DIRECT PRODUCTION OF HYDROCARBONS FROM COAL-STEAM SYSTEMS

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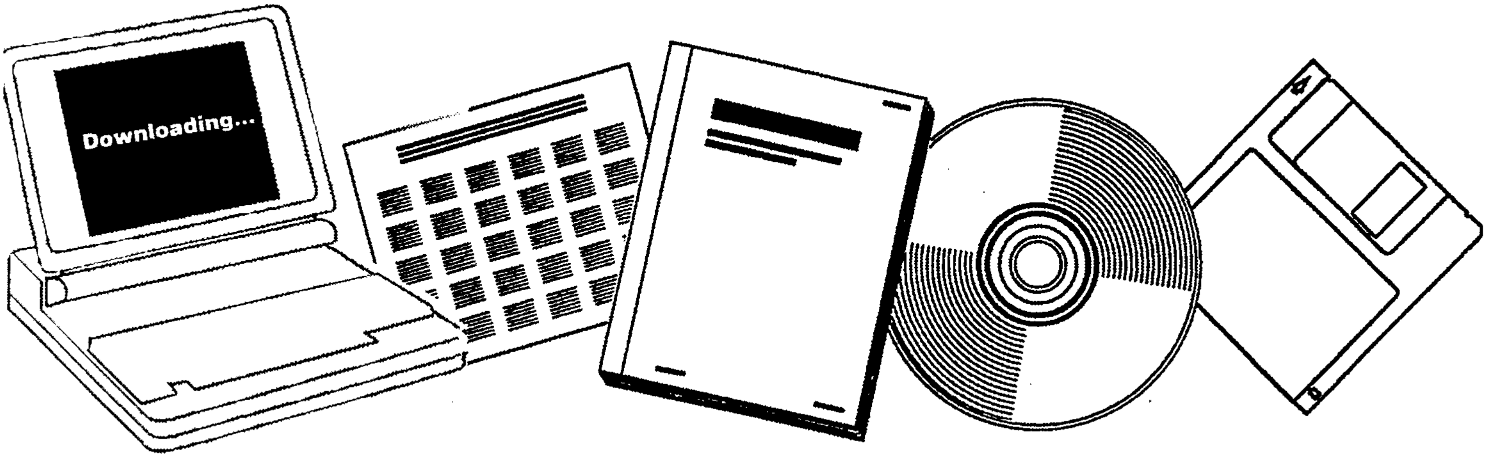

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THE DIRECT PRODUCTION OF HYDROCARBONS FROM COAL-STEAM SYSTEMS

RESEARCH AND DEVELOPMENT REPORT NO. 80

FINAL REPORT

November 1968 - November 1973

Prepared for

OFFICE OF COAL RESEARCH
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Experiments were carried out on the use of a multiple catalyst system consisting of potassium carbonate and a commercial nickel methanation catalyst for the direct production of methane from coal-steam reactions. This system combines the effects of these catalysts to produce in a single-step conversion a product gas consisting primarily of methane and carbon dioxide with a CO_2-free heating value as high as 850 Btu per SCF. Two of the apparent problems inherent with such a system were catalyst recovery and the loss of catalyst activity over prolonged periods of time at the conversion temperatures (1200° and above) in the presence of the various reactants produced from the coal gasification. In conjunction with the latter problems, experiments were also performed on the influence of sulfur compounds produced during gasification upon catalyst life and activity.

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Prepared by:

David K. Bosshardt, John L. Cox, Walter E. Duncan, Edward J. Hoffman,

Robert Hoffman, Francis C. Hoodmaker, Charanjit Rai, L. John Sealock, Jr.

Donald L. Stinson and Warrack Willson

University of Wyoming

Laramie, Wyoming

Contract 14-01-0001-1196

for

Office of Coal Research

Department of the Interior

Washington, D.C. 20240

March 3, 1849

As the Nation's principal conservation agency, the Department of the Interior has basic responsibilities for mineral, water, fish, wildlife, land, park, and recreational resources. Indian and Territorial affairs are other major concerns of America's "Department of Natural Resources."

The Department works to assure the wisest choice in managing all our resources so each will make its full contribution to a better United States -- now and in the future.

Forward

The contents of this report are meant to serve as a summary of the investigations carried out on the NRRI Coal Conversion Process. Since the material being summarized covers a period of five years, only the major accomplishments and results in the opinion of the contributing authors are brought forward at this time. In this way, the overall program has been evaluated from the personnel's point of view with conclusions and recommendations being set forth. This approach has helped to place the accomplishments in clearer perspective as well as define problematic areas and the direction in which the project should proceed.

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THE DIRECT PRODUCTION OF HYDROCARBONS FROM COAL-STEAM SYSTEMS

ABSTRACT

The University of Wyoming has developed a process for the direct production of light hydrocarbons from coal under an Office of Coal Research contract. The process uses a multiple-catalyst system for converting coal to methane and other light hydrocarbons in the presence of steam. The catalysts are mixed with coal in a reactor to maximize the formation of methane. The operating temperatures have been optimized at about 650°C. This is considerably lower than the conventional gasification temperatures thereby permitting use of more economical reactor designs and heat transfer systems.

The program has successfully demonstrated the production of a reactor off-gas that averages over 900 Btu's per standard cubic foot on a carbon dioxide free basis. Gas yields of at least 10,000 standard cubic feet per ton of coal charged indicate a conversion of 65 to 75 percent of the energy originally contained in the coals tested. The low-sulfur Western coals also used in this program do not seriously affect the catalyst activity at these temperatures. Thus, high Btu gas has been produced in a single reactor.

Detailed design engineering toward fabrication of a 6-inch diameter fully continuous fluidized bed reactor has been conducted by Stearns-Roger. This represents a scale-up of a continuous coal feed system tested in the laboratory. This will permit a study of continuous reactor feeding problems, catalyst life and other scale-up problems.

Section I

SUMMARY & CONCLUSIONS

The research and development program on the NRRI Coal Conversion Process was initiated largely through the realization of the potential economic benefit that could be obtained from such a conversion scheme. The process is described under U.S. Patent #3,505,204. The crux of the innovation contained within the patent is the use of a single-stage multiple catalyst system to effect the direct conversion of a carbonaceous material with steam to hydrocarbons. It has been predicted from thermodynamic calculations that such a conversion in a single-stage reactor will approach or possibly even be autothermal, i.e., energy necessary for endothermic reactions will for a large part be supplied by the exothermic hydrocarbon formation reactions. This would permit a large energy input savings over other more conventional multiple-stage coal conversion schemes. This coupled with the simplified processing requirements (single plant in place of two) and pressure independence make it the most attractive and potentially the cheapest process for the production of hydrocarbons from coal.

Although investigations have been limited to small semi-continuous bench scale equipment, the results indicate that the innovative concept continues to have merit. Experimental results that are in strong support of this have been obtained through the gasification of coal at essentially atmospheric pressures and temperatures from 525--725°C, in the presence of alkali and nickel catalysts to a gaseous product which has a heating value in excess of 800 Btu/SCF (CO_2-free). This high heating value is consistent with an approach to autothermisity since the greater the products volumetric heating value the closer the approach to heat balance. Much of the experimental effort has been directed at optimization of conversion conditions and demonstrating the single-stage conversion concept.

It has become apparent through the empirical results that the conversion can be altered in a predictable manner to radically change the nature of the product. The variables include type of coal, catalysts, temperature and regulation of the steam feed rate. Hence, by the proper choice of these conditions a product can be made that consists primarily of a low Btu/SCF gas, a high Btu/SCF gas, hydrogen or predominately liquids. Furthermore, at pressures up to 300 psig a pressure effect upon gasification has yet to be demonstrated. Here again, this observation is consistent with thermodynamic predictions for a direct conversion process.

Various alkali and alkaline earth carbonates have been evaluated as one of the members of the multiple catalyst system. The other member being Group VIII transition metals. It has been found that the three best of the former types of catalysts on an as charged basis are sodium carbonate (Na_2CO_3), trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) and potassium carbonate (K_2CO_3). However, the explicit nature of these catalysts under reaction conditions is not known. Employing K_2CO_3, it has been determined that the optimum quantity of alkali carbonate was 20% of the mass of coal. Furthermore, the recoverability of this catalyst from the ash by a single wash is in the neighborhood of 90%. Of the transition metal catalysts, iron and nickel have received the most attention. The iron catalysts employed have included various commercial types as well as millscale and pyrite cinders. With iron catalysts conversion yields as high as 0.8 bbls of liquids plus over 5MSCF of gaseous hydrocarbons per ton of coal have been realized. On the other hand, the nickel catalysts have been found to be highly selective, producing essentially hydrogen, carbon monoxide, carbon dioxide and methane. Methane yields of over 10MSCF/ton have been realized and the overall product gas has a heating value in excess of 800 Btu/SCF (CO_2-free basis). Gasification yields approaching 75% of the theoretical possible methane have been obtained at 650°C and 30 psia.

In an attempt to address the problems associated with scale-up a continuous feed system that employs a coal-water-alkali slurry has been developed and placed in semi-continuous operation. This system is in addition to the batch charge system that has continually been employed for data aquisition. The experimental gasification results from this system approach those obtained with the batch charge system and provide additional support for the direct conversion concept.

In conjunction with the above experimental investigations and in support of the overall program a vigorous catalytic methanation program has been carried out. The objectives of this segment of the overall program have been to provide answers to problematic areas. The two areas that have received particular attention are the matter of catalyst poisoning, especially from sulfur, and high temperature methanation.

The high temperature catalytic methanation studies have shown the feasibility of obtaining good methanation yields in the range of temperatures employed in the above integrated systems.

Since poisoning of the methanation catalyst by sulfur compounds gasified from coal is one of the areas of major concern, particular attention has been focused here. It is apparent that although the standard methanation catalyst is more resistant to sulfur poisoning at these high methanation temperatures, that poisoning will still occur. In addressing this problem, solutions and alternatives have been sought. Some encouraging success has been obtained at catalyst regeneration by employing a synthesis gas. Other more sulfur resistant methanation catalysts are being considered as well as other regeneration concepts.

In conjunction and in support of the conversion project other pertinent information of general interest is being generated. The development and implementation of both routine and non-routine analytical and petrographic procedures and techniques being one. Three additional areas include the relative low temperature reactivity results of several western coals and gasification conditions, fundamental catalyst investigations employing sophisticated physical techniques and general interest information circulars.

In view of the current development status of the project, it is the general concensus of the investigators that it has been taken as far as practically possible at the small bench scale level. Although there is a need for accompanying bench scale work the process should be scaled as soon as possible to a larger size where continuous operation of the single-stage multiple catalyst direct conversion process can be attained. The larger size conversion unit is to address sulfur poisoning, fluidization, conversion optimization and processing. It is necessary to have a larger continuous reactor to realistically attain these objectives. To, this end, the design and cost estimate of a larger unit has already been performed by Stearns-Roger.

