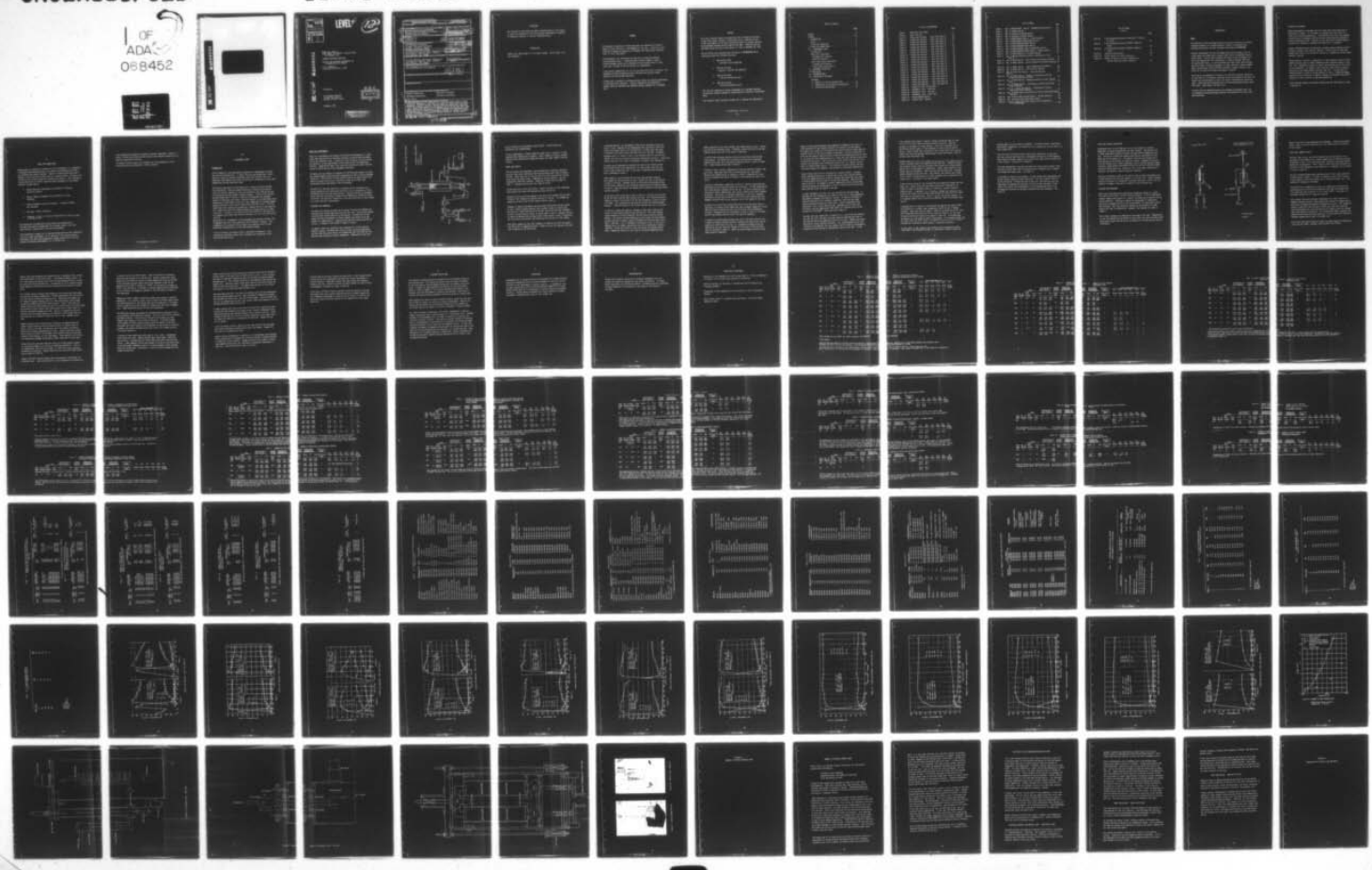
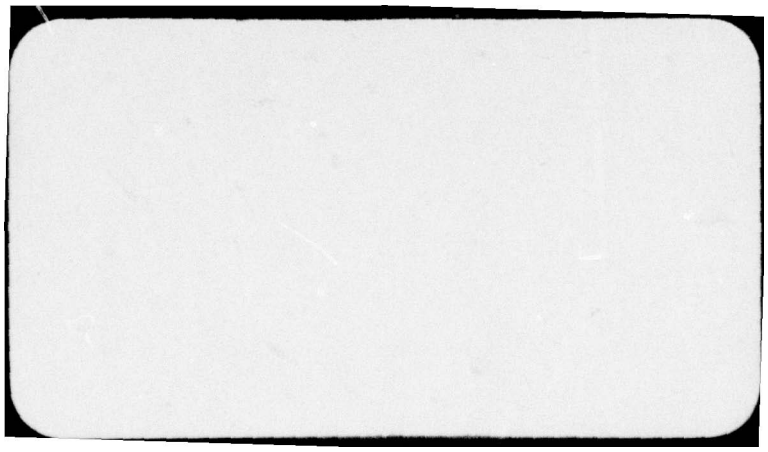
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HYDROGEN GENERATOR SUBSYSTEM

CATALYST AND EQUIPMENT DEVELOPMENT FOR A THERMO-CATALYTIC CRACKER

U.S.A. MERADCOM
Fort Belvoir, Virginia 22060

Prepared by

IIT Research Institute
10 West 35th Street
Chicago, Illinois 60616

November, 1978

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Future Army plans call for generation of silent electrical power in field situations. Hydrogen/air fuel cells are considered viable electrical power generators. Currently available logistic fuels are hydrocarbon; requiring a fuel conditioning process to free hydrogen for use by the fuel cell. This report concerns one such process to obtain hydrogen from hydrocarbon fuels. Experimental work is aimed at optimizing a catalyst for catalytic cracking and the development of a breadboard hydrogen generator. Further work is needed in both these areas.

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SUMMARY

An important alternative in future Army plans for generation of electric power in field situations is the hydrogen air fuel cell. Viability of this alternative depends on generation of hydrogen from logistically available fuels in "fuel conditioners".

A developmental fuel conditioner has been built to generate hydrogen from hydrocarbon fuels. A thermo-catalytic process scheme is used to isolate hydrogen during cyclic operation of twin catalyst beds in a unit which uses a limited air-off gas mixture for regeneration.

A new catalyst composition like this barium stabilized nickel on alumina - was developed to better withstand process conditions and tolerate carbon deposition during hydrogen generation.

Further work is necessary to evaluate design factors and catalyst performance in sustained cyclic operation. Catalyst composition and preparation methods should be optimized and component designs upgraded for a prototype unit.

PREFACE

This final Technical Report was prepared by the IIT Research Institute, 10 West 35th Street, Chicago, Illinois 60616 and is submitted as part of the requirements of the United States Army Mobility Equipment Research and Development Command Contract DAAG 53-76-C-0081. Technical work was performed during the period from January 13, 1976 to September 30, 1978.

Earlier efforts were conducted both internally at USAMERADCOM and by contractors under the following contracts:

1. DAAK 02-69-C-0425
   Institute of Gas Technology

2. DAAK 02-70-C-0547
   Engelhard Minerals and Chemicals

3. DAAK 02-69-C-0453
   Pratt and Whitney Aircraft

4. DAAK 02-70-C-0518
   Pratt and Whitney Aricraft

This work was conducted to further development of a hydrogen generator sub-system to produce hydrogen by thermo-catalytic cracking of hydrocarbon fuels.

This Technical Report has been reviewed and is approved for publication.

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I

INTRODUCTION

SCOPE

The objective of work performed during this contract period was to develop prototype hardware for a thermo-catalytic cracker in accordance with pruchase descriptions and other information provided by USAMERADCOM.

Original requirements for this development work were outlined as part of a long range plan summarized as project SLEEP (Silent Lightweight Electric Energy Plant). Project SLEEP concepts were based on use of hydrogen fuel cells with appropriate "fuel conditioners" to derive hydrogen from logistic hydrocarbon fuels. It was envisioned that these "sets" would provide electrical power to maintain equipment in ready condition, operate command posts, provide power for surveillance equipment in remote locations, and allow use of electrically-powered equipment in general.

Units were to be designed for missions up to 100 hours and have capability of fast start up (15 minutes), operation on any fuel (gasoline, jet fuel, and diesel fuel) was desirable, as was a low level of detectability (noise and heat). Other desirable characteristics included high hydrogen purity, good efficiency, light weight, and small size.

Previous work has addressed process and equipment development tasks, but an acceptable prototype hydrogen generator sub-system unit has not as yet been developed.

HISTORICAL BACKGROUND

Recent developments in hydrogen fuel cells have made silent generation of electricity a reality. It is logical to consider these fuel cells for field use in military applications. This application of fuel cells depends on availability of hydrogen--with the obvious source being the hydrogen in logistic hydrocarbon fuels. However, to make the overall concept workable, a process for isolation of hydrogen from these fuels is necessary.

Several candidate process are available, including steam reforming, partial oxidation, thermal, and catalytic cracking. Previous work has shown the process most likely to be an over-all success is a combination called thermo-catalytic cracking.

Thermo-catalytic cracking is conducted at a lower temperature than straight thermal cracking and at a higher temperature than straight catalytic cracking. This "compromise" process has some of the problems and merits of each of its forerunners. For example, usual catalysts from refinery catalytic cracking are not stable enough to provide long life. Previous work has indicated metallic nickel to be the catalyst of choice. Operating temperatures are not as severe as in thermal cracking, but equipment and material selection is still critical to long term operability.

A more thorough summary of previous contract work and conclusions is given in Appendix A.

II

BASES FOR CURRENT WORK

Thermo-catalytic cracking as a process for fuel conditioning, i.e. production of hydrogen from hydrocarbon fuels, was found to be workable but not without equipment and catalyst problems. Results of previous work were used to present a starting point for design work at a preaward-bidders conference associated with this current request for proposal and contract. This information included definition of several suggested design parameters for the thermo-catalytic cracker reactor:

1. Kinetic data were interpreted as indicative of diffusion controlled reaction.

2. Reactor length to diameter ratio-a minimum of six was indicated.

3. Reactor diameter to particle diameter - a minimum of eight was indicated.

4. Bed type - fixed, cylindrical.

5. Catalysts - 0.5-1% wt. nickel on Norton BA 307; 5-10% wt. nickel on Norton SA 5203.

Desired physical and operating characteristics were summarized in "purchase description" documentation and included; weight, size, fuel specifications, product purity, and yield requirements.

IITRI formulated a concept for an improved thermo-catalytic fuel conditioner to fulfill these requirements. Cyclic operation of two cracker beds was envisioned, with each being regenerated, purged, and fed fuel in turn to provide the hydrogen requirements of a 1.5 KW fuel cell.

A new regeneration concept was proposed to improve temperature control in which a limited air/off-gas mixtures would be used instead of ambient air to moderate regeneration reactions.

A conceptual design layouts and a program plan for development of final design data were also presented in IITRI's proposal.

III

EXPERIMENTAL WORK

INTRODUCTION

Initial emphasis of the experimental program was on development of design data for the prototype unit. A "bench" unit was constructed with a prototype-size reactor to develop information about heat transfer rates, regeneration requirements and product purity/kinetic limitations on cycle time, temperatures and gas production rates.

During early operations with the bench unit, catalyst stability problems were encountered. Physical damage-disruption of catalyst particles-was occurring. Several attempts to solve this problem by heat treating and use of alternative catalyst supports proved fruitless. To more fully evaluate possible mechanisms of failure, a smaller scale apparatus was designed. Advice of consultants and further literature studies let to experiments which showed that a nickel-carbon interaction was responsible for catalyst damage. Several stabilized nickel catalyst compositions were then tried. A barium-stabilized nickel catalyst was prepared by a method similar to that described in several Universal Oil Products patents and showed promise in a small scale test. A sample of this catalyst was then evaluated in the bench unit and appeared more stable than previous catalysts, but with some sacrifice of activity.

Design work for a "breadboard" of the prototype unit was then finished, the "breadboard" was built, and loaded with this "preferred" catalyst. This breadboard will be used to fully evaluate this catalyst as well as the operational characteristics of the IITRI process concept.

A list of catalyst and subtacts used is presented in Appendix B. Also included are analytical results and a procedure for preparation of the barium stabilized nickel

BENCH UNIT EXPERIMENTS

Bench unit experiments were planned to characterize performance of a prototype-sized catalyst bed at conditions necessary to achieve desired product purity and production rates. Evaluation of the limited air-off gas concept was possible, as were measurements of bed pressure drop and temperature profiles. Regeneration times, flow rates and air/off-gas mixtures could be varied to attain desired carbon management conditions.

The bench unit was capable of production of sufficient gas product to allow gas chromatrographic analyses during regeneration as well as during hydrogen production. These analyses allowed characterization of product purity and impurity contents during cyclic operation so that cycle times, heat balances,and purge requirements could be estimated.

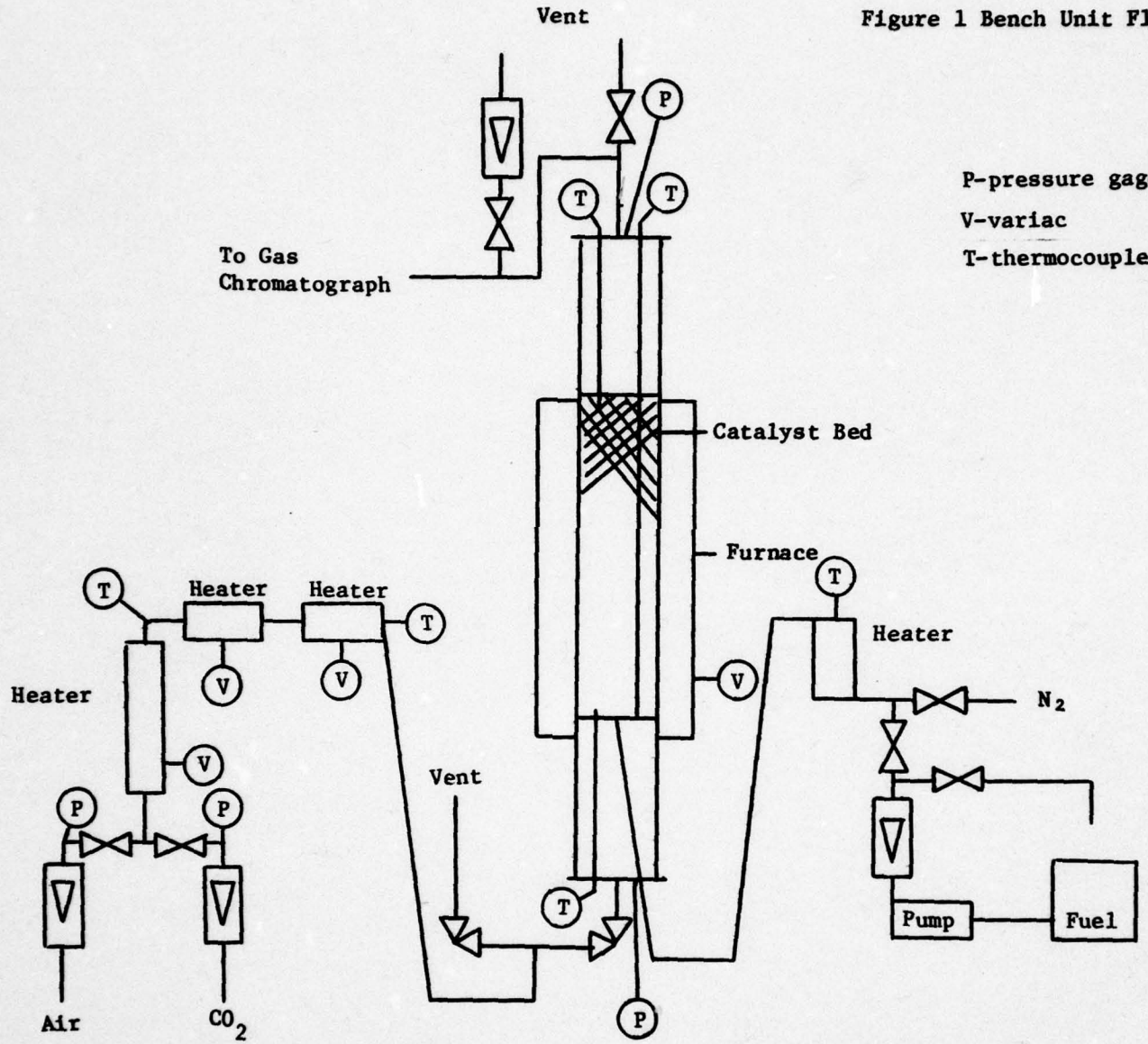
The bench unit provided capability to evaluate overall performance and allowed manipulation of macroscopic variables, but no indications of local performance within the bed were available. Physical handling of equipment during operation and catalyst change-out was hampered by peripheral piping, insulation, and electrical connections, which made evaluation of many samples on a short time basis inconvenient.

EQUIPMENT AND PROCEDURE

The bench unit reactor was made from a section of three inch diameter 347 stainless steel furnace tube which was two feet long. Fuel was fed through an electrically heated vaporizer to the reactor. A mixture of air and carbon dioxide was preheated in electric heaters and either fed to the reactor for regeneration or bypassed during the fuel cracking portion of a cycle. A schematic flow diagram is shown in Figure 1.

In general, bench unit operations were conducted for a given catalyst material loading. Different fuels could be used, starting temperatures and fuel feed times were chosen, and regeneration gas flow rates and composition were adjusted to control temperature. Regeneration times were

Figure 1 Bench Unit Flow Scheme



usually chosen to allow complete carbon burnoff. Product gases were analysed by gas chromatography.

In early experiments, a single sample was taken for G.C. analysis, in later tests, multiple samples were collected. After a number of cycles, catalyst materials were evaluated for damage and weight loss after removal from the reactor.

BENCH UNIT RESULTS

The first bench unit experiment was performed with a catalyst loading of one-third low nickel on Norton BA 307 and two-thirds high nickel on Norton SA 5203. Diesel fuel (No. 2) and jet fuel (JP-4) were each fed for various cycle times and several rates. Temperature, product analyses, fuel and regeneration times were recorded. Summaries of these data are shown in Table 1. Hydrogen purities were less than 80 percent.

At the conclusion of this test series - about five hours of total operating time-catalyst bed volume had decreased by about one-fourth.

Catalyst particles had been damaged to the point that regeneration gas could "fluidize" the fragments and entrain them out of the bed. This damage was thought to be due to the SA 5203 support material break up.

Attempts to improve performance and purity were made during the next series of runs: catalyst support material with a higher surface to volume ratio was used in a single catalyst bed of SA 5503 rings which had been impregnated with 10 weight percent nickel. As may be seen in Table 2, hydrogen purities of nearly 90 percent were obtained several times during 11 hours of operation, but at the end of the series, bed volume was only one half of that loaded.

Once again, damage was such that fragments of catalyst particles and support were entrained in regeneration gases. Higher activity was apparent, but catalyst integrity was not maintained.

A candidate material for replacement of BA 307 was evaluated in the next series of runs. Denstone 57 was impregnated with one percent nickel and used as the bottom layer in the catalyst bed. SA 5503 rings with about 10 percent nickel were used as the upper portion of the bed. Acceptable hydrogen purity, as shown in Table 3, was obtained with JP-4 but not with hexane, which was the lightest hydrocarbon conveniently available. Significant damage occurred to the rings but apparently no damage to the Denstone 57.

A second run with Denstone was aborted when reactor and furnace burnout occurred during the first regeneration. For this series, which was the first in which diesel fuel (No. 1) was used, limited data was available, and is presented in Table 4.

Fresh samples of low nickel/BA 307 and high nickel/SA 5203 catalyst were loaded for the next series of runs. Diesel fuel (No. 1) was fed for a total of 25 cycles. Hydrogen purity of 82 percent was obtained during the first day's operation, but increasing pressure drop was noted as shown in Table 5. When the reactor was opened, only 30 percent of the high nickel catalyst remained.

In the next series, which may be seen in Table 6, a mixture of low nickel/ BA 307 and high nickel/SA 5203 catalyst was used. This mixed bed was preceded by a layer of low nickel on BA 307 and followed by a layer of nickel on SA 5203. This configuration was used to minimize and contain damaged catalyst . About 60 percent of the SA 5203 catalyst was lost in 22 cycles.

In order to increase the physical strength of high nickel catalyst particles, a heat treating operation was carried out. This heat treating caused formation of nickel aluminate from the nickel oxide and alumina present. This spinel structure-$NiAl_2O_4$-is quite strong and heat treated catalyst did hold up better, however, hydrogen purities were quite low as Table 7 indicates. This is presumed to be because nickel is tied up as a compound and is no longer catalytically active for hydrocarbon cracking reactions. During this series of runs, the reactor was opened several times. Damage was minimal at first, but as increased temperatures and

higher hydrogen purities were reached, more damage began to occur. Acceptable purity was obtained rarely. Ultimately, nearly one third of the heat treated catalyst was lost in 80 cycles of operation.

A similiar heat treating step was carried out with high nickel/SA 5503 ring catalyst. Two-thirds-loss of catalyst occurred while acceptable hydrogen purity was only occassionally attained during 71 cycles of operation. These results may be seen in Table 8.

A series of runs in which a combination of new and used heat treated rings was tried. Hopes were that nickel on used catalyst was "activated". Results were disappointing, as apparent in Table 9, hydrogen purity was still not acceptable and nearly 10 percent of the catalyst was lost in 26 cycles.

A series of experiments, summarized in Table 10, aimed at characterizing performance of heat treated catalyst was tried next. At lower temperatures with fresh materials hydrogen purity was low. As time on stream was accumulated and higher temperatures used, purity improved, but never exceeded 80 percent. Once again, as hydrogen production, or activity, improved, degradation started and two percent of the high nickel catalyst was lost. Somewhat improved stability was apparent, but at the expense of activity.

A series of runs with heat treated high nickel on SA 5203 which had an additional 3.5 percent nickel added after heat treatment showed this nickel addition greatly improved activity, but once again severe degradation occurred. Hydrogen purity was acceptable, as seen in Table 11, but about one half the catalyst bed was lost in 30 cycles of operation.

A high-purity alumina-based catalyst was used in the next series of runs. A sample of methane reforming catalyst obtained from Katalco was used for seven cycles with diesel fuel (No. 1). Acceptable hydrogen purity was obtained at low fuel rates but dropped to 35 percent at high fuel feed rate as indicated in Table 12. Nearly 40 percent damage occurred during seven cycles of operation.

Studies of mixed bed performance were temporarily stopped at this point to allow evaluation of each separate material for stability and performance. The reactor was filled with low nickel/BA 307 catalyst and provisions made for internal as well as the usual external pre-heating. Fuel was burned with air below the bed support plate to provide a more uniform temperature profile, that is, to bring the inlet temperature up to a level such that the entire bed would be catalytically active. Most of the runs in this series were not well controlled, but hydrogen purity reached 80 percent prior to a reactor burnout. Table 13 contains these results. This indicated a single-catalyst bed with low nickel catalyst was adequate if maintained at high enough temperatures.

Single catalyst bed work was continued with internal heating. Hydrogen purity reached 89 percent in a shorter bed of low nickel catalyst during a run with temperatures more carefully adjusted and controlled. Once again, a single-catalyst bed was shown to be more than adequate. Results may be seen in Table 14. An attempt to monitor temperature profiles failed when insulation caused the thermocouple to stick in the 1/8 inch well which had been installed along the length of the bed.

