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CATALYTIC CONVERSION OF COAL ENERGY TO HYDROGEN

Monthly Report for The
Period May 1 - May 31, 1977

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1.0 INTRODUCTION

This monthly report describes TRW's technical accomplishments made during the twelfth month under ERDA Contract No. E(49-18)2206. The overall objective of the program is to develop a preliminary assessment of the potential of a hydrogen generation process based upon reactions involving char, steam, lime and metal salt additives. Small scale laboratory studies consisting of both fixed bed and fluid bed experiments will be carried out to characterize the effect of metal additives on the char-steam-lime reaction. These data will support a preliminary engineering study of the technical and economic feasibility of a hydrogen generation process based upon this system.

The technical effort to accomplish these project objectives has been divided into five work areas or tasks each with their own specific objectives. These work areas of project tasks are as follows:

TASK I	FIXED BED REACTION EXPERIMENTATION
TASK II	FLUID BED REACTOR TESTS
TASK III	GASIFICATION REACTION PHYSICAL-CHEMICAL PROPERTIES
TASK IV	STEAM-OXYGEN-CHAR STUDIES
TASK V	ENGINEERING STUDIES

Presented below are brief synopses of the technical accomplishments made in each of the above reporting areas for May and work forecasted for them for the month of June.

2.0 OPEN ITEMS

The technical effort originally scheduled to be completed under the project by June has been extended beyond this date. By mutual agreement with the ERDA project officer, Dr. Kermit Woodcock, and the cognizance of ERDA's contract administrator, Ms. Joanne Finotti, the completion of all technical work under this project including preparation of the project final report has been extended to 30 September 1977. Extention of the period of performance is necessary because of a delay in assembly of an elevated pressure fluid bed reactor required in experiments under the present project's scope of work.

3.0 PROJECT TASK REPORTS

3.1 TASK I - FIXED BED REACTOR EXPERIMENTATION

The objective of this task effort is to determine the effects which selected catalytic metal salt additives have on the rate of hydrogen generation from the reaction of steam, char and lime. It is a further objective of this task to identify and define char gasification and lime regeneration conditions in which optimal char conversion rates and catalyst performance with recycle are obtained. Small fixed bed reactors will be used for carrying out char gasification reactions. The effects of char, acceptor (lime, limestone, and dolomite) and selected catalyst systems on hydrogen production and rate will be studied, as well as the effects of steam reaction and lime regeneration temperatures, catalyst stabilizer and acceptor concentrations, and methods of dispersion.

3.1.1 Accomplishments

No work was performed on this task during May. All experimental work under the task was completed in February and reported on in the quarterly technical progress report for the period 1 January - 31 March 1977.

3.1.2 Work Forecast

Results obtained from the Fixed Bed Reactor Experimentation task will be reviewed and organized for incorporation into the final report. It is anticipated this activity will be completed in July. No further experimental work under this project task is planned.

3.2 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.

3.2.1 Work Accomplishments

During this reporting period the design, construction and preliminary checkout tests of the elevated pressure fluid bed reactor have been completed. In addition a review of the safety of operation of the reactor system was completed, and TRW management approval to operate the system for char gasification studies up to a temperature of 750°C and a pressure of 150 psi was granted. Photographs of the elevated pressure fluid bed reactor system are shown in Figures 1 and 2. A schematic of the reactor systems is presented in Figure 3. The reactor tube is constructed from 0.035 inch wall, 1 inch O.D. tubing, and is 8 feet in length. The tube material is Hastalloy 800. All other tubing and fittings are 304 or 316 stainless steel. The reactor and the four zone furnace, the particle trap, water condensor, water trap, and steam generator are located in a personnel shield constructed of 1/4" lexan polycarbonate sheets supported on a 1 1/2" angle iron frame. These components are labeled in Figures 1 and 2.

In operation steam, and purge gas, are metered and fed to the bottom of the reactor. The plenum chamber evens out the flow prior to its passage through the gas distributor and the fluidized bed. The feed gas and steam are preheated before they enter the plenum chamber. Both the reactor and preheater are electrically heated.

Exit gas leaves the top of the reactor and passes through a heated line and a heated particle trap (to avoid condensation of liquids) to a cooler condensor. Liquid products are collected in a knockout pot and are drained through a manually controlled valve into the liquid receiver.