Section II

Introduction

Over the past seven years research and development has been carried out on the NRRI Coal Conversion Process. In the last five years the work has been supported through a contract (#14-01-0001-1196) with the Department of Interior's Office of Coal Research. The objective of the program is to demonstrate and develop the process concept, which is presented below, for the production of both methane and liquid hydrocarbons from coal.

The NRRI Coal Conversion Process is described under U.S. patent #3,505,204 titled the "Direct Conversion of Carbonaceous Material to Hydrocarbons." The conversion is effected by the reaction of steam with coal in the presence of a two component catalyst and is illustrated by equations 1 and 2. It is apparently the opinion of the Division of Engineering of the National Academy of Engineering that such a conversion could revolutionize coal gasification and as such should be strongly supported.[1]

$$C + H_2O \xrightarrow[\Delta]{\text{catalysts}} \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \qquad (1)$$

$$\frac{(3n + 1)}{2}C + (n \pm 1)H_2O \longrightarrow C_nH_{(2n+2)} + \frac{(n + 1)}{2}CO_2 \qquad (2)$$

The first catalyst component is an alkali metal compound while the second is a transition element compound of Group VIII. By employing this multiple catalyst system, good yields of hydrocarbons can be obtained in a single-stage reaction at temperatures from 500-700°C.

There are obvious advantages of a single- versus a multiple-stage conversion scheme: 1) a single-stage reaction is predicted to require less heat, and 2) a single-stage reaction is predicted to be relatively independent of pressure. Both of these aspects of a single-stage conversion process provide tremendous economic advantages in terms of the plant construction cost and maintenance and energy requirements for the process.

The following report is broken up into several chapters that present areas of research and development in support of the overall program. These chapters include Integrated One-Inch Batch Reactor, Integrated One-Inch Continuous Feed Reactor, Catalyst Studies-Half-Inch Flow Reactor, Analytical Methods and Results, and Petrographic Methods. A section listing the technical publications resulting from this project has also been included. Each chapter has been written by the individual who heads up that area. Included within each of these support areas is a section on recommendations and conclusions.

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[1] R&D Report No. 74 - Interim Report No. 1, "Evaluation of Coal - Gasification Technology, Part I Pipelipe-Quality Gas," Prepared for OCR, Dept. of Interior. Contract #14-32-0001-1216.

Section III

INTEGRATED ONE-INCH BATCH REACTOR

The research and development program initiated previous to January 1, 1971, entailed development of equipment needed to carry forward further work. The reactor system was continually revised until a completely integrated unit was established. As a result of these revisions a single-stage, fixed bed reactor with a lower section for the production of super-heated steam was constructed. The volume of gas produced was measured with a wet test meter. At the same time the gas analysis progressed from an orsat apparatus to an "on-line" gas chromatograph. A flow diagram illustrating the experimental unit is contained in Appendix A, page 33.

The thrust of the work during this time was to examine the influence of various operating variables upon the coal conversion using the NRRI Coal Conversion concept. Variables examined were steam rate, catalysts, temperature and pressure. The emphasis was upon finding the proper conditions for the production of liquid hydrocarbons and a gaseous fuel by-product. There were approximately 250 independent runs made with the integrated system during this phase of the work. The end results were both encouraging and discouraging. However, ideas, information and expertise were accumulated for a more intensive investigation. Some of the earlier observations and results from the single-stage multiple catalyst coal-steam reaction system were: (a) that iron catalysts produce significant quantities of liquid and gaseous hydrocarbons, whereas nickel catalysts form primarily methane and other accompanying gases; (b) the steam rate must be judicially controlled since high steam rates, particularly in the presence of iron catalysts, tend to yield an effluent rich in hydrogen; (c) that the coal-steam reactivity seems to decrease with pressure, but can be off-set by increasing the temperature; (d) carbon monoxide introduced along with the steam enhances the catalyzed coal-steam reaction, and (e) that hydrocarbon production falls off with catalyst temperatures in excess of 600°C. Runs 203-37 in Appendix A present some of these earlier experimental results.

January 1, 1971, saw a change in approach. The emphasis had changed from liquid hydrocarbon to gaseous hydrocarbon production. The earlier investigations had established that nickel catalysts were more suitable for methane production, so a number of nickel catalysts were obtained from commercial sources for testing and evaluation.

The daily activity centered on obtaining reproducible results and pursuing findings obtained earlier. Efforts were confined to holding temperatures constant and finding the range of other variables that would produce the most consistent results. Reproducible results were obtained after two months effort by using a single commercial catalyst and controlling temperatures and water feed within a narrow range. Hence, product gas was regularly 900 Btu/SCF or better, with overall conversions generally greater than 65%. Some of these results are included in Runs 282-9, page 40. The heating value of these product gases, as reported, are thought to be on the order of 50-100 Btu/SCF too high.

The next several months were spent in looking for the best catalyst in respect to size, shape, hardness and percent nickel. In this respect the nickel catalyst, Ni-3210, proved to be superior to the others. Some projections from attrition studies on this catalyst are presented in Appendix A page 48 and 49 . Also contained in Appendix A pages 35 through 38 is a tabulation of catalysts tested in the integrated system.

Variations in coal size, amount of alkali catalyst and water were studied for best results. While the conversion was relatively insensitive to the size of coal employed, it was strongly influenced by the amount of alkali catalyst as well as the amount and technique of water addition. It appeared that in the neighborhood of 20 wt% of alkali was optimum while steam addition was more of an art. Excessive steam appeared to deactivate the methanation catalyst and promote the CO-shift reaction. Both of these effects resulted in a lowering of the heating value of the gas product.

The gas analysis and other analytical support during the preceeding investigative periods left something to be desired. The gas chromatograph was not exacting enough, due to the fact that N_2 and O_2 eluted with the CO, and did not give dependable CO results. Furthermore, H_2 sensitivity was low leading to inferior results. It was also evident that analytical support for the project needed to be expanded to include other areas. The desire to improve the quality of the gas analysis brought a new, dual column, dual detector gas chromatograph into use. Reliable quantitative results were secured after a testing period (Qtr. 9/27/71). All recorded data also improved thereafter. The new equipment gave a better insight into the chemistry involved and consequently provided a better understanding of the multiple catalyst approach.

The nickel catalyst that had been used since the middle of 1970 began to show loss of activity by September 1971 and it was decided to try rereducing to restore its activity. This entailed building and operating a 2" flow reactor for catalyst reduction. Reduction conditions were 650°C at atmospheric pressure under a monitored flow of H_2 for 12 hours. Due to the high reactivity of the rereduced catalyst inert atmosphere techniques had to be developed. The batch-charge reactor was loaded with the coal, alkali and rereduced nickel catalysts in a custom designed glove box under a N_2 atmosphere. This technique, although laborious and time consuming, disclosed the importance of having the catalyst in a highly reduced state. The reproducibility of the results were improved, consequently along with the quality of the product gas.

A period of time beginning about January 1972 was spent evaluating coals and lignites from North Dakota, Montana, Wyoming and Illinois. It was about this time that the analytical support for the project was also increased. It was during this testing that it became apparent that the quality of the coal had an effect on the temperature needed to take it to complete ash. The higher the rank of the coal, the higher the temperature needed for complete ashing. Lignite went to ash in the range of 1200°F. Total volume of gas produced followed the percent of carbon present. Under experimental conditions there was no significant difference observed in the heating value of the product from the various coals. Appendix A, page 34 contains analyses of these coals and what is considered to be representative gasification results for each are contained on page 41.

During this period it was noted that the contact time involved between the nickel catalyst and the effluent gas from the coal-alkali-steam reaction was critical in bringing maximum methanation activity to the catalyst. The shorter the residence time, or higher the flow rate, the lower the activity of the nickel catalyst. In this connection it had been determined previously that the water volume introduced had a great bearing on the catalyst activity, likewise the temperature at which the steam enters the coal-alkali bed. The higher the temperature of the steam, the better the production of CO + H_2 and methane.

August 1972 brought a change in supervision and with it a change in direction. Our research went forward but was directed more toward a basic approach. Many things that had been tried before and evaluated were repeated. The configuration of the reactor was changed to give a less variable temperature profile. A comparison of the temperature profile before and after this modification is shown in Appendix A page 50. Accompanying the more isothermal reaction conditions was a decrease of about 100 Btu/SCF in the gas production, i.e., from about 950 to 850 Btu/SCF (CO_2-free). In contrast to some of the earlier runs using a stratification of reactants, all catalysts and coal were mixed intimately and increased emphasis was placed on securing material balances. The top temperature in the reactor was held at 650°C. The lower super heater section of the reactor had to be increased to 730°C. The result of having increased the steam temperature was that it improved the volumetric heating value of the gas product and increased the overall conversion. This point is demonstrated in Appendix A page 52-54.

It was felt that the alkali to coal ratio might not be determined properly so a good many trials were made using from 12g alkali/100g coal to 60g alkali/100g coal. The end result was that a figure, in agreement with previous results, of about 20g alkali to 100g coal would be optimum. These results are presented in Appendix A, pages 58-59. It was during this period that the analytical group made single ambient temperature wash separations of the alkali from the ash. Results show that 85-99% of the alkali present could be dissolved. In addition it was shown by X-ray diffraction that the alkali carbonate in the ash was the same form as that originally charged.

The suggestion was made that the production of H_2 be tried using high and low temperatures plus high and low water volume. The usual shift reaction, $CO + H_2O = H_2 + CO_2$ occurred at the lower temperatures and gave very good H_2 production from the coal char after first driving off the volatiles in the production of high Btu gas. In excess of 50 MSCF of H_2 per ton of coal was obtained using the multiple-catalyst, single stage reactor approach. A tabulation of some of the results are included in Appendix A pages 42 and 43.

Although considerable earlier efforts were directed at obtaining sulfur material balances within the integrated system, the only attempt to control sulfur deposition on the nickel catalyst has occurred just recently. The purpose of the sulfur balances was to provide information on which to assess the nature and extent of the sulfur-methanation catalyst problem. It was evident from these analytical results that the nickel methanation catalyst was picking up sulfur during the conversion. Various preselected compounds were introduced with the coal and alkali to see if they might act as sulfur scavengers. Initial results look promising. Further work has been planned along this line.