A larger thermowell (1/4 inch o.d.) was installed for the next study. A shielded 1/8 inch thermocouple was placed in the well to allow temperature measurement throughout the length of the bed. To improve uniformity of profiles measured by this technique, additional insulation was added around the reactor bottom and inlet valves. Several experiments were conducted in this closely monitored bed. Hydrogen purity varied from 64 percent with bed temperatures 1250-1400°F to 71 percent with bed temperature of 1370-1400°F. These data are in Table 15.

The bench unit was loaded with 12 inches of low nickel on BA 307 catalyst. This was the first time that a multiple sampling technique was used to describe the entire gas generation portion of a cycle. Samples were taken and stored in glass sampling containers. Gas chromatographic cycle time limited on-line sampling, but many samples could be taken and subsequently analyzed to allow plotting of concentration versus cycle time. In the

first sampled cycle, shown in Figure 3, carbon dioxide was used to flush air out of the reactor before hydrogen generation started. Note the presence of two peaks for carbon dioxide: the first is residual CO_2 in the reactor and the second is from reduction of oxide sites on the catalysts. Figure 5 shows that cracking JP-4 may be much easier than cracking diesel fuel since the hydrogen peak maximum occurred much sooner. Table 16 contains data from these runs.

Uncoated high Al_2O_3 balls were loaded into the reactor. This support, was no nickel, provided a basis for comparison with other runs. Thermal cracking and catalytic effects from the stainless steel reactor wall produced hydrogen but with a large amount of contaminants. Brown liquid observed in the sample tubes was presumably water with soot and uncracked fuel. Hydrogen content dropped rapidly with time. Upon removal, the catalyst had a brown color similiar to that observed in liquid, probably due to oxidation of the reactor walls. See Table 17 for these results.

A bed of twelve inches of low nickel/BA 307 was weighed and loaded into the bench unit. Seven cycles were run before the bed was increased to 18 inches in height to evaluate effects of increase in catalyst volume on product purity. A decrease in C_2's resulted. Higher fuel rates were also tried on the longer bed and yielded approximately the same results as lower fuel rates on the smaller bed. After 11 cycles, the bed was removed. A 2.17 percent weight loss of catalyst was observed. Table 18 containes these results.

A weighed bed of 12 inches of low nickel/BA 307 catalyst was again loaded and operated at a slightly lower temperature (700°C) to see if damage occurred. These four runs are shown in Table 19. Hydrogen purity fell from over 85 percent during the first cycle, shown in figure 17, to less than 80 percent during the fourth cycle, shown in figure 20. A corresponding increase in C_2's was noted to nearly five percent. A six percent weight loss was noted after only four cycles. No apparent solution to catalyst damage problems was indicated by these changes in operating conditions.

At this point in time, emphasis was shifted to more fundamental studies (described in the following section) to characterize catalyst damage and

possible means to solve stability problems. Literature reviews, consultants evaluations, suggestions, and counseling led to preparation of more stable catalyst compositions.

The first trial with one of these "stabilized" compositions in the bench unit was a barium stabilized nickel impregnated catalyst on SA 5202 support. These spheres had more integrity, but activity was lower than non-stabilized nickel catalyst. Results are in Table 20.

This same impregnation of barium and nickel was tried on pure alumina rings. Activity was even lower than the previous batch, presumably due to channeling through the larger rings. See Table 21.

A new batch of catalyst was prepared - SA 5202 spheres were impregnated with barium nitrate instead of barium hydroxide. This led to higher levels of nickel and barium. Propane was used as fuel at a flow rate such that the same amount of hydrogen was produced as with JP-4. This provided a "cross check" with smaller scale experiments in which propane was used as fuel. No damage was observed and hydrogen concentrations were comparable. See Table 22.

VYCOR TUBE FURNACE EXPERIMENTS

Experimental work in the VYCOR tube furnace was planned to evaluate mechanisms of catalyst degradation with small samples. The smaller scale of these experiments allowed for better and more uniform temperature control. The use of a VYCOR tube removed uncertainties associated with the metal wall of the bench unit. The smaller scale also facilitated use of different gases and mixtures for stability studies. Repeated cycling was also facilitated, and in later experiments, use of the Cahn balance allowed continuous sample weight measurement during this cycling to observe changes caused by carbon deposition, carbon burn off, active metal oxidation and reduction, and physical losses of metal or substrate.

The ease of handling allowed by the smaller scale of these experiments also allowed evaluation of many more samples in a shorter time. Sample integrity could be maintained for subsequent microscopic evaluation, since it was not necessary to empty a large bed of catalyst as with the bench unit.

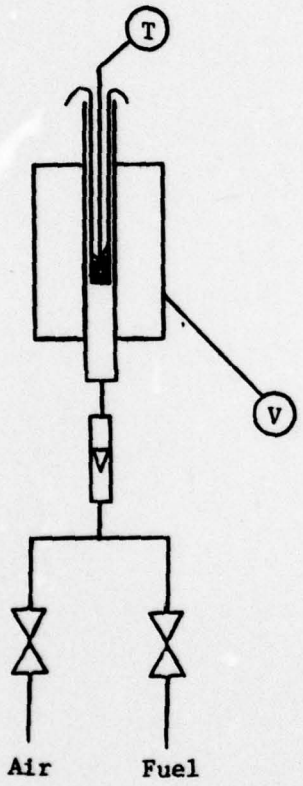
EQUIPMENT AND PROCEDURE

Small scale experiments were conducted by suspending samples in a VYCOR Tube which was enclosed in electric heating elements. In early experiments, catalyst samples were placed in a "basket" and temperatures measured with an optical pyrometer. Handling of samples and measurement of temperature proved to be somewhat difficult with these methods, but some useful results were obtained. Later the system was improved by the addition of a CAHN balance and other instrumentation. Schematic flow diagrams are shown in Figure 2.

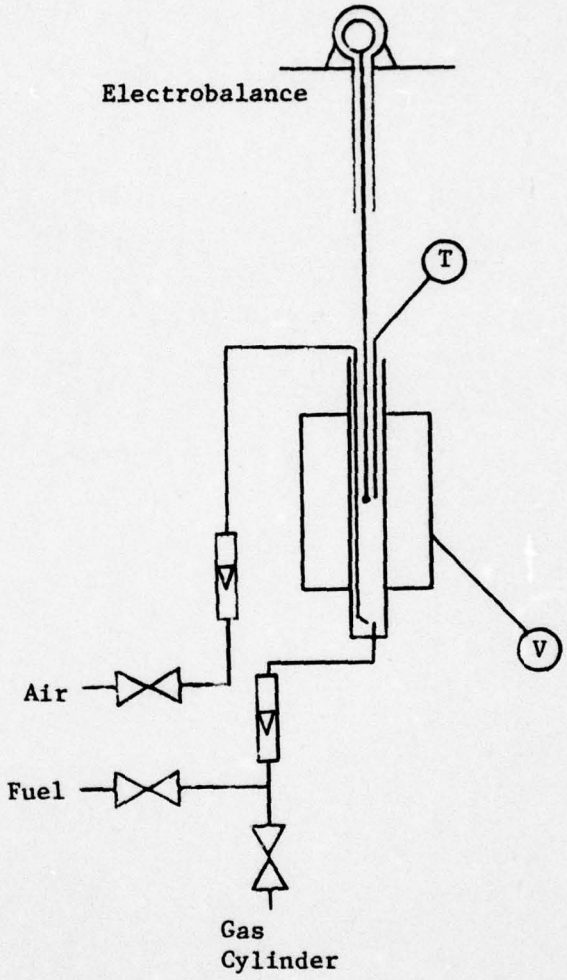
Fuel, usually propane, was admitted at the bottom of the tube. Regeneration air was also admitted at the bottom in early tests, but later stainless steel tubing which passed from the top to the bottom of the VYCOR tube was used as a pre-heater.

Figure 2

VYCOR TUBE UNIT



VYCOR TUBE UNIT WITH
CAHN BALANCE (T.G.A.)



T-Thermocouple

V-Variac

Flows of fuel and air were measured with rotameters. Samples were weighed before, after, and during experiments with the CAHN balance to determine weight changes.

VYCOR TUBE FURNANCE RESULTS

The Vycor tube furnace was usually operated by placing material to be evaluated on the support wires, allowing temperature to stabilize and then introducing a flow. Early experiments were conducted to evaluate possible mechanisms of degradation. Later, relative stabilities were evaluated as a function of time, temperature, and composition. A complete list of results is given in table 23.

The first proposed mechanism was hydrogen attack of the silica portion of SA 5203 catalyst support. Six hours in hydrogen at over 2000°F caused a slight greying of the white spheres, but no noticeable weight loss. This mechanism of damage was eliminated.

The possibility of damage due to high local temperature excursions was evaluated next by artificially impregnating particles with carbon black. This carbon was then burned off in air at over 1800°F. Once again, no noticeable weight loss or damage was observed.

Pure alumina rings which had been impregnated with nickel (Katalco 23-1 methane reforming catalyst) showed damage when exposed to propane gas/air cycles but no damage when exposed to hydrogen/air cycles. This damage was similar to that which had occurred in bench unit tests with vaporized liquid hydrocarbon fuels and justified use of propane as fuel for further small scale material evaluations. This allowed much simpler apparatus and operations than would have been necessary if liquid fuels were required to reproduce damage results seen in the bench unit.

Pure nickel metal balls showed no weight loss when exposed to hydrogen/air cycles at over 1650°F, although slight oxidation was evident.

Several tests were conducted with pressed pellets of powdered nickel, nickel oxide and mixtures of each with carbon. In hydrogen, no damage occured. In air, some dusting was evident with nickel and some damage occurred as carbon was burned from the mixed materials. Hydrocarbon/air cyclic exposure caused severe damage to both nickel and nickel oxide pellets and dusting of nickel balls.

All of these results indicated that damage was occurring during hydrocarbon cracking and not during regeneration. Further experimental work was carried out with several different hydrocarbon fuels. Operation with methane and air showed no apparent damage, while all other hydrocarbons caused damage to both pure alumina and SA 5203 based catalyst. Several tests were performed in which only hydrocarbon was fed to the catalyst bed. No visible damage was detected at short contact times (200 seconds) but at longer times (15 minutes) considerable damage was noted. Results of repeated cycling did indicate that even though damage was not detected in 200 seconds some must have occurred, as a cumulative effect was seen in later repeated cyclic runs.

Damage caused by cyclic hydrocarbon/air operation was demonstrated with several catalyst materials which contained nickel, including nickel on BA 307, nickel on SA 5203, nichrome wire and a new support from Norton, 06233 which had been impregnated with nickel. Catalyst materials without active nickel, BA 307/Pt, SA 5203/NoNi and SA 5203/Ni which had been heat treated to form $NiAl_2O_4$, did not show damage. These materials also did not give appreciable hydrogen concentrations under conditions of these tests.

Several ten-cycle runs were made with nickel on SA 5203 catalyst samples to characterize damage as a function of operating temperature. Start of run temperatures were varied from 1400°F to 1740°F while other operating parameters were constant. Damage ranged from less than one to over 10 percent as shown in Figure 23.

Several individual catalyst spheres were each exposed to hydrocarbon for different times. Each catalyst particle was suspended by a nichrome wire

in the hot zone of the VYCOR reactor. After the desired fuel exposure, particles were lowered out of the hot zone. Results ranged from a small weight gain with nickel on BA 307 to severe damage with nickel on SA 5203. X-ray microprobe analyses showed rapid nickel depletion on BA 307 and Denstone when treated in propane at 1470°F, but essentially no damage at 1290°F. See Table 26-28. No changes in surface composition were noted with SA 5203 catalyst, but damage was evident in that the spheres "shrank" as time progressed.

Methane was found to deposit carbon more slowly than propane at identical temperature. In a series of tests in which nickel on SA 5203 spheres which had carbon deposited for 300 seconds were held at temperature in nitrogen, initial carbon build-up was followed by a weight loss and carbon disappearance. These particular results are not fully understood.

The VYCOR tube reactor was adapted for thermogravimetric analyses (T.G.A.) by the addition of the CAHN micro-balance. The first runs of this kind were performed on BA 307. Practically all the balls lost weight, but more dramatic were changes in the surfaces of the balls. A yellowish-green fluffy powder of nickel oxide was present upon the removal of the balls. The powder had little integrity and no adhesion to the surface of the balls, although ball weight increases during fuel cycles still showed activity from carbon deposition.

A variety of other metals were then tried in T.G.A. tests. Unsupported cobalt metal was tried. Samples yielded lower carbon peaks, indicating less activity. Chromium and solid nickel balls were also tried with poor results. Lower apparent activity was thought to be due to low surface area of the solid metal compared to metal on a ceramic support, which provides much more surface area. Platinum was tried on the BA 307 support and also showed low activity.

Tighter controls were tried on the runs by trying to bring all the different catalyst types to the same state of oxide prior to a test. First, attempts were made to completely reducing the ball to pure metal by passing heated hydrogen over it. This attempt failed due to the hydrogen flame melting the support wire. Different support wires were tried but no practical means was found to hold the catalyst ball. The method then used was to try to have the catalyst in its oxide form when starting a run.

Runs were made on BA 307 in an effort to optimize cycle time and temperature such that minimum damage occurred. Runs were made at temperatures between 700 and 900°C and cycle times from 100 to 500 seconds. Results showed that only at low temperatures and short fuel contact times would damage be low, but hydrogen production would also be low.

A cobalt catalyst was tried in the form of SA 5202 balls coated with cobalt nitrate which was heated to form cobalt oxide. Again, a temperature-time damage distribution was obtained showing results similar to BA 307. Nickel treated SA 5202 was also tried for a direct comparison to the cobalt balls and cobalt was applied to a stripped BA 307 substrate. Damage occurred to all samples.

A very non-porous catalyst, *Denstone* 57 was then tried to test the hypothesis that a non-porous catalyst would suffer less damage. Damage still occurred at all temperatures tried.

Several catalyst prepared by a consultant, C.H. Bartholomew, were examined. These catalyst were in matched pairs to see the results of adding platinum to stabilize a nickel catalyst. Damage occurred on most samples--results were somewhat inconclusive, but indicated no outstanding improvement in stability. These results may be seen in Table 25.

A barium stabilized nickel catalyst was then tried. Initial weight change results did not look encouraging, but there was a great improvement in surface integrity. Additional batches were made varying the procedure slightly each time. Analytical results of metal content for some of these "developmental" catalysts are shown in Table 29.

In one test, 40 fuel/air cycles resulted in only one quarter of one percent weight loss with a barium stabilized nickel on alumina composition. This remarkable improvement in stability led to trial of a similiar composition in bench unit tests and use of this composition in the breadboard unit.

IV

EQUIPMENT DESIGN WORK

A preliminary prototype design was prepared during the proposal stages of this contract work. This design was based on best available information at that time and was refined somewhat during the first months of the contract. A summary of some supporting calculations for this preliminary design is given in Appendix C and includes estimated heat balances, mass balances, and flow requirements for heat-up and operation. Plans were to finalize and optimize design parameters during the period of contract work.

When problems with catalyst stability became evident, design work was stopped in order to concentrate efforts on catalyst development. When an improved catalyst composition was developed, design work was resumed, but sufficient time did not remain to allow for refinement of design concepts.

As a result of these circumstances, the current "breadboard" of the prototype incorporates some of these concepts in a "preliminary" form. Assembly drawings of the breadboard unit are shown in Figures 24, 25 and 25, and pictures in Figures 27 and 28. The reactor or process portion of the breadboard is approximately as envisioned for a prototype, but the heat exchange and heat-up section is still more of a developmental entity. As such, considerable refinement of component designs should be possible and some of the goals set for the prototype have not been met, e.g., weight and size. Once operability of the design features is established, further refinements can be made to more nearly approach desired characteristics as listed in the purchase description.

V

CONCLUSIONS

Development work on catalyst materials and equipment for thermo-catalytic cracking of hydrocarbon fuels to produce hydrogen for fuel cell use has resulted in some improvement of catalyst stability. A "breadboard" unit has been constructed to utilize this new catalyst composition in a dual reactor system which will be evaluated for process concept and equipment viability. Further design refinements will then be possible to enable attainment of equipment goals such as size, weight, etc.

VI

RECOMMENDATIONS

Further work should be carried out to evaluate "breadboard" unit and catalyst for stability, operability and overall performance. If "breadboard" evaluations are satisfactory, design refinements should be undertaken to adapt components for prototype unit and catalyst life should be evaluated.

VII

EVALUATION OF EQUIPMENT

Operation of the breadboard unit will be described in a "Test and Demonstration Report" to be written after testing is carried out.

Detailed drawings are available as "Engineering Data for Research and Prototype Hardware"

Photographs of the breadboard unit are available as "Still Photographic Records".

Each of these items is a separate data requirement of Contract Number DAAG53-76-C-0081.

Table 1 SUMMARY OF BA307 , LOW NICKEL SPHER

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#2	1	22	8	1100	1150	-	20	840	1250	-
				1100	1160	-		1120	>1800	-
D#2	2	22	12.5	1130	1310	-	19	1050	1400	-
				1250	1640	-		1225	1725	-
JP4	2	34.3	13	1080	1160	1515	13	1080	1505	1515
				1200	1505	>1800		1140	1560	1725
D#2	1	22	5	1200	1365	1375	24	925	1285	1050
				1275	1640	1400		1255	1840	1540
D#2	3	22	19	950	990	1125	25	950	1050	1120
				1130	1225	1725		1140	1460	1725
JP4	2	34.4	10	950	1035	1015	14	910	990	1100
				1140	1600	1630		1140	1525	>1800
D#2	2	22	7	980	1210	1460	13	1050	1145	1550
				1125	1590	>1800		1140	1415	1810
JP4	3	34.3	10	900	1015	950	15	900	1235	950
				1030	1600	1330		1050	1690	1480
D#2	4	22	14	970	1375	1425	27	990	1330	1520
				1160	1420	>1800		1160	1940	>1800

[1]Bed loading was used BA307 and SA5203 obtained from MERADCOM.

[2]Tube sample.

When the bed was opened to evaluate catalyst condition, large portion of catalyst particles and dust were evident. Bed volume had decreased by 20

JP4 fuel was fed to the bed so that regeneration could be used for heat u major concerns were 1) heating the bed up rapidly, 2) obtaining a high en

le 1 SUMMARY OF BA307/SA5203 RESULTS [1]
, LOW NICKEL SPHERES/HIGH NICKEL SPHERES

EGENE-RATION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN	MAJOR COMPONENTS (%)					
					H_2	CH_4	CO	C_2H_4	C_2H_6	ΔP
Total min	Inlet	4"	Top	Fuel Cycle Only	Range	Range	Range	Range	Range	Range in H_2O
20	840	1250	-	1	55.4	28.2	0.4	5.0	3.1	-
	1120	>1800	-		55.4	28.2	0.4	5.0	3.1	-
19	1050	1400	-	4	53.2	5.0	1.3	.3	.1	-
	1225	1725	-		65.4	26.7	12.9	7.6	1.0	-
13	1080	1505	1515	3	45.4[1]	2.4	.1			-
	1140	1560	1725		74.9	11.3	6.1			-
24	925	1285	1050	3	43.5	21.5	.8	8.0	1.2	-
	1255	1840	1540		55.9	25.5	1.4	11.9	2.2	-
25	950	1050	1120	5	28.2	13.2	.3	1.5	1.2	-
	1140	1460	1725		78.0	25.8	1.7	13.5	5.5	-
14	910	990	1100	-						-
	1140	1525	>1800							-
13	1050	1145	1550	3	34.9[1]	26.6	.5	6.2	1.8	-
	1140	1415	1810		52.7	27.0	2.5	10.2	3.4	-
15	900	1235	950	-						-
	1050	1690	1480							-
27	990	1330	1520	3	38.4[1]	6.0	2.1			-
	1160	1940	>1800		77.8	10.9	9.9			-

from MERADCOM.

dition, large portion of the SA5203 spheres were spalled, small
olume had decreased by 20-30%.

could be used for heat up. During this run, the
y, 2) obtaining a high enough bed temperature to get improved H_2 production.

Table 2 SUMMARY OF
HIGH NICKEL

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
JP4	3	34.3	13	755	1040	750[1]	37	750	1440	750[1]
				915	1440	1010		900	1710	>1800
D#2	3	22	6	870	1250	-	36	845	1250	-
				925	1325	-		865	1910	-
D#2	3	22	14	1070	1200	1180	30	1250	1260	1180
				1275	2175	1750		1335	2000	>1800
D#2	4	22	18	880	1175	1140	24	1075	1120	1425
				1150	2250	>1800		1160	1880	>1800
HEX	3	58	12	900	900	1080	50	990	1260	1080
				1075	1220	1500		1160	2005	>1800
HEX	3	58	12	1025	1175	990	41	1075	965	990
				1250	1485	1590		1270	1635	>1800
JP4	1	34.3	5	995	1415	1350	12	995	1440	1460
				1200	-	1500		1290	-	>1800
JP5	1		3	1010	1120	1330	10	1010	1280	1060
				1100	1200	-		1210	1620	>1800

Table 2 SUMMARY OF SA5503 RESULTS
HIGH NICKEL RINGS

GENE-TION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN	MAJOR COMPONENTS (%)					
					H_2	CH_4	CO	C_2H_4	C_2H_6	ΔP
tal In	Inlet	4"	Top	Fuel Cycle Only	Range	Range	Range	Range	Range	Range in H_2O
7	750	1440	750[1]	-	-	-	-	-	-	-
	900	1710	>1800		-	-	-	-	-	-
6	845	1250	-	-	-	-	-	-	-	-
	865	1910	-		-	-	-	-	-	-
0	1250	1260	1180	2	-	-	-	-	-	-
	1335	2000	>1800		-	-	-	-	-	-
4	1075	1120	1425	1	73.1	9.4	0.6	-	-	-
	1160	1880	>1800		73.1	9.4	0.6	-	-	-
0	990	1260	1080	2	71.3	11.4	-	-	-	-
	1160	2005	>1800		73.2	14.9	-	-	-	-
1	1075	965	990	2	72.1	6.4	.3	-	-	6
	1270	1635	>1800		80.3	11.4	2.7	-	-	14
2	995	1440	1460	2	83.5	1.9	.2	-	-	-
	1290	-	>1800		83.8	8.1	4.6	-	-	-
0	1010	1280	1060	-	-	-	-	-	-	5
	1210	1620	>1800		-	-	-	-	-	-

Table 2 (cont.) SUMMARY OF S
HIGH NICKEL

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top	N F
JP4	2	34.3	8	1040	1100	1360	23	1135	1335	1200	
				1260	1180	1700		1310	1750	>1800	
D#2	1	22	5	1130	1330	1560	15	1120	1340	1385	
				1220	1350	1690		1220	1685	1660	
D#2	2	22	6	950	1100	950	22	1030	1075	900	
				1120	1350	1330		1170	1840	1635	
JP4	4	34.3	17	885	990	840	45	905	1110	865	
				1200	1400	1680		1225	2010	1680	
D#2	4	22	20	1040	1225	1255	41	1050	1200	1285	
				1335	1420	1680		1210	1835	1725	
D#2	12	22	50	825	1075	820	81	925	1310	990	
				1260	1680	1685		1265	2220	1825	
D#2	4	22	16	970	1200	1050	25	1015	1160	1050	
				1160	1700	1440		1180	1910	1530	

[1]Top Thermocouple inoperative after first regeneration.

