11	3.28	3.18	3.01	2.51	0.77	0.44	30	0.325
19% COED	76% CaO	5% Na_2CO_3	Wet	3.09	2.97	3.15	3.00	2.91	2.83	2.55				>26	<0.37

[a] Moles product gas produced per mole carbon per hour.

[b] Weight char catalytically gasified per unit weight of alkali catalyst employed.

[c] Ratio of mole catalyst used to moles SiO_2 in 7th cycle or deactivated reaction residue.

performance. For K_2CO_3 solution impregnation appears to improve catalyst recyclability. While the activity of the dry blended catalyst is equal to or greater than that shown by the wet impregnated catalyst through the third reaction cycle, its activity rapidly diminishes for the solution dispersed catalyst in reaction cycle four through six. The wet impregnated catalyst is still effective through the seventh cycle thus attaining a usage ratio of something greater than 26, an increase of at least 40% over the usage ratio for the dry blended catalyst. Whether any improvement in catalyst recyclability is achieved with solution impregnation for sodium carbonate is undeterminable owing to the limited number of reaction cycles completed. There does, however, appear to be some detectable loss of catalyst activity relative to the dry mixed catalyst after the fourth reaction cycle. From these results, it appears that only modest improvements in catalyst performance for the char-lime steam reaction can be attained with solution dispersion of catalyst. The small apparent advantage to be realized in catalyst performance would probably not be sufficient to compensate for the additional complexity and catalyst recovery costs in a gasification process to warrant this approach being taken for dispersing catalyst. To confirm that no significant improvement in catalyst performance is to be achieved with solution impregnation, evaluation tests using a fluid-bed reactor should be performed and a reaction cycle employed in which catalyst, char ash and acceptor are exposed to high temperature acceptor regeneration treatment.

4.1.2 Work Forecast

Work finished this quarter under the fixed-reactor experimentation task complete the experimental effort planned for this task and no future work is contemplated. During the next reporting period, experimental results obtained under this task will be compiled, analyzed and incorporated into a project final report.

4.2 TASK II - FLUID BED REACTOR STUDIES

The objectives of this task are to demonstrate the effectiveness of various stabilized catalyst systems which will retain their activity through many recycles, and to generate data on the performance of these systems under conditions which more closely approximate the anticipated operations of commercial systems. These data will be used in the economic analyses of conceptualized commercial systems and in conceptual commercial plant design studies. Two concepts are currently being investigated: one involving recalcining of acceptor as might be used in a CO_2-acceptor process, and the second involving a non-coal impregnated resident catalyst which remains in the fluid bed without including a recalcining step.

4.2.1 Work Accomplishments

During this reporting period (Jan-Mar 1977) the majority of the atmospheric pressure fluid-bed experiments to determine catalyst performance have been completed. The data from these experiments have been reduced and analyzed. Additionally most of the components for the elevated pressure fluid-bed reactor have been received and the assembly of the laboratory reactor started. Finally, several experiments have been conducted to observe the behavior of the acceptor material and to resolve certain difficulties concerning the performance of these materials.

Presented below, in the remainder of this section, are more detailed descriptions of the activities, observations, and results obtained in the Fluid-Bed Reactor Studies task.

4.2.1.1 Catalyst Recyclability Experiments

Catalyst recyclability tests using the fluid-bed reactor are continuing. Tests with four catalyst systems, Na_2CO_3, K_2CO_3, Na_2CO_3 with CaF_2, and K_2CO_3 with CaF_2, are being performed to determine their performance with recycle. Catalyst recycle performances are being evaluated for the carbon oxide acceptor gasification process concept, and a resident catalyst or non-carbon oxide acceptor application. Recycle tests with K_2CO_3 and K_2CO_3-CaF_2 catalyst systems are totally complete, while approximately six recycle experiments with Na_2CO_3 and Na_2CO_3-CaF_2 catalyst systems remain to be completed. A series of experiments using $Na_2B_4O_7$ catalyst have been initiated. At present this catalyst has shown only minimal catalytic activity in atmospheric pressure fluid-bed reactor tests. This is in contrast to the behavior observed for this catalyst in the fixed-bed reactor experimentation. Further experiments to determine whether a fluidization or reactor channelling problem exists are planned. No other single based catalyst system has been identified from the fixed-bed experiments which warrant testing in the fluid-bed reactor at this time.

The results obtained for the catalyst recycle tests completed to date are shown in Table 4-3. Here usage figures for each catalyst system are shown. These are the weight ratios of char catalytically gasified per unit weight of alkali catalyst employed. For the non calcined K_2CO_3 catalyst the effect of the CaF_2 stabilizer is to approximately double the life of the catalyst. This has been discussed previously in earlier monthly reports. The effect of the stabilizer on the Na_2CO_3 catalyst is less pronounced in these experiments. In fact a decrease is observed which is within experimental tolerance. This decrease (or lack of improvement) is inconsistent with the fixed-bed experiments, which show definite increases in usage ratio due to addition of CaF_2. Furthermore rerunning the Na_2CO_3 + CaF_2 catalyst for two additional cycles showed the catalyst to be inactive. The reason for this discrepancy in the results obtained with fixed-bed and fluid-bed reactor is not known.

Since several recycles remain to be completed with the recalcined Na_2CO_3 catalyst, the effect of the CaF_2 addition on catalyst recyclability has not been determined.

The $Na_2B_4O_7$ catalyst has been very surprising in that it has shown no catalytic activity in these experiments. Additionally, the bed temperature has been raised from 650°C to 700°C without any observable effect. Further tests at a bed temperature of 750°C will be conducted to determine whether this catalyst is active in a fluid-bed reactor.

Table 4-3. Summary of Catalyst Recyclability Performance Observed From Fluid-Bed Reactor Experiments

Catalyst System		Usage Ratio
K_2CO_3	Non-Calcined	12.5
$K_2CO_3 + CaF_2$	Non-Calcined	22.5
$NaCO_3$	Non-Calcined	25.0
$Na_2CO_3 + CaF_2$	Non-Calcined	20.0
K_2CO_3	Reclacined	17.5
$K_2 CO_3 + CaF_2$	Recalcined	20.0
Na_2CO_3	Recalcined	>33[a]
$Na_2CO_3 + CaF_2$	Recalcined	>12[a]
$Na_2B_4O_7$	Non-Calcined	0[b]

[a] Test still in progress.

[b] Has shown no activity in 4 experiments.

4.2.1.2 Analysis of Recycle Test Data

The data from the atmospheric pressure fluid-bed gasifier experiments have been reduced, and the specific gasification rates (grams char gasified per gram char in bed per hour), the specific water feed rates (gram water/gram char-hr), steam utilizations (%) and the apparent water gas equilibrium constant have been calculated from the data. These data, together with the gasifier product composition, provide considerable information on the performance of the catalytic fluid-bed reactor.

Gas Composition

Figures 4-1 through 4-4 show the H_2, CH_4, CO, and CO_2 product gas composition (volume percent on a dry basis) from the reactor as a function of carbon utilization and the specific steam rate (gms steam/hr/gm carbon in the bed). The specific steam rate is related to the carbon utilization by the equation

$$Sp_{H_2O} = H_2O_{in}/((1-X)\cdot W\cdot\xi)$$

where

Sp_{H_2O} = specific steam rate (gm/gm-hr)

H_2O_{in} = steam feed rate (gm/hr)

X = fraction of carbon reacted

W = initial weight of char in the bed (gms)

ξ = weight percent of carbon in the char

For the particular experimental arrangement used in these experiments the specific steam rate is inversely proportional to the carbon utilization. A continuously fed fluid-bed reactor experiment would have a different form for this equation.

For all catalysts and both process concepts the gas composition is similar with the exception of the experimental series using recalcined K_2CO_3 catalyst. In this series the concentrations of CO are too low while those of CO_2 are too high in comparison to the other series. A gas chromatograph calibration error is suspected but no reason for this difference has been determined at this time. With the exception of this series a fairly consistent pattern emerges.

In Figure 4-1 the hydrogen percent in the gasification products is seen to increase from a mean value of 55% to mean value of 65% as the

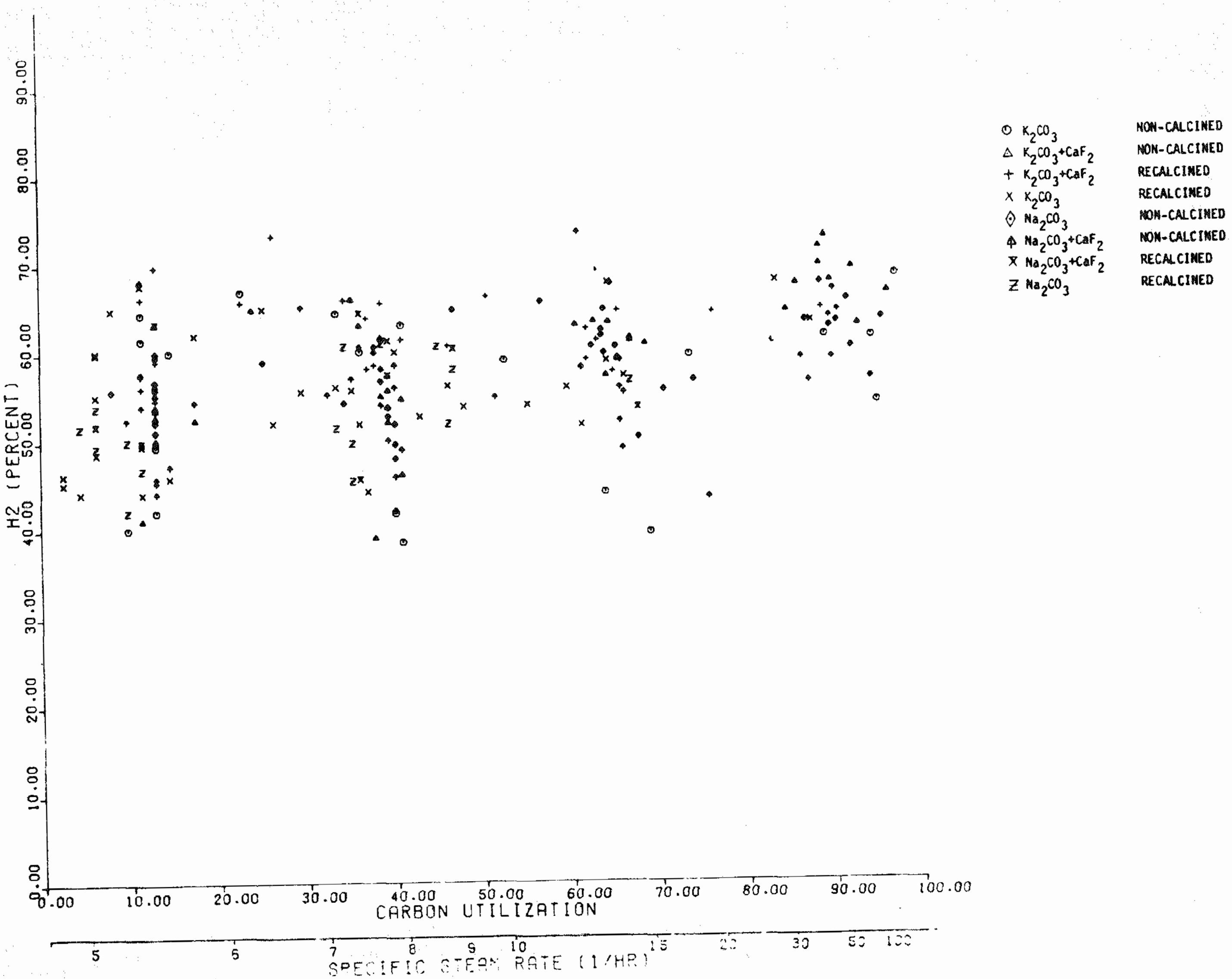


Figure 4-1. H_2 Percent As a Function of Carbon Utilization and Specific Steam Rate