Conclusions and Recommendations

1. Following the preliminary investigations up to January 1, 1971, it would be pertinent to point out that some significant results, using Group VIII metal catalysts, were forthcoming. Namely the production of liquid hydrocarbons and methane gas.
2. The apparent pressure independence of this system is a plus factor. The advance from a fixed bed reactor to a fluidized bed could be accomplished on a reasonable budget. The design and cost estimate for such a unit has already been worked up by Stearns-Roger. Looking at all our reactor runs using pressure and disregarding mass balances, we can find no effect upon the volume or quality of the off gas. This observation is consistent with thermodynamic predictions for a single-stage conversion process.
3. It appears that the alkali and alkaline earth carbonates lend themselves well as catalysts for the production of CO + H_2 and methane from the coal-steam reaction. The availability of such catalysts speaks well for their use.
4. The necessity of solving continous reactor feeding problems requires that we have a larger unit to work with. Two approaches need to be tried, i.e., slurry feeding and dry coal into steam. Reactor feeding with the small unit we were working with was too much of a problem to be solved using dry coal into steam. The result was to stay with the fixed bed and hope for a larger reactor unit so more development work could be done on feed problems. It might be pertinent to say that the problem would be easier solved where pressure need not be considered.
5. One of the critical factors demonstrated in our numerous reactor runs is "residence" time during the methanation reaction. Some criticism has been leveled at the multiple catalyst idea because of the large volume of nickel catalyst used in relation to the coal volume in our reactor set-up. This is only due to establishing a proper contact time for the methanation reaction, i.e., need for a long column of catalyst to establish the proper contact time in a fixed bed. There is no relationship between a fixed bed and a commercial approach with a fluidized bed and a continous feed as to residence times. Hence, further reason for the necessity of scale-up. One is very apt to be in a different ball game with a fluidized unit.

   The reason most apparent is that in a batch charge fixed bed reaction the composition of the reactants is constantly changing while with a fluidized bed the feed of coal and steam would be of a stable nature, giving a more constant composition in the reacting gas. Other variables enter into the reaction which may tend to supress methanation, i.e., excess oxygen, poor ratio of CO_2, CO and H_2. Based on the difference between gas-solids contacting between a fluidized and fixed bed reactor, one could expect different results.

   The recommendation here is that no hard judgement of the process be made until proven results are obtained by using a fluidized bed reactor. The concept of continous feed, recycle of off gas and catalyst life cannot be prejudged or even the extent of the problem adequately defined by fixed bed results. In fact analytical results from recent runs using Fe_2O_3 as a sulfur scavenger indicate nearly all the sulfur is retained on the scavenger in the ash.

The investigation of sulfur scavengers has barely been touched. Other compounds could very well combine more readily or at least compete with the nickel catalyst for the forms of sulfur given off during the conversion process. Catalyst alternatives and regeneration techniques also would appear to have merit and deserve consideration.

6. The evaluation of numerous nickel catalysts as methanation agents has demonstrated what is needed for this type of process catalyst. The Harshaw nickel catalyst Ni-3210 has been shown to be satisfactory for fluidization techniques. Attrition loss stablized after the sharp edges were worn off. Activity wise nothing better has been found. This also applies to high temperatures on the order of 1200°F to 1350°F.

Section IV

INTEGRATED ONE-INCH CONTINUOUS FEED REACTOR

Prior to January 1, 1972, the initiation of this portion of the study, no significant success had been achieved with small-scale apparatus for feeding either coal-water slurries or dry pulverized coal.

Coal-water slurries were very unstable unless they were kept agitated, a condition that could not be maintained with small scale equipment. It was found that the addition of alkali to the slurry formed a more stable slurry. This was determined to be due to the formation of Na^+ or K^- salts with the acidic groups present in the coal forming compounds with a thixotropic nature. Alkalis function as catalysts in the production of synthesis gas. It was decided to concentrate efforts on the feeding of coal-water-alkali slurries so all raw materials would be introduced into a reactor simultaneously.

Due to the capacity limitations of our equipment it was decided to use a variable speed screw drive piston pump. Slurries containing 50% to 60% coal with 5% to 6% trona could be successfully pumped with this equipment at rates ranging from 75 ml/hr to 300 ml/hr.

Numerous failures were encountered when it was attempted to pump slurries through a tube heated to 700°C. The bulk of our studies have been run with Glenrock coal, a low-sulfur, sub-bituminous, Wyoming coal. Glenrock coal does not fuse or coke when heated in a crucible to 700°C. However, when alkali is added to the coal a fusion does occur. The relative hardness of fused coal-alkali mixtures was found to range in the descending order of hardness of KOH, NaOH, K_2CO_3, and trona. The failures were due to a plugging in the area where the slurry came in contact with the heated portion of the tube. This was determined to be caused by the fusion or coking of the coal alkali mixtures. It was found that placing a rotating agitator in the heated tube resulted in keeping the coke broken up as it was being formed, giving a smooth flow discharging steam, gas, and powdered coke.

In all subsequent studies a one-inch reactor, 70 inches long, heated to 700 - 720°C with electric furnaces was used. A thermocouple placed in the reactor top determined the gas temperatures to be 450 to 490°C. Operating pressures were maintained at 20 - 22 psig. The pre-heater was a 20-inch length of 3/4 inch stainless steel tubing heated to 800 - 820°C with electric furnace. The pre-heater contained a rotating agitator to break-up the coke as it was being formed and conserve the volatile components of the coal. After a series of preliminary studies, a wet test meter was used to measure the volume of gas produced and a gas chromatograph to determine the gas composition was installed.

A screw-drive piston pump with a capacity of 154 ml (1.25 inch bore) was used in a series of studies with the reactor. Fifty percent coal-water slurries containing 5% trona were used in these studies. Pumping rates were maintained at approximately 75 ml/hr. By alternating pumps successful runs of 6 hrs. have been made.

A series of single pump runs produced an average of 3.8 cu. ft. of synthesis gas consisting of 52.2% H_2, 13.4% CO, 6.3% CH_4, 0.9% C_2H_6, and 27.2% CO_2. This gas on a CO_2-free basis had a heating value of 400 Btu/cu. ft.

Char recoveries showed a conversion of approximately 55 - 60% of the carbon in the coal.

The addition of methanation catalysts to the reactor was then initiated. In these studies a catalyst column of approximately 3 ft. was placed in the reactor prior to the introduction of the slurry, the catalysts were reduced in place with the flowing H_2 at 20 psi and oven temperatures of 700°C and gas temperatures of approximately 475°C. With the methanation catalysts, no hydrocarbons larger than CH_4 were detected.

When the slurries were pumped at a rate of 75 ml/hr the activity of several nickel catalysts (1/8 inch extsusion) ranged from 11 to 23% CH_4 and, on a CO_2-free basis, 430 to 560 Btu/cu. ft. It was determined that better methanation was achieved with the softer, more porous catalysts. The rougher surface, exposing more area to the synthesis gas may account for the better activity. It was found that the degree of methanation could be improved by crushing the catalyst pellets (removing the fines) and by decreasing the pumping rate.

Up to seven separate runs have been made with a single charge of catalyst. When this was done, the reactor was charged with the catalyst which was then reduced in place with H_2. After the run was completed H_2 was passed through the catalyst for two hours after which the reactor was sealed with an atmosphere of H_2 until the following day when another run was made and the procedure repeated.

In the study to be reported slurries of 45% Glenrock coal (-100 mesh) prepared with 4.5% trona were used. The reactor was charged with a 20% nickel catalyst, pellet form in one series, and crushed pellets with the fines removed in the other series. The slurries were pumped at a rate of 0.33 ml/min for a volume of 50 ml, the average reaction runs being $2\frac{1}{2}$ hrs. The reactor temperature was maintained at 450 - 480°C as determined by an internal thermocouple. Operating pressure was maintained at 20 - 22 psi. Gas production was measured with a wet test meter. Product gas composition was determined at 15 min. intervals for the final $1\frac{3}{4}$ hrs. of the run. Values shown are the averages of eight determinations. Gas volumes were corrected for the flow through the gas chromatograph.

The results shown in Table 1 show the marked influence of crushing the catalyst pellets thus increasing the surface area exposed to the synthesis gas resulting in an improved methanation.

These data show that in successive runs there is a gradual decrease in the degree of methanation. During the series of seven runs with the crushed catalyst, the reactor was maintained at the reaction temperature for a period of 13 days. Work carried on by another group suggests that there is an increase in the nickel crystal size when the catalysts are subjected to heat. If this is the problem in this work there would be a decrease in the surface area of the catalyst. More meaningful data would be obtained if we had the equipment so that a continuous run could be made instead of daily runs of $2\frac{1}{2}$ hours followed by a shut down of $21\frac{1}{2}$ hours to $69\frac{1}{2}$ hours.

It is impossible to achieve fluidization of the catalyst bed in our reaction. Char does pass through the catalyst bed during a run and is collected in a trap. It is also conceivable, therefore, that a channelization can develop through the catalyst bed, in effect reducing the catalyst contact area. Fluidization of the catalyst bed would prevent this possibility.

Table 1. Crushed Pellets With Fines Removed

Date of run	Run No.	Gas produced cu. ft.	% H_2	% CO	% CH_4	% CO_2	CO_2-free Btu/cu. ft.
6/28	1	0.63	32.6	0.7	34.7	32.0	677.0
6/29	2	0.74	36.9	0.9	29.3	32.9	626.2
7/2	3	0.89	42.8	1.7	22.5	36.8	556.7
7/3	4	0.90	49.0	1.1	20.1	29.8	522.5
7/6	5	0.94	51.7	1.0	21.6	25.6	525.5
7/9	6	1.20	52.7	3.5	17.5	26.1	488.7
7/10	7	1.00	55.8	2.4	14.6	27.2	463.3

Intact Pellets

7/11	1	0.76	45.3	5.8	21.4	27.5	528.4
7/12	2	0.90	47.1	6.7	21.3	25.0	520.4
7/13	3	1.17	53.6	8.3	14.6	23.5	456.3
7/16	4	0.92	56.3	6.8	12.3	24.6	437.3

The poisoning of the catalyst by sulfur does not appear to have been a serious factor in this series of runs. Unused catalyst contained 0.05% sulfur. The sulfur levels in the catalyst at the conclusion of the series of seven runs in the top, center, and bottom of the reactor were found to be 0.19%, 0.13% and 0.50% respectively.

Plans for Future Work. - The results obtained to date have demonstrated several serious short-comings with our present equipment which could, at least in part, be overcome by the use of a larger reactor.

The objective is to produce a high Btu gas that must have a high level of methane and low level of hydrogen and carbon monoxide. To achieve this goal several factors must be brought into balance. These are slurry composition, slurry pumping rate, and methanation capacity. Though not ideal our best balance is obtained by pumping a slurry containing 45 - 50% coal at a rate of 0.33 ml/min into the reactor. Faster pumping rates increase the flow of synthesis gas, lowering the contact time with the methanation catalyst, thus reducing the reduction of carbon monoxide to methane.