The bed was repacked with SA5503 rings which had been impregnated with 10% N
Diesel #2 fuel. Again JP4 was used with Air/CO_2 mix to bring the bed up to
to withstand thermal stresses better, after the 11.6 hours of operating time
decreased by about 1/2.

2 (cont.) SUMMARY OF SA5503 RESULTS
HIGH NICKEL RINGS

ENE-TION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN	H_2	CH_4	CO	C_2H_4	C_2H_6	ΔP
al in	Inlet	4"	Top	Fuel Cycle Only	Range	Range	Range	Range	Range	Range in H_2O
3	1135	1335	1200	2	84.1	6.9	.3	-	-	2
	1310	1750	>1800		86.9	7.5	.7	-	-	14
5	1120	1340	1385	2	84.5	2.7	.9	-	-	6
	1220	1685	1660		88.4	5.4	1.8	-	-	8
2	1030	1075	900	-	-	-	-	-	-	-
	1170	1840	1635		-	-	-	-	-	-
5	905	1110	865	3	74.6	6.0	0.4	2.6	-	-
	1225	2010	1680		88.2	15.0	2.1	6.2	-	-
1	1050	1200	1285	2	80.5	4.3	5.3	-	-	5
	1210	1835	1725		85.5	6.3	7.5	-	-	15
1	925	1310	990	2	74.7	3.7	5.3	-	-	-
	1265	2220	1825		76.4	18.3	15.1	-	-	-
5	1015	1160	1050	-	-	-	-	-	-	-
	1180	1910	1530		-	-	-	-	-	-

ion.

n impregnated with 10% Ni. Good H_2 production was obtained from
to bring the bed up to operating temperature. Although the rings were expected
hours of operating time, they were also found spalled and the bed volume had

Table 3 SUMMARY OF DENSTO
LOW NICKEL SPHER

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
HEX	5	58	16	950	1005	860	67	990	995	1035
				1120	1100	1660	-	1170	1120	1800
HEX	4	58	16	-	-	-	64	-	-	-
				-	-	-	-	-	-	-
JP4	6	34.3	23	990	-	935	95	950	950	1035
				1250	-	1615	-	1280	1280	2025

[1]28 in H_2O at end of final cycle.

Catalyst charged to the reactor was 4½-5" of Denstone 57[R] (1% Ni), covering
originally packed 1" from the top with catalyst, upon opening on 8/3/76, aft
2½"-3" below the top. Catalyst degradation and loss was apparent.

Initially, the catalyst was treated with hydrogen, 4 H_2-air cycles covering
to reduce and stabilize the catalyst entirely before start-up.

Table 4 SUMMARY OF DENSTONE 5
LOW NICKEL SPHERES/HI

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
Hydrogen Treatment of catalyst bed. 2 air-H_2 cycles were run total time 7										
D#1	2	32.6	9	925	1050	1015	33	940	1045	1030
				1080	1220	1590	-	1165	1310	>1800

The experimental bed was charged with 5" of Denstone 57[R] (1% Ni) and cover
12% Ni. Only two cycles were run because the Stainless Steel tube was melt
had melted.

3 SUMMARY OF DENSTONE 57/SA5503 RESULTS
LOW NICKEL SPHERES/HIGH NICKEL RINGS

TEMPERATURE REGENERATION			NO.OF G.C. TAKEN	MAJOR COMPONENTS (%)					
				H_2	CH_4	CO	C_2H_4	C_2H_6	ΔP
Inlet	4"	Top	Fuel Cycle Only	Range	Range	Range	Range	Range	Range in H_2O
990	995	1035	2	73.6	10.8	.4	2.5	.4	5
1170	1120	1800	-	77.6	14.8	.7	6.1	.9	20
-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-
950	950	1035	2	84.4	7.6	.3	-	-	9
1280	1280	2025	-	89.5	9.0	.8	-	-	28[1]

57^R (1% Ni), covering the T.C. which is 4" up. Though the bed was opening on 8/3/76, after 4.6 hours of run the bed top was found was apparent.

H_2-air cycles covering a period of 104 min were run. Purpose was start-up.

SUMMARY OF DENSTONE 57/SA5203 RESULTS
LOW NICKEL SPHERES/HIGH NICKEL SPHERES

TEMPERATURE REGENERATION			NO. OF G.C. TAKEN	H_2	CH_4	CO	C_2H_4	C_2H_6	ΔP
Inlet	4"	Top	Fuel Cycle Only	Range	Range	Range	Range	Range	Range in H_2O
were run total time 77 min.									
940	1045	1030	-	-	-	-	-	-	-
1165	1310	>1800	-	-	-	-	-	-	-

57^R (1% Ni) and covered with 13½" of SA5203 balls with balls with ss Steel tube was melted in specific areas, also the heater wires

Table 5 SUMMARY OF BA307/

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
Newly packed bed was treated with hydrogen. 3 Air-H_2 cycles were run takin										
D#1	3	32.6	12	1150	1085	1300	45	1125	1190	1275
				1250	1320	1710		1245	2140	>1800
D#1	5	32.6	15	970	1025	1250	70	870	980	1235
				1215	1225	1735		1190	1480	>1800
D#1	4	32.6	12	865	990	1220	37	770	865	1180
				1100	1160	1600		1060	1310	1950
D#1	7	32.6	25	835	975	1435	41	835	1015	1035
				950	1000	1800		960	1220	2010
D#1	6	32.6	22	900	975	1185	30½	885	1025	1375
				1100	1210	1660		1085	1350	1835

The first 2" of catalyst at the bed entrance was BA307 with the remaining
to about 900°F and pure H_2 was passed through the bed to reduce the catalys
subsequently noted that the catalyst bed was not performing well, produc
than cracking. On 9/30/76 the experimental bed was cooled and disassemble
the bed was empty. Serious deterioration of SA5203 catalyst was apparent.

Table 6 SUMMARY OF BA307/BA3

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	To
D#1		32.6	15	1075	1115	1650	53.5	1065	1075	150
				1150	1180	1890		1120	1180	175
D#1	8 (6)	32.6	33.5	925	1040	1290	65.5	940	985	104
	(2)	13.0		1225	1285	1560		1225	1285	175
D#1	3	13.0	22½	1160	1420	1125	41	1065	1375	140
				1290	1650	1725		1255	1580	172
D#1	7 (3)	32.6	37	1060	1140	1525	85	1100	1160	120
	(4)	13.0		1250	1320	1770		1230	1310	178

The bed was packed on 10/6/76 with BA307 (1% Ni) for the first 4½" above
(equal volume) containing BA307 and SA5203. The final portion of the bed
run the bed was opened and discharged noting that a number of fueling per
58% of the high Ni catalyst was lost.

e 5 SUMMARY OF BA307/SA5203 RESULTS

ENE-TION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN						
tal in	Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
l2 cycles were run taking 46 min.										
5	1125	1190	1275	-	-	-	-	-	-	-
	1245	2140	>1800		-	-	-	-	-	-
0	870	980	1235	1	82.1	5.0	2.0	-	-	-
	1190	1480	>1800		82.1	5.0	2.0	-	-	12
7	770	865	1180	1	77.8	8.1	2.7	-	-	11
	1060	1310	1950		77.8	8.1	2.7	-	-	28
1	835	1015	1035	1	71.8	4.5	6.7	-	-	6.7
	960	1220	2010		71.8	4.5	6.7	-	-	22[1]
0½	885	1025	1375	1	79.6	10.4	2.3	2.7	.8	8
	1085	1350	1835		79.6	10.4	2.3	2.7	.8	22[1]

307 with the remaining 15 1/4" being SA5203. The bed was first heated
ed to reduce the catalyst. 25 cycles of kerosene were run. It was
performing well, product gas was more the result of a thermal degradation
cooled and disassembled for inspection of the catalyst. The top 10" of
catalyst was apparent.

SUMMARY OF BA307/BA307-SA5203/SA5203 RESULTS

GENE-ATION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN						
otal in	Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range in H_2O
53.5	1065	1075	1500	2	72.6	15.7	0	.5	.7	8
	1120	1180	1750		78.0	22.8	2.3	1.9	1.5	13
55.5	940	985	1045	2	G.C. were analyzed incorrectly					5
	1225	1285	1750		-	-	-	-	-	5
61	1065	1375	1400	2	76.0	12.4	.7	-	-	18
	1255	1580	1725		84.4	15.3	5.3	-	-	>24
35	1100	1160	1200	4	34.6	2.6	1.5	-	-	6
	1230	1310	1780		82.9	19.8	5.3	-	-	14

r the first 4½" above the fuel entrance. The next 9" was a homogenous mixture
nal portion of the bed contained 4½" of SA5203. After ?? cycles of fuel were
number of fueling periods were 7-8 minutes long. It was discovered that

Table 7 SUMMARY OF BA307/SA5203HT LOW NICKEL SPHERES/$NiAl_2O$ NICKEL SPHERES

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	6	(1)32.6	38	960	1050	1425	73	920	1045	1500
		(5)13.0		1230	1625	1800		1185	1625	1820
D#1	4	13.0	36	1090	1150	1230	40½	1040	1120	1230
		-		1180	1215	1355		1180	1230	1355
D#1	10	13.0	62.5	1170	1225	1515	102½	1170	1250	1515
		-		1420	1730	1700		1220	1620	1800

Reactor was disassembled because the pressure drop during regeneration was on the catalysts spheres. All the spheres appeared to be intact. The bed bed height was 1/2" lower than upon charging. The run was continued with

Table 7 (cont.)

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	6	(2)32.6	28	990	1140	1380	30	910	1080	1390
		(4)13.0		1110	1200	1765		1100	1335	1870
D#1	8	(1)13.0	24	925	915	1440	35	910	1045	1500
		(7)32.6		1080	1280	1675		1090	1250	1850
D#1	5	(2)13.0	15	970	1120	1290	23	880	1120	1315
		(3)32.6		1040	1165	1485		1030	1190	2130
D#1	11	(7)32.6	40.5	960	1075	1210	50.5	950	1050	1600
		(4)13.0		1200	1420	1750		1035	1530	1935

The catalyst bed was opened, the bed height was found 2" below the origi of which 3.6% was dust. The bed was recharged with the same catalyst re

MARY OF BA307/SA5203HT/BA307 RESULTS
NICKEL SPHERES/$NiAl_2O_4$ SPHERES/ LOW
CKEL SPHERES

ME-ION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN						
l	Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range in H_2O
	920	1045	1500	6	49.6	23.0	5.5	1.1	.3	4.4
	1185	1625	1820		69.1	36.7	5.5	9.7	1.4	5.4
½	1040	1120	1230	2	10.6	24.0	-	17.4	5.8	3.6
	1180	1230	1355		11.2	28.1	-	20.7	7.7	3.8
½	1170	1250	1515	6	56.7	12.3	4.1	.1	-	4.3
	1220	1620	1800		75.1	30.9	6.9	6.9	-	7.2

during regeneration was increasing. This problem was due to carbon build-up
to be intact. The bed weight had increased by 8% due to the build up. The
run was continued with the same charge.

Table 7 (cont.)

ENE-TION	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN						
tal In	Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range in H_2O
30	910	1080	1390	3	32.0	7.1	2.4	18.4	3.1	3.5
	1100	1335	1870		82.2	33.4	9.2	18.4	3.1	5.7
35	910	1045	1500	2	70.6	11.5	9.20	-	-	4.5
	1090	1250	1850		74.9	25.3	9.20	-	-	5.0
23	880	1120	1315	-	-	-	-	-	-	3.0
	1030	1190	2130		-	-	-	-	-	7.6
50.5	950	1050	1600	2	78.5	6.9	11.8	-	-	4.2
	1035	1530	1935		86.2	11.6	11.8	-	-	6.6

nd 2" below the original charge height. The total charge weight was recovered
the same catalyst removed.

Table 7 (cont.)

Fuel Type	FUEL No. of Cycles	Feed Rate cc/min	Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top	NO Fu
D#1	13	(12)13.0	45	900	1010	1180	56.5	870	1095	1380	
		(1)32.6		1075	1160	1635		1055	1160	2100	
D#1	17	13	67½	865	970	1290	90	750	990	1120	
				1050	1120	1760		1040	1150	2200	

After 6 hrs. of operation the spheres still appeared whole, though after 14 ho
30% weight loss and extensive degradation.
Heat treated balls (blue balls) - Work had been done to improve the strength o
to 2700°F for 4 hours. This treatment was to improve the catalyst strength.
and no NiO remained. Initially the bed was charged with 3" of BA307 catalyst
treated SA5203, topped off by another 2" of BA307 catalyst.

Table 8 SUMMARY OF BA307/SA5503HT/BA3

Fuel Type	FUEL No. of Cycles	Feed Rate cc/min	Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top	NO Fu
D#1	16	(3)23.0	56½	950	1080	1360	67	1050	1120	1440	
		(13)13.0		1165	1500	1965		1165	1250	1880	
D#1	10	13.0	41	985	1080	1450	47	1015	1080	1485	
				1135	1230	1940		1140	1245	1940	
D#1	6	13.0	22	1060	1145	1420	31½	1050	1155	1285	
				1125	1195	1500		1125	1210	1785	
D#1	17	13.0	74	1040	1250	-	79½	1080	1320	-	
				1180	1465	-		1205	1550	-	
D#1	6	13.0	24	950	1070	-	26½	930	1035	-	
				1080	1220	-		1035	1290	-	
D#1	16		64½	950	995	-	72½	960	985	-	
				1035	1085	-		1045	1120	-	

The experimental bed was charged with heat treated SA5503 rings and nickel co
that 550g supported the rings and 295g were placed on top to prevent the loss
run over a period of 10 hours. The bed was evaluated after the 55th and 71st
6% HiNi rings had deteriorated. This weight loss was reclaimed as dust. The
a configuration similar to the original. After the 71st cycle the bed was op

Table 7 (cont.)

E- N	TEMPERATURE REGENERATION			NO.OF G.C. TAKEN						
	Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range in H_2O
5	870	1095	1380	4	71.2	19.5	-	-	-	1.8
	1055	1160	2100		76.2	22.6	-	-	-	6.6
	750	990	1120	6	58.3	17.6	-	-	-	3.0
	1040	1150	2200	-	-	-	-	-	-	6.0

whole, though after 14 hours of run even the heat treated 5203 balls showed

to improve the strength of Ni coated 5203 catalyst. The catalyst was heated
e the catalyst strength. X-ray analysis showed that $NiAl_2O_4$ had formed and
with 3" of BA307 catalyst at the fuel entrance covered by 9 1/4" of heat
talyst.

ARY OF BA307/SA5503HT/BA307 RESULTS

E- N	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
	Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range in H_2O
	1050	1120	1440	5	62.6	20.2	-	-	-	4.2
	1165	1250	1880		76.1	29.0	-	-	-	6.9
	1015	1080	1485	5	69.8	18.0	-	-	-	6.4
	1140	1245	1940		79.2	24.0	-	-	-	8.3
	1050	1155	1285	2	73.1	17.7	-	-	-	6.6
	1125	1210	1785		79.5	21.8	-	-	-	9.5
	1080	1320	-	6	55.9	6.4	-	-	-	5.0
	1205	1550	-		90.3	22.1	-	-	-	7.4
	930	1035	-	3	72.2	13.0	-	-	-	2.0
	1035	1290	-		82.8	21.3	-	-	-	15.4
	960	985	-	6	63.0	14.6	-	-	-	5.1
	1045	1120	-		81.8	32.0	-	-	-	18.5

5503 rings and nickel coated BA307 spheres. The BA307 catalyst was divided such
top to prevent the loss of any ring fragments during operation. 71 cycles were
after the 55th and 71st cycles. After the 55th cycle the 1% LoNi BA307 and
reclaimed as dust. The intact catalyst particles were returned to the bed in
1st cycle the bed was opened and the catalyst removed. 67.4% of NiHi rings were lost.

Table 9 SUMMARY OF BA307/SA5503HT (N

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	26	-	78	-	-	-	78	-	-	-

The bed was recharged with 3" LoNi BA307 at the entrance, covered with 11 1/
and finally by 2" LoNi BA307. The bed was run for 2 1/2 hrs and then discha
were lost.

Table 10 SUMMARY OF BA307/SA5203H

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	52	12	156	-	-	-	156	-	-	-

The experimental bed was loaded with LoNi BA307 at the fuel entrance, heat
A total of 52 - 6 min fuel on-off cycles were run, with the bed being exami
was intact. After 52 cycles bed examination showed that about 1% of the B
the first 14 cycles the bed was operated between 1000 -1800°F with H_2 purity
run at 1050-1900°F, with improved H_2 purity ranging from 60-78% for the la

Table 11 SUMMARY OF BA307/SA5

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	13	(5) 32.6 (8) 13	39	-	-	-	39	-	-	-
D#1	17	12	51	-	-	-	51	-	-	-

Bed was charged on 1/28/77 with LoNi BA307 at fuel entrance covered with
and topped off with LoNi BA307. 30 cycles were run, the bed was examined
showed 0.95% weight loss of BA307 and 52% weight loss of SA5203 balls.

Y OF BA307/SA5503HT (NEW & USED)/BA307 RESULTS

- TEMPERATURE REGENERATION			NO.OF G.C. TAKEN						
Inlet	4"	Top	Fuel Cycle Only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range in H_2O
-	-	-	7	52.1 78.5	16.8 29.8	-	-	<	-

nce, covered with 11 1/4" new, 2 1/2" old SA5503 heat treated rings
i/2 hrs and then discharged. 9.3% of the HiNi heat treated rings (SA5503)

UMMARY OF BA307/SA5203HT/BA307 RESULTS - SECOND LOADING

GENE- TION	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
tal in	Inlet	4"	Top	Fuel Cycle only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
156	-	-	-	10	1.3 45.0	3.8 46.1	- -	.3 20.0	3.2 11.5	- -
				12	30.2 77.8	11.6 28.0	- -	1.7 13.5	- -	- -

he fuel entrance, heat treated SA5203 spheres, and topped off with LoNi BA307.
ith the bed being examined after 14 cycles -- finding that the catalyst still
that about 1% of the BA307 and 2% of the heat treated SA5203 were lost. During
00 -1800°F with H_2 purity ranging from 1.3- 36% . The remaining 38 cycles were
from 60-78% for the last 20 cycles.

1 SUMMARY OF BA307/SA5203HT+Ni/BA307 RESULTS

GENE- TION	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
tal in	Inlet	4"	Top	Fuel Cycle only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
39	-	-	-	5	76.0 81.2	8.2 16.5	-	-	-	-
51	-	-	-	3	82.9 88.7	10.3 12.0				

entrance covered with heat treated HiNi 5203 which was re-impregnated with 3.5% Ni
, the bed was examined and found to be 5½" below its initial loading point. Weighing
ss of SA5203 balls.

Table 12 Sum. of Methane
α Al_2O_3

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	6	12	50	-	-	-	87	-	-	-

The experimental bed was loaded with c[illegible]cial methane reforming catalyst
of run time. The bed was opened 38.7% of the high Ni catalyst had been lo

Table 13 SUMMARY OF BA307 RESU
INTERNAL AND EXTERNAL

Fuel Type	No. of Cycles	FUEL Feed Rate cc/min	FUEL Total min	TEMPERATURE OF FUEL PROFILE Inlet	4"	Top	REGENERATION Total min	TEMPERATURE REGENERATION Inlet	4"	Top
D#1	1	12	5	1500	-	1400				
				>1800	-	1500				
D#1	3	12	24	1250	-	1100	26	750	-	108
				1750	-	1400		1750	-	150
D#1	1	12	11	1400	-	1600				
					-	>1800				

Reactor burned out on regeneration cycle. No record of catalyst conditio
Loading was all BA307 low nickel spheres. Heating was partially by fuel

le 12 Sum. of Methane Reforming Catalyst Nickel/Pure α Al_2O_3

NE-ION	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
l	Inlet	4"	Top	Fuel Cycle only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
	-	-	-	5	80.0	1.8	-	-	-	-
					90.1	12.7	-	-	-	-
					34.8			9.62	2.9	

ne reforming catalyst and run for 7 cycles of fuel-air totaling about 2¼ hours
l catalyst had been lost.

SUMMARY OF BA307 RESULTS
INTERNAL AND EXTERNAL HEATING

NE-ION	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
l n	Inlet	4"	Top	Fuel Cycle only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
	750	-	1080	3	27.3	.8	1.2	-	-	-
	1750	-	1500		73.8	20.8	2.6	-	-	-

of catalyst condition. Reactor was rebuilt and reloaded.
as partially by fuel burning at inlet.

Table 14 SUMMARY OF B
SECOND LOADI
AND EXTERNAL

		FUEL		TEMPERATURE OF FUEL PROFILE			REGENE-RATION	TEMPERATURE REGENERATIO		
Fuel Type	No. of Cycles	Feed Rate cc/min	Total min	Inlet	4"	Top	Total min	Inlet	4"	T
D#1	2	11	7	1600	-	1350	21	1200	-	13
			7	1660	-	1460	21	1600	-	14

Loading was 12" BA307 low nickel catalyst. Heating was partially by bu

Table 15 SUMMARY OF BA307
TEMPERATURE P

		FUEL		TEMPERATURE OF FUEL PROFILE			REGENE-RATION	TEMPERATURE REGENERATIO		
Fuel Type	No. of Cycles	Feed Rate cc/min	Total min	Inlet	4"	Top	Total min	Inlet	4"	T
D#1	1	11	3	1373	-	1412	9	1400	-	>1
	1	11	6	1255	-	1410	16	1250	-	>1

Loading was 12" BA307 low nickel catalyst. Thermowell was fitted throu
profile measurement.

able 14 SUMMARY OF BA307 RESULTS
SECOND LOADING WITH INTERNAL
AND EXTERNAL HEATING

EGENE-ATION	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
Total min	Inlet	4"	Top	Fuel Cycle only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
21	1200	-	1300	2	80.4	4.1	6.7	.1	.1	1.0
21	1600	-	1400		89.0	5.8	7.8	4.1	1.9	-

g was partially by burning of fuel at reactor inlet.

15 SUMMARY OF BA307 RESULTS LOWER
TEMPERATURE PERFORMANCE

EGENE-ATION	TEMPERATURE REGENERATION			NO.of G.C. TAKEN						
Total min	Inlet	4"	Top	Fuel Cycle only	H_2 Range	CH_4 Range	CO Range	C_2H_4 Range	C_2H_6 Range	ΔP Range In H_2O
9	1400	-	>1800	2	71	23	.7	-	-	-
16	1250	-	>1800	-	64	-	-	-	-	-

well was fitted through reactor bed to enable temperature

Table 16 Summary of BA307 Results Performance of Single-Catalyst Bed with Multiple Sampling Technique

Fuel			Initial Temp	Regeneration		Number	Max. Percentage
Type	Rate cc/min	Time sec.	Top/6"/Inlet °F	Time sec.	Max. Temp Top/6"/Inlet	of G.C.'s	$H_2/CH_4/CO$
D #1	11	300	1400/1430/1260	1310	1725/-/1350	-	-
D #1	11	300	1450/-/1300	1930	1725/-/1350	-	-
D #1	11	300	- /-/ -	1030	- /-/ -	3	77.5/22.3/1.2
D #1	11	330	- /-/ -	1560	- /-/ -	2	78.8/15.1/0.8
D #1	11	300	1550/1600/1375	1350	- /-/ -	-	-
D #1	11	300	1460/1500/1290	970	- /-/ -	15	Fig 3
D #1	11	300	1580/1570/1326	1090	- /-/ -	15	Fig 4
D #1	11	360	1505/1525/1305	-	- /-/ -	-	-
JP4	11	300	1550/1490/1175	1000	1625/-/1250	-	-
JP4	11	300	1470/1480/1250	1520	1625/-/1350	15	Fig 5
JP4	11	600	1475/1490/1275	1750	1625/-/1300	13	Fig 6

The bed was dismantled and discharged on 8/19/77.