A back-pressure regulator connected to the reactor controls the reactor pressure and reduces the pressure of the exit gases. The volume of exit gases are measured with a wet-test meter. A gas sample can be withdrawn and periodically analyzed with a gas chromatograph. Primary gas analysis is for H_2, CO, and CO_2. Minor components of O_2, N_2, and CH_4, are also present, and analysis for their presence is made. The gas from the wet-test meter is finally vented.

Initial gasification experiments at atmospheric pressure using K_2CO_3, COED char and CaO acceptor have been conducted. In the remainder of the

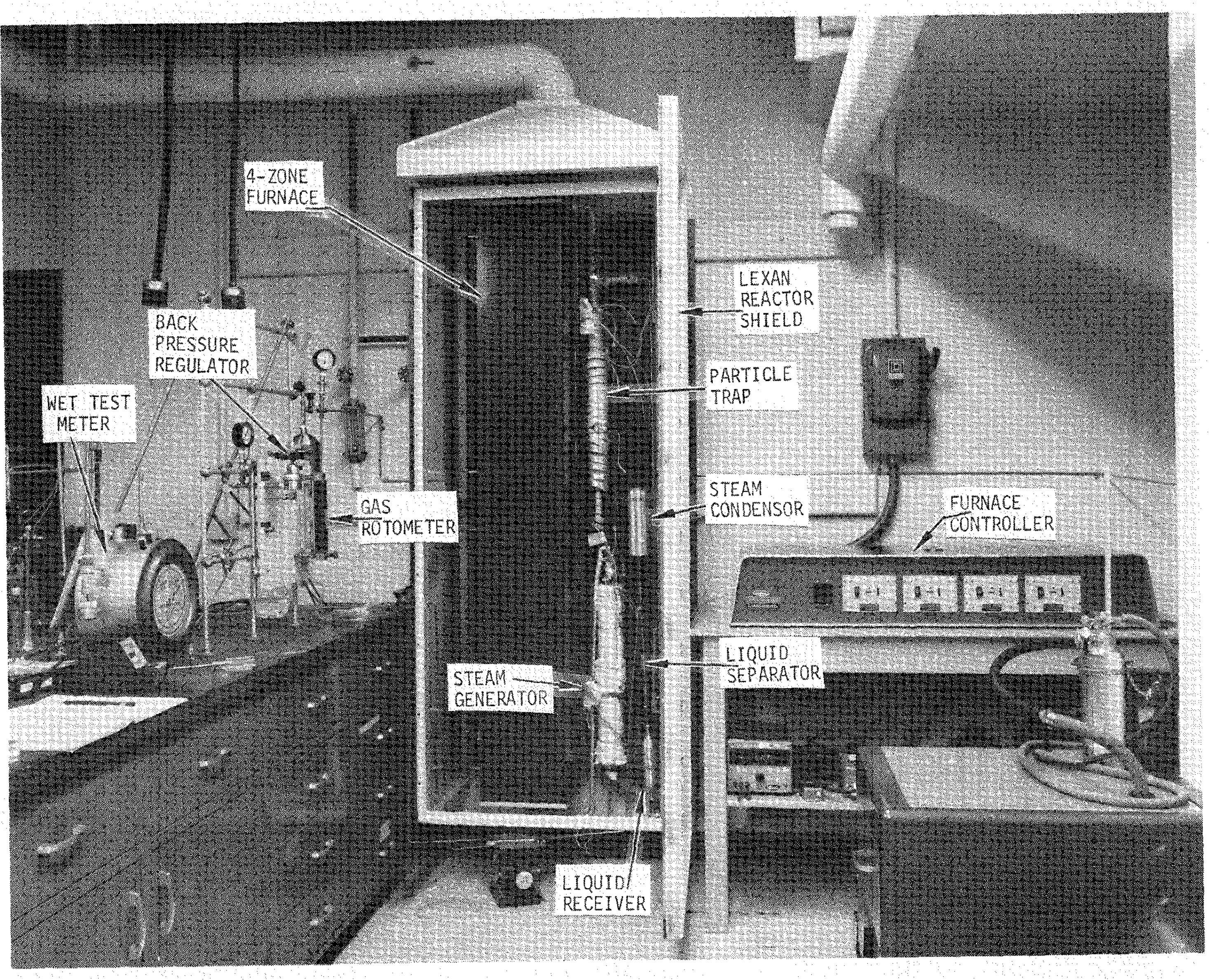

Figure 1. Photograph of Elevated Pressure Fluid Bed Reactor System. (View A)