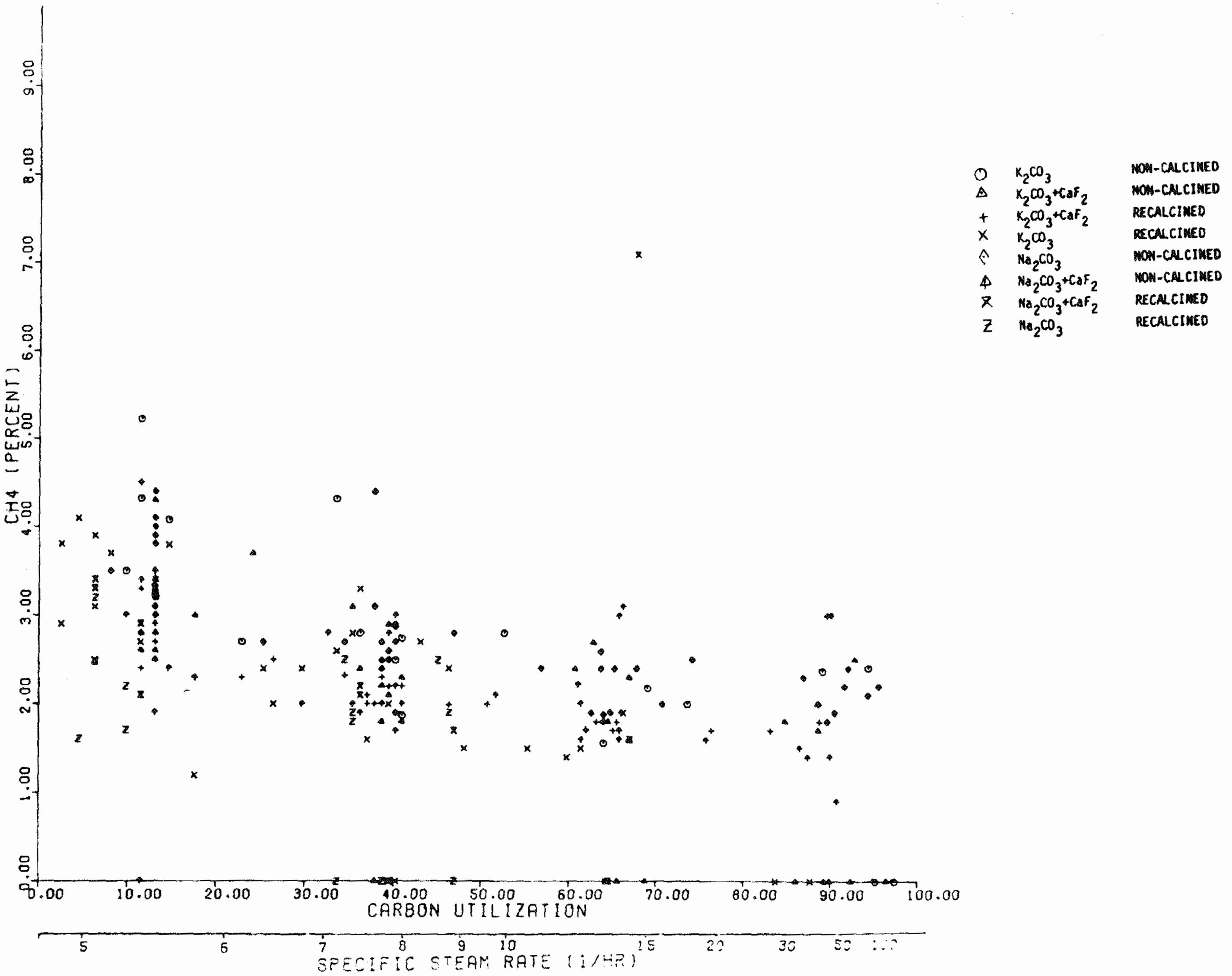


Figure 4-2. CH_4 Concentration as a Function of Carbon Utilization and Specific Steam Rate

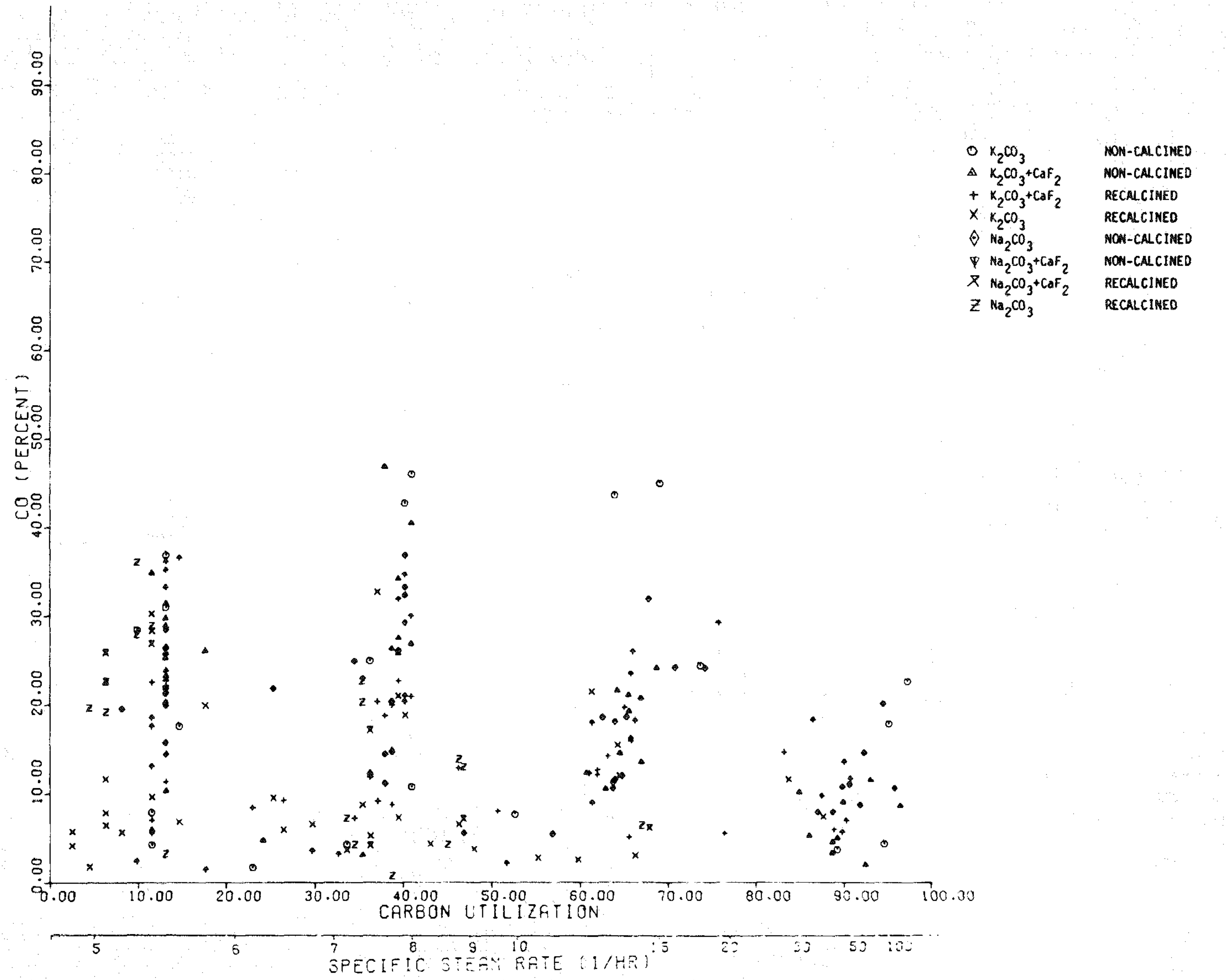


Figure 4-3. CO Concentration as a Function of Carbon Utilization and Specific Steam Rate

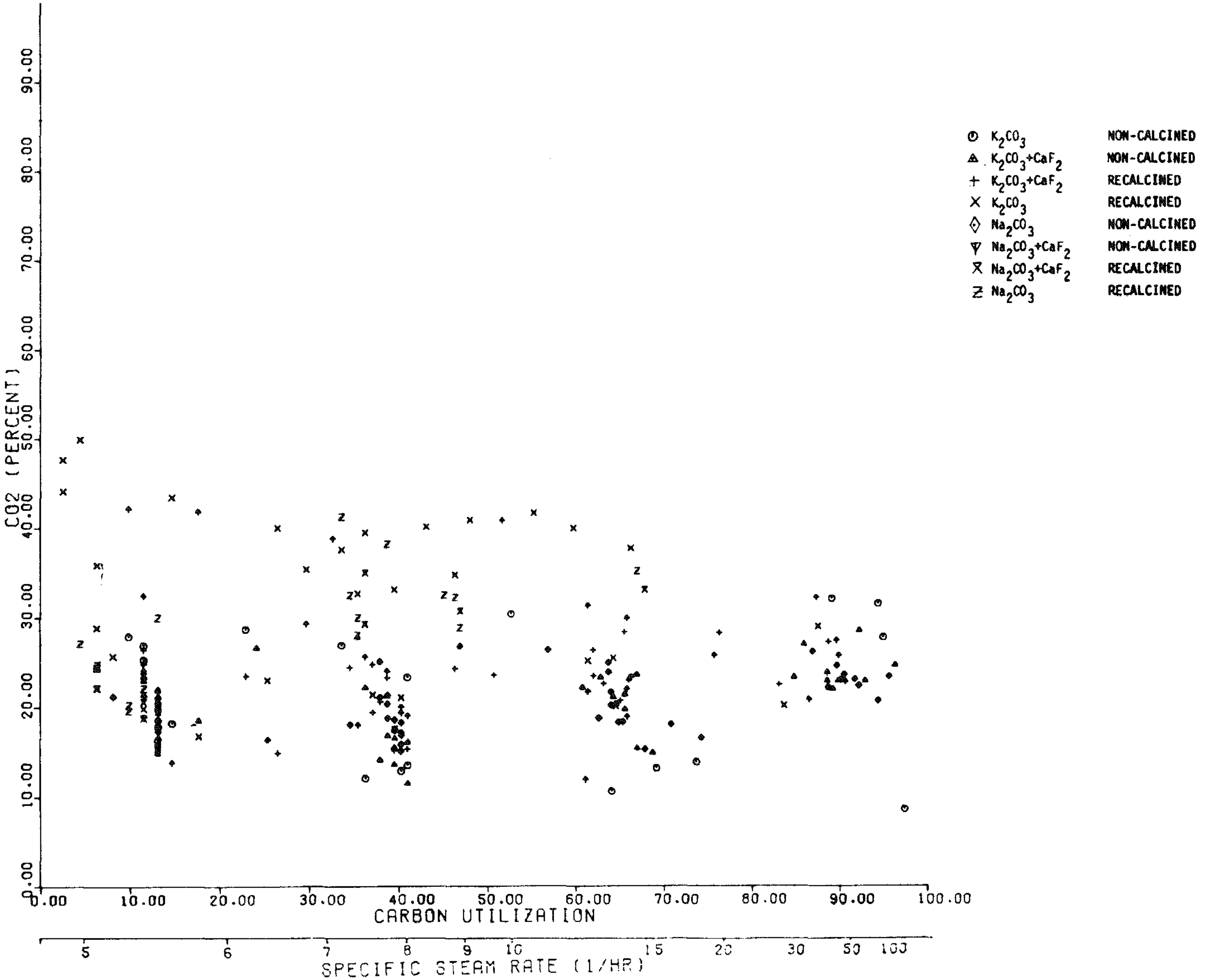


Figure 4-4. CO_2 Concentration as a Function of Carbon Utilization and Specific Steam Rate

carbon utilization changes from 5% to 95%. This change in the carbon utilization corresponds to change in the specific steam rate of 5 to 100 (hr^{-1}). Figure 4-2 shows that the mean methane concentration varies from 3.5% to 2% for the same range of carbon utilization.

Figures 4-3 and 4-4 show the carbon monoxide and carbon dioxide concentrations which unlike the H_2 and CH_4 composition curves show very large scatter in the observed values. Much of the variation as previously mentioned is due to the series using K_2CO_3 with recalcining. Neglecting this series reduces the scatter and mean values for CO show a decrease from 25% to 10% as the carbon utilization increases from 5% to 95%. At the same time the CO_2 concentration, shown in Figure 4-4, increases from 20% to 25%. This observed behavior is consistent with the increasing unreacted steam in the reactor effluent which occurs with increasing specific steam rate. In other words with an increasing excess of steam available for the water gas shift reaction more CO is shifted to CO_2 thus lowering the CO content in the product gas while increasing the H_2 and CO_2 concentrations. It is also observed that the acceptor material does not appear to remove very much CO_2 in the recalcining experiments. Calculations based on the CO and CO_2 contents in the effluent gas indicate about 5%-10% removal. This is discussed further in later sections.