Table 17 Summary of High Al_2O_3 Results Performance of Single-Catalyst Bed With Non-Catalytic Material

Fuel			Initial Temp.	Regeneration		Number	Max. Percentage
Type	Rate cc/min	Time sec.	Top/ 6" /Inlet °F	Time sec.	Max. Temp of Top/ 6" /Inlet	of G.C.'s	$H_2/CH_4/CO$
JP4	11	220	1470/1523/1250	800	1425/-/1125	4	Fig 7
JP4	11	150	1475/1500/1250	-	1400/-/1175	2	-
D #1	11	125	1450/-/1250	-	1500/-/1300	4	Fig 8
D #1	11	100	1470/1520/1230	300	1500/-/1300	2	-

The bed was emptied and much of the balls obtained a brown color.

Table 18 Summary of BA307 Results
Change in Performance with Bed
Volume and Feed Rates Varied

Fuel			Initial Temp.	Regeneration		Number	Max. Percentage
Type	Rate cc/min	Time sec.	Top/ 6" /Inlet °F	Time sec.	Max. Temp of Top/ 6" /Inlet	of G.C.'s	$H_2/CH_4/CO$%
D #1	11	300	1450/-/1250	1730	1600/-/1300	12	-
D #1	11	320	1480/1475/1230	1500	1625/-/1300	15	Fig 9
JP4	11	200	1430/1425/1240	-	- /-/ -	-	-
JP4	11	320	1480/1475/1235	1680	1625/-/1275	15	Fig 11
JP4	11	360	1500/-/1250	2040	1600/-/1300	15	Fig 12
D #1	11	120	- /-/ -	-	- /-/ -	-	-
D #1	11	360	1505/1515/1255	1770	1625/-/1300	15	Fig 10
D #1	11	340	1485/1460/1255	1810	1600/-/1275	15	Fig 13
D #1	16.2	330	1510/1490/1245	2110	1650/-/1300	15	Fig 14
JP4	11	315	1515/1470/1255	1485	1650 /-/1275	12	Fig 15
JP4	16.4	325	1520/1505/1255	-	- /-/ -	15	Fig 16

The bed was removed after eleven cycles, and a 2.17% weight loss was noted.

Table 19 Summary of BA307 Results
Damage Evaluation at
Lower Temperature

Fuel			Initial Temp.	Regeneration		Number	Max. Percentage
Type	Rate cc/min	Time sec.	Top/ 6" /Inlet °F	Time sec.	Max. Temp of Top/ 6" /Inlet	of G.C.'s	$H_2/CH_4/CO$
JP4	11	400	1274/1328/1130	1660	1450/-/1175	13	Fig 17
JP4	11	310	1292/1275/1184	1760	1500/-/1273	7	Fig 18
JP4	11	310	1274/1328/1148	1420	1500/-/1175	7	Fig 19
JP4	11	310	1292/1346/1148	1490	1475/-/1175	8	Fig 20

The bed was discharged and a 6.0% weight loss was noted.

Table 20 Summary of SA5202 Results
Performance of Barium Stabiliz
Nickel Catalyst

Fuel			Initial Temp.	Regeneration		Number	Max. Percentage
Type	Rate cc/min	Time sec.	Top/ 6" /Inlet °F	Time sec.	Max. Temp of Top/ 6" /Inlet	of G.C.'s	$H_2/CH_4/CO$
JP4	11	220	1425/-/1200	-	1600/1600/1250	7	73.9/24.4/3.2
JP4	11	220	1475/1450/1250	-	1675/1700/1275	6	Fig 21
JP4	11	310	1525/1475/1275	740	1650/1725/1300	6	78.6/23.1/5.9
JP4	11	300	1525/1475/1275	840	1625/1750/1300	4	Fig 22
JP4	11	300	1500/1450/1275	965	1625/1700/1300	5	77 5/23.3/5.0

The bed was discharged and a 2.0% weight loss was noted.

Table 21 Summary of αAl_2O_3 Ring Results
Performance of A Barium Stablized
Nickel Catalyst

Fuel			Initial Temp.	Regeneration		Number	Max. Percentage
Type	Rate cc/min	Time sec.	Top/ 6" /Inlet °F	Time sec.	Max. Temp. of Top/ 6" /Inlet	of G.C.'s	$H_2/CH_4/CO$
JP4	11	215	1525/1425/1300	590	1650/1550/1275	4	-
JP4	11	300	1525/1450/1275	730	1650/1600/1325	7	74.5/26.8/5.6
JP4	11	300	1550/1500/1300	1455	1700/1650/1300	9	75.0/26.6/4.9

Suspect channeling past the larger rings lowered performance.

Table 22 Summary of SA5202 Results
Performance of Barium Stablized
Nickel Catalyst - Propane Fuel

Fuel			Initial Temp.	Regeneration		Number	Max. Percentage
Type	Rate ft^3/min	Time sec.	Top/ 6" /Inlet ^0F	Time sec.	Max. Temp of Top/ 6" /Inlet	of G.C.'s	$H_2/CH_4/CO$
Propane	0.156	300	1500/1475/1250	525	1550/1500/1250	-	-
Propane	0.156	300	1600/1525/1275	450	1575/1550/1300	-	-
Propane	0.156	300	1500/1450/1225	1300	1650/1550/1275	7	80.6/22.8/91
Propane	0.156	300	1550/1500/1300	1500	1700/1675/1300	-	-

A weight gain was noted upon discharging the bed.

Table 23 SUMMARY OF VYCOR TUBE FURNACE RESULTS VARIOUS MATERIALS

Material	Temperature °F	Gases	Cycles/time	Comments/results
5203 NoNi	1760-1800	H_2	6 hours	White 5203 turned gray
5203 NoNi	2100-2150	H_2	6 hours	negligible weight change
5203 NoNi/C	1905-1920	Air	10 minutes	carbon burned off
Al_2O_3NoNi/C	1905-1920	Air	10 minutes	negligible weight change
Al_2O_3/Ni (rings)	1740 start	C_3/air	9-3-4min/3-4 min	cracking and dusting
Al_2O_3/Ni (rings)	1740 start	H_2/air	10-4 min/4 min	essentially no changes
Ni Balls	1740 start	H_2/air	10-4 min/4 min	
Ni powder (pelletized)	1670-1715	H_2	30 minutes	slightly sintered
NiO powder (pelletized)	1670-1715	H_2	30 minutes	slightly sintered
Ni/C powder (pelletized)	1670-1715	H_2	30 minutes	slightly sintered
NiO/C powder (pelletized)	1670-1715	H_2	30 minutes	slightly sintered
Ni powder (pelletized)	1700-1790	Air	10 min - heated in helium	some dusting
Ni/C powder (pelletized)	1700-1790	Air	10 min - heated in helium	some damage (carbon gone)
NiO/C powder (pelletized)	1700-1790	Air	10 min - heated in helium	some damage (carbon gone)
Ni powder (pelletized)	1750 start	C_3/air	3 - 200 sec/200 sec cycles	much damage
NiO powder (pelletized)	1750 start	C_3/air	3 - 200 sec/200 sec cycles	much damage
Ni metal balls	1690 start	C_3/air	3 - 200 sec/200 sec cycles	slight dusting
Al_2O_3/Ni (rings)	1535 start	CH_4/air	9 - 2 min/2 min	no damage
Al_2O_3/Ni (rings)	1700 start	C_2H_2/air	4 - 2 min/2 min	inconclusive
5203/Ni (partially $NiAl_2O_4$	1660 start	C_4H_{10}/air	9 - 3 min/5-10 min	11% wt. loss
Al_2O_3/Ni (rings)	1800 start	C_3H_6/air	9 - 200 sec/300-400 sec	much degradation
Al_2O_3/Ni (rings)	1815 start	CH_4/air	9 - 200 sec/200 sec	no damage
5203/Ni	1815 start	CH_4/air	9 - 200 sec/200 sec	no damage

Table 23 (cont.)

Material	Temperature °F	Gases	Cycles/time	Comments/results
5202/Ni	1470	C_3/Air	10-300/300	24.22% wt. loss
5202/Ni	1290	C_3/Air	10-300/300	Much destruction/74.45% wt. loss
5202/Ni	1290	C_3/Air	10-100/100	8.58% wt. loss
5202/Ni	1290	C_3/Air	10-500/500	N.A.
307/Ni Retreat	1470	C_3/Air	10-300/300	0.61% wt. loss
307/Ni Retreat	1470	C_3/Air	10-500/500	0.39% wt. loss
307/Ni Retreat	1290	C_3/Air	10-100/100	0.24% wt. loss
307/Ni Retreat	1290	C_3/Air	10-500/500	0.50% wt. loss
307/Ni Retreat	1650	C_3/Air	10-100/100	0.21% wt. loss
307/Ni Retreat	1650	C_3/Air	10-500/500	0.47% wt. loss
307/Co	1470	C_3/Air	10-300/300	0.26% wt. loss
307/Co	1470	C_3/Air	10-500/500	0.14% wt. loss
307/Co	1470	C_3/Air	10-100/100	0.27% wt. loss
307/Co	1650	C_3/Air	10-500/500	0.107% wt. loss
307/Co	1650	C_3/Air	10-100/100	0.30% wt. loss
307/Co	1650	C_3/Air	10-300/300	1.24% wt. loss
307/Ni	1470	C_3/Air	5-300/300	0.25% wt. loss
Denstone 57/Ni	1470	C_3/Air	10-300/300	0.88% wt. loss
Denstone 57/Ni	1380	C_3/Air	10-300/300	0.68% wt. loss
Denstone 57/Ni	1560	C_3/Air	10-300/300	0.10% wt. loss
Denstone 57/Ni	1650	C_3/Air	10-300/300	0.80% wt. loss
23-1/Ni	1470	C_3/Air	4-200/400	0.30% wt. loss
307/Ni	1470	C_3/Air	15-*	2.269% wt. loss

* A varing Air and CO_2 mixture was used to regenerate

Table 23 (cont.)

Material	Temperature °F	Gases	Cycles/time	Comments/results
Al_2O_3/Ni (rings)	1740-1790	CH_4	(15 min at temp - heated	destroyed
5203/Ni	1740-1790	CH_4	\and cooled in CH_4	damaged
Al_2O_3/Ni (rings)	1770	C_3H_8	(15 min at temp - heated	damaged
5203/Ni	1770	C_3H_8	\and cooled in C_3H_8	damaged
Al_2O_3/Ni (rings)	1725	CH_4	(200 sec - heated and	no damage
5203/Ni	1725	CH_4	\cooled in Helium	no damage
Al_2O_3/Ni (rings)	1650	C_3H_8	(200 sec - heated and	no damage
5203/Ni	1650	C_3H_8	\cooled in Helium	no damage
307/Ni	7715-start	C_3/air	5 - 200 sec/200 sec	1.47% wt. loss- most of the nickel
5203/Ni($NiAl_2O_4$)	1650 start	C_3/air	10 - 200 sec/200 sec	no damage (low hydrogen purity)
307/Ni	1365 start	C_3/air	10 - 200 sec/200 sec	dusting - Ni content reduced 0.6-0.12%
307/5203	1570 start	C_3/air	10 - 200 sec/200 sec	307 lost wt. 2.4%; 5203 lost 35%
NiCr Wire	1470 start	C_3/air	11 - 200 sec/200 sec	2% wt. loss
307/Pt	1545 start	C_3/air	10 - 200 sec/200 sec	no damage (25-27% H_2)
5203/Ni	1645 start	C_3/air	5 - 200 sec/400-900 sec	2.8% wt. loss- 65-80% H_2
307/Ni	1645 start	C_3/air	5 - 200 sec/200-400 sec	1.7% wt. loss
5203/Ni	1520 start	C_3/air	4 - 200* sec/400-800 sec	5.3% wt. loss *(one fuel cycle 550 sec)
5203/Ni	1535 start	C_3/air	11 - 200 sec/400 sec	4.6% wt. loss (50-70% H_2) 60-80% H_2
5203/NoNi	1545 start	C_3/air	4 - 200 sec/200 sec	no damage (27% H_2)
5203/Ni($NiAl_2O_4$)	1545 start	C_3/air	4 - 200 sec/200 sec	no damage (25 - 30% H_2)
5203/Ni	1510 start	C_3/air	30 - 200 sec/400 sec	3.7% wt. loss
Empty Tube	**	C_3		(23.5% H_2)
Wire support only	**	C_3		(26% H_2)
96233/Ni(0.59%)	1560 start	C_3/air		0.45% wt. loss (23% H_2)

** Same furnace setting as previous run.

Table 23 (cont.)

Material	Temperature °F	Gases	Cycles/time	Comments/results
307/Ni	1290	C_3	12 Balls/50 sec	Fuel only for S.E.M.
Denstone 57/Ni	1470	C_3	12 Balls/50 sec	Fuel only for S.E.M.
307/Ni	1200	C_3/Air	13-300/300	2.27% wt. loss
307/Ni	1290	C_3/Air	5-300 / 300	0.19% wt. Gain
307/Ni	1290	C_3/Air	5-300/300	No change
307/Ni	1320	C_3/Air	5-300/to level*	0.52% wt. loss
307/Ni	1320	C_3/Air	3-300/300	No change
5203/Ni	1305	C_3/Air	10-300/400**	1.50% wt. loss
307/Ni	1275	C_3/Air	10-300/to level*	0.05% wt. loss
307/Ni	1455	C_3/Air	10-300/300	2.7% wt. loss
5203/Ni	1480	C_3/Air	5-300/400	4.09% wt. loss
307/Ni	1505	C_3/Air	10-300/300	3.91% wt. loss
307/Ni	1485	C_3/Air	10-300/300	3.5% wt. loss
5203/No Ni	1490	C_3/Air	2-300/300	0.33% wt. gain
307/Ni	1400	C_3/Air	10-300/300	0.4% wt. loss
Solid/Co	1490	C_3/Air	10-300/300	1.3% wt. loss
Solid/Ni	1525	C_3/Air	10-300/300	1.06% wt. loss
Solid/Cr	1510	C_3/Air	8-300/300	No change
Solid/Co	1290	C_3/Air	10-300/300	0.87% wt. gain
Solid/Ni	1275	C_3/Air	6-300/300	0.24% wt. loss
307/Pt	1275	C_3/Air	5-300/300	0.99% wt. loss

* .Regeneration Until Complete
** Regneration Air Rate Reduced by 33%

Table 23 (cont.)

Material	Temperature °F	Gases	Cycles/time	Comments/results
307/Ni	1470	C_3/Air	8-300/300	Pre-reduced/N.A.
307/Ni	1470	C_3/Air	10-300/300	0.758% wt. loss
307/Ni	1650	C_3/Air	10-300/300	0.328% wt. loss
307/Ni	1650	C_3/Air	9-500/500	2.66% wt. loss
307/Ni	1290	C_3/Air	10-100/100	0.09% wt. loss
307/Ni	1290	C_3/Air	10-300/300	1.02% wt. loss
307/Ni	1110	C_3/Air	2-500/500	0.76% wt. loss
307/Ni	1200	C_3/Air	3-500/500	2.80% wt. loss
307/Ni	1290	C_3/Air	4-300/300	0.94% wt. loss
307/Ni	1290	C_3/Air	4-300/300	0.51% wt. loss
307/Ni	1560	C_3/Air	10-500/500	1.21% wt. loss
5202/Co	1290	C_3/Air	10-100/100	No change
5202/Co	1290	C_3/Air	10-500/500	Flaking of surface/3.75% wt. loss
5202/Co	1290	C_3/Air	10-300/300	Flaking of surface/0.717% wt. loss
5202/Co	1470	C_3/Air	10-300/300	7.16% wt. loss
5202/Co	1470	C_3/Air	10-100/100	0.317% wt. loss
5202/Co	1470	C_3/Air	2-500/500	51.39% wt. loss
5202/Co	1650	C_3/Air	10-100/100	3.86% wt. loss
5202/Co	1200	C_3/Air	10-300/300	10.57% wt. gain
5202/Co	1650	C_3/Air	3-300/300	Fell apart/75.28% wt. loss
5202/Co	1380	C_3/Air	10-300/300	0.09% wt. loss
307/Ni	1470	C_3/Air	10-100/100	0.02% wt. loss
307/Ni	1470	C_3/Air	10-300/300	2.71% wt. loss
307/Ni	1470	C_3/Air	10-500/500	2.11% wt. loss

Table 23 (cont.)

Material	Temperature °F	Gases	Cycles/time	Comments/results
307/Pt/5203/Ni	1550 start	C_3/air	10 - 200 sec/400 sec	0.06/6.14% wt. losses (60-75% H_2)
5203/Ni	1550 start	C_3/air	10 - 200 sec/400 sec	2.9% wt. loss (45-65% H_2)
5203/Ni	1550 start	C_3/air***	10 - 200 sec/400 sec	1.2% wt. loss (55-60% H_2)
5203/Ni	1400 start	C_3/air	10 - 200 sec/400 sec	.7% wt. loss (45-60% H_2)
5203/Ni	1740 start	C_3/air	10 - 200 sec/400 sec	5.9% wt. loss (65-80% H_2)
307/Ni	1470	C_3	50,100,150,200,250,300,400, 500,600,700,800,900 sec	Small carbon buildup (0-1%)
5203/Ni($NiAl_2O_4$)	1470	C_3	30,125,160,200,250,300,400, 500,600,700,800,975 sec	negligible change
5203/Ni	1470	C_3	50,100,150,200,250,300,400, 500,600,700,800,900 sec	wt. gain followed by severe loss
5203/Ni	1470	CH_4	50,100,150,200,250,300,400, 500,600,700,800,900 sec	slower buildup of carbon than from C_3
5203/Ni	1470	C_3/N_2	300/600,900,1200,1500, 1800 sec	carbon buildup followed by wt. loss
307/Ni	1290	C_3	12 Balls/ 50 sec	Fuel Only for S.E.M. Samples
57/Ni	1470	C_3	12 Balls/ 50 sec	Fuel Only for S.E.M. Samples
307/Ni	1200	C_3air	13-300/300	2.2% wt. loss
307/Ni	1290	C_3air	5-300/300	0.19% wt. gain
307/Ni	1290	C_3air	5-300/300	No change
307/Ni	1320	C_3air	5-300/to level*	0.55% Wt. Loss

*regeneration until complete

***double C_3 rate

Table 24 SUMMARY OF BARIUM STABILIZED NICKEL RESULTS

CATALYST	TYPE	STARTING TEMPERATURE °F	RUN SUMMARY CYCLE-FUEL/AIR TIME SECONDS	WEIGHT LOSS %	COMMENTS
SA5202	Ni+Ba	1470	10-200/400	0.258	
SA5202	Ba/Ni	1470	10-200/400	0.222	
SA5202	Ni/Ba	1470	10-200/400	0.140	intact damaged flaking,
*SA5202	Ni/Ba	1470	10-200/400	2.456	dusting.
α-Al_2O_3	Ni+Ba	1470	10-200/400	0.217	
α-Al_2O_3	Ba/Ni	1470	10-200/400	1.319	surface degradation evidence of powder
SA5202	Ni+Ba	1470	10-300/400	0.476	gained weight
SA5202	Ba/Ni	1470	10-300/400	0.211	
SA5202	Ni/Ba	1470	10-300/400	0.265	surface degradation cracking.
α-Al_2O_3	Ni+Ba	1470	10-300/400	0.294	
α-Al_2O_3	Ni/Ba	1470	10-300/400	3.790	surface showed powder
*SA5202	Ni/Ba	1470	10-300/400	0.488	no damage
*SA5202	Ni/Ba	1470	10-300/400	0.545	surface degradation evidence of cracking
*SA5202	Ni/Ba	1470	10-300/400	0.257	
*α-Al_2O_3	Ni/Ba	1470	10-300/400	0.319	some visible dusting
*SA5202	Ni/Ba	1470	10-300/400	1.195	surface degradation cracking
SA5202	Ni+Ba	1470	10-100/400	0.092	
SA5202	Ni/Ba	1470	10-100/400	0.294	
α-Al_2O_3	Ni+Ba	1470	10-100/400	0.264	
α-Al_2O_3	Ba/Ni	1470	10-100/400	0.223	
SA5202	Ni/Ba ($Ba(NO_3)_2$)	1470	10-200/400	2.474	light yellow
SA5202	Ni/Ba ($Ba(NO_3)_2$)	1470			
SA5202	Ni+Ba	1380	10-200/400	0.250	
SA5202	Ba/Ni	1380	10-200/400	1.116	visible dusting
SA5202	Ni/Ba	1380	10-200/400	N.A.	fell apart, cracking
*SA5202	Ni/Ba	1380	10-200/400	0.180	
α-Al_2O_3	Ni+Ba	1380	10-200/400	0.329	
α-Al_2O_3	Ba/Ni	1380	10-200/400	0.127	

* Bench Unit made catalyst. All others made for T.G.A. runs only.

Table 25 PLATINUM STABLIZED NICKEL CATALYST

PAIRS PREPARED BY C.H. BARTHOLOMEW

CATALYST TYPE	STARTING TEMPERATURE°F	CYCLES-PROPANE/AIR TIMES--SECONDS	WEIGHT LOSS %	COMMENTS
12% Ni/Al_2O_3 ASTM	1470	10-200/400	26.82	destroyed cracking and dusting
0.5% Pt 12% Ni/Al_2O_3 ASTM	1470	10-200/400	12.05	black color flaking and dusting
KATALCO Al_2O_3 1% Ni	1470	10-200/400	0	
KATALCO 0.9% Ni 0.1% Pt/Al_2O_3	1470	10-200/400	0.376	dusting
4.5% Ni 0.5% Pt on Al_2O_3 Reduced 4 hrs	1470	10-200/500→1100*	gained	intact but crisp
4.5% Ni 0.5% Pt on Al_2O_3 Reduced 5 hrs	1470	10-200/500→1300*	3.62	intact
5% Ni/Al_2O_3 Conoco Catapol Al_2O_3	1470	10-200/400→800	gained	cracked

* Air time until complete regeneration

Table 26 X-RAY MICROPROBE ANALYSES
Ni/Denstone 57 Treated At 1470°F

Ball # *	Time (sec)	Mg%	Al%	Si%	K%	Ni%	Ti%	Fe%
0	0	3.04	4.24	9.09	-	83.61	-	-
0	0	1.74	5.73	9.90	-	82.62	-	-
1	50	2.93	13.87	19.77	2.66	60.76	-	-
1	50	1.65	12.28	16.88	3.42	65.76	-	-
3	150	1.89	32.15	46.81	4.83	12.62	0.64	1.06
3	150	4.30	32.02	20.59	2.78	38.47	0.76	1.07
5	250	2.11	36.36	53.04	4.61	1.98	1.31	0.38
5	250	1.09	42.35	48.26	4.94	1.40	1.16	0.78
8	400	0.83	34.33	53.34	5.74	3.80	1.03	0.92
8	400	0.94	32.94	54.33	5.83	3.37	1.40	1.18
10	500	1.74	36.77	48.52	6.03	5.55	1.87	-
10	500	3.72	35.03	51.38	5.01	2.20	1.71	0.94
12	600	1.10	35.14	55.10	5.05	1.39	1.44	0.77
12	600	1.48	32.93	44.69	10.08	3.76	4.61	2.44

* Two different areas of same ball.