Probably the first problem to be solved is that of slurry composition. Slurries of coal, water, and alkali are thixotrophic in nature, Slurries with a higher coal concentration than we are presently using cannot be pumped with our present equipment at our optimal rate. This is because of the thixotropic nature of the slurry that in the absence of agitation sets-up to a solid plug in the pump. With a faster pumping rate we have successfully pumped slurries containing 55 to 60% coal. The use of a more concentrated slurry would result in two important benefits: the deactivation of the catalyst caused by the steam would be reduced, and the level of hydrogen in the product gas would be reduced. A solution to this problem would be to use a pump similar to the Moyno pump that does supply a continual agitation. However, the smallest Moyno pump available has a slowest pumping rate of approximately 10 liters per hour. The present reactor is too small to handle even this low rate.

The one-inch (0.75 in. i.d.) reactor we are presently using is too small to permit a fluidization of the catalyst bed. This could lead to the channelization of the gas through the catalyst bed thus reducing the efficiency of methanation and overall quality of the results.

It is therefore recommended that a larger reactor capable of continuous operation be constructed for future studies.

Section V

CATALYST STUDIES - HALF-INCH FLOW REACTOR

A variety of catalyst investigations in connection with the NRRI Coal Conversion Process have been undertaken with a 1/2-inch (o.d.), adiabatically operated, tubular flow reactor. A flow diagram and further details of this on-site designed and constructed experimental unit have been included in Appendix B, page 61.

The 1/2-inch flow reactor was used for screening and evaluation of both laboratory and commercial catalyst formulations, methanation studies on the influence and interrelation of various operating variables and synthesis gas compositions, as well as catalyst poisoning and regeneration studies. A brief discussion of the results of each of these areas is presented. Additional details and supporting information are included in the Appendices.

Catalyst Formulations. - A variety of both laboratory prepared and commercial methanation catalysts were investigated with the 1/2-inch catalyst test unit. Active metals in these catalysts are nickel, cobalt and iron. Information about their composition and preparation are contained in Appendix B, Part I, pages 62 and 63.

The laboratory catalyst preparations were undertaken early in the program with the objective of obtaining a more active catalyst that showed a greater resistance to sulfidation, carbon deposition and loss from attrition. However, it soon became apparent that it would be advantageous to initiate liaison with various catalyst manufacturing companies so that they could develop superior methanation catalysts. We in turn would evaluate the custom and commercial preparations in view of the requirements of the process.

Methanation Studies. - Catalytic methanation studies have been carried out with the 1/2-inch catalyst test unit where both H_2-CO and H_2-CO_2 synthesis gas mixtures were employed. The objective of this investigation was to provide catalyst evaluation information as well as to examine the influence of operating variables on the methanation. In addition to synthesis gas composition, such variables as temperature, pressure and space velocity were examined. The results of these investigations were in general in accord with guidelines set forth in the literature.

a. Synthesis Gas Composition

Synthesis gases of approximate mole % compositions of 80% H_2 - 20% CO_2, 75% H_2 - 25% CO and 67% H_2 - 33% CO were investigated. The formation of carbon deposits on the catalyst, apparently associated with the Boudouard reaction, was observed with the hydrogen-carbon monoxide mixtures but not

$$2CO = CO_2 + C$$

with the hydrogen-carbon dioxide mixture. The severity of carbon deposition increased with decreasing H_2 to CO ratio and with increasing pressure. Although the Boudouard reaction is thermodynamically favored at low temperatures, the rate was noted to jump markedly in the region of 480°C. Carbon deposition was catalyzed more by iron than nickel or cobalt catalysts. Additional information and results on carbon deposition are presented in Appendix B, Part II, pages 64 and 65.

Carbon deposition has long been recognized as a cause of catalyst fouling in catalytic processing of synthesis gas. Some preliminary investigations were directed at this problem. Three approaches that have been suggested were employed to alleviate the carbon deposition during catalytic methanation with $2H_2/CO$. One was by steam addition to the system, another consisted of doping the catalyst with sulfur and the third involved the addition of H_2S to the synthesis gas stream. Although each of these approaches inhibited carbon deposition, they also had a marked inhibition on the catalytic methanation. Thus, the methanating activity decreased so that the product gas composition changed from over 50 mole % to less than 10 mole % CH_4. More specific information concerning these experiments is contained in Appendix B, Part II, pages 64 and 65.

b. Methanation Catalyst Screening

A variety of both laboratory prepared and commercial methanation catalysts were investigated in the 1/2-inch catalyst test unit. Active metals in these catalysts are nickel, cobalt and iron. The activity of these metals toward the methanation of synthesis gas followed the order $Ni \gg Co \geq Fe$. In contrast to the nickel, both cobalt and iron catalysts, under similar synthesis conditions, produced higher molecular weight hydrocarbons, the effect being the most pronounced for iron. Although several of these catalysts demonstrated a high activity, a commercial nickel catalyst (Ni-3210) showed an overall superiority, particularly in regard to its spalling and attrition resistance. Analogous conclusions were drawn from investigations performed with the batch charge integrated reactor.

c. Methanating Variables

Several variables influencing catalytic methanation were examined with the 1/2-inch catalyst test unit. In addition to synthesis gas composition, temperature, pressure and space velocity were investigated. As expected, catalytic methanation with synthesis gases composed of $4H_2/CO_2$ and $3H_2/CO$ was superior to that obtained with $2H_2/CO$. Some results for each of these compositions are listed in Appendix B, Part III, page 66. Under optimized conditions CO conversions are generally in excess of 90% with greater than 50% methane in the product gas.

Many catalytic methanation studies with different catalysts and synthesis gas compositions indicated that the following chemical reactions would describe the methanating system. These results indicate that there are competing reactions within the system which can be influenced by the catalyst employed in the synthesis, as well as the synthesis conditions.

$$3H_2 + CO = CH_4 + H_2O$$

$$H_2O + CO = H_2 + CO_2$$

$$2CO = C + CO_2$$

The influence of temperature and pressure upon catalytic methanation was, without expectation, in qualitative agreement with thermodynamic predictions. The optimum average methanation temperature for the catalysts employed was from 300-400°C. At a given temperature the catalytic conversion of synthesis gas to methane increased markedly with increasing pressure. Some of these temperature and pressure dependent results are demonstrated by figures in Appendix B, Part III, pages 67-72. Hence, a good run would produce a product gas, from $3H_2/CO$ @ 325°C, and 100 psig and 1300 hr^{-1} space velocity, composed of 85% CH_4, 10% H_2, and 5% CO_2.

Since the 1-inch integrated system was generally operated in the 600-700°C temperature range, catalytic methanation with synthesis gas was also investigated in this temperature range. Some of the high temperature results which are shown in Appendix B, Part IV, page 84 show that at pressures up to 100 psig using synthesis gas composed of ~ $3H_2/CO$, catalytic methanation will produce a product containing about 50 mole % CH_4 in the 600-700°C range with better than 90% CO conversion. Increased pressures should further improve the CO conversion and methane yield at these high temperatures.

Recently some effort has been directed at carrying out quantitative thermodynamic calculations for the methanation reactions aforementioned in order that correlations between experimental and theoretical results can be made. This has required a considerable amount of computer programming and tabulation of thermodynamic data. The preliminary results for the 1/2-inch catalyst test unit have indicated that within experimental error, there is reasonable good agreement between the predicted and observed product compositions.

In as much as space velocity versus conversion data is reflective of the catalyst activity and methanation rate, investigations in this area have also been carried out. Results indicate that catalytic methanation with $4H_2/CO_2$ occurs at a lower rate than with $3H_2/CO$ mixtures. The high activity of the nickel catalyst, Ni-3210, has been repeatedly observed. Some of the results of space velocity investigations have been presented in Appendix B, Part III, page 73-74. As one example, using $3H_2/CO$ synthesis @ 400°C, 0 psig and a space velocity of 14,200 hr^{-1} a product was produced (with 100% CO conversion) composed of 17.6% H_2, 0.0% CO, 82% CH_4, and 0.3% CO_2.

<u>Catalyst Poisoning and Regeneration Studies</u>. - Catalyst poisoning by carbon deposition, steaming and sulfur gases have been investigated. Carbon deposition has previously been discussed in connection with the influence of synthesis gas composition. The formation of carbon deposits not only lead to excessive pressure drops across the reactor and eventual plugging, but also decrease the catalyst activity because of surface coverage and pore plugging.

Since steam is present during catalytic methanation ($3H_2 + CO = CH_4 + H_2O$) in the 1-inch integrated system, attempts were made to examine its influence on catalytic activity using the 1/2-inch catalytic test unit. The nickel catalyst was first pretreated at ~ 870°C in a steam-hydrogen atmosphere. This was followed by an examination of the change in its nickel crystallite size and finally by testing its activity with $3H_2/CO$ in the 1/2-inch flow reactor. Even for short periods of time the steaming resulted in a six fold increase in the nickel crystallite size. This in turn paralleled a decrease in the activity of the nickel catalyst which was most noticeable at low temperature methanation. For high temperature (~ 650°C) methanation the change in crystallite size had only a small effect on the catalytic activity, but had a marked effect upon the ease of reducing the catalyst prior to initiating methanation. This activation difficulty is presumably associated with spinel formation ($NiAl_2O_4$) during the steaming.

Since the NRRI Coal Conversion process is operated as a single-stage unit no prior sulfur removal from the coal is carried out. Some of the sulfur is consequently given off in the form of sulfur gases which are known to poison methanation catalysts. This situation has prompted some catalyst sulfur poisoning studies with the 1/2-inch catalyst test unit.

It was established that hydrogen sulfide was a definite poison for nickel catalysts through the formation of nickel sulfide according to the following reactions. Furthermore, the poisoning was very rapid and required only small concentrations of H_2S in the synthesis gas.

$$3Ni + 2H_2S = Ni_3S_2 + 2H_2$$

$$NiO + H_2S = NiS + H_2O$$

The thermodynamics of the preceeding reactions show that the sulfidation is independent of pressure and that although the sulfide formation is extremely favorable, larger H_2S concentrations can be tolerated by employing higher temperatures. Some of the sulfur poisoning results and thermodynamic considerations are listed in Appendix B, Part IV, pages 75-79.
Hence, by employing a synthesis gas composed of about $3H_2/CO$, which contained about 0.06% H_2S, the catalytic activity decreased from an initial value of 950 to 100 cm^3 CH_4/g cat/hr in 25 hours at a space velocity of 1665 hr^{-1} and a temperature of 325°C. This corresponds to an initial gas product composition of about 88% CH_4, 10% H_2, and 2% CO_2 and a final one of 5% CH_4, 20% CO and 75% H_2.

In view of the findings in connection with the preceeding discussion, it was decided to look for solutions or alternatives to alleviate the sulfur poisoning problem. Two lines of attack were planned which included catalyst regeneration and catalyst alternative. The majority of the effort was spent in the former area.