It is interesting to compare the gas composition measured in these experiments with those reported for several uncatalyzed commercial scale reactors. Figures 4-5, 4-6 and 4-7 show the calculated equilibrium constant and measured values for the reactions:

$$CO + H_2O \text{ ——— } CO_2 + H_2 \qquad K_1 = \frac{[CO_2]\,[H_2]}{[H_2O]\,[CO]}$$

$$CO_2 + C \text{ ——— } 2CO \qquad K_2 = [CO]^2/[CO_2]$$

$$2H_2 + C \text{ ——— } CH_4 \qquad K_3 = [CH_4]/[H_2]^2$$

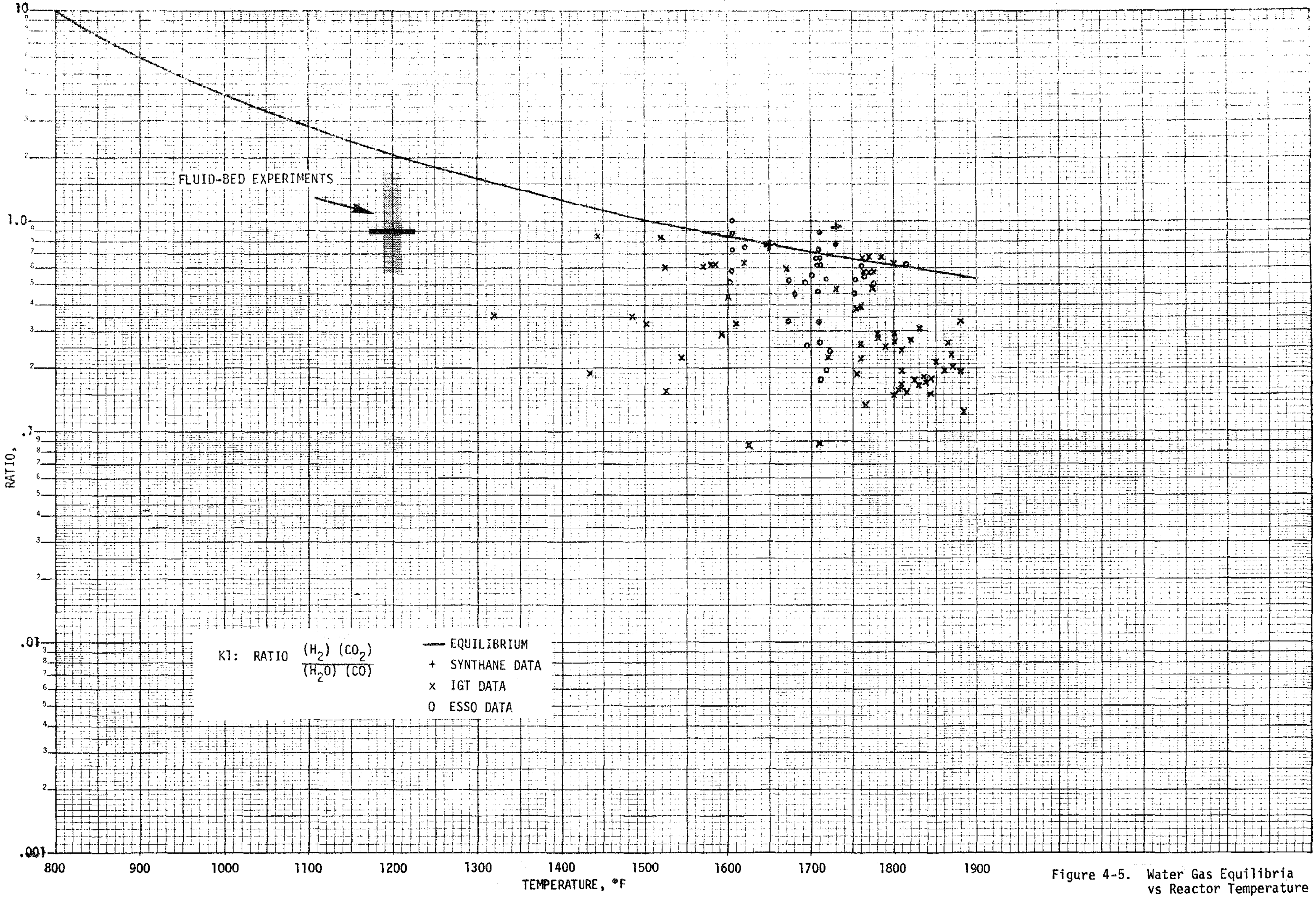


Figure 4-5. Water Gas Equilibria vs Reactor Temperature

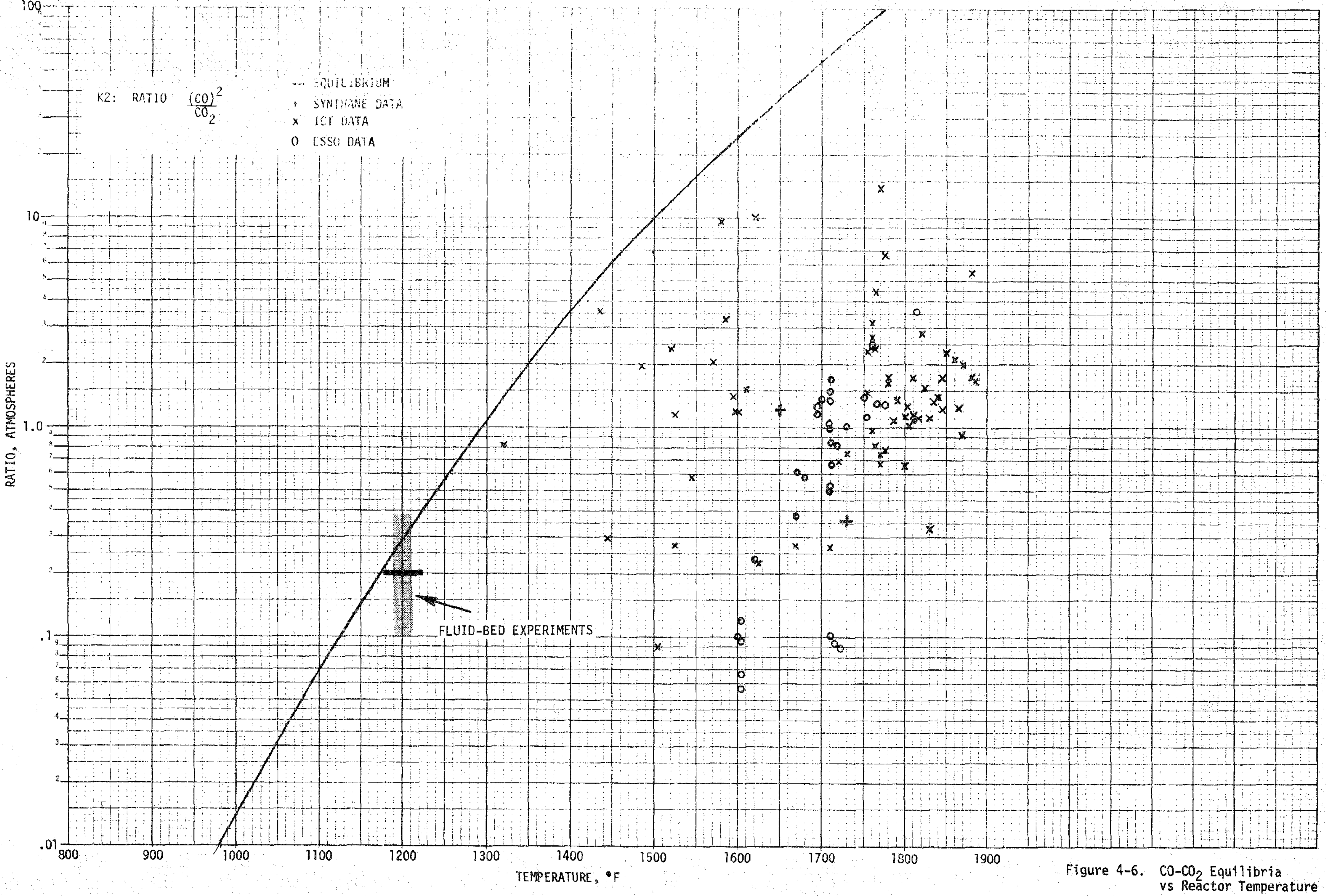


Figure 4-6. CO-CO_2 Equilibria vs Reactor Temperature

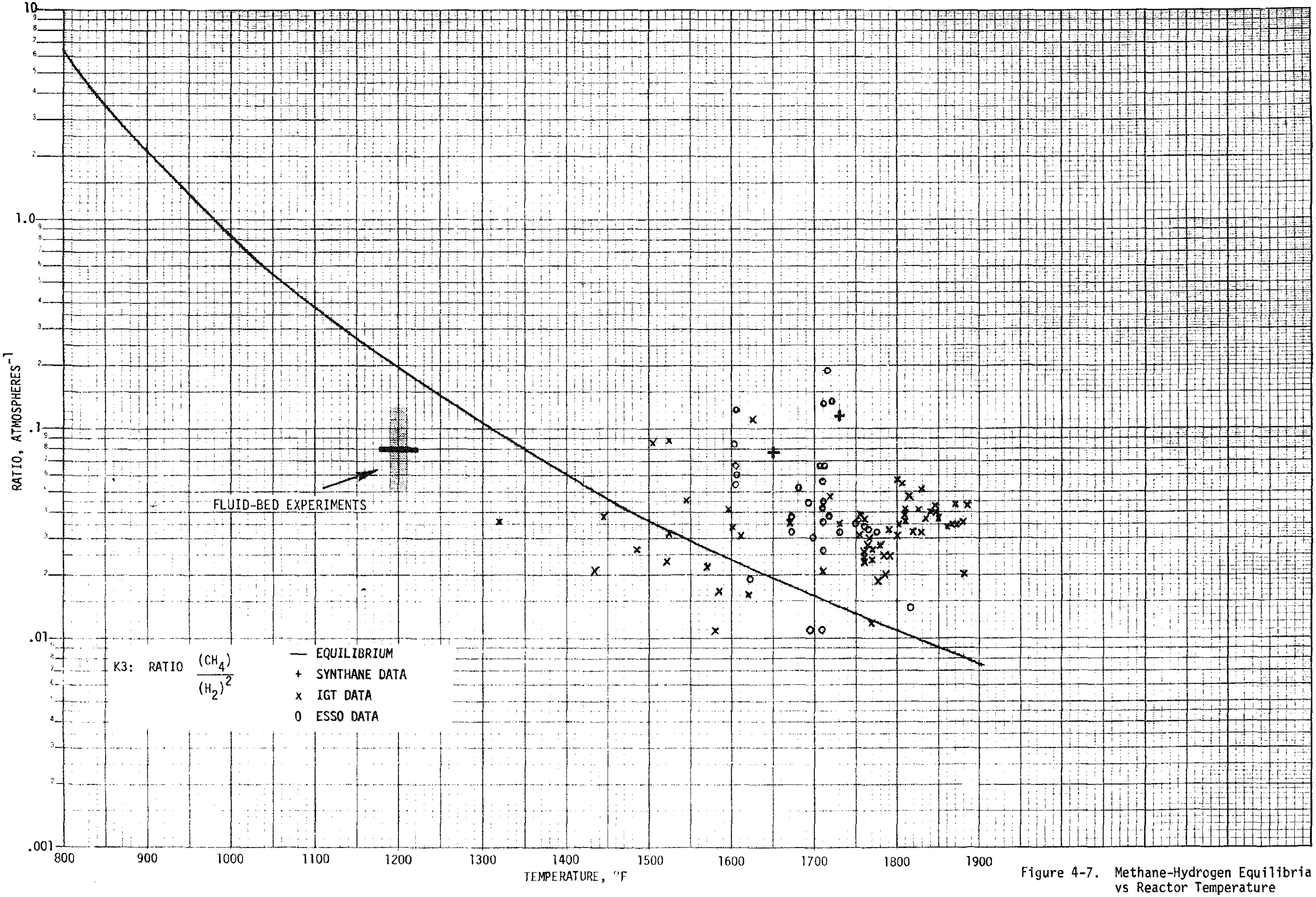


Figure 4-7. Methane-Hydrogen Equilibria vs Reactor Temperature

These data were compiled by Crawford et al[3] are taken from 63 IGT tests on Illinois No. 6 char and 32 ESSO tests on Disco (Pittsburgh) char. The range of ratios found in this investigation are also shown in the figures. The mean value for K_1 computed from these experiments was one-half of the equilibrium value and is very close to that reported in the other work. The range of K_1 from these experiments is rather large since no attempt was made to smooth the data screen. This result suggests that it may be beneficial to incorporate a shift catalyst in order to improve the hydrogen yield observed in this work.

The mean value of K_2 is about equal to equilibrium value, although at high specific steam rate it decreases to 20% of equilibrium. This is much higher than the IGT and ESSO data. This implies that the catalysts accelerate the carbon-dioxide-carbon reaction. This is consistent with acceleration of steam-carbon reaction. One expects both reactions to be accelerated since a similar kinetic mechanism is probably involved.

The observed value for the ratio of CH_4/H_2^2 approaches the equilibrium value initially but decreases as the gasification reaction progresses. This is in contrast to IGT and ESSO data which generally tend to get greater than equilibrium methane concentrations. One possibility here is that for the IGT and ESSO data, methane is formed by hydrogen position shift during the carbon ring fracture rather than the reaction of gaseous H_2 with graphite carbon. In the absence of a catalyst the methane could then persist in above equilibrium concentrations. Alkali catalysts are known to be good reforming catalysts, thus greater than equilibrium concentrations of methane are not to be observed in these catalytic gasification experiments.