Denstone 57
Fuel Only
Fuel o Propane
1470°F

Table 27 X-RAY MICROPROBE ANALYSES
Ni/Ba307 Treated at 1290°F

Ball # *	Time (sec)	Al%	Si%	Ca%	Ni%
0	0	27.59	-	3.96	68.44
1	50	19.76	-	4.93	75.31
1	50	22.42	5.96	3.10	68.51
3	150	28.74	5.01	10.8	65.16
3	150	21.50	4.81	3.22	70.45
5	250	34.47	1.91	3.55	60.07
5	250	56.33	4.17	2.00	37.49
8	400	22.28	4.00	5.58	68.13
8	400	22.16	4.63	5.81	67.40
10	500	29.14	4.80	5.46	60.59
10	500	33.97	4.73	5.43	55.87
12	600	24.91	4.01	4.66	66.33
12	600	26.71	4.13	5.39	63.76

* Two different areas of same ball

BA 307
Fuel Only
Fuel Propane
1290°F

Table 28 X-RAY MICROPROBE ANALYSES
Ni/BA307 TREATED AT 1470°F

Time (sec)	Al%	Ni%
0	17	83
50	18	82
150	31	69
250	68	32
400	91	9

BA 307
Fuel Only
Fuel Propane
1470°F

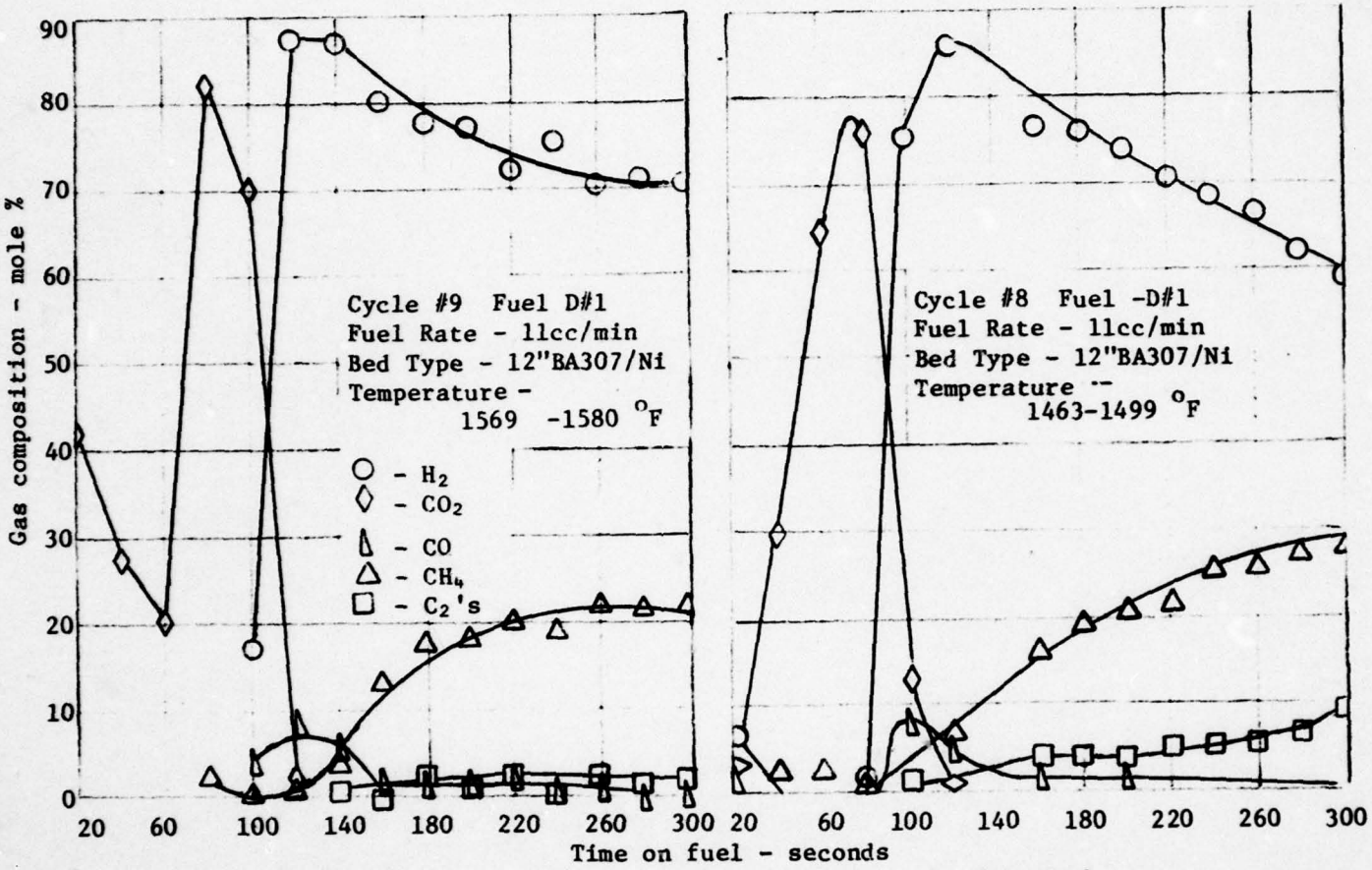


Figure 3

Figure 4

Product Gas Analyses - Runs from Table 16