The catalyst alternatives that have been considered are: (a) cheaper catalysts such as mill scale, iron ore or red mud and (b) sulfur resistant catalysts such as sulfides of various transition elements. As previously noted, the less expensive iron catalysts have been generally less active than the nickel and tend to form liquid products. A sulfided form of a nickel catalyst has shown high temperature methanating activity. The results are presented in Appendix B, Part IV, page 81.

Regeneration investigations of sulfur poisoned nickel methanation catalysts have sought suitable chemical reactants to react with the nickel sulfide with the objective of evolving the sulfur as a gaseous compound. Both gaseous and liquid reactants have been used in this respect with some success.

Employing oxygen or air for sulfur removal results in the following competing reactions:

$$Ni_3S_2 + \tfrac{1}{2}O_2 = NiO + 2NiS$$

$$NiS + \tfrac{3}{2}O_2 = NiO + SO_2$$

$$NiO + SO_2 + \tfrac{1}{2}O_2 = NiSO_4$$

$$NiS + 2O_2 = NiSO_4$$

Although considerable sulfur reduction in the catalyst is effected, the sulfate formation is a very undesirable feature. The high temperatures required for its decomposition are likely to cause sintering and loss of catalyst surface area and pore structure as well as nickel crystallite growth.

The use of solutions of oxidizing agents and acids for the removal of sulfur has also been examined. The desired reactions in each instance are generalized below.

$$NiS + Ox(soln) = NiO + SO_2$$

$$NiS + H_2A\ (soln) = NiA + H_2S$$

Although sulfur removal with acids was successful, there was an accompanying undesirable degradation of the physical structure of the catalyst and solubilization of the nickel through coordination complex formation.

The use of solutions of oxidizing agents such as hydrogen peroxide and peracids have produced the best solution results to date. It appears that about 1 - 2% sulfur can be removed by this technique under mild conditions with little nickel solubilization and degradation of the physical structure.

Finally the use of sulfur free synthesis gas composed of $3H_2/CO$ for the regeneration of a sulfur poisoned nickel methanation catalyst was investigated. The results presented in Appendix B, Part IV, page 83. demonstrate that this technique can apparently be successfully used for sulfur removal and restores the catalyst to nearly its original high temperature methanating ability. Hence the sulfur content of the catalyst was reduced from 9.4 wt.% to 0.4 wt.% while a parallel increase in CH_4 concentration of 2.0% to 25% in the product was observed.

<u>Conclusions</u>. - Catalyst screening tests have provided several very active methanation catalysts. Those containing nickel were found to be more active than cobalt or iron. One of the nickel catalysts, Ni-3210 has shown a superiority over all the rest in the single-stage coal conversion concept.

Catalytic methanation with various compositions of synthesis gas have shown the necessity of maintaining high H_2/CO ratios to minimize carbon formation. Both steam and sulfur compounds in the H_2-CO synthesis gas decreased the rate of carbon formation but also decreased methanation. The steam strongly favored the CO-shift reaction. In contrast to H_2-CO synthesis gas mixtures the $4H_2/CO_2$ showed no tendency to form carbon deposits and also gave good methanation results with the same catalysts used with the H_2-CO mixtures.

Some preliminary thermodynamic calculations have produced reasonably good correspondence between theoretical and experimental results from the 1/2-inch catalyst test unit.

Methanation results support the competitive reactions occurring during catalytic methanation with $3H_2/CO$. Thus, the production of water, carbon dioxide and carbon from these reactants was observed.

Sulfur poisoning experiments have demonstrated the severity of sulfur poisoning, particularly at low temperatures, in the 1/2-inch catalyst test unit. At higher temperatures the nickel catalyst is slightly more resistant to sulfur poisoning. Furthermore, a nickel sulfide catalyst has shown significant methanability at the higher temperatures.

Encouraging catalyst regeneration results have been obtained. Several techniques for removing sulfur from sulfur poisoned catalysts and restoring them to their original activity were investigated. Air, oxygen, acid solutions, solution oxidizers and synthesis gas were employed. The latter two methods, appear to hold the most promise. Using synthesis gas $(3H_2/CO)$ nearly all of the sulfur from a nickel poisoned catalyst was removed and its high temperature methanation activity was restored to near its unpoisoned level.

Recommendations. - There are several areas that deserve additional investigation. However, the emphasis is on those programs that provide direct support for the development of the NRRI Coal Conversion Process. Investigations of high temperature catalytic methanation, catalytic kinetics of competitive reactions occurring during methanation, thermodynamic modeling of methanation and integrated systems, catalyst poisoning (sulfur compounds, steaming, high temperature, carbon formation), catalyst regeneration and a consideration of catalyst alternatives appear to have much merit.

Section VI

ANALYTICAL METHODS AND RESULTS

A. CLASSICAL AND INSTRUMENTAL METHODS

Before May 1972 only a limited amount of analytical work had been carried out. It consisted primarily of coal analyses and Leco sulfur analyses. After May 1972 considerably more analytical work was initiated. At that time most of the work undertaken involved developing analytical procedures and techniques which were needed to produce reliable data that would give valuable information to the overall process.

The Leco Sulfur Analyzer. - Because sulfur poisoning of methanation catalyst by sulfur compounds gasified from coal has been a major concern, development of sulfur analysis was initiated. Poor sulfur mass balances had been obtained by the use of the Leco Sulfur Analyzer and for this reason the Leco analysis became suspect. Because of this suspicion, ASTM methods of analysis for sulfur were performed on the nickel catalysts. The method is known as sulfur by the Gravimetric Method In the Chemical Analysis of Nickel (designation E-39). This method has proven to be accurate and reproducible. The results have been in agreement with those of independent laboratories. The results of these gravimetric methods have been used to check Leco results and have also been used in the standardization of the instrument. The major drawback of the gravimetric method is that it is very time-consuming. A major advantage of the gravimetric method is that by varying the procedure, the forms of sulfur present (sulfide, sulfate) can be determined and their percentage of the total sulfur can also be calculated.

Other aspects of analytical techniques have been worked out to help bring the Leco's sulfur values into line. Some of these would be proper sampling methods, grinding, proper sample sizes, proper amount and proportions of Fe and Sn accelerators, standardization of the Leco Analyzer daily, and replacement of weights in the analytical balance. Sulfur samples of over 1.5 percent were run by wet methods because it was found that the Leco gives low results at about that percentage because of the concentration of the potassium iodate solution was too small to keep up with the sulfur dioxide evolved at the titration rate of the apparatus. The higher percentages of sulfur could be analyzed if a stronger iodate solution was used.

Leco sulfur balances have been improved to consistent values of 95 to 105 percent recoveries for each daily reactor run. The following table shows the improvement of sulfur balances since May 1972.

Table I. Comparison of Leco Balances

Quarterly Report Date	Average Deviation from 100 % in %
May, 1974	20.1
August, 1972	20.5
November, 1972	18.8
February, 1973	6.9
May, 1973	4.2
August, 1973	2.4

From Table I it can be seen that the Leco data has improved and can now be used as an accurate analytical tool to study sulfur problems.

Mechanical Attrition of Catalysts. - Studies were made in May 1972 on a limited number of catalysts to determine the amount of attrition on these catalysts caused by fluidization. These studies were made at excessive flow rates and at rates that approach the flow that would be normal for our gasification reaction. In these tests air was used as the fluidization medium and was supplied by a compressor-blower.

A run was made on Harshaw Ni-3210, 1/8-inch tablets in a 6-inch diameter glass column at velocities of about 819 cubic feet per hour. This rate corresponds to a linear superficial velocity of 1.16 ft/sec. Fluidization is normally expected to occur at gas velocities of around 0.5 to 1.0 ft/ sec depending upon particle size, density, and properties of the fluid. By looking into the glass column it could be seen that fluidization was taking place.

If the gasification reaction proceeds as $C + H_2O \longrightarrow 1/2CH_4 + 1/2CO_2$ and 100 percent excess steam was used, then 819 SCF of gas corresponds to 1.1 moles of carbon, or about 25 pounds of coal per hour. This figure corresponds to about 205 SCF/hr of methane produced. This fluidization was carried out for 107 hours corresponding to 21,935 SCF of methane produced. The amount of loss due to attrition was measured at intervals and catalyst cost was figured on a basis of $2.76 per pound of catalyst (the cost of this catalyst for larger operations might be considerably lower).

The cost due to attrition ranged from 8.91 cents per MSCF in the first hour to 0.09 cents per MSCF during the last 60 hours. This run showed an initially high attrition loss which then leveled off. The average catalyst cost per MSCF was .58 cents. This in turn means that the catalyst attrition cost for production of 21,935 SCF of methane is in the neighborhood of $.13. Finally it should be noted that this was for 1/8-inch tablets and the cost due to attrition for spheres with the same physical strength would be expected to be somewhat lower.

Total Potassium Recoveries. - Total potassium recoveries have been made on selected runs with balances between 95 to 105 percent. The methods used for analysis are as follows. For the potassium combined or adhering to the catalyst an acid digestion method was developed consisting of heating in HNO_3 to a sirup and then heating to dryness twice in HCl. A small addition of HCl was made followed by 150 ml of boiling water then the solution was boiled. It was filtered and washed with hot water and diluted to 500 mls. The solutions were then analyzed for potassium by atomic absorption. The potassium remaining in the coal ash was determined by the J. Larence Smith Ignition method described in the Determination of Potassium and Sodium in Coal Ash.[1] After the J. Larence Smith Ignition was completed the fused mass was dissolved in hot water, filtered, diluted to volume, and analyzed for potassium by atomic absorption.

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[1] R. Belcher. A. J. Nutlen, and H. Thomas, Analytica Chimica Acta 2 120, (1954).

Carbonate Recoveries. - Carbonate determinations were made on coal ashes by evolution of carbon dioxide when treated with a 1:1 HCl solution. The evolved gases were aspirated through a purifying train and the carbon dioxide was collected in a tube of ascarite and magnesium perchlorate. This tube was weighed before and after evolution and the weight of carbon dioxide was calculated to a carbonate basis. Carbonate recoveries in the ash have ranged from 95 - 105 percent.

Potassium Washings. - Potassium recoveries by a simple water wash have been carried out with an average potassium recovery of 85 percent of the original potassium. The washings were carried out at ambient temperature for one hour. It should be noted that some recoveries as high as 95 percent have been made and if washings were made in hot water at temperatures around 80° - 90°C the total recoveries may increase further. Some impregnations of coals with these washes have been made, but the impregnated coals at this point have produced erratic results.

Sulfur Scavengers. - With sulfur poisoning of methanation catalysts being a critical problem, the idea of sulfur scavengers to take up sulfur has been with the process for some time. With other work being more pressing, actual sulfur scavenger experiments were not undertaken until July 1973. The experiments consisted of adding about 1 gram of the scavenger material to the 100 grams of coal charge and mixing thoroughly. The different scavengers that have been tried at this point are MgO, CaO, ZnO, and Fe_2O_3. The results show that the use of sulfur scavengers was helpful in preventing sulfur deposits on the catalysts. Runs were made using 100 grams of Glenrock coal and Ni-3210 catalyst and therefore each run should have the same amount of sulfur going into the reactor. For all runs sulfur mass balances were between 95 to 105 percent.