Gasification Rate and Steam Utilization

The calculated specific gasification rates and the percent steam utilization for the K_2CO_3 + CaF_2 catalyst with recalcining are shown in Figures 4-8 and 4-9 as a function of carbon utilization. The gasification rate for all experiments is seen to rise during the transient heat-up of the reactor for both the catalyzed and uncatalyzed char. At about 10%-20% carbon utilization, the uncatalyzed rate becomes stable and then decreases

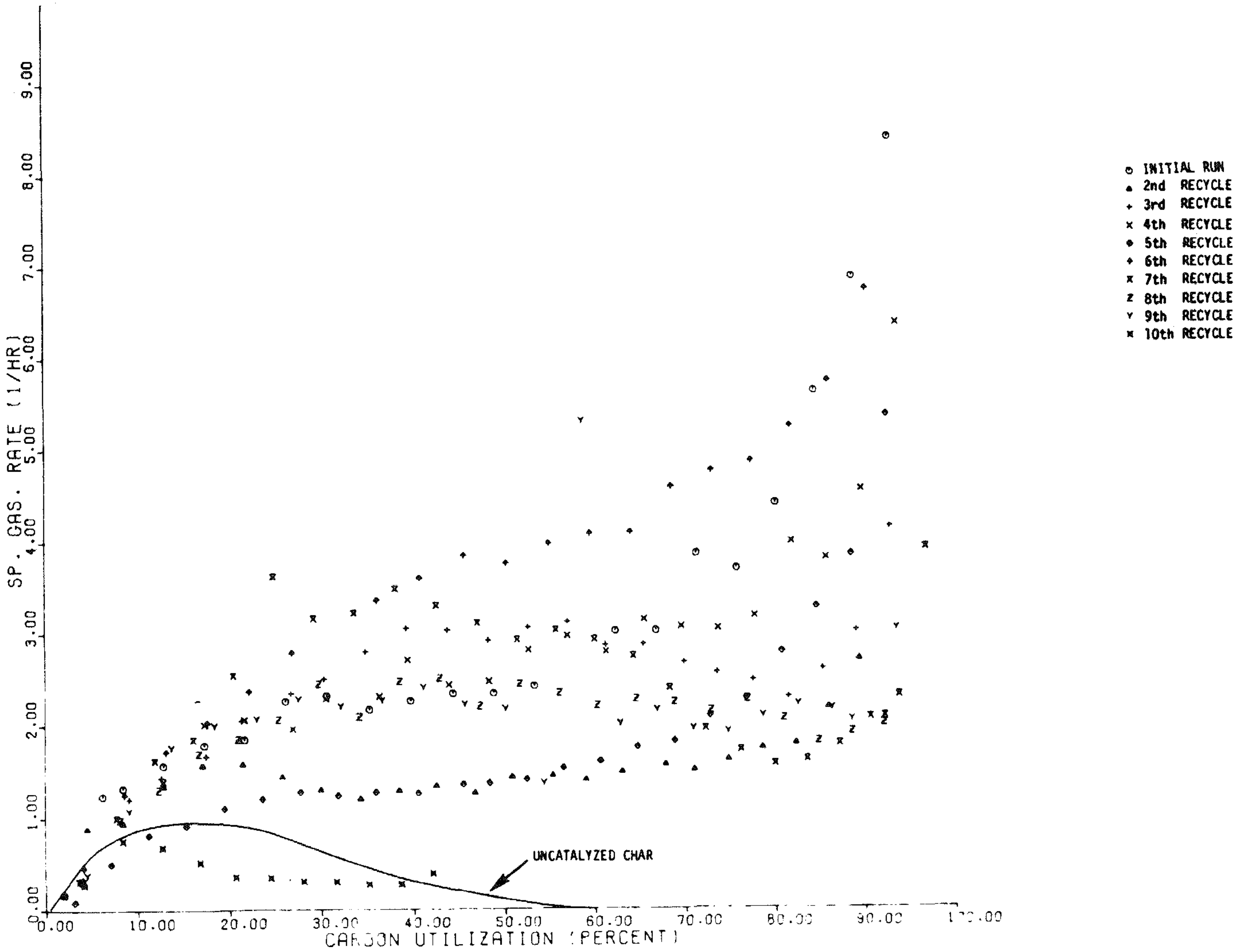


Figure 4-8. Specific Gasification Rate as a Function of Carbon Utilization K_2CO_3 + CaF_2 Non-Recalcining

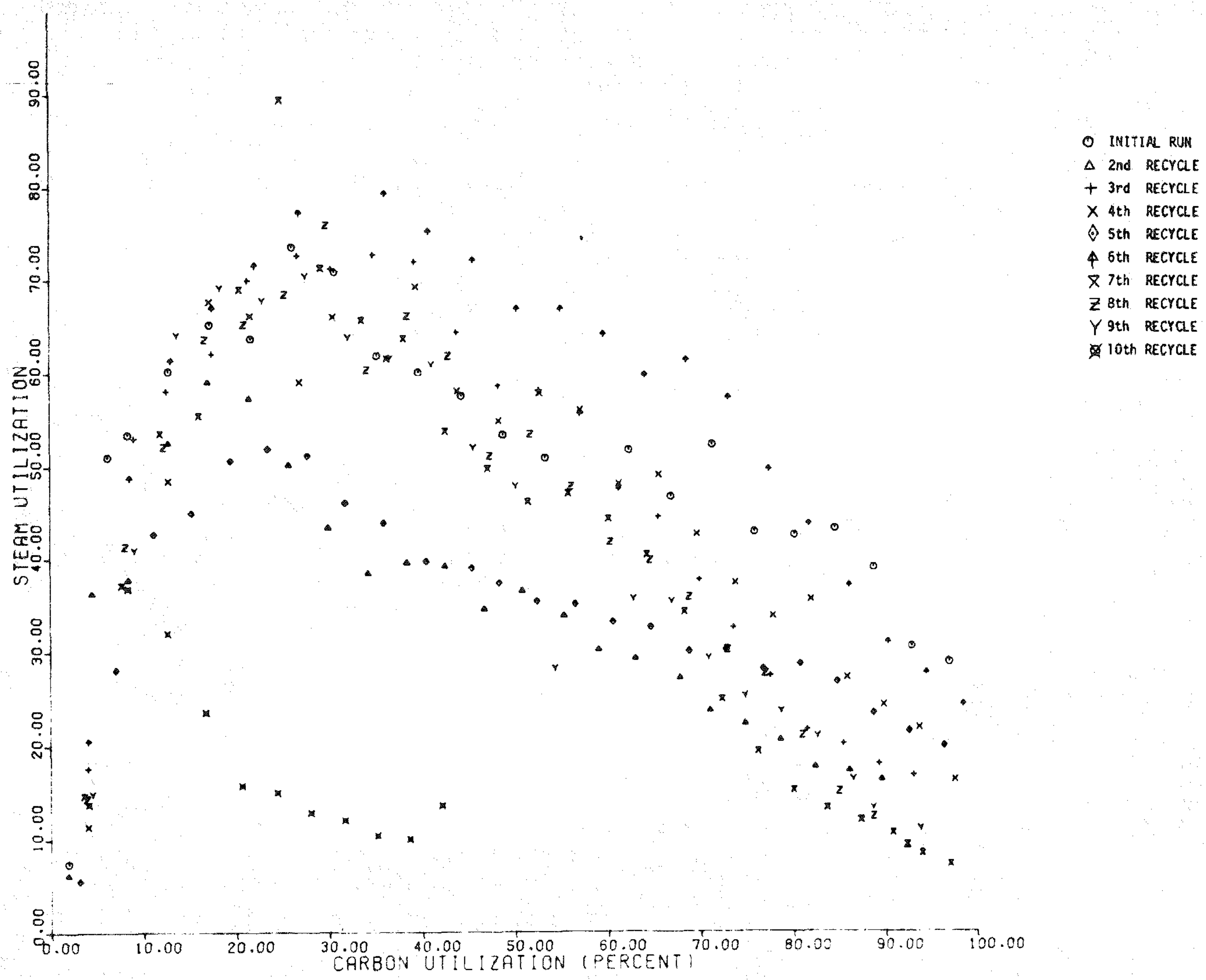


Figure 4-9. Steam Utilization as a Function of Carbon Utilization. $K_2CO_3 + CaF_2$ Non-Recalcining

to zero around 60% carbon gasification. The catalyzed rate however, never goes to zero and is always greater than the uncatalyzed rate. Despite considerable variation in the catalyzed rate, it is seen that the trend is toward stable or increasing gasification with increasing carbon utilization. (This variation in the gasification rate may result from bubbling or slugging in the fluid bed.) A conclusion to be drawn from a comparison of the catalyzed and uncatalyzed rates is that for the char and temperature selected, gasification beyond 60% of the original carbon present is not possible without a catalyst. Chars of different reactivity may show different maximum uncatalyzed utilizations.

A typical steam utilization vs carbon utilization curve is plotted in Figure 4-9 for a K_2CO_3 catalyzed reaction. For all experiments steam utilization is seen to increase early in the reaction and then decrease during the later stages of gasification. This result is expected from considerations of the specific gasification rate.

The gasification rate is constant or slightly increasing (in the catalyzed case), but the amount of char present in the bed decreases in relation to the fraction char remaining. Since the amount of steam fed to the system is constant, the amount reacted or the utilization should decrease as observed. Of course when the gasification rate goes to zero, as in the uncatalyzed case, the steam utilization also goes to zero.

Acceptor Characterization

As mentioned previously it was observed that the recalcined acceptor used in these experiments did not show the CO_2 absorption which was expected on the basis of a simple gas-solid equilibrium reaction. Reagent grade CaO was used, as the acceptor. This result is contrary to very early experiments in this program when Hollister dolomite was used as an acceptor in conjunction with Synthane char. In the experiments with the natural acceptor material, it was found that the dolomite removed about 30% of stoichiometric amount of CO_2 based on complete conversion of $CaO \longrightarrow CaCO_3$.

To determine the source of this discrepancy a series of experiments were run in which the fluid bed was charged with only acceptor or acceptor and catalyst. The bed was then heated and fluidized with a 30% CO_2-70% Ar mixture. The composition of the exhaust stream was measured and after the experiment the acceptor was weighed to determine its weight gain. The results of these experiments are shown in Table 4-4.

It is seen that the Hollister dolomite retains about the same amount of carbon dioxide as previously observed, while the CaO appears to be ineffective as an acceptor. It was further observed from the gas composition that the absorption occurred early in the experiment during the transient warm-up period. This period as a typical gasification experiment corresponds approximately to the time required for achieving 20% char gasification. Thus, absorption is not rate limiting in these experiments It is clear from these experiments that acceptor selection for use in a catalyzed acceptor gasification process is going to be important. Additional work is needed in determining what the range of absorption properties are for several natural acceptor materials, educating what factors are responsible for the limitations in carbon dioxide absorption for these materials, and identifying suitable materials for use in the gasification reaction.

Table 4-4. Effect of Acceptor Material on 650°C Carbon Dioxide Absorption

Material	% Stoichiometric CO_2 Absorption
Hollister dolomite	35
Hollister dolomite + K_2CO_3	35
CaO	0
CaO + K_2CO_3	0

4.2.1.3 Elevated Pressure Fluid Bed Experiments

The furnace and other major pieces of equipment for the reactor have been received and assembly of the apparatus has been initiated.

4.2.2 Work Forecast

During the next reporting period the following activities are planned under the Fluid-Bed Reactor Studies task:

- Complete fabrication of the pressured fluid-bed reactor
- Complete recycle tests with Na_2CO_3 and $Na_2B_4O_7$ catalyst in the atmospheric pressure fluid-bed reactor
- Initiate catalyst performance tests using either K_2CO_3 or Na_2CO_3 catalyst using the elevated pressure fluid-bed reactor
- Complete analysis of experimental data generated from atmospheric pressure fluid-bed reactor experiments.

4.3 TASK III - CATALYST-ACCEPTOR PHYSICAL-CHEMICAL PROPERTIES

The objective of this task is to determine how catalysts function during gasification and acceptor regeneration, and to identify the mechanisms associated with their deactivation and stabilization. A second objective of the task is to assess the coal-char-sulfur retention characteristics of an acceptor-catalyst system during char gasification and acceptor regeneration. Information gained in this task will hopefully be useful in improving catalyst effectiveness during gasification and performance with recycle.

4.3.1 Work Accomplishments

Significant experimental accomplishments made under this task during the reporting period have included: 1) determination of the char-sulfur retention properties of acceptor-catalyst systems, 2) completion of optical, scanning electron microscope, and X-ray diffraction analysis of deactivated catalyst systems in reaction ash residues, 3) determination of the relative carbon dioxide absorption properties of chemically pure lime and a recalcined natural dolomite, and 4) an assessment of the loss of alkali catalyst from recycled reaction residues. Presented below in the remainder of this section are more detailed descriptions of the experimental work, as well as the observations and results obtained. Also included is a description of the work planned to complete this task during the next reporting period.

4.3.1.1 Char-Sulfur Retention Studies

An important set of catalyst-acceptor system properties that was demonstrated during the quarter was 1) the ability of various acceptor-catalyst systems to retain a significant fraction of the char-sulfur during the combined steps of char gasification and acceptor regeneration, and 2) the ability of acceptor-catalyst systems to remain active as sulfur absorbents with recycle. The sulfur retention properties of the catalyst-acceptor systems were determined by analyzing aliquot samples of reaction residues from catalyst system recycle experiments for their sulfur contents. Residue samples from recycle experiments carried out using both the fixed-bed reactor and the atmospheric pressure fluid-bed reactor were analyzed for their sulfur contents. Knowing the number of reaction cycles, the amount of char used in each cycle, and the sulfur content of the char, the total weight of sulfur charged to the reactor could be determined. The fraction sulfur retained by a catalyst-acceptor system was then determined as the ratio of the product of the sulfur content of the solid residue multiplied by the weight of reaction residue to the total weight of sulfur charged to the reactor. The sulfur content of the reaction residues was determined by an ASTM procedure.[4] A reaction temperature of 650°C was used for the steam gasification reaction. Other experimental conditions used in the sulfur retention studies as well as the results obtained are summarized in Table 4-5.

As can be seen from the results presented, sulfur retention by the acceptor-catalyst systems is generally more than 50% for gasification reactions carried out using the fluid-bed reactor. Considerably lower sulfur retentions are observed with the fixed-bed reactor. The difference in retention figures with the two reactors is probably due to much poorer contacting or mixing of sulfur gases evolved during gasification with lime absorbent in the fixed-bed reactor. While high percentage of sulfur retention is attained with the fluid-bed reactor, the actual percentage utilization of lime or acceptor for sulfur retention is rather low suggesting that a greater degree of utilization may be attainable if catalysts remained effective in promoting the char-lime-steam reaction longer. For the fluid-bed results, there is no readily discernable trends of sulfur retention with catalyst system or acceptor regeneration treatment although too few results are available at this time to firmly draw this conclusion. For the fixed-bed reactor K_2CO_3 based catalyst systems appear to show slightly higher sulfur retention, especially in the case where 950°C acceptor regeneration treatment was included as part of the reaction cycle. The high sulfur retention demonstrated in these fluid-bed experiments are encouraging and suggest that perhaps higher sulfur retention may be expected from batch fluid-bed reactions carried out at elevated pressures.