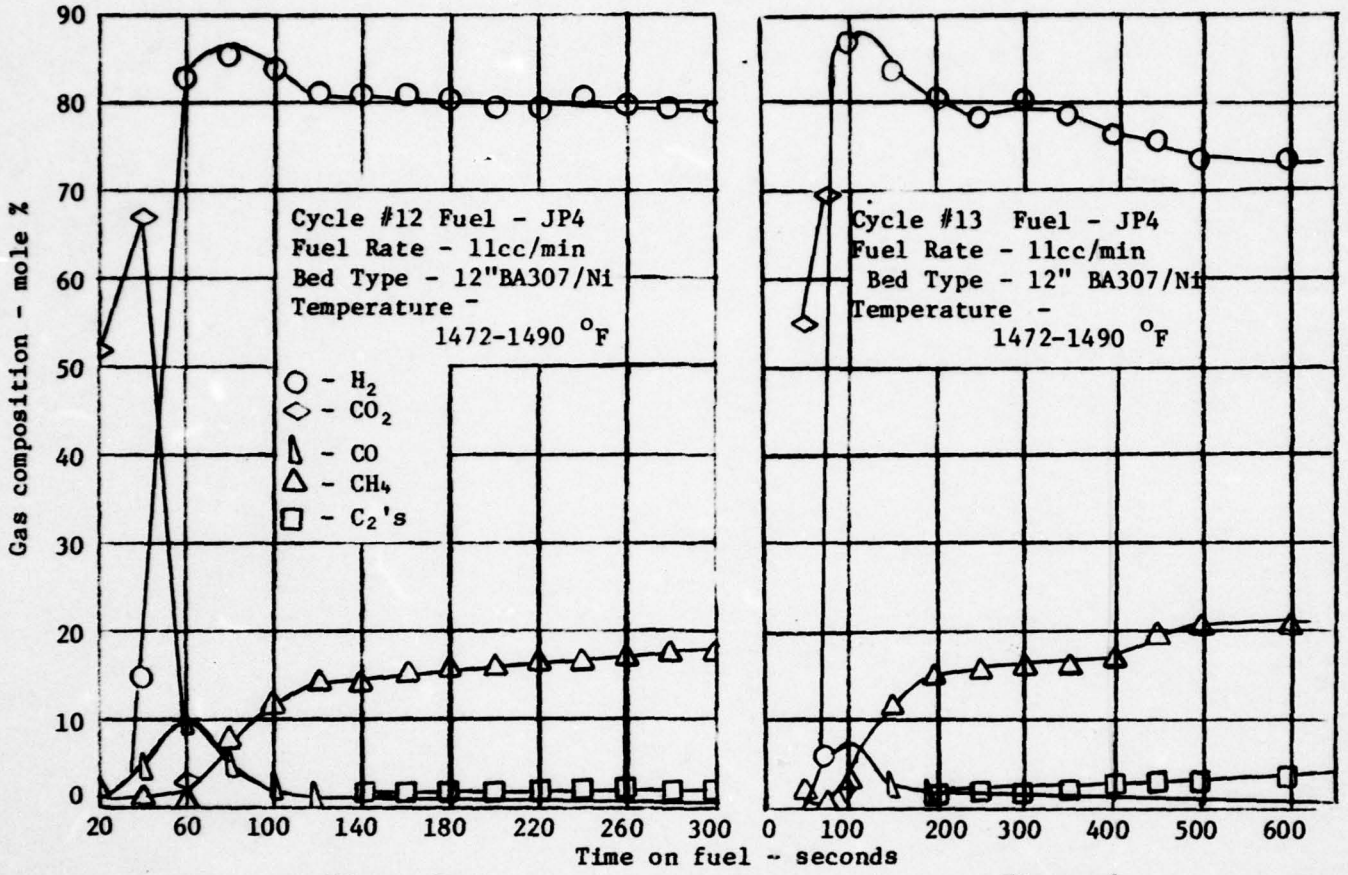


Figure 5

Figure 6

Product Gas Analyses - Runs from Table 16

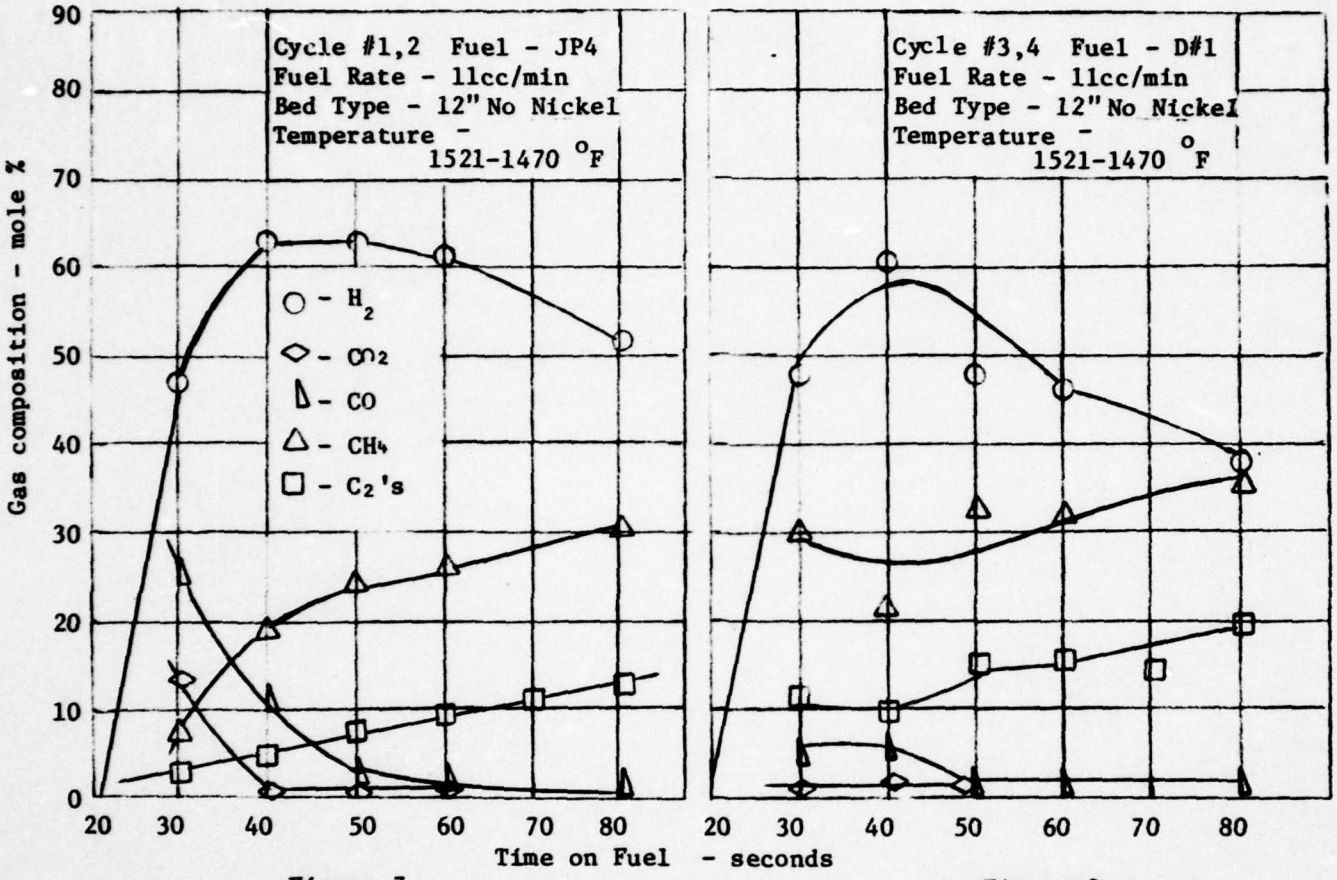


Figure 7

Figure 8

Product Gas Analyses - Runs from Table 17

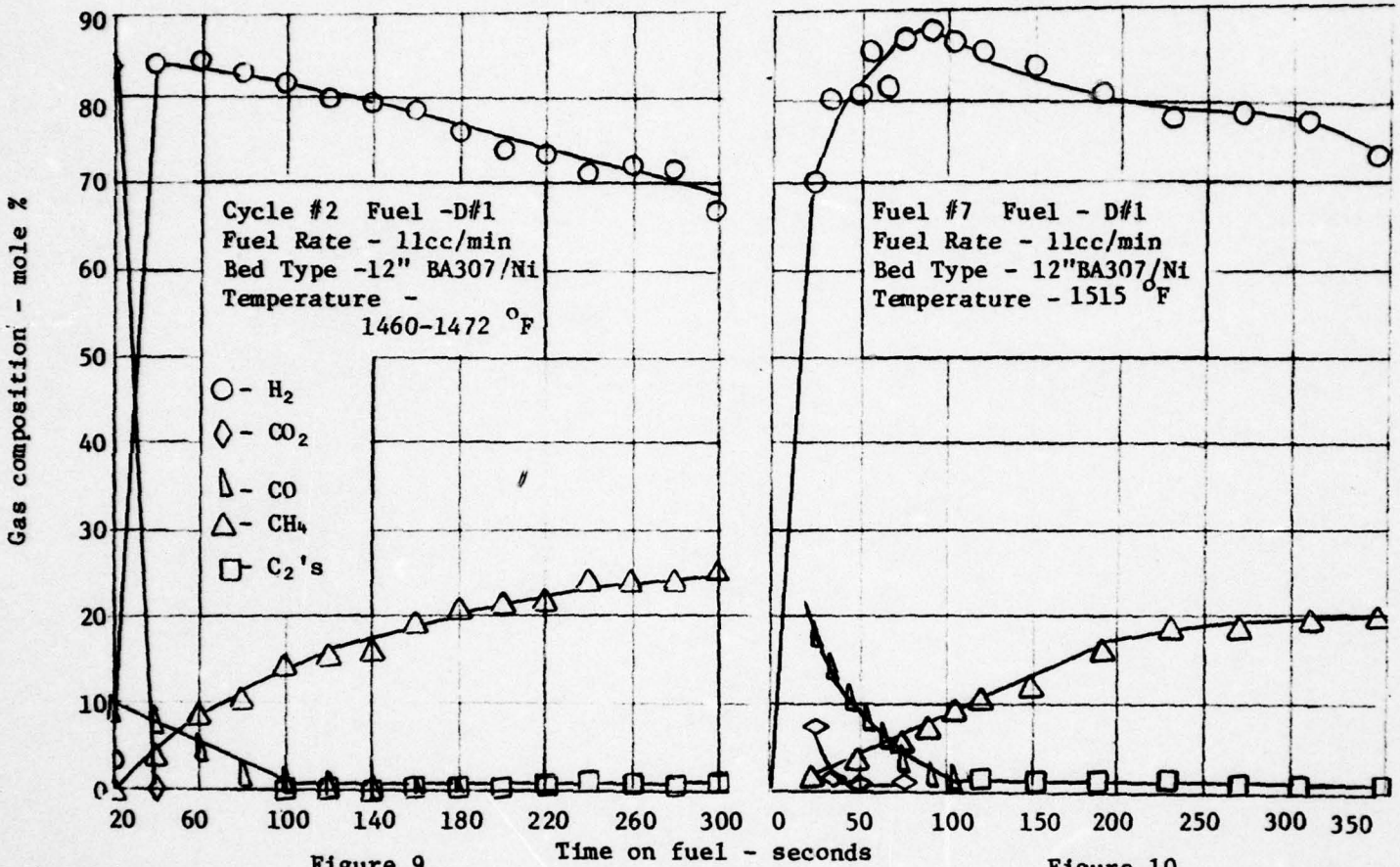


Figure 9

Figure 10

Product Gas Analyses - Runs from Table 18

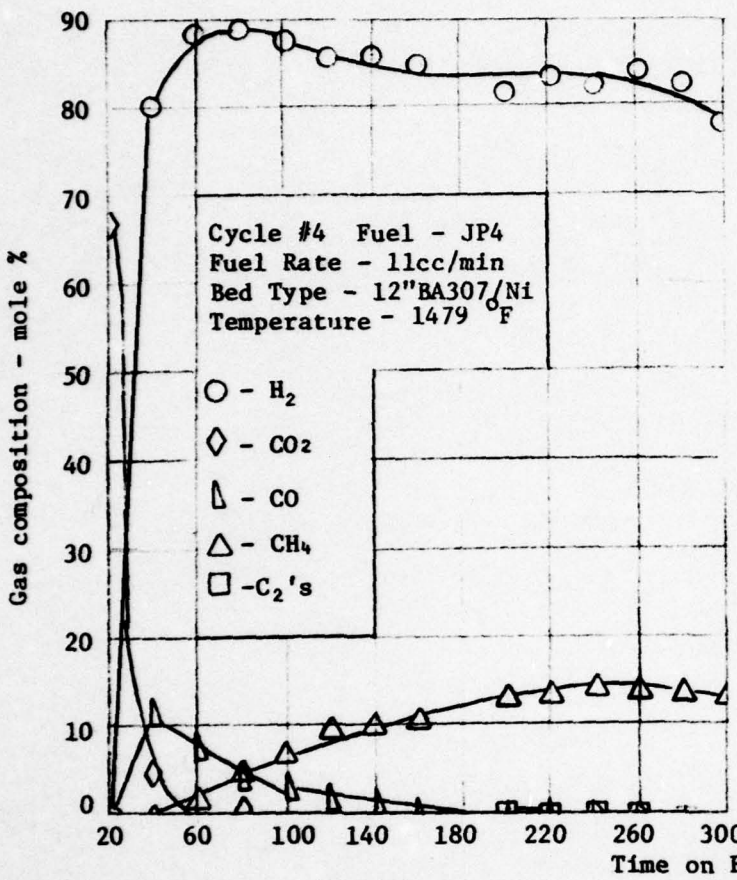


Figure 11

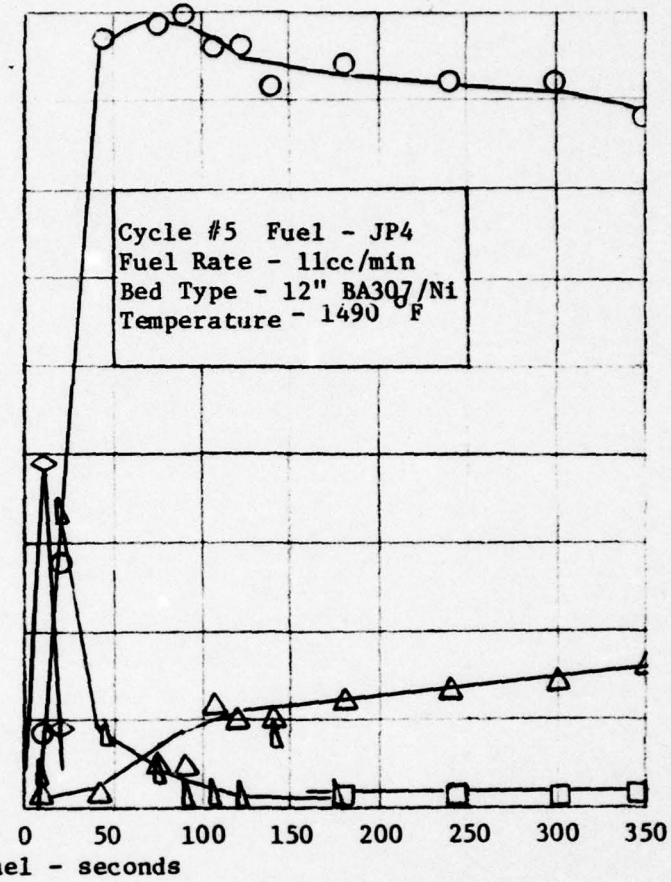


Figure 12

Product Gas Analyses - Runs from Table 18

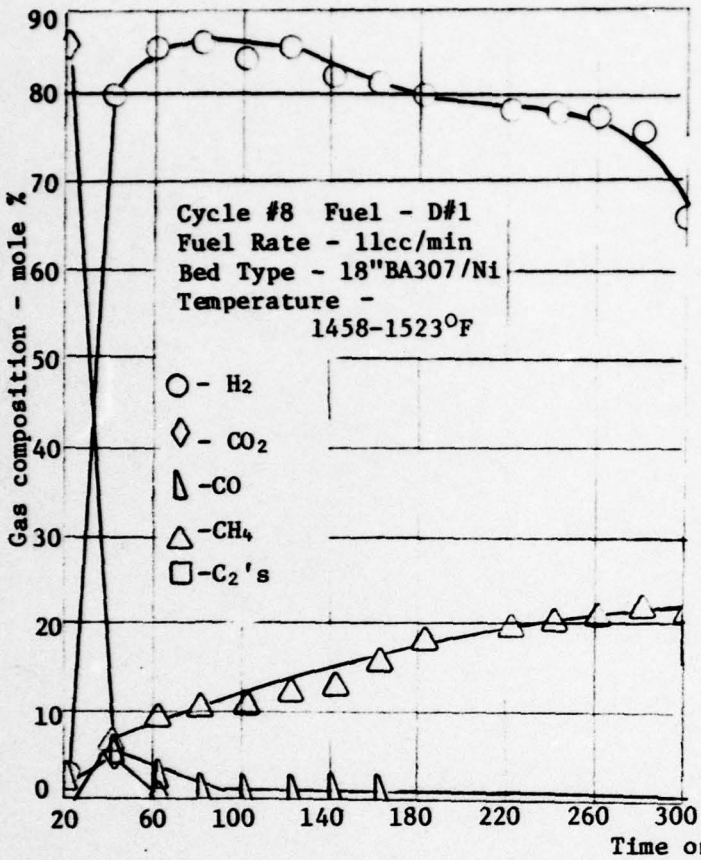


Figure 13

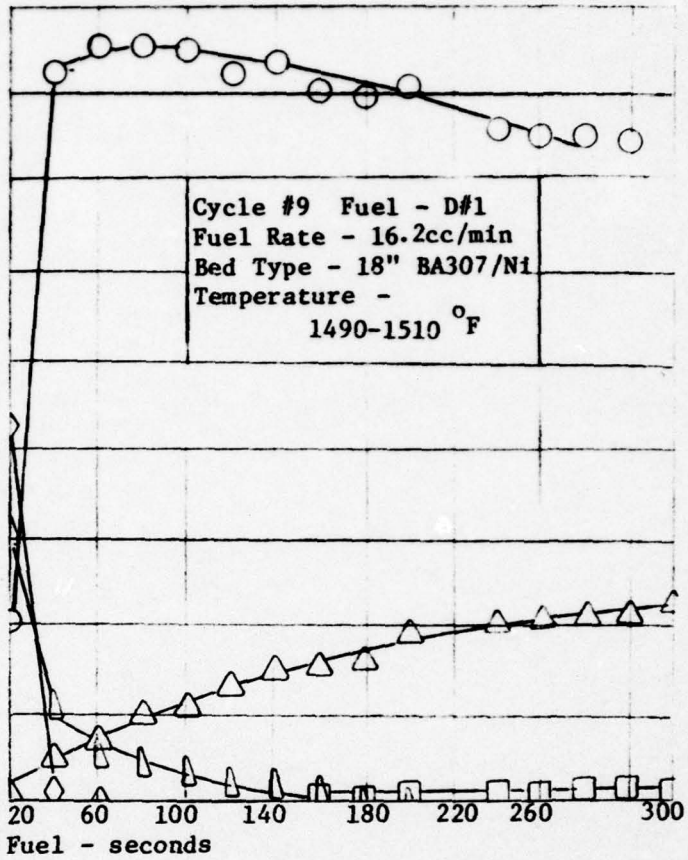


Figure 14

Product Gas Analyses - Runs From Table 18

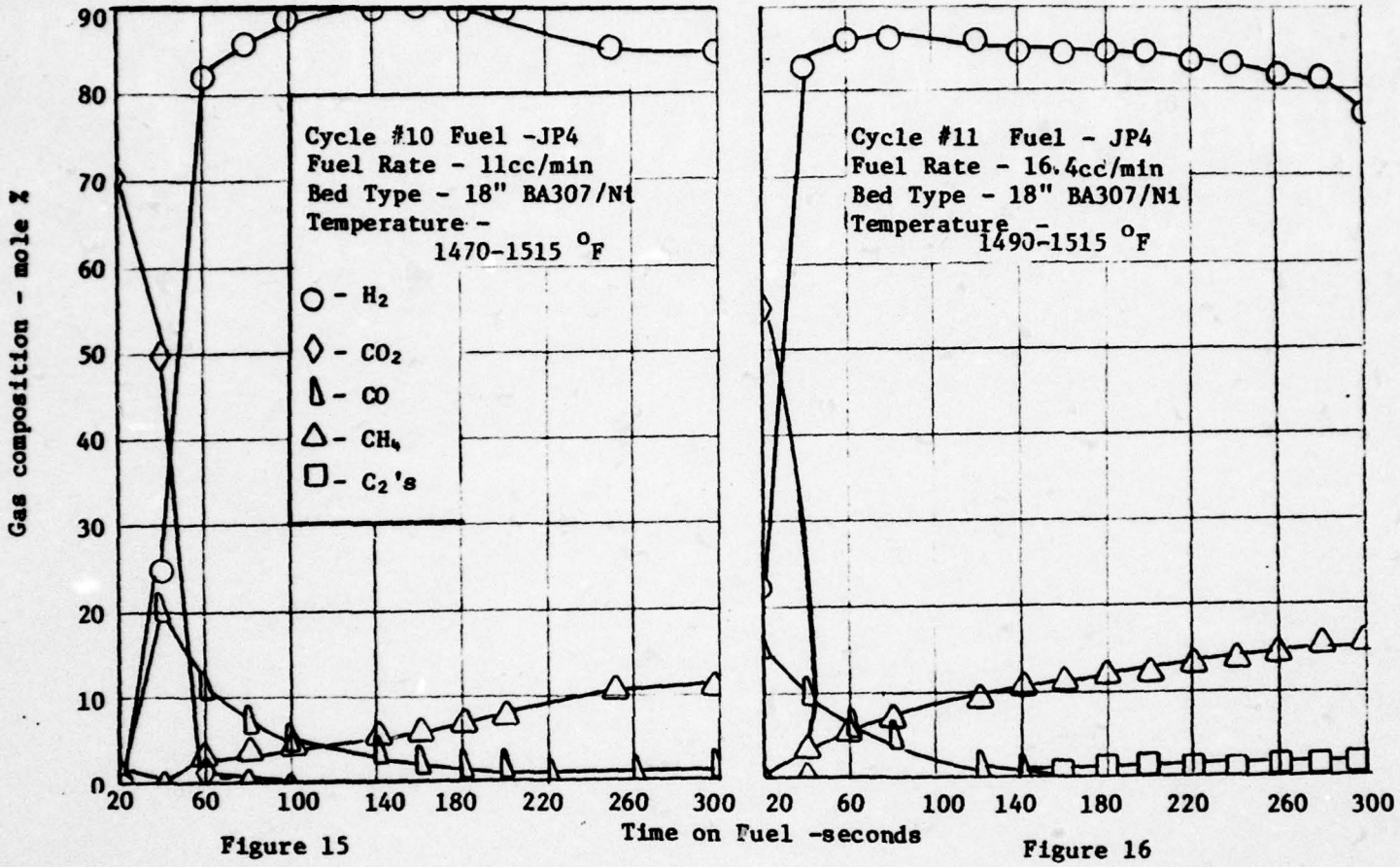


Figure 15

Figure 16

Product Gas Analyses - Runs from Table 18

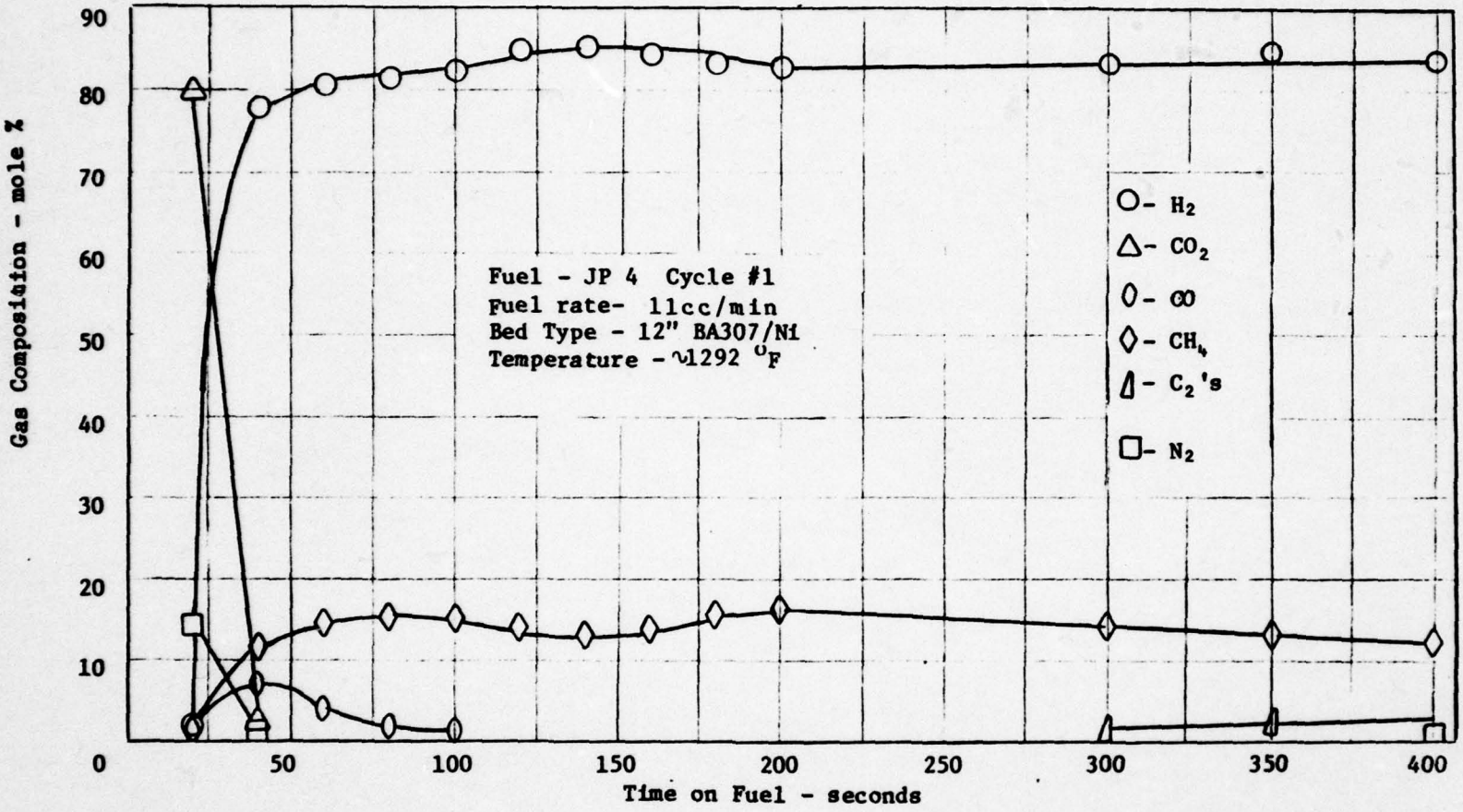


Figure 17 Product Gas Analyses - Runs from Table 19

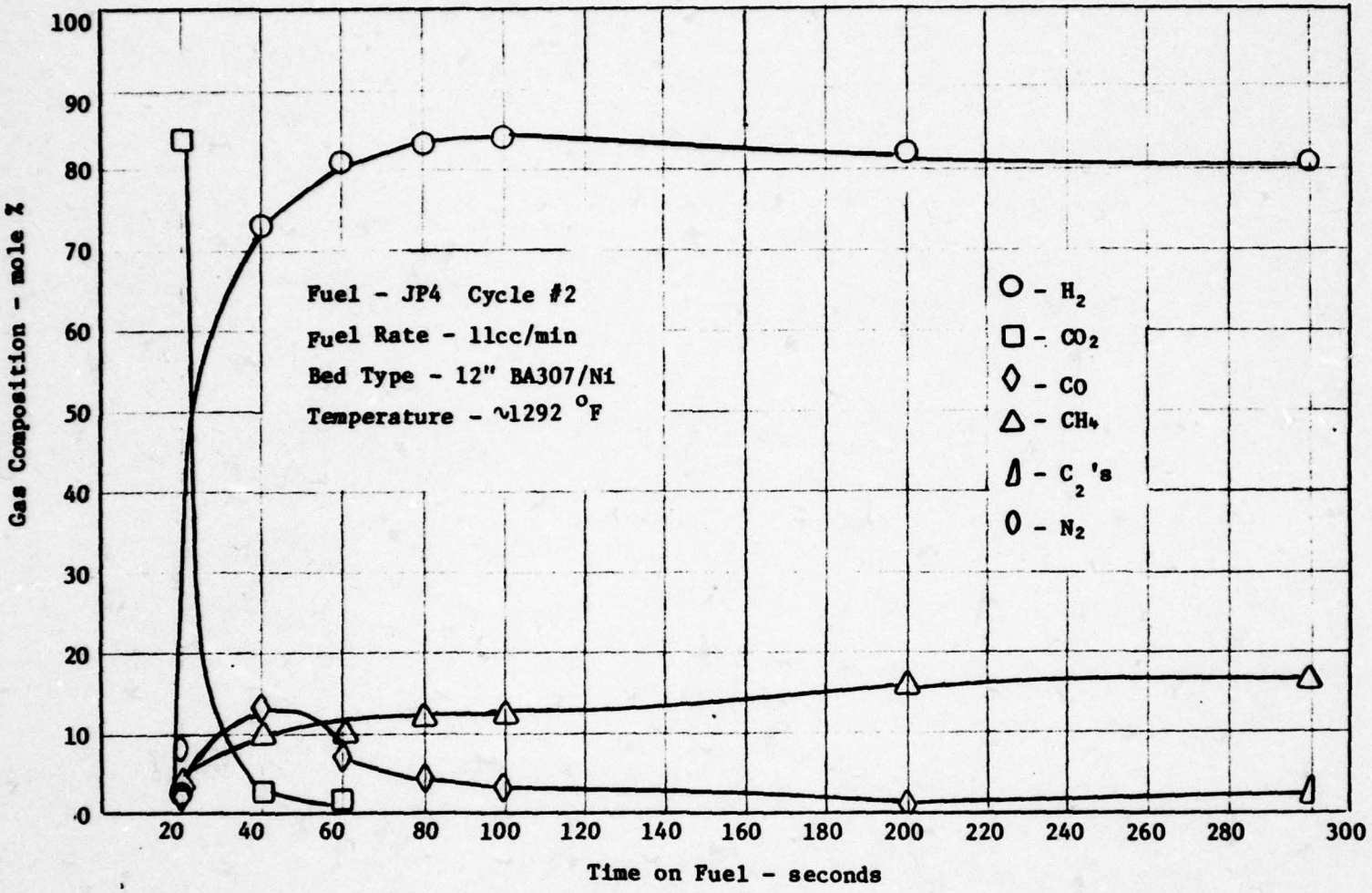