Table II. Sulfur in the Ash and Used Catalyst

	Avg. g. Sulfur in the ash	Avg. g. sulfur in the used cat.	Avg. g. sulfur recovered
Typical runs made in July	.0643	.6305	.6948
Runs using 1% MgO	.2795	.4039	.6834
Runs using 1% CaO	.2941	.3820	.6761
Runs using 1% Fe_2O_3	.4991	.2221	.7212
Runs using 1% ZnO	.6540	.1068	.7607

From Table II it can be seen that all of the sulfur scavengers retained more sulfur in the ash than would remain in a typical run. Also from the table it is apparent that Fe_2O_3 and ZnO are the best of the scavengers that have been tested at this time. The Fe_2O_3 was able to retain about 8 times more sulfur in the ash than is normal while allowing only 35 percent of the normal amount of the sulfur onto the catalyst.

Some work has been done in understanding why the sulfur scavengers work and to give an insight into what properties a scavenger must have to make it economically feasible and efficient.

Table III. Types of Sulfurs Present in Ash and Catalyst

	Total Sulfur Present (%)	% of Total Sulfur in Sulfate form	% of Total Sulfur in Sulfide form
New Catalyst 3210	.10	77.8	22.2
Used Catalyst typical run	.53	9.0	91.0
Used Catalyst when Fe_2O_3 was used	.22	68.2	31.8
Typical Ash	.13	70.4	29.6
Ash when Fe_2O_3 was used	.76	60.5	39.5

From Table III it can be seen that for a sulfur scavenger to be effective it must be ready to pick up sulfur in the sulfide form. It is this sulfide sulfur that is the major cause of sulfur poisoning on the nickel catalyst. For sulfur scavengers to be feasible as a solution to sulfur poisoning, the compounds chosen must be obtainable in large quantities at low prices. More work needs to be done in the evaluation of sulfur scavengers.

Regeneration of Catalysts. - At the present time little work has been done on regeneration of catalysts by the analytical section but thought has been given to the problem. It was found that passing oxygen and air over the heated catalyst removed a small portion of the sulfur from the catalyst. The major drawback for this procedure was that it converted more of the sulfur to the sulfate form than it removed. It was found that a mixture of CO and H_2 would remove sulfur over a period of time. Washing the catalyst with acid and hydrogen peroxide has been studied but has not been very successful, because leaching of nickel was observed. Of these, mild H_2O_2 has given best results but considerable work needs to be performed.

Conclusions and Recommendations. - Since May of 1972, considerable work has been done in the development and implementation of the analytical methods. Many hours were spent in developing techniques to give reliable results. Techniques have been perfected to meet the immediate project needs, but there is still need for development and application of additional analytical methods. Work is being initiated on the types of sulfur gases in coal by gas chromatography. Expanded and improved material balances need to be made along with analysis of the water for collected liquids. Other areas that need to be worked on are ash washes, impregnation of coals, effect of contaminents in the ash, sulfur poisoning, and regeneration of both nickel and carbonate catalysts. Many of these problems are fundamental to gasification processes.

Finally, it should be stated that analytical techniques have been developed or can be developed to answer important questions that will further the overall process and coal gasification.

B. PETROGRAPHIC METHODS

Introduction

A number of Ni methanation catalysts were examined by x-ray diffraction (XRD) and x-ray fluorescence (XRF) during the final six quarters of the project. Those studied more throroughly were Ni-5105, Ni-0104, G-65RS, Ni-3250, NA-2-V, HSC-102, 715X2-5X1 and Ni-3210. Owing to Ni-3210 having been used more than the other catalysts in the reactors, it was studied in more detail. The catalysts were characterized according to compounds. elements, metallic Ni crystallite sizes, and changes occurring under different experimental conditions. Crystallite sizes of Ni-3210 and 715X2-5X1 were measured in angstroms (A) for the major Ni peak at 44.5° 2θ using the technique described by Klug and Alexander[1], whereas the sizes for other catalysts were described as small, medium or large according to variations in intensity of the 111 reflecting plane. Crystallite sizes of metallic Ni in used Ni-3210 from the one-inch batch reactor were correlated with various reactor operating parameters.

Ashes from the one-inch batch reactor and impregnated coal were also studied by x-ray techniques.

Results

Ni-5105 Catalyst. - The as received catalyst contains metallic Ni with large crystallites, NiO, possibly SiO_2 and $CaCO_3$, and unidentified material by XRD; the largest amounts of Ca and smallest amounts of Fe and Mn of four different catalysts examined by XRF. Reduced as received catalyst contains metallic Ni of increased crystallite size, possibly SiO_2 and $CaCO_3$, and unidentified material. After use in the one-inch batch reactor, the catalyst has the same content as the "reduced as received" sample, except the amount of Ni has decreased and the metallic Ni crystallite size has increased. In one reactor run the used catalyst has a metallic-appearing surface coating and contains Ni_3S_2.

Ni-0104 Catalyst. - The as received catalyst contains metallic Ni with large crystallites, SiO_2, and unidentified material. The used catalyst from the one-inch batch reactor has the same contents, except the Ni crystallites are larger.

G-65RS Catalyst. - The as received catalyst contains metallic Ni with medium size crystallites, NiO, SiO_2 and unidentified material. Used catalyst from the one-inch batch reactor has the same contents, except the metallic Ni crystallites are larger and quantity of Ni is less. Both the as received and used samples have the smallest amounts of Ca, Ti, Fe, and Zn of four different catalysts examined by XRF.

Ni-3250 Catalyst. - The as received catalyst contains metallic Ni with medium size crystallites, SiO_2, $CaCO_3$, CaO? or NiO?, and unidentified material. The used catalyst from the one-inch batch reactor contains metallic Ni with

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[1] Klug H. P. and L. E. Alexander, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, John Wiley & Sons, Inc., New York, 1954, Chapter 9, pp. 512 and 530-531.

increased crystallite size, SiO_2, $CaCO_3$, and unidentified material.

NA-2-V Catalyst. - The as received catalyst contains NiO and $NiAl_2O_4$. Reducing the as received catalyst converts the NiO to metallic Ni having relatively small crystallites, whereas the $NiAl_2O_4$ appears unchanged. Contrary to other catalyst examined, four of five used catalyst samples from 399°C and 538°C runs in the one-inch batch reactor show decreases in crystallite sizes, whereas one run at 649°C showed a small increase in crystallite size compared to the reduced as received sample. In one of the 538°C runs the catalyst was segregated; that portion from the inlet gas area contains metallic Ni, whereas that from the outlet gas appears to have NiC instead of metallic Ni. In two runs Ni_3S_2 formed in the catalyst. Peak intensities of the $NiAl_2O_4$ in both portions of the segregated catalyst are about the same as for the as received and reduced as received samples.

HSC-102 Catalyst. - The as received catalyst contains NiO and η - Al_2O_3. Used catalyst from the continuous feed reactor contains metallic Ni with the largest crystallites of all catalysts examined and η - Al_2O_3. Activity of the catalyst decreased at the end of the reactor run.

715X2-5X1 Catalyst. - The as received catalyst contains NiO and $3NaAlSiO_4 \cdot Na_2CO_3$. Reducing the as received catalyst converts the NiO to metallic Ni having a crystallite size of 137 A, whereas the $3NaAlSiO_4 \cdot Na_2CO_3$ remains unchanged. Used catalyst after three runs in the continuous feed reactor contains metallic Ni with 196 A crystallites, $3NaAlSiO_4 \cdot Na_2CO_3$ with peak intensities less than the as received and reduced as received samples, and some unidentified material. Used catalyst after an eight-day continuous feed reactor run has the same contents and peak intensities as the catalyst after three runs, except the metallic Ni has 203 A crystallites. Catalyst activity declined during both reactor runs.

Ni-3210 Catalyst. - The as received catalyst contains metallic Ni with 54 A crystallites (the smallest of all catalysts examined), CaO, and SiO_2. After the catalyst container had been opened a number of times to obtain charges for the reactors, the CaO became hydrated to $Ca(OH)_2$.

Two samples of as received catalyst from a freshly opened container, which had been re-reduced six to eight hours and twenty-four hours, have the same contents as the as received non-reduced catalyst, except both re-reduced samples have larger metallic Ni crystallites. Furthermore, the twenty-four hour sample has larger crystallites than the 6-8 hour sample. Crystallites average 82 A in the re-reduced catalyst. Re-reduced samples in which the CaO has hydrated, the resultant $Ca(OH)_2$ appears to be converted to $CaCO_3$ during re-reduction.

Sulfided Ni-3210 was prepared in the one-half inch flow reactor by passing H_2S over the catalyst. It contains $NiS_{1.03}$, β Ni_7S_6, and SiO_2. No metallic Ni was detected. This is the only sample of Ni-3210 in which sulfides were detected by XRD.

Ni-3210 from a freshly opened container, which was fluidized 107 hours in the fluid bed reactor, contains metallic Ni with crystallites about the same size as in the as received catalyst, $Ca(OH)_2$, and SiO_2.

Samples of Ni-3210 were steamed for 3, 6, and 12 hours at average temperatures of 857°C. All contian metallic Ni, α $CaSiO_3$, and some unidentified material. The Ni crystallite sizes are 275 A, 293 A, and 303 A for the 3, 6, and 12 hour samples respectively. By comparison the Ni crystallites in the as received catalyst are 54 A; five to six times smaller than in the steamed samples.

Used Ni-3210 from the one-inch batch reactor contains metallic Ni, $CaCO_3$, and SiO_2. Samples from all reactor runs examined show increases in metallic Ni crystallite sizes. For example, for 11 runs in the #665-677 one-inch batch reactor series, the size range is 90-172 A, the average being 112 A. The crystallite sizes for these 11 runs were graphically plotted against Btu/SCF (CO_2-free), H_2O added (ml.) and recovered (ml.), run time (hrs.), catalyst (°C) and coal (°C) temperature, unreacted coal (g.), catalyst activity (cc/hr./g.cat.) and selectivity (cc/hr./g.cat.), overall conversion (%), and gas composition (%) C, H_2, CO, and CO_2 to determine if correlations could be made.

Segregated used Ni-3210 from the inlet, middle, and outlet areas of the one-inch batch reactor for runs #616-625 showed metallic Ni crystallite growth. However, there were variations in crystallite sizes in the three areas.

XRF indicates that the total amount of Ni decreases in used Ni-3210.