Table 4-5. Char Sulfur Retention Results for Catalyst-Acceptor Systems

Reaction System			Reactor	950°C Acceptor Regeneration	Number of Reaction Cycles	% Sulfur[a] Retention	% Acceptor[a] Utilization
Char	Acceptor	Catalyst					
25% COED	65% CaO	10% Na_2CO_3	Fluid Bed	No	12	56	13
24% COED	62% CaO	10% Na_2CO_3-4% CaF_2	Fluid Bed	No	11	68	14
25% COED	65% CaO	10% K_2CO_3	Fluid Bed	Yes	9	60	10
24% COED	62% CaO	10% K_2CO_3-4% CaF_2	Fluid Bed	No	10	36	7
24% COED	62% CaO	10% K_2CO_3-4% CaF_2	Fluid Bed	Yes	9	50	9
19% COED	76% CaO	5% K_2CO_3	Fixed Bed	No	11	4	0.5
19% COED	76% CaO	5% K_2CO_3	Fixed Bed	Yes	4	34	1.6
18% COED	72% CaO	5% K_2CO_3-5% CaF_2	Fixed Bed	No	12	2	0.4
18% COED	72% CaO	5% K_2CO_3-5% CaF_2	Fixed Bed	Yes	4	35	1.6
19% COED	76% CaO	5% Na_2CO_3	Fixed Bed	No	18	2	0.4
19% COED	76% CaO	5% Na_2CO_3	Fixed Bed	Yes	8	6	0.6
18% COED	72% CaO	5% Na_2CO_3-5% CaF_2	Fixed Bed	No	14	2	0.5

[a] Computed as ratio of weight sulfur in reaction residue after nth reaction cycle to weight sulfur fed from char times 100.

[b] Computed as ratio the moles sulfur retained after nth reaction cycle to moles lime charged times 100.

4.3.1.2 Acceptor Carbon Dioxide Absorption Studies

As mentioned in Section 4.2.1.2, a problem with carbon dioxide absorption was noted in the fluid-bed reactor tests. Little or no carbon dioxide absorption occurred with calcium oxide acceptor during gasification while in an experiment completed last quarter in which calcined Hollister dolomite was used as an acceptor, significantly more carbon dioxide was absorbed, thus leading to a product gas with a higher hydrogen composition. It was desired to confirm whether a real difference in CO_2 absorption capacity and/or rate existed between the two acceptor materials. To determine whether this difference in acceptor properties existed, the reactions between carbon dioxide and the two acceptor materials were conducted separately in a special reactor in the absence of a char gasification reaction. In these experiments a sample of the acceptor was placed in a constant volume reactor heated to 650°C and evacuated. Precise volumes of carbon dioxide gas was admitted to the reactor in a series of repetitive additions and the pressure of the heated reactor system allowed to equilibrate before addition of another volume of carbon dioxide. The pressure of the reactor system was recorded as a function of time during its decay to an equilibrium or resting value. In this manner the comparative kinetics of the absorption reaction for the two acceptor materials could be ascertained as well as the total quantity gas absorbed by a known weight of an acceptor before a certain standing pressure in the reactor was developed. The constant volume reactor system used in these experiments is shown schematically in Figure 4-10.

The first series of pressure decay or absorption measurements was made using chemically pure lime (powder) in which each addition volume of carbon dioxide represented approximately one percent of the stoichometric amount of carbon dioxide that could theoretically combine with the lime. The observed pressure decay-time curves are shown in Figure 4-11. for the first, fourth and sixth (1%, 4%, and 6% respectively) additions of carbon dioxide. The decay curves are exponential in all cases and show that the attainment of an equilibrium pressure is more rapidly attained

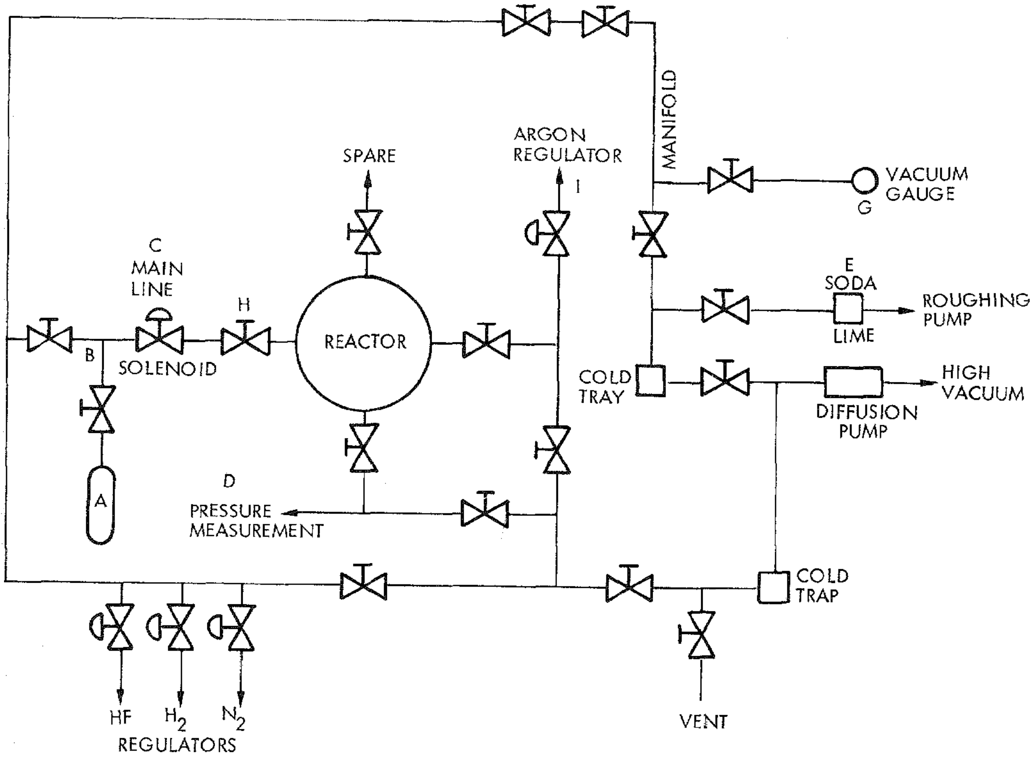


Figure 4-10. Schematic Diagram of Constant Volume Reactor System Used in Acceptor Absorption Tests

with early additions of carbon dioxide. The pressure decay curves also show an apparent increase in the equilibrium carbon dioxide pressure over the partially reacted acceptor with each addition of carbon dioxide. After the third addition, the observed equilibrium pressure was 10 torr. After this addition the reactor was evacuated and the formed solid allowed to re-establish an equilibrium pressure. A pressure of 6 torr was established which is in good agreement with the 6.90 torr equilibrium vapor pressure reported for calcium carbonate at this temperature.[5] Failure to return to the apparent equilibrium pressure of 10 torr after evacuation suggests the possibility of an inert gas contamination of the reactant CO_2. Mass spectrometric analyses of the reactant gas indicated trace oxygen levels and a

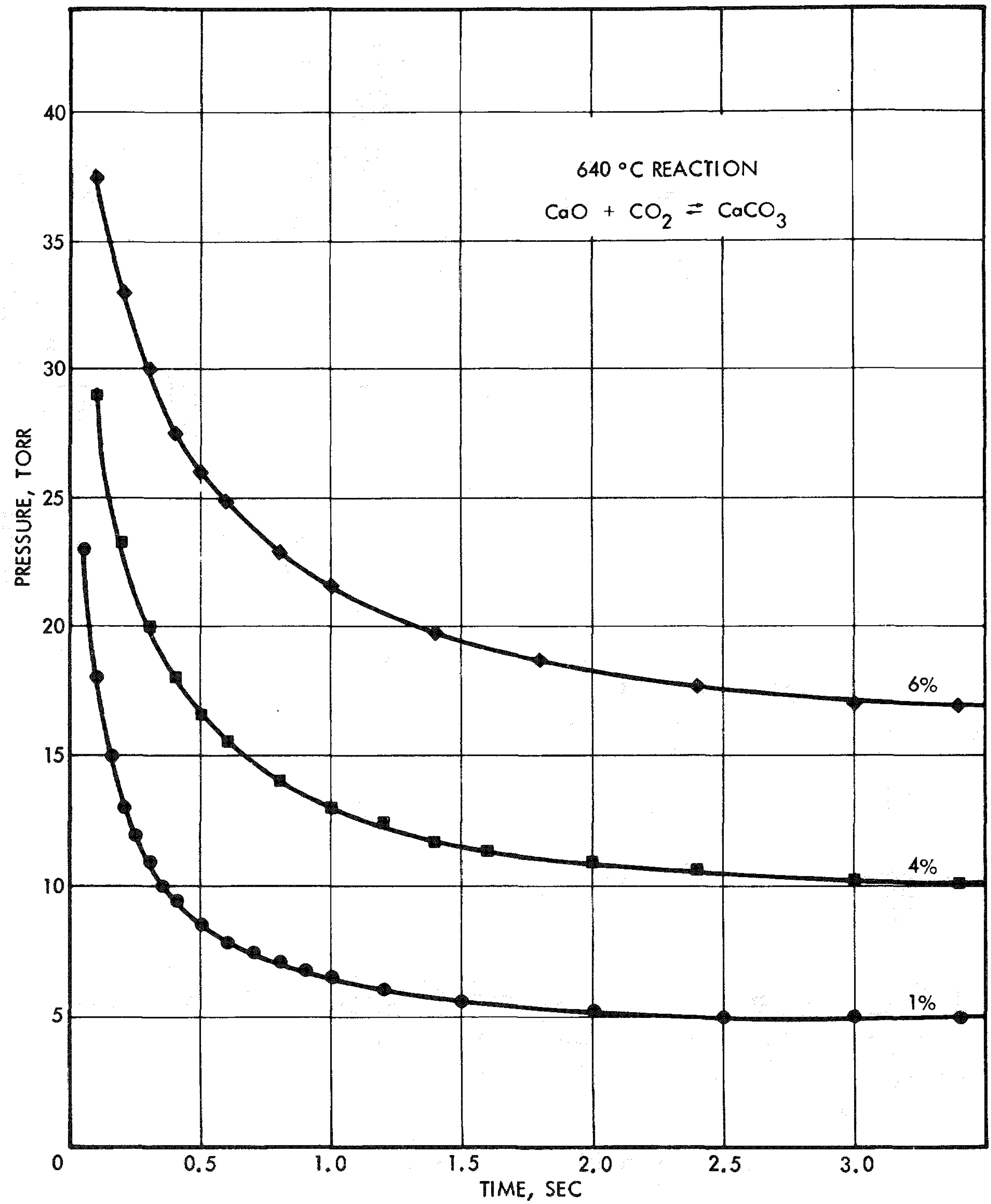


Figure 4-11. Pressure Versus Time Curves for Carbon Dioxide Absorption Reaction with Lime.

nitrogen content of 0.5% or less. No additional impurities were found and reactant gas impurities can not explain the constant change in apparent equilibrium pressure or the failure to reestablish this apparent equilibrium pressure after reactor evacuation. After a total of eight 1% pulses, carbon dioxide was slowly admitted to the reactor from the manifold. Sufficient CO_2 was added (from pulse and slow addition) to form approximately 15% of the theoretical amount of calcium carbonate possible on the basis of the initial amount of lime charged to the reactor. The standing pressure in the reactor at this reaction extent was 35 torr.

The same experimental procedure was employed with a sample of calcined Hollister dolomite. The sample used contained an equivalent amount of CaO by weight as that employed in the first experiment. The pressure decay results are presented in Figure 4-12. for the 1%, 4% and 6% pulses. Again, as for CaO, the pressure decay appears to be exponential and the equilibrium pressure increases with each pulse. The reactor was evacuated after the third pulse and the pressure reestablished itself at 11 torr at 660°C. By slowly adding the CO_2 from the manifold after the seventh pulse, sufficient CO_2 could be admitted to form 30% $CaCO_3$ before a standing pressure of 40 torr in the reactor was reached. Thus, when compared to the CaO sample, the natural dolomite acceptor material has nearly twice absorption capacity of chemically pure lime. These findings agree with the results obtained in the fluid-bed gasification experiments which indicated that the dolomite is a much better acceptor than pure calcium oxide. These results demonstrate that appreciable differences in acceptor absorption properties do exist and that a screening of several acceptor materials is probably needed to identify an optimum acceptor for the gasification reaction. Because of the limited amount of experimentation conducted in this study, no explanation of the apparent changes in equilibrium pressure with percent carbonate formed is offered. Additional experiments would be needed to assess this phenomena.