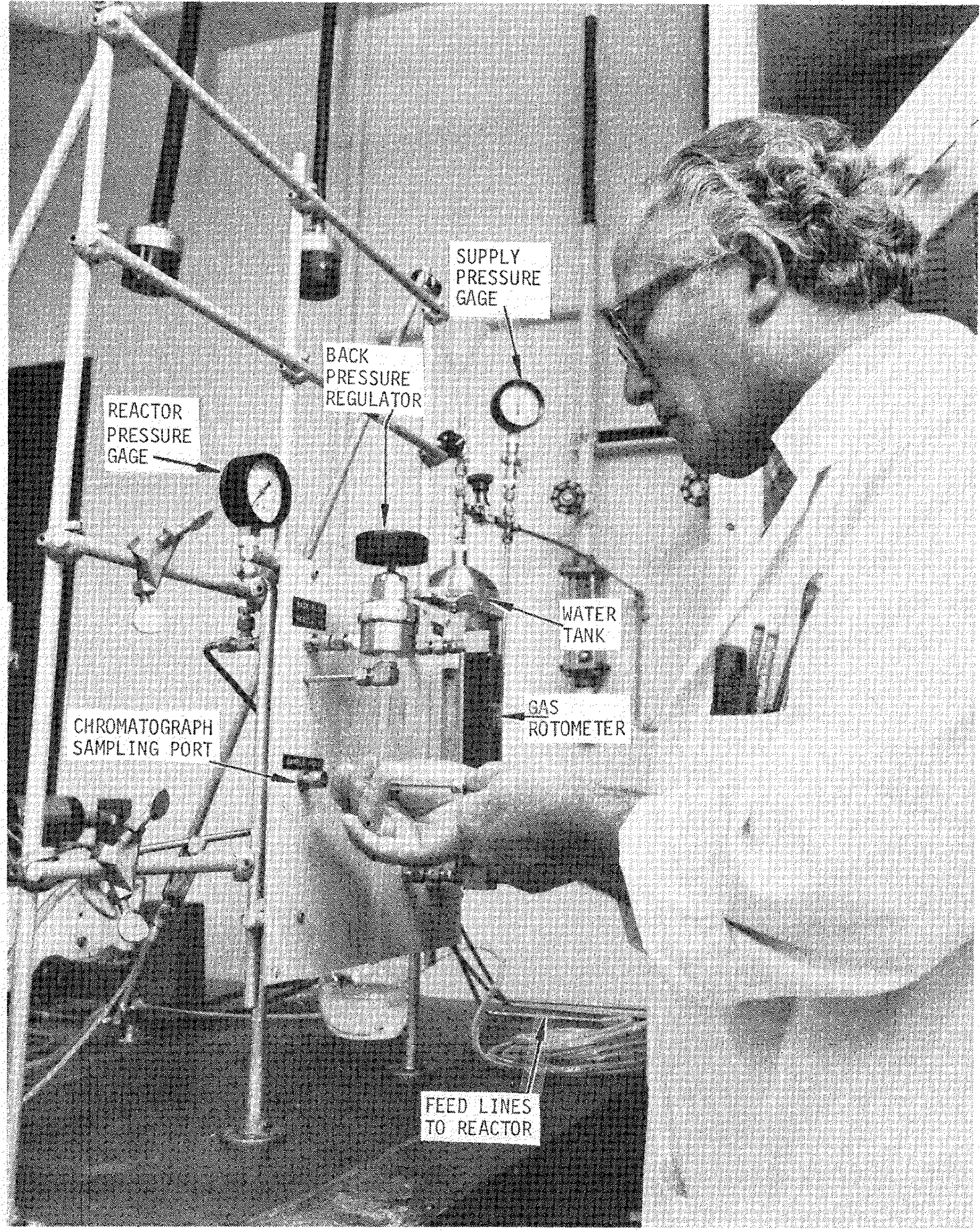

Figure 2. Photograph of Elevated Pressure Fluid Bed Reactor System. (View B)