Ash. - Ash from 12 runs in the one-inch batch reactor were examined by XRD to determine if any of the alkali catalyst, a hydrated form of K_2CO_3, in the reactor charges had been carried over into the ash. Zero to 60 grams of hydrated K_2CO_3 had been used in the charges. Runs containing 15 grams showed no hydrated K_2CO_3 in the ash, whereas runs containing 20 to 60 grams showed amounts approximately proportional to those in the reactor charges.

Impregnated Coal. - Samples of pulverized Glenrock coal were prepared for one-inch batch reactor charges by dry-mixing coal and K_2CO_3, by impregnating the coal with a solution of K_2CO_3 washed from the ash of a previous reactor run, and by impregnating the coal with a KOH-K_2CO_3 solution. A 1:5 K_2CO_3/coal mixture was used for all samples, except one, which was 1:1.

XRD indicates that all samples of the 1:5 K_2CO_3/coal mixtures, except the dry-mixed sample, do not contain K_2CO_3 after impregnation. On the other hand, the 1:1 mixture clearly shows the presence of K_2CO_3 after impregnation. XRF, however, shows that all samples, including the as received non-impregnated coal, contains elemental K. The use of KOH in sample preparation appears to increase the total K.

Conclusions

As received Ni methanation catalysts contain either metallic Ni and/or NiO depending upon the manufacturer. Some contain other Ni compounds as well, e.g., $NiAl_2O_4$. Crystallite size of the metallic Ni also varies with the manufacturer. Catalysts having the smallest metallic Ni crystallites in the as received state (e.g., 54 A in Ni-3210) generally produce the greatest activity in the one-inch batch reactor. Reducing the as received catalysts in a hydrogen atmosphere prior to use in a reactor increases the metallic Ni crystallite sizes and converts the NiO to metallic Ni. Additional increases in metallic Ni crystallite sizes occur when the catalysts are used in the reactors, with some catalysts showing larger increases than others. One exception is NA-2-V, which experienced size decreases in four out of five one-inch batch reactor runs.

There is evidence that crystallite sizes of used catalysts are related to temperature increases. Although NA-2-V crystallite sizes at 399°C were smaller than in the as received catalyst, crystallite sizes from these two runs and one at 649°C when compared with each other show small increases, which correlate with temperature increases. Used Ni-3210 displayed similar results.

In two cases metallic Ni crystallite growth appeared to be related to length of runs when temperatures were constant. Catalysts indicating this were 715X2-5X1 samples from three runs vs. eight days in the continuous-feed reactor and Ni-3210 steamed for 3, 6, and 12 hours. Steamed Ni-3210 experienced its largest crystallite growth sometime during the first 3 hours of the experiment. Perhaps the greatest growth occurred instantaneously when steam was applied, with progressively slower growth thereafter. Evidence for the latter is that the amount of crystallite growth was 18 A and 10 A, respectively, between the 3 to 6 hour and 6 to 12 hour samples compared to 221 A from zero to 3 hours.

In addition, the amount of metallic Ni crystallite growth appears to vary according to the catalyst location in a reactor. For example, the segregated Ni-3210 from the one-inch batch reactor runs #616-625 had larger crystallites in the outlet area of the reactor than the inlet area, whereas the middle area displayed intermediate size crystallites.

Graphical plotting of used Ni-3210 metallic Ni crystallite sizes against the previously mentioned reactor parameters indicates that the best correlations of size are with coal temperature, catalyst temperature, amount of unreacted coal, and the percentage of overall conversion. In general, crystallite size increases with coal and catalyst temperature and overall conversion, but decreases with an increase in the amount of unreacted coal. At this time, it is believed that crystallite growth in Ni-3210 and other catalysts is primarily a function of temperature in the reactors. However, additional study is needed to prove this.

In all catalysts examined by XRF it was determined that elemental Ni decreases in amount during reactor runs. Perhaps it is the result of volatilization of some of the Ni or nickel compounds.

Unusual compounds were formed in two of the catalysts under reactor conditions. A material, which remains unidentified, in used 715X2-5X1 from the continuous-feed reactor may have formed from a reaction of the $3NaAlSiO_4 \cdot Na_2CO_3$ in the catalyst. Evidence for this is that the intensities of the $3NaAlSiO_4 \cdot Na_2CO_3$ peaks are less in the used catalyst. The α $CaSiO_3$ which formed in Ni-3210 during the steaming experiment was not detected under any other experimental conditions.

The formation of the unidentified material in 715X2-5X1 and/or the increase in metallic Ni crystallite size may have been responsible for the catalyst's decline in activity during continuous-feed reactor runs. On the other hand, no new material was formed in HSC-102 during continuous-feed reactor runs. However, a similar decline in activity was experienced. Perhaps the increase in metallic Ni crystallite sizes in both catalysts may offer the best explanation for the decline in activity. Only additional examinations of these and other catalysts will provide evidence for a firm explanation of the declines in activity.

Only four samples of used catalyst out of the many examined by XRD during the project contained evidence of possible sulfur poisoning. They included the synthetically sulfided Ni-3210 from the one-half inch flow reactor, Ni-5105 from run 544 in the one-inch batch reactor, and NA-2-V from runs 588 and 592 in the one-inch batch reactor. In run 592, which was a segregated catalyst set-up, the sulfur compound was found only in catalyst from the inlet gas area of the reactor. In all cases the sulfur compounds were nickel sulfides.

XRD and XRF suggest that the K_2CO_3 in the 1:5 impregnated coal samples may have reacted with the coal to form a different K-containing compound. However, to date, such a compound has not been identified.

On the other hand, when an abundance of K_2CO_3 is used for impregnation, such as in the 1:1 sample, not all of the K_2CO_3 is involved in a reaction with coal.

Recommendations

It is recommended that additional studies of the catalysts utilized, or to be utilized, in the NRRI Coal Conversion Process be made with the scanning electron microscope, reflected and transmitted light microscopy, the electron microprobe, XRD, and XRF. The purposes of these investigations are: (1) to characterize the catalyst, (2) to provide additional evidence for the correlation of metallic Ni crystallite growth and other physical properties with reactor conditions and catalyst activity, (3) to aid in the determination of which catalysts are most suitable for the process, (4) to provide data that will help to determine the most effective catalyst regeneration technique, and (5) to provide data on the behavior of catalysts in various types of reactors.

The same instruments are recommended to be used for a comprehensive petrographic study of Wyoming coals. This study would be designed to determine the physical characteristics of the coals, their ranks, and which coals are most suitable for gasification, liquefaction, and hydrogenation.

In addition, it is proposed that an investigation of the trace elements in Wyoming coals and coal ashes be made. The purpose of this study would be to determine the types and amounts of trace elements present, as well as the compounds or materials in which they occur. Such a study will serve to analyze trace elements which may be deleterious to the environment as well as those which may create problems during or after coal conversion. XRF, XRD, electron probe microanalysis, and chemical techniques would be employed in the project.

Section VII

LIST OF PUBLICATIONS GENERATED IN CONJUNCTION WITH THE PROJECT

1. Hoffman, Edward J., "Product Breakdown and Cost Estimate for Proposed Steam-Coal Process," NRRI, Univ. of Wyo., April, 1966, 20 pp.
2. Hoffman, Edward J., "Coal Conversion and the Direct Production of Hydrocarbons from Coal-Steam Systems," Information Circular #44, NRRI, Univ. of Wyo., Aug., 1966, 134 pp.
3. Hoffman, Edward J., "A Program for Research and Development in Coal Conversion," NRRI, Univ. of Wyo., 1966, 35 pp.
4. Hoffman, Edward J., "Water Requirements for Coal Conversion," Information Circular #52, NRRI, Univ. of Wyo., Oct., 1967, 8 pp.
5. Hoffman, Edward J., "Energy Transformations," Energy Conversion, 10, 33-9 (1969).
6. Morrison, Robert G., "Generation and Recovery of Carbon Monoxide," Information Circular #70, NRRI, Univ. of Wyo., Jan., 1971, 56 pp.
7. Cox, John L., "A Survey of Iron Catalysts for Fischer-Tropsch Type Reactions," Information Circular #71, NRRI, Univ. of Wyo., Feb., 1971, 23 pp.
8. Sutherland, Robert L., "Investigation of Mechanical Behavior of Fluidized Beds," Information Circular #72, NRRI, Univ. of Wyo., Sept., 1971, 33 pp.
9. Hoffman, Edward J., "Overall Efficiencies of Nuclear Power," Information Circular #73, NRRI, Univ. of Wyo., Dec., 1971, 69 pp.
10. Hoffman, Edward J., "The Direct Production of Hydrogen from Coal-Steam Systems," Preprints, Div. of Fuel Chemistry, ACS, 15(1), 1971.
11. Hoffman, Edward J., Conference on Financing Synthetic Fuels and Related Problems Sponsored by NRRI, Univ. of Wyo., Cheyenne, Wyo., April 25-26, 1972.
12. Hoffman, Edward J., Cox, John L., Hoffman, Robert W., Roberts, Jake A., and Willson, Warrack G., "Behavior of Nickel Methanation Catalysts in Coal-Steam Reactions," Preprints, Div. of Fuel Chemistry, ACS, 16(2), 64-7 (1972).
13. Cox, John L., Hoffman, Edward J., Hoffman, Robert W., Willson, Warrack G., Roberts, Jake A., and Stinson, Donald L., "Gasification of Organic Waste," Preprints, Div. of Fuel Chemistry, ACS, 18(1), 1-14 (1973).
14. Willson, Warrack G., Sealock, L. John, Jr., Hoodmaker, Francis C., Hoffman, Robert W., Cox, John L., and Stinson, Donald L., "Alkali Carbonate and Nickel Catalysis of Coal-Steam Gasification," Preprints, Div. of Fuel Chemistry, ACS, 18(2), 29-42(1973).
15. Cox, John L., "Selected Thermodynamic Values of Coal Gasification Reactions," Information Circular #74, NRRI, Univ. of Wyo., May, 1973, 50 pp.
16. Cox, John L., "Catalyst for Coal Conversion," Symposium on Clean Fuels from Coal, IGT, Sept., 10-14, (1973).
17. Willson, Warrack G., Sealock, L. John, Jr., Hoodmaker, Francis C., Hoffman, Robert W., Cox, John L., and Stinson, Donald L., "Alkali Carbonate and Nickel Catalysis of Coal-Steam Gasification," ACS Advances in Chemistry

Series on Fuel Gasification, 1974 (in press).

18. Cox, John L., Sealock, John, Jr., and Hoodmaker, Francis C., "Sulfur Problems in the Direct Catalytic Production of Methane from Coal-Steam Reactions," Am. Chem. Soc., Div. Fuel Chem., Preprints 19, (1974) (in press).