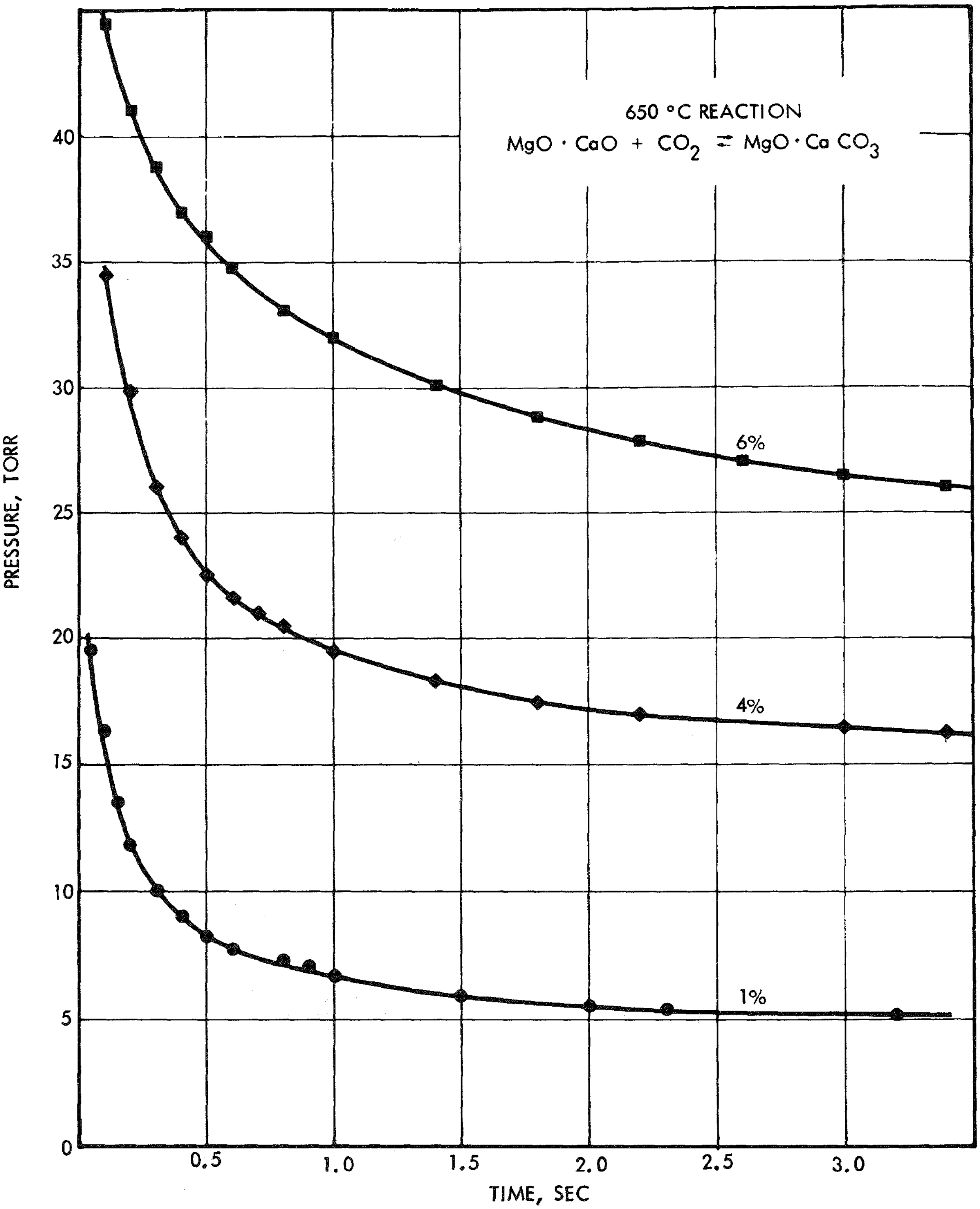


Figure 4-12. Pressure Versus Time Curves for Carbon Dioxide Absorption Reaction with Calcined Hollister Dolomite.

4.3.1.3 Optical and SEM Examination of Reaction Ash Residues

Three samples of reaction residue materials were microscopically examined to determine what visual and morphological changes occur in catalyst-acceptor-char ash systems with recycle. The three samples selected for examination were residue specimens from gasification reactions carried out in the fixed-bed reactor using test mixtures originally consisting of 72 wt.% lime, 18% FMC COED char, 5% flurospar and 5% sodium carbonate catalyst. A reaction cycle consisted of a one-hour exposure to steam (flow rate 0.33 mole min^{-1}) at 650°C followed by a one-half hour exposure to air at 500°C to burn off unreacted carbon in the sample. One sample, hereafter designated as A, received one steam exposure, while a second sample (B) received four complete steam reaction/char burn off treatments, and the third sample (C) was put through eighteen complete reaction cycles. Samples A and B contained active catalyst as demonstrated in subsequent reaction cycles while sample C was not active in promoting char gasification. Small samples of these residues were mounted on gold sample stages and examined at 100X using an optical microscope. The same samples were SEM imaged using a JEOL model JSM-U3 instrument. Additionally, sample C was partially examined using a Princeton Gamma model SEM equipped with an energy dispersive X-ray analysis (EDAX) attachment. Key observations made in the examination of the reaction ash residues are summarized below.

- Color of reaction ash changed from gray-white to light tan, to darker shade of brown with increasing degree of recycle.
- Particles in samples irregular in shape and appear as aggregate clusters. Sample C also contained some smoother surface single particles.
- Size of aggregate particle clusters were relatively uniform within each sample, but appeared to vary with degree of recycle. Largest particle clusters observed for sample C.
- Elements detected on surface of particle clusters in sample C included: calcium, iron and silicon. Elements detected on surface of larger smoother, single particles included: iron, potassium and silicon.

SEM photographs of reaction residues for samples A and C are presented in Figure 4-13. On the basis of the observations it appeared that some ash fusion may be occurring with recycle and could be responsible for the formation and growth of aggregate clusters.

Sample A

Sample C

Figure 4-13. SEM Photomicrographs of Fixed-Bed Reaction Ash Residues (Magnification: 1000X)

4.3.1.4 X-Ray Diffraction Analysis of Deactivated Catalyst Systems

Two samples of recycled catalyst systems which contained char ash residues from gasification reactions were analyzed by X-Ray diffraction. The objective of the analyses effort was to determine in what chemical forms deactivated catalyst systems existed and what compounds the acceptor had formed with sulfur and other char ash constituents. The two samples selected for analysis were reaction residues from fluid-bed reactor experiments in which the catalyst-acceptor systems had been recycled a number of times until they were ineffective in promoting the 650°C COED char-lime-steam gasification reaction. Sample A was a reaction residue sample from the fluid-bed tests involving the sodium carbonate-calcium fluoride catalyzed reaction while Sample B was a residue sample from a potassium carbonate catalyzed reaction. The initial composition of the recycled reaction mixtures were: Sample A - 10% Na_2CO_3, 5% CaF_2, 62% CaO and 24% COED char; Sample B - 10% K_2CO_3, 65% CaO, and 25% COED char. In addition to being reacted with steam and recycled, the reaction residue from Sample B was also treated to a 12-hour, 950°C acceptor regeneration step after each steam reaction cycle. All diffraction measurements were made using a GE-XRD-5 X-ray diffractometer with pulse height discrimination recording and Ni filtered Cu K_α radiation. A 100 milligram sample of the reaction residue was ground, ultrasonically dispersed in a Collodian-alcohol mixture and spread uniformly on a glass support. A 5 cm length of sample was illuminated by means of a 3° divergent slit. The X-ray diffraction spectrum of the sample was recorded for a 2θ angle from 5-50°. A number of specific compounds were looked for. Identification was made on the basis of agreement within $\pm$ 0.02° of the reported compound spacings. Because of overlap of spacings for several of the compounds, unambiguous identification of all the compounds was not possible.

Summarized in Table 4-6 is a list of the compounds looked for and detected in the samples. As the results in the table indicate a large number of specific compounds were looked for though only relatively few compounds were found. It should be noted that only crystalline compounds present in the samples at concentrations generally greater than 1-3 weight percent can be detected. It is possible that some of the compounds looked for could be in an amorphous phase in which case they would not be observed.

Table 4-6. Summary of X-Ray Diffraction Analyses of Char and Reaction Residues

Compound	Sample			Remarks
	COED Char	Residue A	Residue B	
K_2CO_3	ND[a]	ND	ND	
$KHCO_3$	ND	ND	ND	
KOH	ND	ND	Possible	
KO_2	ND	ND	ND	
K_2S	ND	ND	ND	
KHS	ND	ND	ND	
$K_2S_2O_3$	ND	ND	ND	
$KHSO_3$	ND	ND	Possible	
K_2SO_4	ND	ND	Possible	
$KHSO_4$	ND	ND	ND	
$KSiO_3$	ND	ND	ND	
$K_xSi_4O_2$	ND	ND	ND	
$KAlO_2$	ND	ND	ND	
$K_xAl_ySi_2O_4$	ND	ND	ND	
$K_2Fe_2O_y$	ND	ND	ND	
$KCa(CO_3)_2$	ND	ND	Possible	Most probable in B
Na_2CO_3	ND	Possible	ND	
$NaHCO_3$	ND	ND	ND	
NaOH	ND	Possible	ND	
NaO_2	ND	ND	ND	
Na_2O	ND	ND	ND	
Na_2O_2	ND	ND	ND	

* a - Not Detected

Table 4-6. (Continued)

Compound	Sample			Remarks
	COED Char	Residue A	Residue B	
Na_2S	ND[a]	ND	ND	
$Na_2S_2O_3$	ND	ND	ND	
$NaHSO_3$	ND	ND	ND	
Na_2SO_4	ND	ND	ND	
$NaHSO_4$	ND	ND	ND	
Na_2SiO_3	ND	ND	ND	
$Na_xSi_4O_2$	ND	ND	ND	
$NaAlO_2$	ND	ND	ND	
$Na_xAl_ySi_zO_t$	ND	Possible	ND	In form of $NaAlSiO_4$
$NaFeO_2$	ND	ND	ND	
$Na_2SiO_2F_2$	—	—	—	Probably non-crystalline
Na_2CaSiO_4	ND	ND	ND	
$Na_2Ca(CO_3)_2$	ND	Possible	ND	
$Na_3Ca(SiO_3)_3$	ND	Possible	ND	
SiO_2	ND	ND	ND	
FeC	Possible	Possible	Possible	Similar to graphite spectra
Fe_xC_y	ND	ND	ND	
FeO	ND	ND	ND	
Fe_2O_3	ND	ND	ND	
Fe_3O_4	ND	ND	Possible	
FeS	ND	ND	ND	
Fe_2S	ND	ND	ND	

* a - Not Detected

Table 4-6. (Continued)

Compound	Sample			Remarks
	COED Char	Residue A	Residue B	
Fe_2S_3	ND[a]	ND	ND	
$FeSO_3$	ND	ND	ND	
$Fe_2(SO_3)_3$	ND	ND	ND	
$FeSO_4$	ND	ND	ND	
$Fe_2(SO_4)_3$	ND	ND	ND	
$FeSiO_3$	ND	ND	ND	
$Fe_2(SiO_3)_3$	ND	ND	ND	
$Fe_xSi_yO_z$	ND	ND	ND	
$Fe_xAl_yO_z$	ND	ND	ND	
$Fe_xAl_ySi_zO_t$	ND	ND	ND	
FeF_2	ND	Possible	ND	
C	Possible	Possible	Possible	Graphite
$Fe(HCO_3)_2$	ND	ND	Possible	
$Ca_3Fe_2Si_3O_{12}$	Possible	Possible	Possible	
$CaCO_3$	ND	ND	ND	
$Ca(OH)_2$	ND	ND	ND	
CaO_2	ND	Yes	Yes	CaO content greater in B than in A
CaS	ND	Yes	Yes	CaS content greater in A than in B
$CaSO_3$	ND	ND	Possible	
$CaSO_4$	ND	ND	Possible	
$CaSiO_3$	ND	ND	Possible	

* a - Not Detected

Table 4-6. (Continued)

Compound	Sample			Remarks
	COED Char	Residue A	Residue B	
$Ca_xSi_yO_z$	ND[a]	Possible	ND	In form of $Ca_3Si_2O_7$
$Ca(AlO_2)_2$	ND	ND	ND	
$Ca_xAl_ySi_zO_t$	ND	ND	ND	
$CaFe_2O_y$	ND	ND	Possible	
CaF_2	ND	ND	ND	
CaC_2	ND	ND	ND	
$Ca_xAl_yS_xO_t$	ND	ND	ND	
$Ca_{10}Si_{30}O_{15}F_2$	ND	ND	ND	
$Ca_5(SiO_4)_2CO_3$	ND	Possible	Possible	
CaO_2	ND	Possible	Possible	
$CaFeSiO_4$	ND	ND	Possible	

* a - Not Detected

The presence of compounds where unambiguous identification could not be made due to spectral overlap has been termed "possible" in the results presented in the table. As can be seen from the results, the presence of alkali carbonate catalyst could not be detected in the reaction residues except possibly in the case of sodium carbonate. Nor was it possible to positively identify any compound that the carbonate catalyst was converted to. Several forms of the deactivated catalyst however were identified as possible. These include silicates, aluminates, alumino-silicates, sulfates, sulfites, and some complex calcium-alkali carbonates. From the results it is apparent that sulfur is retained in the residues as calcium sulfide and possibly as the sulfate and sulfite in the case were reaction residues are subjected to the high temperature acceptor regeneration treatment. Char sulfur does not appear from the results to be retained as an alkali sulfide.