Figure 18 Product Gas Analyses - Runs from Table 19

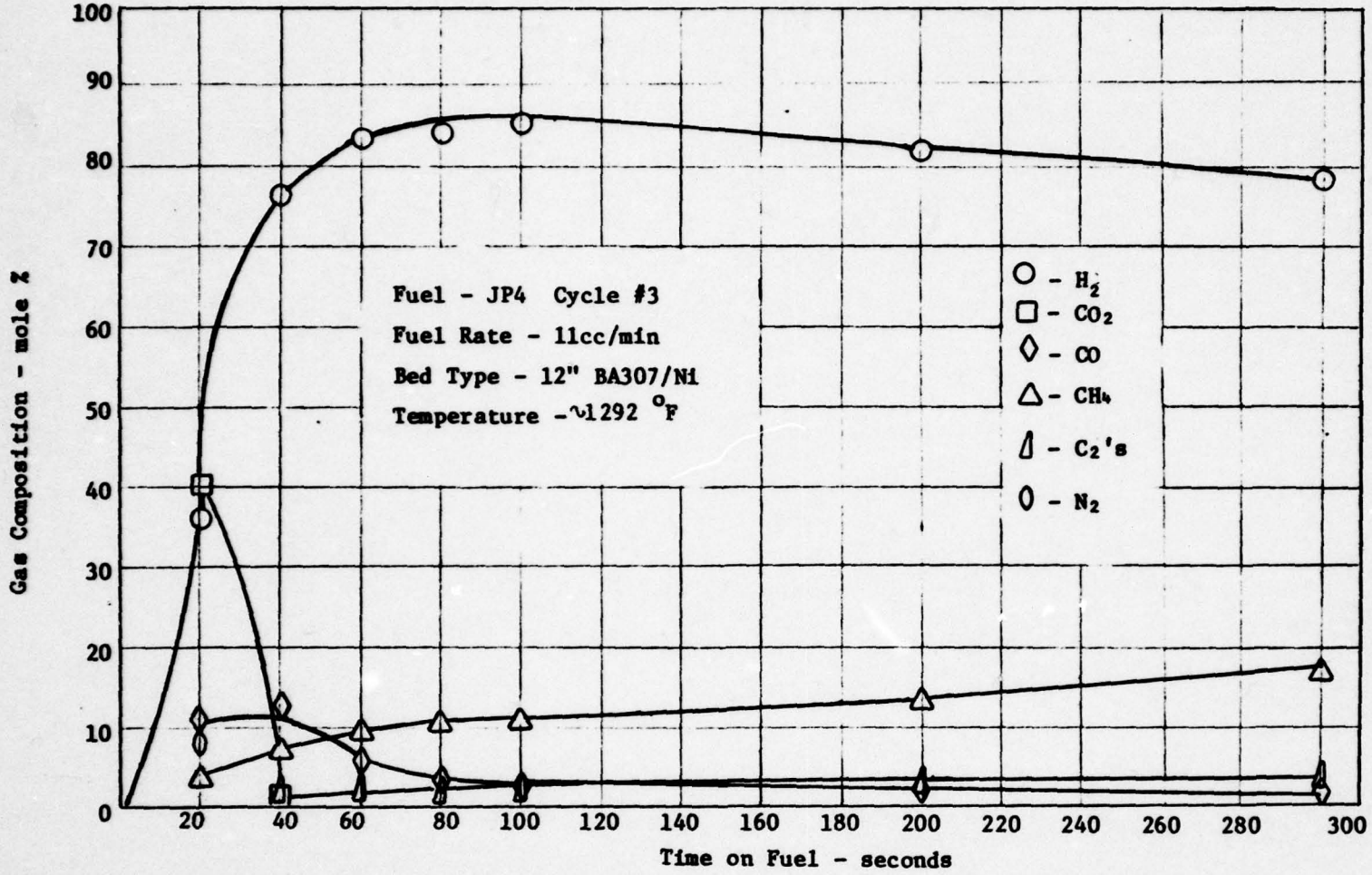


Figure 19 Product Gas Analyses - Runs from Table 19

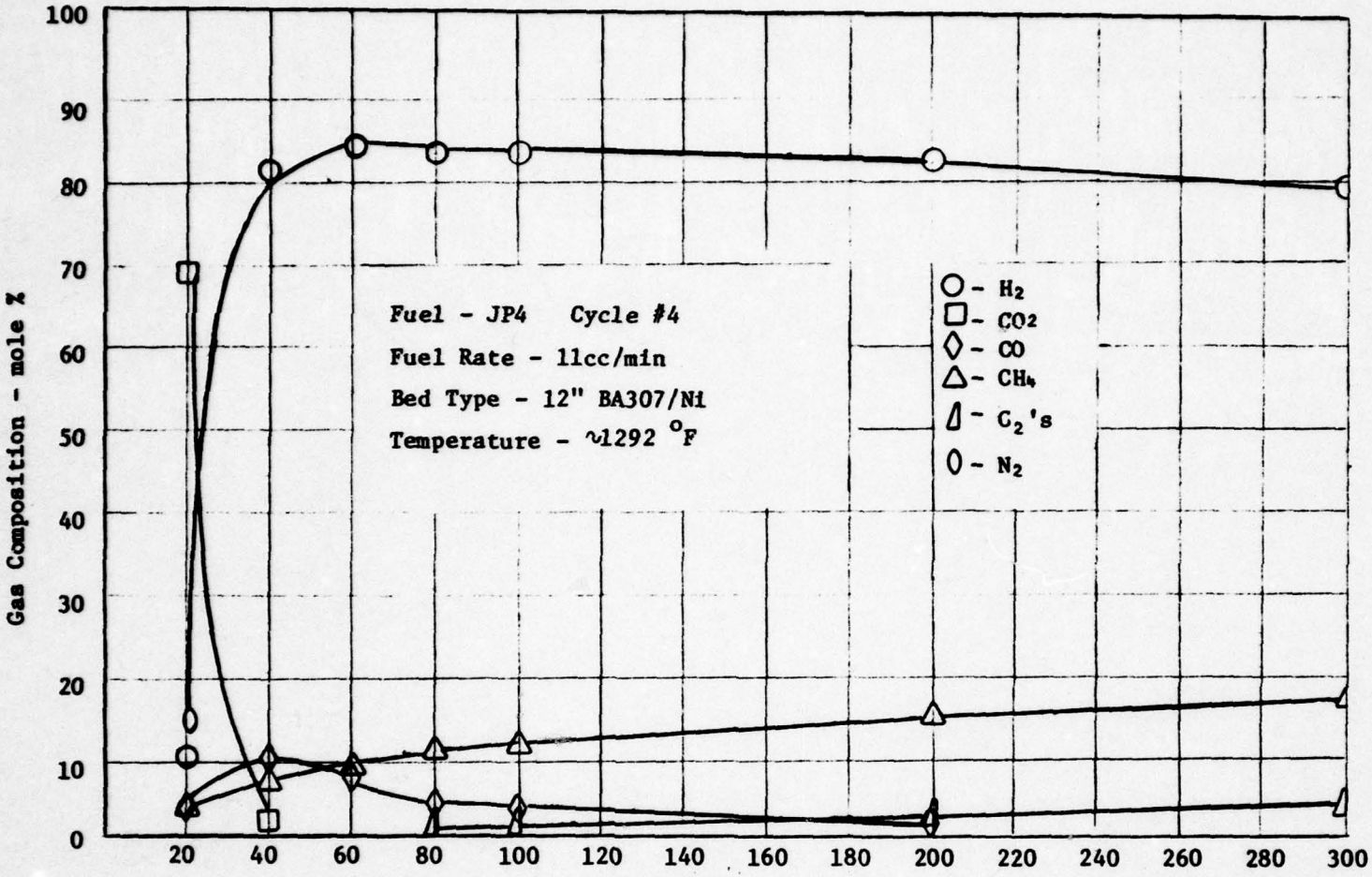


Figure 20 Product Gas Analyses - Runs from Table 19

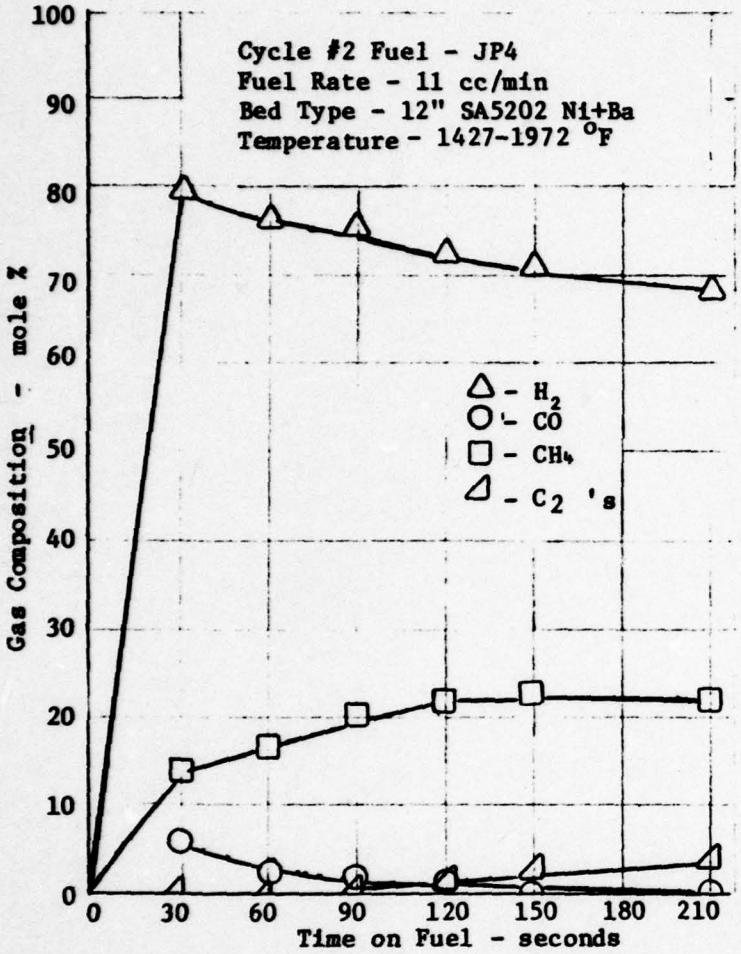


Figure 21

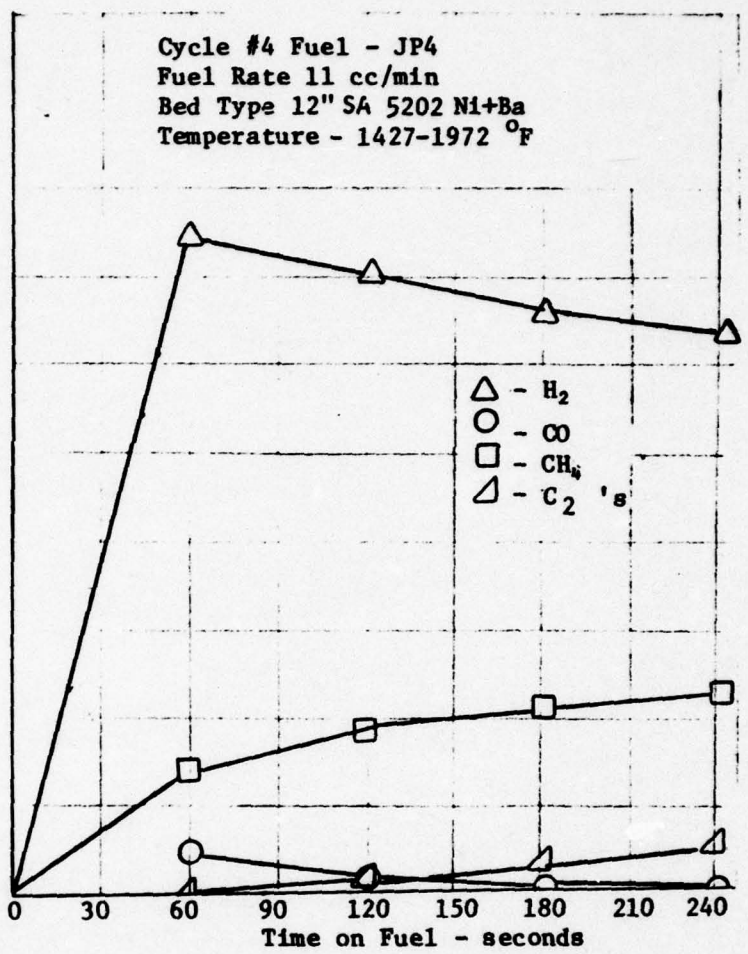


Figure 22

Product Gas Analyses - Runs from Table 20

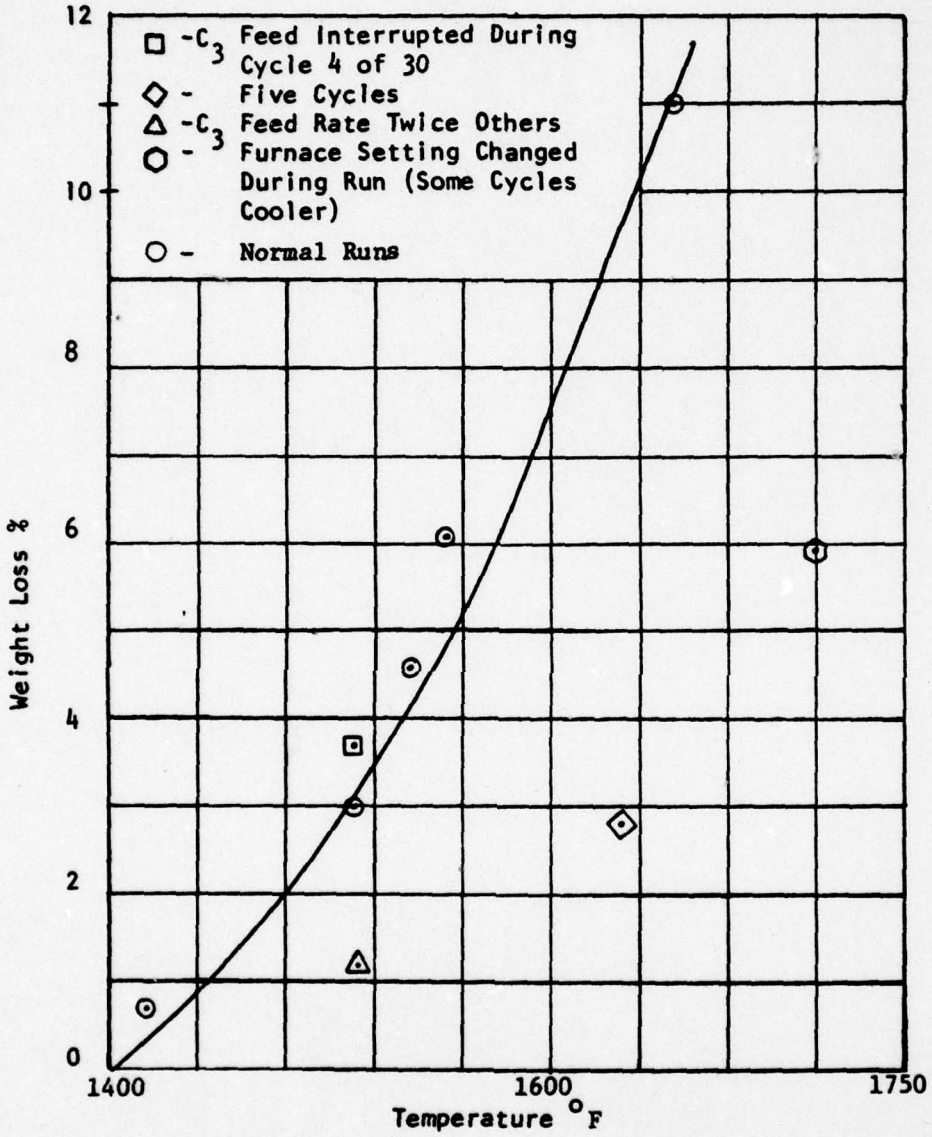
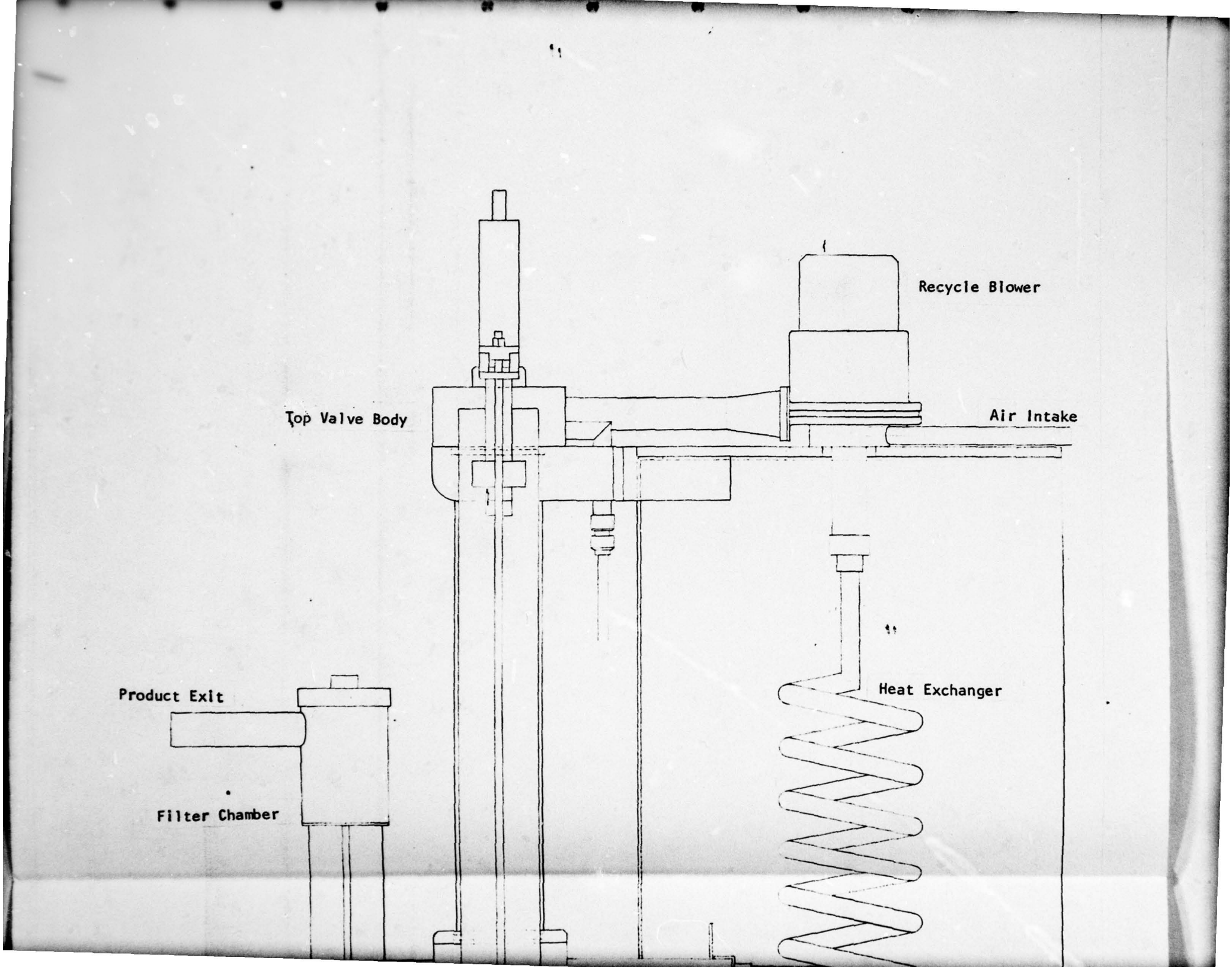


Figure 23 SUMMARY OF TUBE FURNACE DATA

SA5203 High Nickel Catalyst
Propane/Air 10 Cycles


Recycle Blower
Top Valve Body
Air Intake
Heat Exchanger
Product Exit
Filter Chamber

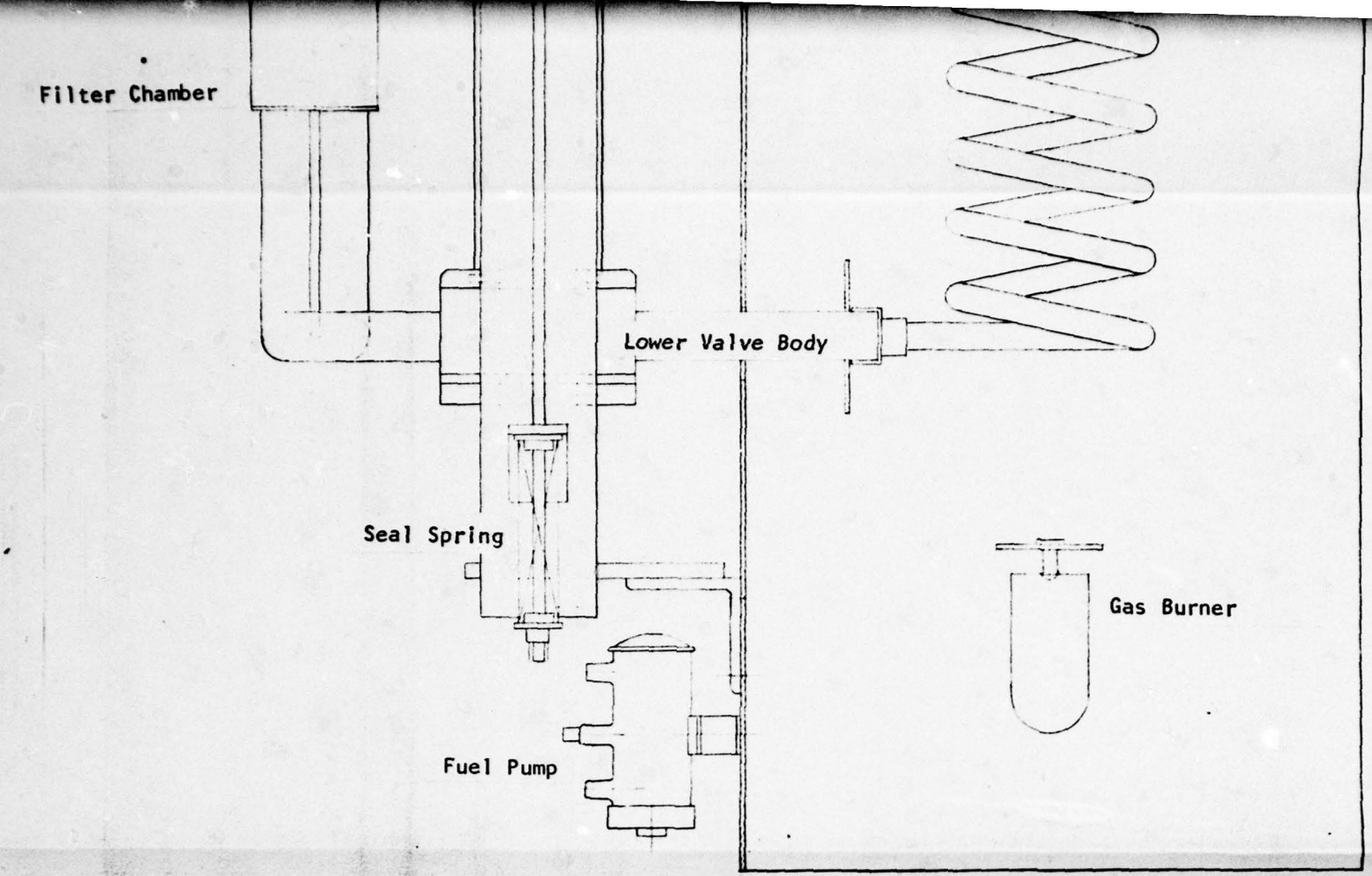


Figure 24 Breadboard Unit - Side View

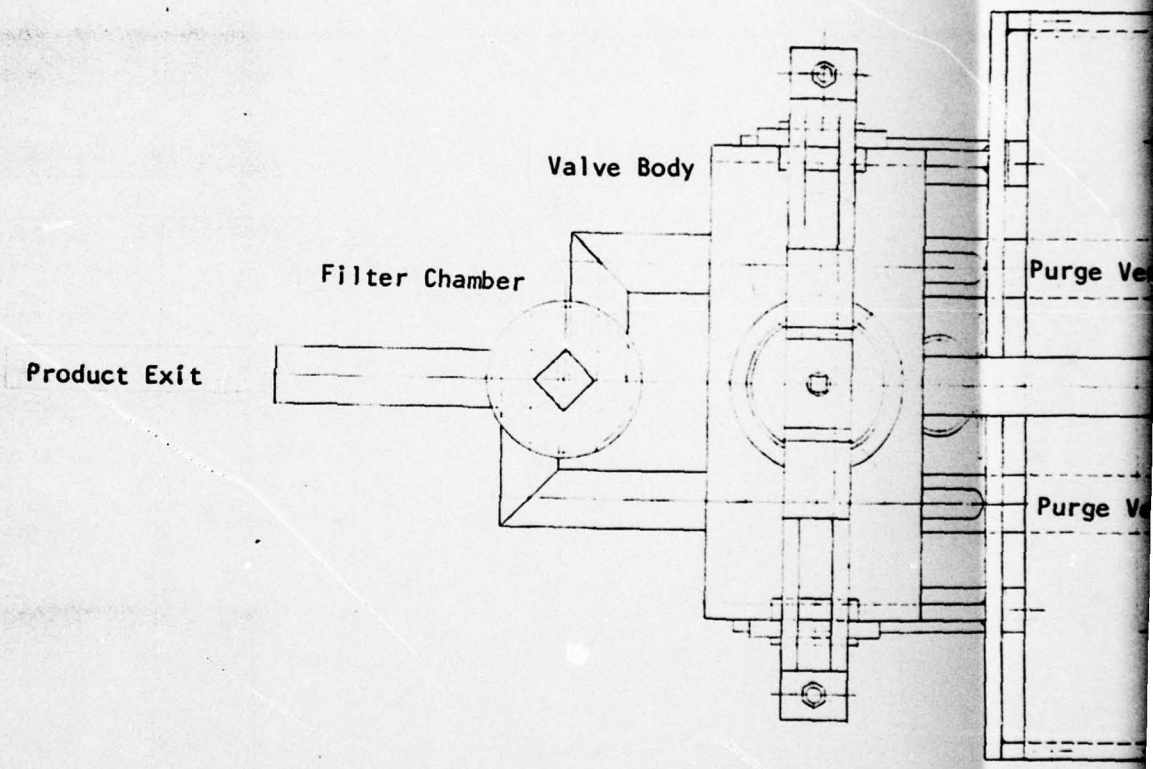


Figure 25 Breadb

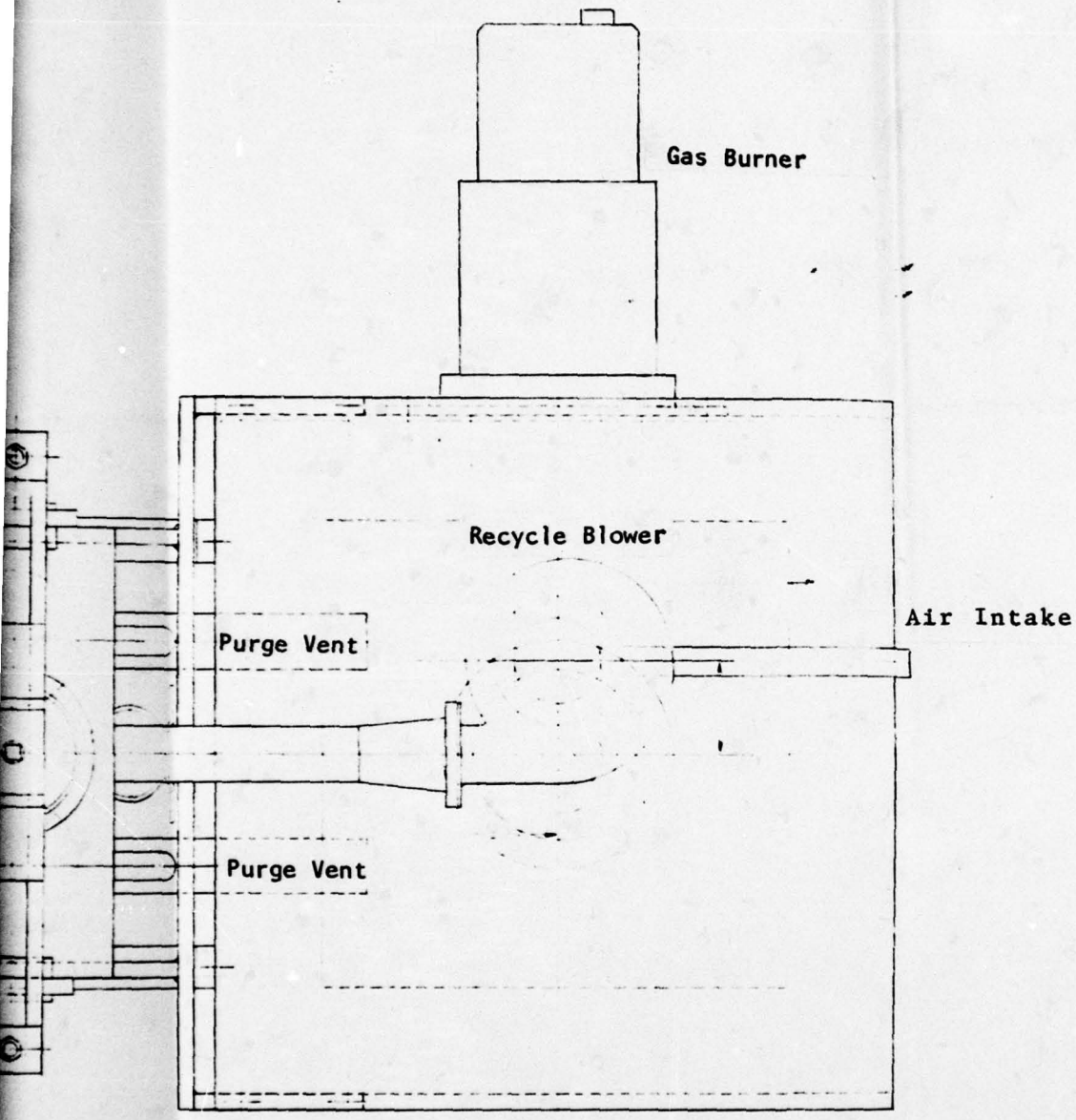
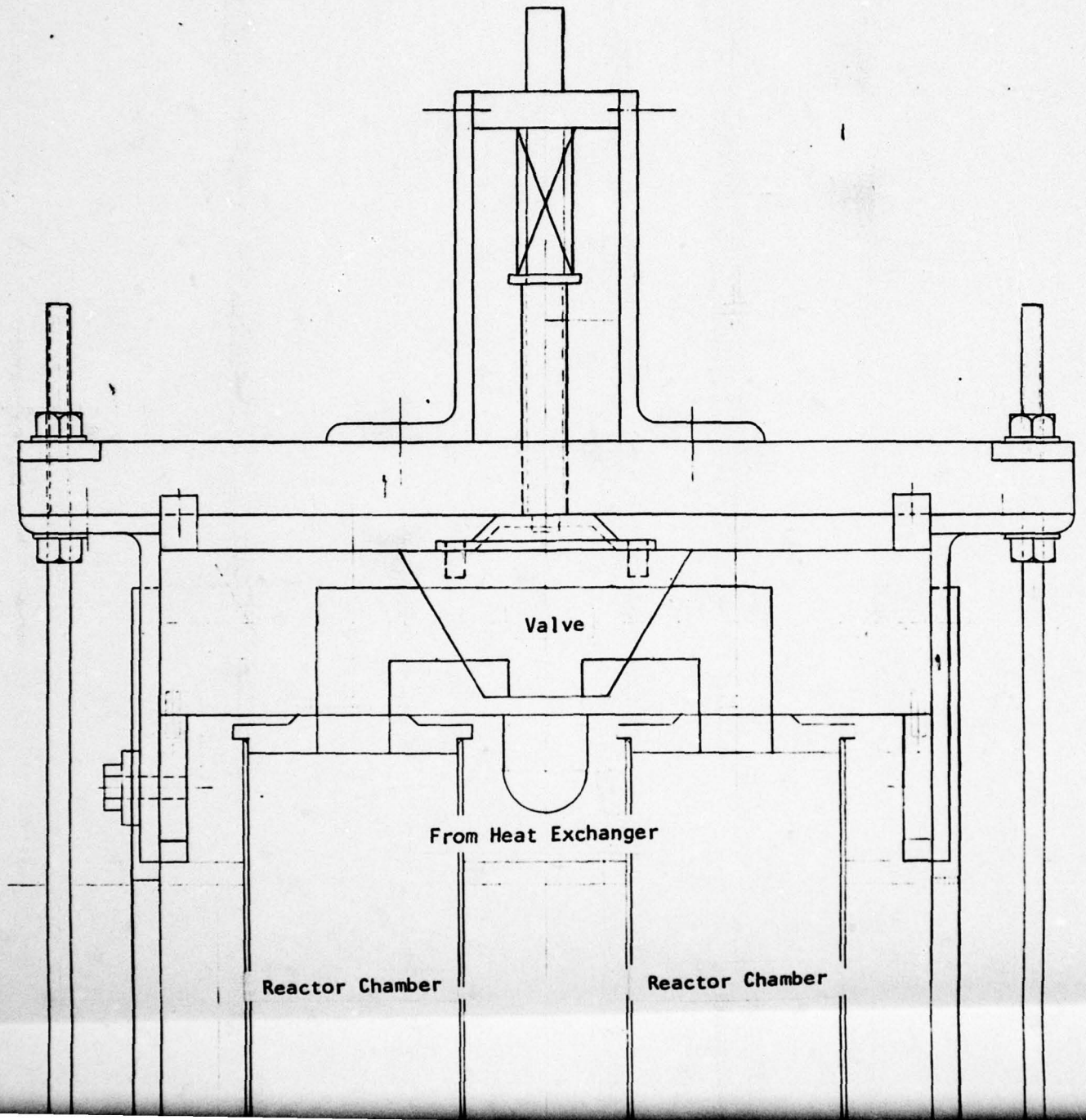