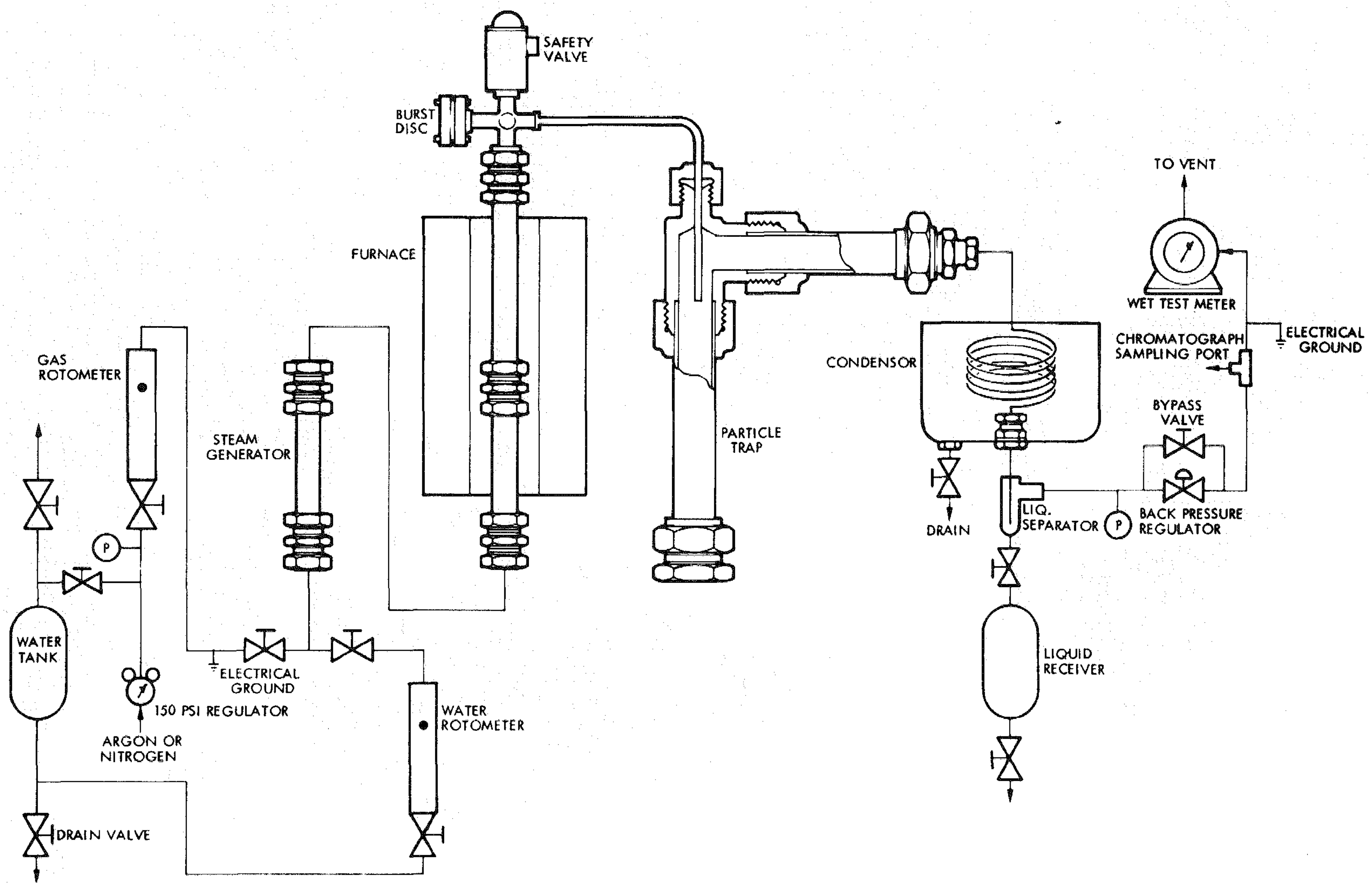

Figure 3. Schematic of Elevated Pressure Fluid Bed Reactor System.

experimental effort under this task two brief series of experiments will be performed to preliminarily show the effects of elevated reaction pressure on char gasification kinetics, product composition, sulfur retention and catalyst recyclability. The reaction conditions to be used for these experiments are summarized in Table 1. A total of approximately ten experimental runs with pressure fluid bed reactor will be conducted.