4.3.2 Work Forecast

It is expected that the Catalyst-Acceptor Physical-Chemical Properties task will be completed during the next reporting period. Work planned under this task includes: 1) completion of elemental chemical analysis of recycled reaction ash residues for determining alkali losses, 2) differential thermal analysis of reacted ash residues for determining phase transformation and ash reaction temperatures, and 3) sulfur retention determinations on residue samples from elevated pressure fluid-bed reactions.

4.4 TASK IV - CATALYZED STEAM-OXYGEN-CHAR REACTION STUDIES

The objective of this task is to assess the capability of stabilized alkali catalyst systems to promote the steam-char and char-oxygen-steam reactions. To be specifically accomplished under this task will be the determination of the temperature and contacting conditions under which the catalyst remains active and stable for the gasification of char with varying ash contents. A small fixed-bed reactor system similar to the ones used in Task I will be used for most of the studies. Some confirmatory tests of the catalyst performance characteristics for an optimized catalyst system will be performed using a small fluid-bed reactor.

4.4.1 Work Accomplishments

Principal accomplishments made under this task during the reporting period include completing experiments to measure the effect that catalyst concentration has on the rate and product composition of the char-steam reaction, and determining the recyclability performance of five catalyst systems for the char-steam reaction, using the fixed-bed reactor. Results obtained from this experiment are presented and discussed below.

4.4.1.1 Effect of Catalyst Concentration on Char-Steam Reaction Rate and Product Composition

Results obtained from experiments completed earlier in which the effect of sodium and potassium carbonate catalyst concentrations had on the char-steam reaction half-life appeared as if they may have been nonreproducible. Particularly the results obtained for potassium carbonate seemed uncertain, since the reaction half-life showed excessive scatter and did not appear to be a smooth continuous function of catalyst concentration. It was felt, therefore, that repeating the series of measurements would be worthwhile.

For these experiments various concentrations of Na_2CO_3 and K_2CO_3 were dry blended with FMC COED char then exposed to steam in the fixed-bed reactor. The reaction conditions involved a 650°C steam reaction temperature and a 0.33 mole min^{-1} steam flow rate. Catalyst concentrations studied ranged from 10-25 weight percent. Product gas evolution and composition were measured during the course of the reaction period. Reaction half-lives were determined from the product volume and composition data by noting the time required for one-half of the initial carbon charged to the reactor to be gasified.

Product gas composition observed for both the Na_2CO_3 and K_2CO_3 catalyzed char-steam reactions were similar and relatively constant over the entire reaction period. Product gas produced from the fixed-bed gasification reactions consisted of approximately 70% hydrogen, 25%-30% carbon dioxide and 1%-3% carbon monoxide. Only trace amounts of methane were observed in the product gases. Carbon mass balances for the reactions ranged from 102%-108%. These observations regarding product distribution and constancy with reaction extent agree with the results obtained from earlier experiments.

The effect of Na_2CO_3 and K_2CO_3 catalyst concentration on reaction half-life for the COED char-steam reaction can be seen from Figure 4-14. These curves are similar in shape to those obtained earlier though the half-lives measured for some concentrations differ substantially from those previously obtained. Some part of the observed differences in results may be due to the differing amounts of char or carbon used in the experiments and an improved experimental technique used in these latter experiments. As observed perviously the effect of catalyst concentration on reaction half-life are substantial increases in catalyst concentration from 10%-25% can lower reaction half-lives by approximately an order of magnitude. The highest rate of change of reaction rate with catalyst concentration is observed to occur for the lower concentration levels of catalyst. At higher catalyst concentrations around 20%-25%, a leveling effect in the rate of improvement reaction rate with catalyst concentration is observed to occur. This is in agreement with the results reported earlier and confirm the conclusion that little improvement in char-steam reaction rate is gained through utilization of higher catalyst concentrations than 20%-25%.

4.4.1.2 Catalyst Performance Tests for the Char-Steam Reaction

The objective of these experiments were to determine whether alkali catalyst systems were effective in promoting the char-steam reaction

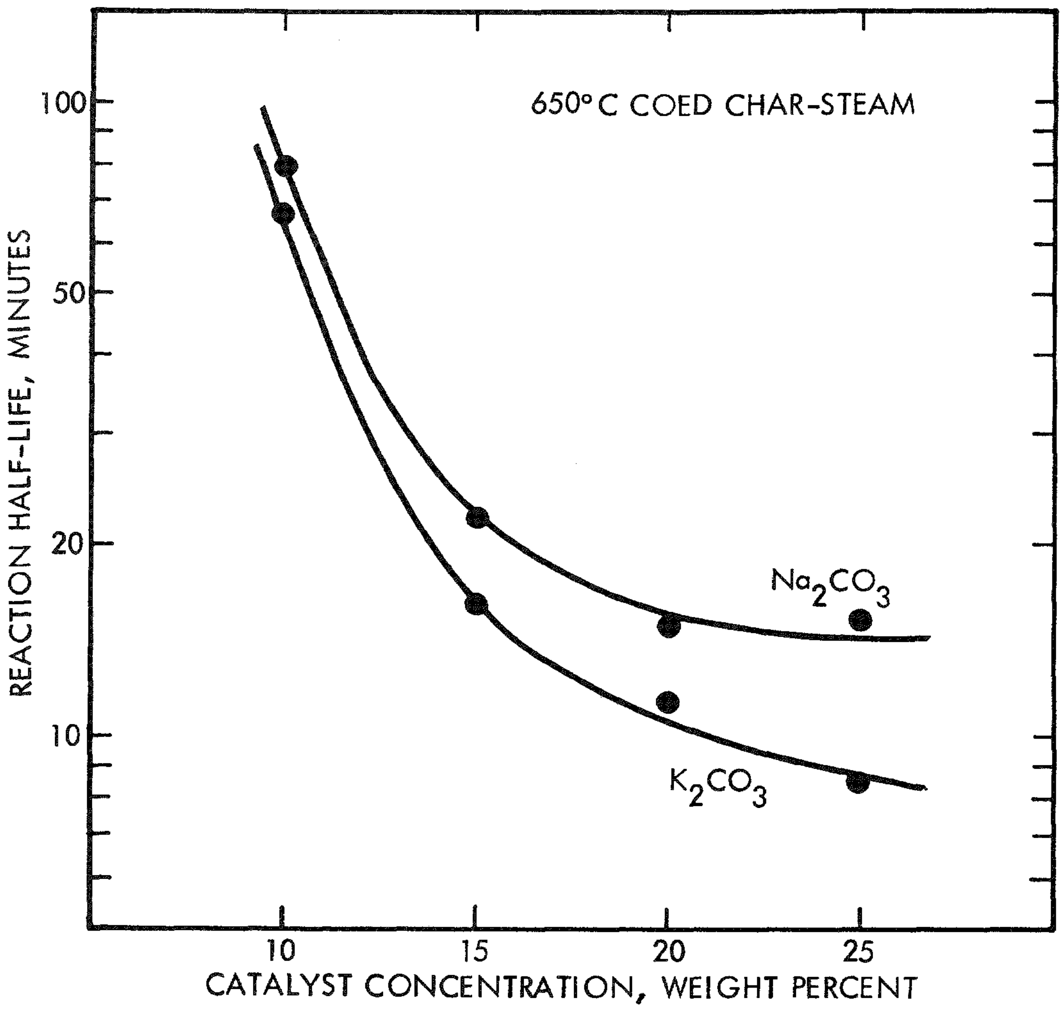


Figure 4-14. Effect of Catalyst Concentration on COED Char-Steam Reaction Half-Life

without the high concentrations of carbon dioxide acceptor that are used for the char-lime-steam reaction, and to determine whether reduction in acceptor concentration affected catalyst recyclability or usage ratio. The catalyst screening tests were conducted using the fixed bed reactor previously described[1] and the general reaction conditions employed in catalyst performance tests for the char-lime-steam reaction. COED char was used as the carbon source for the studies along a 650°C reaction temperature and reactor steam flow rate of 0.33 mole min^{-1}. Included in the catalyst recycle tests for this reaction, was a one hour, 500°C char burn off treatment. Gas evolution rates and product gas compositions were measured during the gasification reactions. Usage ratios (recyclability figures) for the catalyst systems were computed by dividing the weight char that could be catalytically gasified by the weight of alkali catalyst used. The weight char used in calculating the usage ratio was the weight char gasified before a significant decrease (50%-60%) in the product gas evolution rate was observed. Catalysts were rapidly deactivated in the experiments, usually in one to two reaction cycles, owing to the high ratio (16:1) of char to catalyst in the reaction mixtures. Because of the reduced number of reaction cycles completed by the catalyst systems there is an increased uncertainty in the usage ratios determined for the char-steam reaction over the uncertainty connected with usage ratios determined for the char-lime-steam reaction where char to catalyst ratios in test mixtures were much lower and a greater number of cycles were obtainable. Nevertheless, the range and approximate degree of catalyst system recyclabilities are available from the measurements.

The results of the catalyst performance tests for the char-steam reaction are summarized in Table 4-7. As can be seen from the results, the alkali catalyst systems were capable of increasing reaction rate two to sevenfold over the non-catalyzed gasification rate. The most effective catalyst tested at the 5% level appeared to be the K_2CO_3-CaF_2 system while $Na_2B_4O_7$ was the least effective. The activity of Na_2CO_3 was comparable to that observed for K_2CO_3. These results parallel observations made for these catalysts with the char-lime-steam reaction. Catalyst usage ratios determined for both reactions are also similar. In fact, the only major difference in catalyst performance results observed for the char-steam reaction in which a considerably lower concentration of lime or limestone is used and results obtained for the char-lime-steam reaction, is the significantly lower product evolution rates observed for the char-steam reactions. The lower reaction rates, however, can readily be explained on the basis of the high char to catalyst ratios (lower catalyst concentrations) used in the char-steam reaction tests. As reported above in Section 4.3.1.2, reaction rates for the char-steam reaction are highly

Table 4-7. Summary of Catalyst Performance Results for 650°C Char-Steam Reaction

Reaction System			Product Evolution Rate[a]			Useage Ratio[b]
			Reaction Cycle			
Char	Sulfur Acceptor	Catalyst	1	2	3	
80% COED	15% $CaCO_3$	5% K_2CO_3	0.40	0.22	0.13	16-32
80% COED	15% $CaCO_3$	5% Na_2CO_3	0.47	0.20	0.10	16-32
80% COED	15% $CaCO_3$	5% $Na_2B_4O_7$	0.16	0.09	0.09	16
80% COED	10% $CaCO_3$	5% K_2CO_3-5% CaF_2	0.62	0.23	—	16-32
80% COED	15% MgO	5% K_2CO_3	0.47	0.16	0.16	16
80% COED	20% CaO (or $CaCO_3$)	No Catalyst	0.09			—
90% COED	5% $CaCO_3$	5% Na_2CO_3	0.48			—
90% COED	5% $CaCO_3$	5% NaF	0.48			—
90% COED	—	5% Na_2CO_3-5% NaF	0.46			—
90% COED	—	5% Na_2CO_3-5% K_2CO_3	1.89			—
90% COED	—	10% Na_2CO_3	1.87			

[a] Moles product gas evolved per mole of carbon per hour.

[b] Weight char catalytically gasified per unit weight alkali catalyst employed.

dependent on catalyst concentration in the range of 5%-20% catalyst. Thus it would appear on the basis of these results that the performance of dry admixed, alkali catalyst systems is not significantly affected by the reduction of lime or limestone in gasification mixtures. It remains to be determined whether this is true for reactions carried out in a fluid-bed reactor, and whether sulfur retention by lime or limestone, another performance objective not tested in these experiments, is affected by reduced lime concentrations.

4.4.2 Work Forecast

The Steam-Oxygen-Char Reaction studies task will be completed during the next reporting period. To be completed under the task are experiments to evaluate the effect of a partial atmosphere pressure of oxygen on the gasification rate of the char-steam reaction, and the performance of alkali catalyst systems for this reaction.

4.5 TASK V - ENGINEERING STUDIES

An engineering analysis effort is planned to parallel the laboratory research. The objectives of this effort are:

- To provide a preliminary design basis for initial investigation of the economic viability of a commercial catalytic gasification process
- To provide guidelines for the laboratory research in terms of catalyst recycle requirements, catalyst and acceptor (quick-lime) loss limitations, impact of product gas quality and so forth.
- To assist in prioritizing research to treat those areas which have significant impact on the process scale-up and economic characteristics.
- To provide a progressively upgraded conceptual commercial-scale design for use in assessing technology requirements in terms of industry practice and for comparison with other synthetic fuel processes.

4.5.1 Work Accomplishments

Accomplishments made under this task during this reporting period have included: preparing a block diagram of a conceptualized catalytic gasification process, developing a design basis for the conceptualized process, completing mass and energy balances for each of the unit operations involved in the process and preparing a preliminary process flow diagram for the process. In addition, identification and sizing of the major pieces of process equipment was initiated. Presented below in the remainder of this section are more detailed descriptions of the conceptualized catalytic hydrogen process, the design basis for the process, and a summary of the material balances around each processing step or operation of the gasification process. Details of the energy balances for each of the unit operations and the process flow diagram will be presented in the next project technical report. Work forecasts for the next reporting period under the engineering studies task are also presented in 4.5.2.