Figure 25 Breadboard Unit - Top View


Valve
From Heat Exchanger
Reactor Chamber
Reactor Chamber

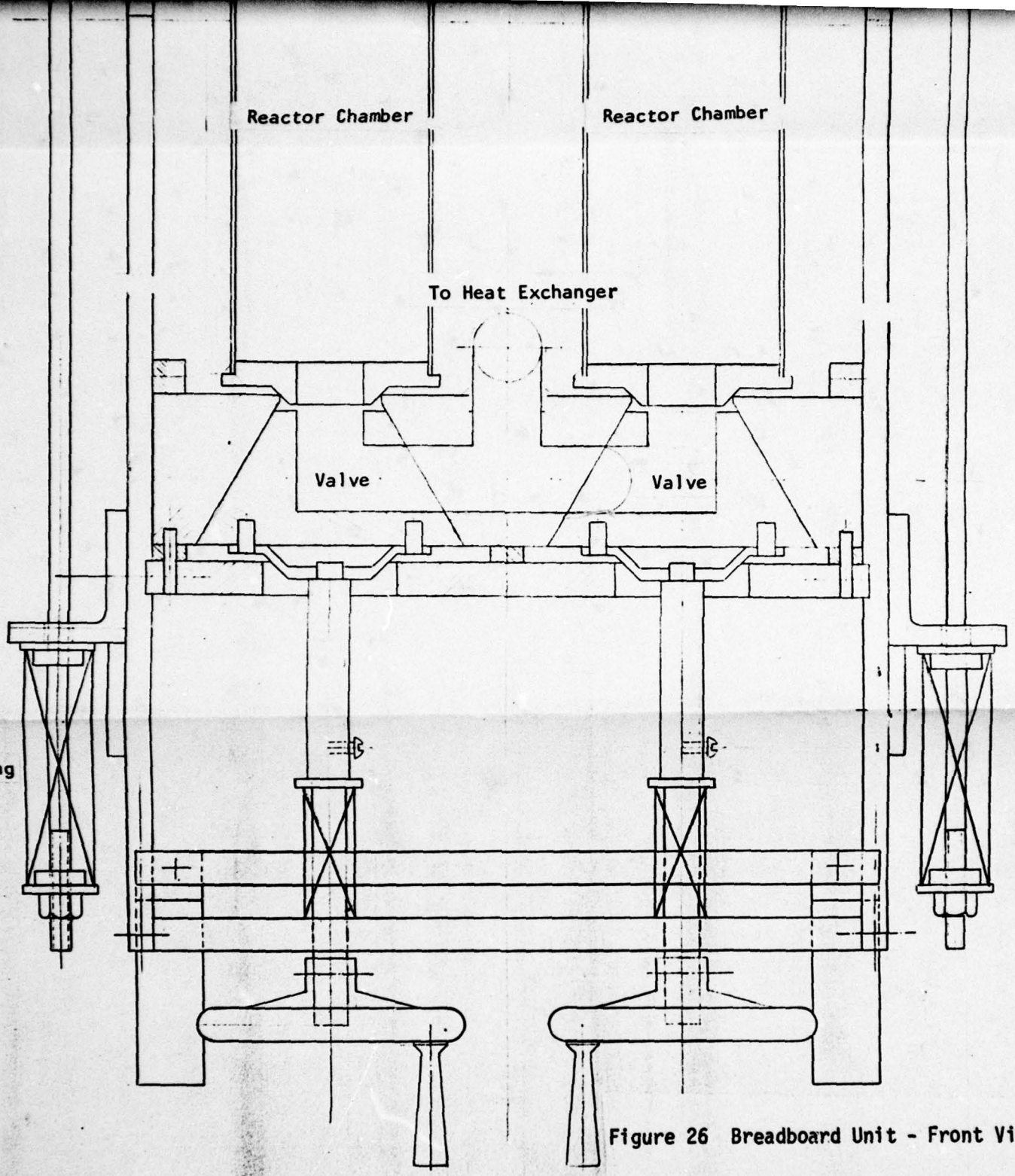


Figure 26 Breadboard Unit - Front View

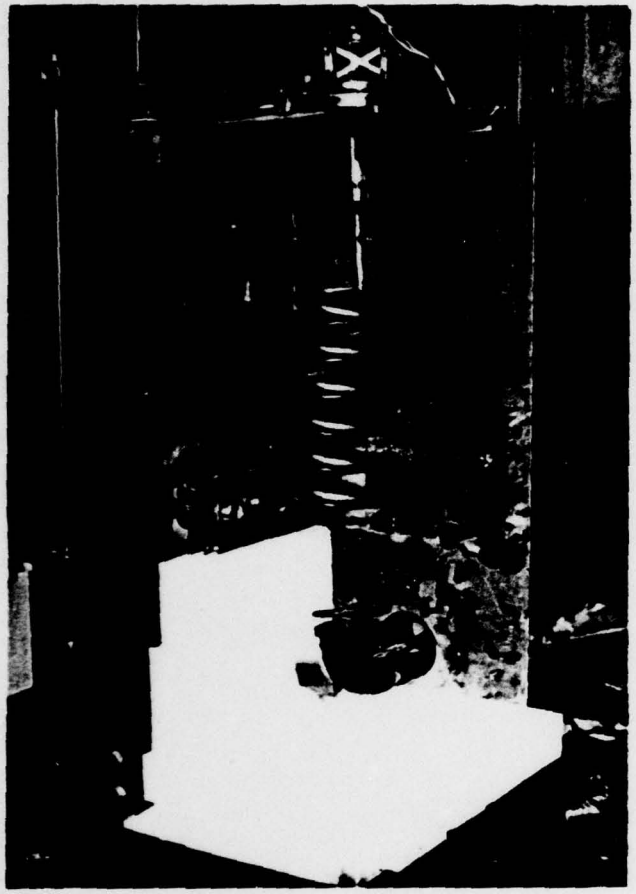


Figure 27 - Heat Exchange Section

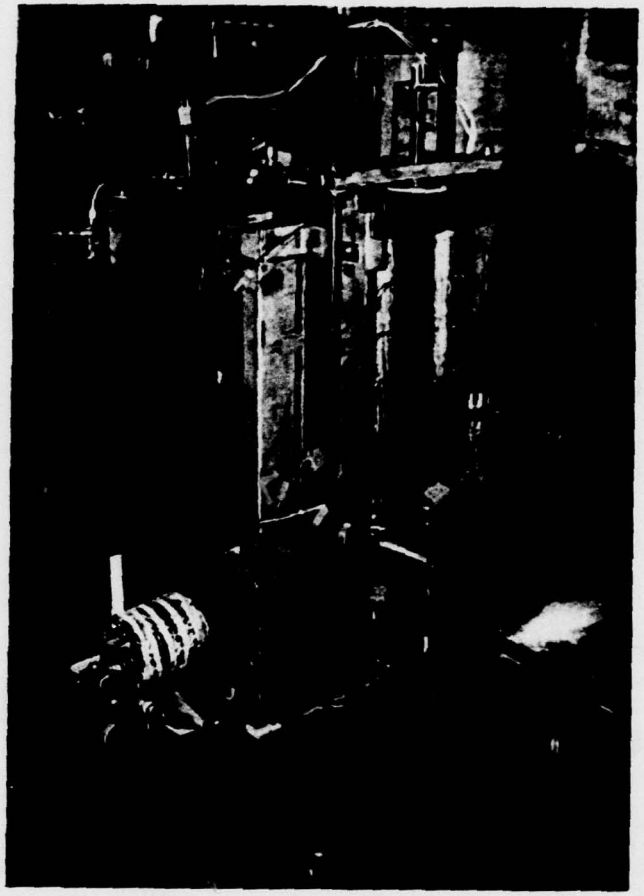


Figure 28 - Overall View - Reactors

APPENDIX A
SUMMARY OF PREVIOUS CONTRACT WORK

SUMMARY OF PREVIOUS CONTRACT WORK

IITRI's work on a "Hydrogen Generator Subsystem" was influenced by previous work performed by:

Institute of Gas Technology
Engelhard Minerals and Chemicals Corporation
Pratt and Whitney Aircraft

Several system concepts were evaluated on paper and in some cases experimentally. Among these concepts were steam reforming, partial oxidation and thermal or catalytic cracking. Prototype hardware was constructed by Pratt and Whitney to further evaluate thermo-catalytic cracking as a "combined" process.

Steam reforming is a continuous process which involves conversion of hydrocarbon fuels and water vapor to hydrogen, carbon monoxide, and carbon dioxide over a suitable catalyst. This process was considered to have the highest yield with excellent product purity, contaminated by only a low level of carbon monoxide. The need forwater in this system posed logistic problems. Since a self-contained unit was desired an outside source of water was ruled out and recycle water was necessary. This recycling would involve large heat exchangers to condense water from exhaust gases. In extremely dry operating areas, exhaust gases would have to be cooled to near or below ambient temperatures. Steam-reforming catalyst could not withstand lead or sulfur found in fuel. Pretreating of the fuel would require added equipment in the hydrogen generator "package". High efficiency and product purity were offset by need for complicated equipment which dictates large unit sizes.

The second type of fuel conditioner considered was partial oxidation of hydrocarbons to carbon monoxide, hydrogen,and water with subsequent processing over a shift catalyst to produce carbon dioxide and water.

Again, as in the steam reforming case, the shift catalyst is poisoned by sulfur and lead,and thus,a pre-conditioner is needed. Weight could be saved, compared to the reforming type, since there is no need for water, but efficiency and product purity are lower. To remove carbon monoxide, more air is necessary, this adds to the nitrogen which acts as a diluent. This lowers the hydrogen concentration and efficiency of the fuel cell. Also, as the fuel cell uses up hydrogen, the concentration drops below the useful limit and product must be discarded or burned for heat. Purification processes are available for the hydrogen stream, such as diffusion though metal films, but these involve complicated equipment or high working pressures. Potential advantages of light weight of a partial oxidation system are offset by poorer product purity and lower efficiency.

The third type of fuel conditioner involves a cyclic process of pyrolysis of the hydrocarbon to its basic elements, hydrogen and carbon. Gaseous hydrogen would then leave while carbon would be left behind. A stream of air would then be passed over the carbon to burn it and supply the heat necessary for the reaction. This cyclic process has advantages and disadvantages. One disadvantage is the need for duplicate reactors, dual sets of piping, and high temperature valves to switch reactors from a generation cycle to regeneration. One advantage of this system is that most impurities in the fuel are deposited on the bed and burned off during regeneration. In this way, the product stream is free from these impurities. Efficiency and purity are as high as the steam reformer, but higher temperatures are involved, 1500-2400°F for catalytic cracking and 2000-3000°F for straight thermal cracking. Materials of construction must then be high quality stainless steels or ceramics.

Each of these process options was considered for use in a "Hydrogen Generator Subsystem" by previous contract workers. A summary of work, results, and conclusions follows.

INSTITUTE OF GAS TECHNOLOGY-DAAK-02-69-C-0452

I.G.T. chose thermal pyrolysis over catalytic pyrolysis as they felt it would be easier to find materials and design for the high temperatures rather than find a catalyst material that will operate at "moderately" high temperature. Catalytic cracking takes place at 1500-2400°F. The lower temperature is about the minimum temperature at which carbon will oxidize, while the upper operating limit is defined by catalyst stability. Primary products of the reaction are hydrogen and methane, with higher temperatures favoring hydrogen. Kinetic effects cause more methane to form than equilibrium predicts. This advantage of higher temperature led to use of straight thermal cracking. These higher temperatures (2500°F) dictated use of ceramic materials for construction. Heat loss becomes critical as one approaches adiabatic flame temperatures so regenerative heating is needed.

A ceramic test reactor and two types of high temperature valves were constructed. One valve was a four way poppet valve much like an automotive exhaust valve, but with stainless steel valves and a seat of boron nitride. The second was a rotary plug valve constructed out of Inconel and boron nitride. Both valves experienced slight leakage, but were considered acceptable for low working pressures. Carbon management in the test reactor was a problem and caused local hot spots that spalled and fused the ceramic balls.

Design information from the test reactor, together with mathematical models led to construction of a breadboard unit. Design information from this led to a prototype design.

ENGELHARD MINERALS AND CHEMICAL CORP. - DAAK-0270-C-0547

Engelhard Minerals and Chemical Corporation also worked on development of a hydrogen generator subsystem. Their approach, unlike I.G.T.'s, was based on thermo-catalytic cracking. Catalysts investigated by Engelhard were platinum on alumina, nickel on alumina, nickel on other ceramics, metallic nickel and Inconel.

Catalyst screening was conducted in a small Inconel test reactor. Results showed no advantage was gained with platinum catalyst. Solid nickel chips were the catalyst of choice for their breadboard system.

After experimentation with a breadboard unit, some problems were observed with metalic nickel as a catalyst. Plugging was observed from carbon deposition, indicating a very active area at the front of the bed. This active area also created hot spots and melting during carbon burn off. Carbon monoxide and water were formed early in the generation cycle from reduction of nickel oxide on the surface to metalic nickel. The large amount of carbon monoxide made it necessary to add a methanator (to convert the poisonous carbon monoxide to harmless methane) to protect the fuel cell. This was done at the expense of hydrogen and lowered efficiency of the unit. A 20-30 hour initiation time was observed for the catalyst to reach full activity. The reason for this time was assumed to be nickel migration, where a layer of nickel was deposited on alumina Raschig rings which were used as a bed diluent. To solve plugging and overheating problems, a graded bed, consisting of four percent metalic nickel at the inlet increasing to 30 percent nickel at the exit, was used. This bed performed well with no plugging or hot spots.

PRATT AND WHITNEY - DAAK-02-69-C-0453

Pratt and Whitney also evaluated different methods of cracking fuel to give hydrogen for fuel cell operation. They concluded that catalytic cracking was the most advantageous method and designed a cracker based on a rotary ceramic honeycomb wheel coated with nickel.

As the wheel was slowly rotated different sectors of the wheel went through alternating generation and regeneration stages. This eliminated the need for separate high temperature valves or two reactor chambers and was light weight and compact.

This system had problems caused by fuel cracking in the vaporizer section. Carbon built up and plugged the seals to the wheel. Part of the honeycombs of the wheel also were plugged such that no air could pass through to burn off carbon.

Catalyst integrity in general was acceptable, although some wheels did develop cracks.

A new rotary cracker was designed based on data from the first model. The bed consisted of an annulus with U-shaped passages for catalyst. The catalyst was a pelletized form of supported nickel. Much higher yields resulted from the combination of more catalyst area and less leakage past the seals. Introduction of fuel directly into the bed eliminated carbon formation on the seals.

PRATT AND WHITNEY - DAAK-02-70-C-0518

Objectives were to improve performance and durability of the thermal cracker, verify suitability of the fuel cell and stack configuration, improve voltage regulator design and performance, and verify integrated operation of the several functional sections of the automatic unit.

Further catalyst investigations indicated that one half inch alumina spheres in a bed "graded" from one percent nickel at the beginning to 20 percent nickel loading at the exit of the outer space of an annular reactor provided the best performance. This kept the inside space, which served as fuel vaporizer, cool enough so as not to prematurely overheat the fuel. Tests with leaded gasoline and sulfur "doped" fuel showed no loss of performance but increased soot levels resulted with high amounts of sulfur. Prototype units were built, but performance was not adequate due to hot spots, bed plugging and other non-uniformities.

APPENDIX B

COMPOSITION OF CATALYSTS AND SUBSTRATES

AD-A068 452 IIT RESEARCH INST CHICAGO ILL F/G 10/2
HYDROGEN GENERATOR SUBSYSTEM. CATALYST AND EQUIPMENT DEVELOPMEN--ETC(U)
NOV 78 R HENRY DAAG53-76-C-0081
UNCLASSIFIED IITRI-C6363-33 NL

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COMPOSITION OF CATALYSTS AND SUBSTRATES

Major components of substrates used in the preparation of catalysts which were evaluated in the course of work on this contract are listed in Table B-1.

Table B-2 lists free nickel content for each of the catalysts used and in bench unit studies.

A summary of barium and nickel contents of stabilized catalysts is shown in Table B-3. Methods of preparation for these catalyst materials are summarized in the following sections.

The initial preparation of a barium-stabilized nickel catalyst involved re-impregnation of Katalco 23-1 reforming catalyst in a hot saturated barium hydroxide solution. Several rings were soaked for 15 minutes in the solution which was held near the boiling point. The samples were then allowed to dry and calcined at 1350°F for two hours. A sample was then heat-treated at 2200°F for three hours.

Compairson of these three samples: 1) untreated 23-1; 2) barium-treated 23-1; 3) heat-treated, barium-treated 23-1 - gave the following results in a "fuel-only" test at 1475°F: a) 13 minutes to damage, b) 23 minutes to damage, c) no activity.

Further catalyst preparations used uncoated substrates so that impregnation of both nickel and barium could be varied. Samples of alumina rings (un-impregnated Katalco 23-1) and Norton SA5202 spheres were both treated with a solution of 10.37 g $Ni(NO_3)_2 \cdot 6H_2O$ and 1.6 g $Ba(OH)_2 \cdot 8H_2O$ per 100 cc water. A 15 minute soak was followed by drying at 300°F for one hour, calcining at 1100°F for an hour and hydrogen reduction at 1350°F for an hour. Two other sets of samples were prepared by similar procedures except that barium and nickel impregnation were separate. This resulted in their sets of samples, Ni + Ba together, Ni/Ba, and Ba/Ni in order.

Tests of all three types showed great improvement with fuel only tests showing no damage after an hour of exposure. However, in cycling fuel-air experiments in the TGA, samples which were impregnated with barium first tended to show lower activity and more damage. Bench unit evaluation of these samples also showed lower activity.

Slightly higher metal loading was obtained when barium nitrate was used. Solutions of 15.08 g $Ni(NO_3)_2 \cdot 6H_2O$ and 2.55 g $Ba(NO_3)_2$ per 100 cc water were used. Soaking times were 45 minutes in each solution and initial drying was at 350°F. Calcining was carried out at 1100°F, followed by reduction at 1350°F in hydrogen.

Table B-1

SUBSTRATE CONSTITUENTS

Substrate	Major Components	
	Al_2O_3	SiO_2
Norton BA307	92.6	6.0
SA5203, 5503	86.9	11.6
SA5202	99.6	<.05
Denstone 57	38.1	56.4
Katalco 23-1	Balance	<.2

Table B-2

NICKEL CONTENT OF VARIOUS CATALYSTS

Type	% Nickel
BA307	0.64
SA5203	10.4
SA5203 Heat Treated	<.01
SA5203 Heat Treated, Recoated	5.25
Katalco 23-1	7.86
SA5503	11.42
Denstone 57	0.57

Table B-3 ANALYTICAL RESULTS BY ATOMIC ABSORPTION ON BARIUM STABLIZED NICKEL CATALYST

Type	% Nickel	% Barium	Comments
23-1 Katalco	8.236	-	Nickel coated ring
23-1 Katalco	2.468	1.381	Nickel coated ring treated with $Ba(OH)_2$
23-1 Katalco	0.031	2.209	Same batch as above - heat treated
SA5202	0.484	0.019	Alumina ball treated with $Ni(NO_3)_2$+ $Ba(OH)_2$
SA5202	0.608	0.043	Alumina ball treated with $Ni(NO_3)_2/Ba(OH)_2$
SA5202	0.707	0.069	Alumina ball treated with $Ni(NO_3)_2$+ $Ba(NO_3)_2$
SA5202	0.653	0.041	Same batch as above
SA5202	0.668	0.049	Alumina ball treated with $Ni(NO_3)_2$/ $Ba(NO_3)_2$
SA5202	0.564	0.045	Same batch as above.
SA5202	0.451	0.023	Same batch as above.

APENDIX C

PRELIMINARY DESIGN BASIS

PRELIMINARY DESIGN BASIS

Conceptual design of the two-bed cracker subsystem was based on a cycle similar to that used previously. Use of a recycle gas - air mixture for regeneration of reactor beds was the major process change, while use of cylindrical beds with length to diameter ratio of six was the major physical change.

Initital design calculations used preliminary data taken with JP-4 fuel at USA MERADCOM. Eighty-five percent conversion at a space velocity of 0.6 volume fuel per hour per volume of bed and operating temperatures of 1600-1800 F were used as a basis. A cycle of 2.5 minutes regeneration; 0.5 minute purge; and 3 minutes hydrogen production was planned for each of the reactor beds. Production of one cubic foot of hydrogen per minute could be accomplished with a fuel flow of 26 cc/min and catalysts beds of 2600 cc (160 cubic inches) which would be about three inches in diameter by nineteen inches long.

Steady state operation of these two beds would require heat removal of about 18,000 Btu/hour and a circulating gas flow during regeneration of 11 SCFM. This would result in an estimated system pressure drop of 10 inches of water and requires heat exchange area of about one square foot.

A summary of preliminary calculations for each of these design parameters follows:

1. Hydrogen Production

26 cc fuel/minute x 0.76 g fuel/cc x 85% conversion
x 15% hydrogen x 22.4 liters/2g x 1 ft^3/28.32 liters
= 1.0 ft /minute

2. Heat Release During Regeneration

Assume:
40% carbon to CO_2 40% x 94050 cal/mole x mole/12gC
60% carbon to CO 60% x 26420 cal/mole x mole/12gC
= 3135
1321
4456 cal/gc

26 cc fuel/minute fed x 3.5 minutes fed/3 minutes x 0.76 g fuel/cc
x 85% carbon x 85% conversion x 4456 cal/g carbon
x Btu/252cal x 60 minutes/hour
= 17670 Btu/hour

3. Pressure Drop

11 SCFM 48 ft^3/minute @ 1800°F
D reactor = 3" Vs = 16.3 ft/sec
D pipe = 1" V = 147 ft/sec
L bed = 2' Dp = 3/8" ρ1800 = 0.018 lb/ft ε = 0.38 μ1800 = 0.049 cp

ΔP bed = 1.75 L/Dp x $\rho V / g$ x $1-\varepsilon/\varepsilon$
= 0.6 inch H_2O

Assume System = 5-90° turns; 4' of 1" pipe; reactor; 1-expansion;
1 contraction; neglect blower

90° turn - 30 equivalent diameters
Expansion - 35 equivalent diameters
Contraction - 18 equivalent diameters

Total equivalent length - 21 feet

P pipe: $N_R = VD\rho/\mu$ = 6700, f = 0.033
$\Delta P = f \ V^2 \Sigma L / 2gD$
= 9.6 inch H_2O

Total ΔP = 10.2 inches H_2O

4. Heat Transfer Requirements

ΔT: 17670 Btu/hr x hr/60 minutes x minute/11 SCF x $lb^{o}F$/0.25 Btu

x ft^3/0.0808 lb = $1325^{o}F$

Thot = $1800^{o}F$ Tcold = $475^{o}F$

ΔThot = 1725 ΔTcold = $400^{o}F$ ΔTlog mean = $900^{o}F$

A: 17670 Btu/hour x hour $ft^{2o}F$/20 Btu x 1/900 F = 1 ft^2

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US Army Mobility Equipment R&D
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Fort Belvoir, VA 22060

Director (1)
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