3.2.2 Work Forecast

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

1. Complete the matrix of elevated pressure fluid bed experiments.
2. Analyze data from the elevated pressure experiments.
3. Begin preparation of the Final Report of this activity.

3.3 TASK III - GASIFICATION REACTION PHYSICAL-CHEMICAL PROPERTIES

The objective of this task is to determine the chemical and physical forms of both active and spent catalysts and how they are distributed and function during both char gasification and lime or acceptor regeneration. It is a second objective of this task to determine whether sulfur present in coal char is retained during char gasification and acceptor regeneration reactions.

3.3.1 Accomplishments

During May catalyst transport studies were completed under the Gasification Reaction Physical-Chemical Properties task. In the studies completed potassium carbonate catalyst, applied to a high surface area silicon carbide support material and immersed in a char bed, was shown to be mobile during the char-steam reaction and able to catalyze, though somewhat ineffectually, the char gasification reaction(s). In other transport studies completed, recycled reaction ash residues from previous fluid bed reactor experiments were chemically analyzed, and a partial depletion of alkali catalyst in them was observed. This finding supports the hypothesis that alkali catalysts are indeed mobile during char gasification. The moderate alkali volatilization losses observed appear to be significant and thus capable of explaining in part the observed reduction and loss of catalyst activity with recycle.

Table 1. Reaction Conditions for Elevated Pressure Fluid Bed Reactor Studies

Test	Steam Reaction Temperature	Pressure (psig)	Acceptor Regeneration Temperature and Time	System
Pressure Effects	650°C	0, 50, 100	———	K_2CO_3, COED Char Hollister Dolomite
Recycle Effects	650°C	50 or 100	900°C, 2 Hr.	K_2CO_3, COED Char Hollister Dolomite

The mobility of a supported alkali catalyst during the char-steam reaction is readily apparent from the photomicrograph shown in Figure 4. Shown in this figure is a photograph of a bed of char which has been exposed to a flow of steam in a fixed bed reactor system. Embedded in the char bed are several silicon carbide beads that have been impregnated with K_2CO_3. The char bed with embedded catalyst beads were reacted for one hour at 750°C with a 0.33 mole min^{-1} steam flow. The support beads used in the experiments were spheroidal in shape, nominally 3.7 mm x 1.8 mm in dimension and coated with approximately 1.2 mg of K_2CO_3. As can be seen from the photograph considerable char in the vacinity of each bead has been reacted as is evidenced by the large cavities or void volumes created by the gasification reaction. The large extent of reaction that has occured in the vacinity of the beads can be taken to signify that a significant concentration of catalyst existed in the region during steaming and that the catalyst was effective in promoting the carbon-steam reaction. In similar experiments performed with SiC beads not impregnated with catalyst, little or no reaction was observed to occur. Electron microprobe analyses of the white regions or zones surrounding each reaction cavity and bead in the photograph show high concentrations of potassium and indicate that effective alkali gasification catalysts, such as potassium carbonate are mobile during reaction.

Presented in Table 2 is a summary of the results obtained from the analysis of recycled residue materials from catalyzed gasification reactions carried out using the atmospheric pressure fluid bed reactor. As can be seen from the results presented, the amount of alkali found in the recycled reaction residues was generally considerably less than the amount initially taken except for the Na_2CO_3-COED-CaO system. The high recovery observed in this case is believed to be due to a contamination problem which may have occured in the analysis of this residue sample. To confirm that the loss of alkali from the reaction residues is real and not due to simple mechanical losses in handling or ash entrainment during gasification, the observed and expected alkali to calcium weight ratios were computed for each sample. As can be seen from the tabulation of results presented in the table, the observed alkali: calcium ratios are less than the expected values confirming that preferential volatilization or loss of

Table 2. Summary of Reaction Residue Analyses and Alkali Losses.