4.5.1.1 Conceptual Process Description and Design Basis

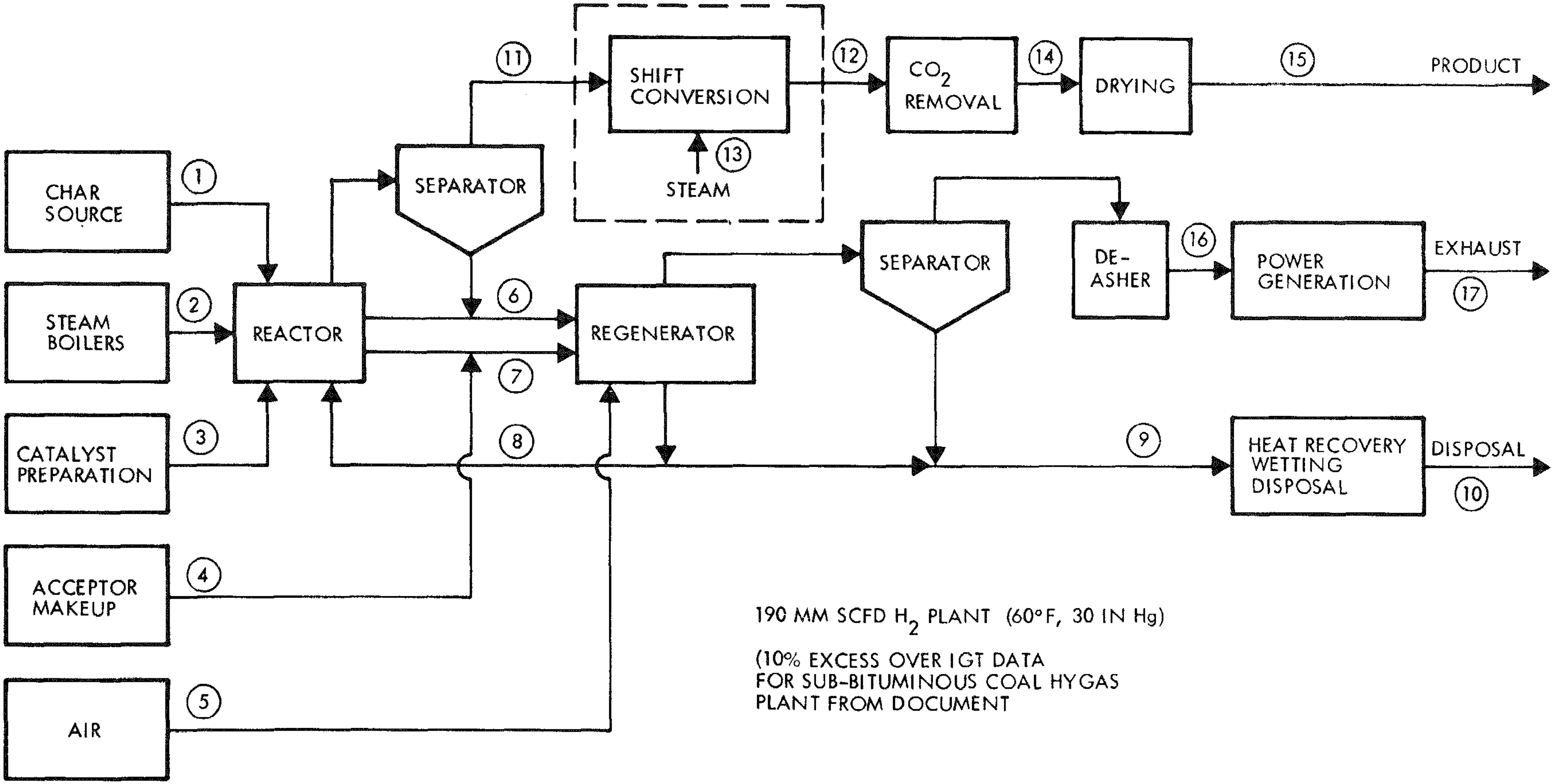
A block diagram of the Catalytic Hydrogen Process appears in Figure 4-15. Coal char from a coal gasification reactor is pneumatically transported to the reactor where it can be fluidized with steam and mixed with calcined dolomite, or limestone, to produce a product gas which is 80% hydrogen, H_2, on a dry basis. This gas is then further converted to hydrogen by reacting with steam over a shift conversion catalyst. The product of shift conversion is scrubbed to remove carbon dioxide, CO_2, and dried to produce a final product that is greater than 95% hydrogen. The reactor solids are pneumatically transported to the regenerator where limestone can be calcined with char and air at 1800°F to produced lime which is then recycled to the reactor. Gaseous products are deashed in order to be expanded through a power turbine. Heat is recovered from the ash before it is wetted and shipped to disposal. It should be noted that in the proposed processing scheme no oxygen plant and special sulfur gas cleanup operations are required.

The design basis for the conceptual process is based partially on extrapolations of laboratory data and necessarily in part on some reasonable assumptions. Laboratory data utilized in the design basis include product compositions at specific carbon and steam utilization rates at the temperature (1200°F) of the envisioned commercial plant. The data were, however, acquired at a reactor pressure somewhat lower than that proposed for the commercial plant, 15 as opposed to 150 psia. In order to reflect the effect of higher pressure on the system, adjustments were made to the laboratory data. Details of the design basis developed are presented below.

1. Feed char composition, dry basis, was taken originally from a Coalcon design for Illinois No. 6 coal (*).

	wt%
C	64.16
H	2.94
O	1.78
S	3.93
Ash	27.19

It is assumed that this char composition is not a function of particle size and that the size of the feed will be that size required for reactor operability.



190 MM SCFD H_2 PLANT (60°F, 30 IN Hg)

(10% EXCESS OVER IGT DATA
FOR SUB-BITUMINOUS COAL HYGAS
PLANT FROM DOCUMENT

Figure 4-15. Block Diagram of the Catalytic Hydrogen Production Process

2. This char, assumed to be produced in another part of the plant, is conveyed from a 150 psia, 1040°F vessel to the acceptor reactor at a rate consistent with the production of 190 MM scfd of 95 percent (by volume) hydrogen gas. Standard conditions are 60°F and 30 in.Hg.

3. Acceptor material composition is representative of Hollister dolomite.

	wt%
$CaCO_3$	56.11
$MgCO_3$	42.27
CaO	31.4*
MgO	20.2*
SiO_2, Al_2O_3, Fe_2O_3	.93
Acid Solubles	.69
LOI	46.8

4. Process steam will be generated at higher pressures and superheated to drive turbines before being exhausted to the process at approximately 165 psia and the temperature required to heat balance the reactor.

5. No process oxygen will be required.

6. Process water will be used as required for hydrogen generator temperature control.

7. The hydrogen generator reactor will be designed for the following operating conditions:

   T = 1200°F

   P = 150 psia above the bed

   Gas residence time ∿ 10 sec

   Superficial Gas Velocity ∿ 4 FPS

8. Residue char is assumed to be composed of only ash: the char which is gasified reacts completely. The char which passes through the reactor is completely unchanged.

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* Calculated on basis of carbonate present in material.

9. The hydrogen generator effluent gas composition will be as follows:

	Vol %, dry basis
H_2	80
CO_2	5
CO	12
CH_4	3

10. The overall hydrogen generation reaction for calculation purposes is:

$$\begin{aligned} CaO + char + H_2O + catalyst \longrightarrow CO_2 + CO + CH_4 \\ + H_2 + H_2O + CaS + CaCO_3 + Residue \\ + Catalyst \end{aligned}$$

11. The acceptor regeneration reactor will be designed to operate at the following conditions:

T = 1800°F

P = 150 psia above the bed

Gas residence time - to be determined from Consol data
Superficial Gas Velocity - to be determined from Consol data

12. The basic regeneration reaction for calculation purposes is:

$$\begin{aligned} CaCO_3 + char + Residue + Air + CaS + catalyst \\ \longrightarrow CaO + CO_2 + NO + O_2 + N_2 + H_2O + CaSO_4 \\ + catalyst + Residue \end{aligned}$$

4.5.1.2 Material and Energy Balances

Material flow rates for steams 1 through 17, shown on the process block diagram (Figure 4-15) have been determined and are summarized in Table 4-8. It should be noted that the material balance is presented in terms of pounds per hour. Energy balances for the reactor, regenerators and shift converters have also been completed. This information as well as all the energy balance data will be presented in the next project technical reports.

Table 4-8. Material Balance for TRW 190 MM SCFD Conceptual Coal Energy to Hydrogen Process (rates = lb/H)

	1 Char feed	2 Steam	3 Makeup Catalyst	4 Makeup Acceptor	5 Air	6 Coal & Residue to Regenerator	7 Spent Acceptor	8 Regenerator Recycle	9 Bleed plus Ash to Disposal	10 Solids to Disposal	11 Reactor Product Gas	12 Shift Conversion Product Gas	13 Steam	14 Benefield Unit Product Gas	15 H_2 Product	16 Regenerator Product Gas	17 Exhaust
Char																	
C	217,740					89,882											
H	9,978					4,119											
O	6,041					2,494											
S	13,337					5,506											
Ash	92,275					38,091											
CaO								354,730	80,735								
Catalyst			9,964				53,747	43,783	9,964								
$CaCO_3$				185,727			608,673										
$MgCO_3$				139,916													
MgO							293,924	293,924	66,896								
Other				5,362			23,561	23,561	5,362								
CaS							17,621										
$CaSO_4$							248,811	248,811	56,629								
H_2O		434,886			18,527						133,718	1,185,283	1,099,523	TBD	381	55,333	
CO_2											50,212	167,370		9,647	9,647	751,674	
CO											76,705	2,140		2,140	2,140		
CH_4											10,983	10,983		10,983	10,983		
H_2											36,799	42,165		42,165	42,165		
N_2					1,138,016											1,137,871	
O_2					345,529											51,829	
NO																312	
Residue						459,617		405,433	92,275								
Total	339,371	434,886	9,964	331,005	1,502,072	599,709	1,246,339	1,370,242	311,861	TBD	308,417	1,407,941	1,099,523	TBD	64,935	1,997,019	TBD

4.5.2 Work Forecast

It is planned to complete the engineering studies task during the next reporting period. To be completed are the identification and sizing of the major pieces of process equipment, and process costing economic analyses and parameter sensitivity evaluations.

5. REFERENCES

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APPENDIX

Table A-1. Summary of Catalyst Recycle Experimental Results

SYSTEM				PRODUCT EVOLUTION RATE[a]														Usage[b] Ratio	C/S[h] Ratio
Char	Acceptor	Catalyst	Stabilizer	Cycles															
				1	2	3	4	5	6	7	8	9	10	11	12	13	14		
19% COED	76% CaO	5% K_2CO_3	——	2.87	3.00	3.13	2.47	1.47	0.44	0.33								19	0.399
18% COED	72% CaO	5% K_2CO_3	5% CaF_2	2.46	2.89	2.78	2.92	3.14	3.03	3.03	3.21	3.37	2.90	1.06	0.47			40	0.191
19% COED	76% CaO	5% Na_2CO_3	——	2.75	3.20	3.22	3.11	3.28	3.18	3.01	2.51	0.77	0.44					30	0.325
18% COED	72% CaO	5% Na_2CO_3	5% CaF_2	2.57	3.15	2.90	2.89	2.78	3.08	3.03	3.27	3.26	3.45	3.49	2.90	1.03	0.46	47	0.211
19% COED	76% CaO	5% $Na_2B_4O_7$	——	1.89	2.31	——[c]	0.46	0.46										11[d]	0.457
18% COED	72% CaO	5% $Na_2B_4O_7$	5% CaF_2	1.63	2.11	2.16	2.47	1.60	0.48	0.24								18	0.289
19% COED	76% CaO	5% NaF	——	2.64	3.01	2.87	2.78	3.11	3.09	3.13	3.15	3.09	3.13	3.05	1.33	0.44		46	0.547
19% COED	76% CaO	——	5% $Ca_3(PO_4)_2$	0.21														—	-
18% COED	72% CaO	5% K_2CO_3	5% $Ca_3(PO_4)_2$	3.01	2.94	3.04	3.42	3.09	2.25	0.92	0.81							22	0.351
17% COED	68% CaO	5% K_2CO_3	10% $Ca_3(PO_4)_2$	3.27	2.87	3.24	3.43	3.06	2.56[e]	1.19	0.76	0.66						22	0.318
17% COED	68% CaO	5% K_2CO_3	10% NaH_2PO_4	3.21	3.31	2.89	2.91	2.63	2.87	2.85	3.00	2.97	3.07	1.56	0.46			37	0.203
18% COED	72% CaO	10% NaH_2PO_4	——	0.10	0.31	0.53	1.05[g]											—	—
19% COED	76% CaO	5% K_2CO_3[f]	——	2.87	2.97	2.63	2.68	1.77	1.87	1.63								> 26	<0.29
19% COED	76% CaO	5% Na_2CO_3[f]	——	3.09	2.97	3.15	3.00	2.91	2.83	2.55								> 26	<0.37

a. Moles product gas produced per mole carbon per hour

b. Weight char catalytically gasified per unit weight of alkali catalyst employed

c. Leak in gas collection system noted

d. Usage ratio may be as low as 8

e. Estimate value due to system power failure during reaction

f. Catalyst dispersed by solution impregnation

g. Ash residue from 3rd cycle exposed to gas mixture of CO_2 in steam (0.2 mole fraction) at 650°C for 90 minutes.

h. Ratio of number of moles of catalyst used to mole SiO_2 in deactivated reaction mixture.

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