Original Reaction Test Mixture Composition[a]				Reaction Cycles[b]	Acceptor Regeneration	Reaction Residue Alkali Content		% Alkali Recovery	Alkali: Calcium Weight Ratio		% Reduction in Alk: Ca Ratio
Catalyst	Char	Acceptor	Stabilizer			Observed (grams)	Theoretical[d] (grams)		Observed	Expected	
10% Na_2CO_3	24% COED	62% CaO	4% CaF_2	11	No	0.702	1.138	62	0.081	0.093	13
10% K_2CO_3	24% COED	62% CaO	4% CaF_2	10	No	0.682	1.483	46	0.105	0.120	13
10% K_2CO_3	24% COED	62% CaO	4% CaF_2	9	950°C	0.666	1.476	45	0.0907	0.119	24
10% K_2CO_3	25% COED	65% CaO	—	9	950°C	0.591	1.475	40	0.0788	0.126	37
10% Na_2CO_3	25% COED	65% CaO	—	12	No	1.138	1.143	>99	0.157	0.0972	(-62)[c]

a. Compositions expressed in terms of weight percentage.

b. Reaction-regeneration cycles completed before analysis of reaction residue performed.

c. Observed increase in alkali: calcium ratio. Result considered to be spurious due to a possible contamination problem.

d. Computed on the basis of the amount of alkali catalyst used and the weight of alkali contributed by char ash.

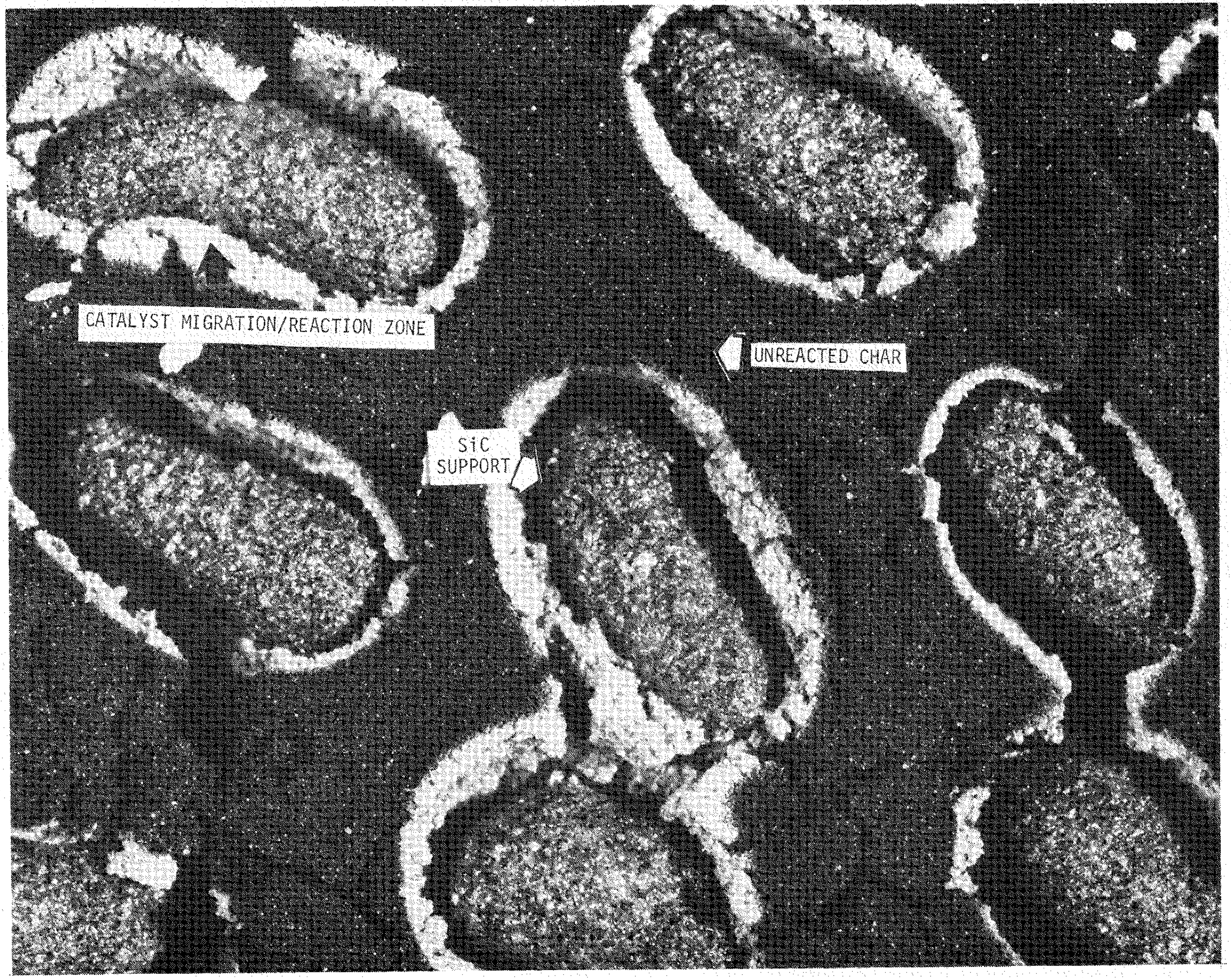

Figure 4. Photomicrograph of Partially Reacted Char Bed with SiC Supported K_2CO_3 Catalyst.

alkali from the reaction residue is occuring. The percentage loss of alkali from the reaction residues, corrected for mechanical losses by the ratioing technique, indicates that the magnitude of the volatilization loss ranges from 13 to 37% depending on the catalyst and reaction conditions employed.

3.3.2 Work Forecast

During June it is planned to obtain differential thermograms on COED Char and four unreacted char-acceptor-catalyst mixtures in order to determine whether any phase changes or chemical transformation occur under an inert atmosphere and at what temperature they occur. If such changes or reactions do take place, the observation could possibly be used to identify the processes responsible for catalyst transport. With the acquisition and interpretation of the differential thermograms, the experimental effort under the Catalyst and Acceptor Physical-Chemical Studies task will be completed. No further work under this task is planned except for reviewing all of the task's experimental results and organizing and interpreting them for the final project report.

3.4 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.

3.4.1 Work Accomplishments

During May gasification experiments were carried out in the fixed-bed reactor system to determine the effects which a small oxygen partial pressure would have on the product composition and gasification rate of the potassium carbonate catalyzed steam-char-limestone reaction. The series of experiments are not complete at this time so that a full presentation and discussion of the results is not possible. It appears from the reactions so far completed though, that a small partial pressure of oxygen, 5 mole percent, in the steam stream can significantly lower the temperature at which a rapid gasification reaction occurs, and also significantly alter the composition of the gaseous products, over that obtained with a pure steam feed.

3.4.2 Work Forecast

During June it is planned to complete the steam-oxygen experiments started last month. With the completion of this experimentation and interpretation of results, the experimental work planned for this task will have been completed. Some effort during June will be spent in organizing the experimental results obtained under this task for incorporation into the project final report.

3.5 TASK V - ENGINEERING STUDIES

An engineering analysis effort is planned to parallel the laboratory research. This effort is designed to serve the following purposes:

- To provide a preliminary design basis for initial investigation of the economic viability of a commercial 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.

3.5.1 Work Accomplishments

The engineering analysis effort has paralleled the laboratory research to the extent that selected laboratory data has been incorporated into an updated version of the conceptual commercial process design for the TRW coal to H_2 process.

The design basis, material balances and block diagram were presented in the recently submitted Quarterly Technical Progress Report (April 1977). Work is continuing on the final sizing and costing of processing equipment for the conceptualized plant. A detailed flow diagram for the conceptual process has been completed.

3.5.2 Work Forecast

During June the following engineering tasks will be accomplished.

- Perform parametric cost analysis for showing the significance of variations in catalyst cost of ±50% on product costs. Determine qualitatively the effects of catalyst attrition and poisoning rates on the conceptual process.
- Produce sensitivity graphs of the effects of variations in char, catalyst and capital cost on hydrogen cost.
- Complete an economic comparison of the conceptualized TRW catalytic coal to hydrogen process and an advanced technology pipeline gas process and liquefaction process, a Lurgi pipeline gas process, the Kopper-Totzek synthesis gas process and the steam-iron process for hydrogen.