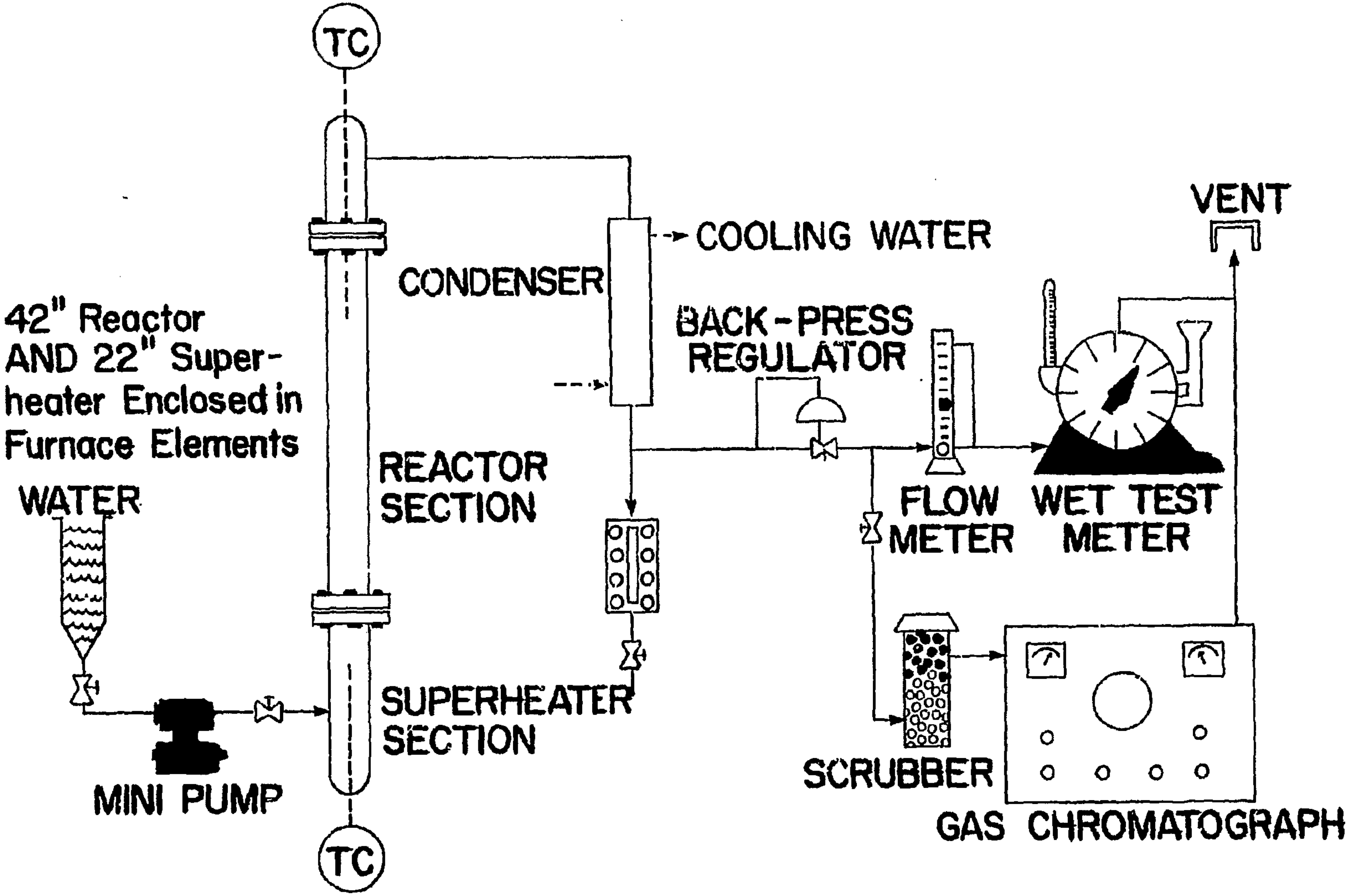


FIGURE I. SCHEMATIC OF EXPERIMENTAL SYSTEM.

COAL ANALYSES

	Glenrock coal		Reynolds coal		Consol lignite		Minnkota lignite		Old Ben coal	
	Air Dried	Moist. Free	As Rec'd	Moist. Free	Air Dried	Moist. Free	As Rec'd	Moist. Free	As Rec'd	Moist. Free
Proximate										
moisture	6.5	----	19.3	----	2.0	----	11.5	----	4.9	----
ash	8.5	9.1	13.5	16.7	8.5	8.7	7.5	8.5	16.3	17.1
volatile matter	41.7	44.6	30.3	37.5	40.9	41.7	37.0	41.8	31.0	32.6
fixed carbon	43.3	46.3	36.9	45.8	48.6	49.6	44.0	49.7	47.8	50.3
Ultimate										
carbon	59.6	63.7	36.7	56.4	63.4	64.7	58.5	66.1	62.8	66.0
hydrogen	5.1	4.7	6.8	4.4	4.8	4.7	5.8	5.1	5.1	4.8
oxygen	25.5	21.2	42.5	17.7	21.9	20.5	26.9	18.8	12.1	8.1
sulfur	0.6	0.6	0.4	0.7	0.8	0.8	0.6	0.7	2.4	2.5
nitrogen	0.7	0.7	0.4	0.6	0.6	0.6	0.7	0.8	1.4	1.5

TABLE I

COMPILATION OF TESTED CATALYSTS

Catalyst Designation	Catalyst Description	Run Nos.
Nickel		
Ni-0104	A reduced and stabilized hydrogenation catalyst containing 58% nickel in kieselguhr with a reduced-to-total nickel ratio of 0.60-0.65. Supplied by Harshaw Chemical.	26-29, 37, 56, 212, 214, 216, 225, 227, 231, 237, 251, 256, 261-285, 287-292, 294-307, 319, 321-325, 331, 346, 353-365, 367-370, 377-394, 403-407, 433-444, 448-449, 451-456, 459-462, 505-507
Ni-0101	A hydrogenation and methanation catalyst containing 44% Ni present as the hydrate in kieselguhr which must be reduced before use. Purchased from Harshaw Chemical.	37, 59
Ni-3210	A reduced and stabilized hydrogenation catalyst containing 35% nickel on a high strength proprietary support. Purchased from Harshaw Chemical.	314, 317, 320, 326-327, 333-344, 347-352, 366, 371-375, 421-424, 430-432, 445-446, 450, 457-458, 463-480, 496-497, 500-504, 513, 524, 538-41, 547-8, 553, 55-60, 574-78, 583, 600-11, 614-26, 630-7, 643, 648-52, 654-706, 708-14, 716, 723, 725-9
Ni-3250	A reduced and stabilized hydrogenation catalyst containing 50% nickel. Obtained from Harshaw Chemical.	328-330, 409-420, 481-495, 514, 523
Ni-0104, CuO	Harshaw's Ni-0104 catalyst mixed with copper.	395-401
Ni-3250, Cr_2O_3	Harshaw's Ni-3250 catalyst mixed with Cr_2O_3.	426-427
Ni-3250, Fe_2O_3	Harshaw's Ni-3250 catalyst mixed with Fe_2O_3.	425

G-48	An iron base catalyst used for the dehydrogenation of butenes to butadiene. Purchased from Girdler Catalysts.	253
Pyrite Cinders	Received from Allied Chemical Corporation's sulfuric acid plant in Denver, Colorado.	72-74, 93, 98, 100, 126, 128
Fixed Bed	A sintered, fixed-bed, Fischer-Tropsch iron catalyst from Ruhrchemie Aktiengessellschaft.	78-81, 86, 89, 92, 94, 103-104, 107, 111, 129-131, 148-149
Ruhrchemie	An unreduced iron catalyst from Ruhrchemie Aktiengessellschaft.	83, 177
Magnetite	An iron ore concentrate catalyst from the Wyoming Copper Mountain Iron Formation. The ore was concentrated by grinding to 100 mesh and using a Davis tube.	22-25, 41, 115
Iron Mountain	A magnetite (Fe_3O_4) ore from Iron Mountain, near Laramie, Wyoming.	190-191
CMIF	A native iron ore from Copper Mountain Iron Formation, Wyoming.	178-179
Fe-USBM	An iron catalyst containing 50.8% FeO, 42.5% Fe_2O_3, 4.6% MgO, 1% SiO and 0.6% K_2O from the U. S. Bureau of Mines, Pittsburgh, Pa.	173-176
T-1844	An iron oxide catalyst with 25% Na_2CO_3 which had been sintered at 2000°F. Purchased from Girdler Catalysts.	238-243, 248-250, 254, 257-260
T-1845	An iron oxide with 25% Na_2CO_3 which had been sintered at 2500°F. Purchased from Girdler Catalysts.	247, 718-19
T-1846	An iron oxide which had been sintered at 2000°F. Obtained from Girdler Catalysts.	245
T-1847	An iron oxide which had been sintered at 2500°F. Purchased from Girdler Catalysts.	244
Alumina	A high alumina fluid cracking catalyst, F-1-25, from Davison Chemical.	315, 707, 717

G-52	A prereduced methanation catalyst used for the removal of carbon oxides and oxygen from hydrogen and ammonia synthesis gas streams, containing about 33 wt. percent nickel in a refactory oxide support. From Girdler Catalysts.	58, 67-70, 82-83, 85, 87-88, 90-91, 95, 105-106, 114, 141-145, 162-165, 172, 215, 286, 318
G-65RS	An improved form of G-52 which is more active and can withstand temperatures in excess of 2200°F without noticeable shrinkage or fusion. From Girdler Catalysts.	308-313, 508-509, 515-522, 527-531, 532-7, 550, 554
G-87RS	A prereduced and stabilized methanation catalyst similar to G-65, but containing 40.3 wt. % nickel. From Girdler Catalysts.	510-511, 525-526
DMS-Ni	A nickel loaded molecular sieve from Davison Chemical containing 13% Ni in 40-80 mesh beads.	429, 498
DA1S-Ni	An unreduced 40-80 mesh novel alumina spheres containing 30 wt. % Ni. Supplied by Davison Chemical.	512, 563
544MS-Ni-A	A nickel loaded zeolite which contains 12% nickel on 8-12 mesh beads.	428, 499
Co-0101	A hydrogenation catalyst containing 35% cobalt present as the oxide in kieselguhr. Purchased from Harshaw Chemical.	102
Millscale	Received from the CF&I plant in Pueblo, Colorado.	42-55, 57, 61-62, 71, 84, 96-97, 99, 108-110, 112-113, 116-118, 122, 132-135, 138-140, 146-147, 150-161, 166-171, 180-189, 192-202, 206-211, 213, 217-218, 222-224, 229-230, 232, 236
G-3	A chromium promoted iron oxide catalyst used to promote the water-gas shift reaction. Obtained from Girdler Catalysts.	60, 119-121, 123-125, 219-220, 226, 228, 233-235
G-47	An ammonia dissociation catalyst composed of iron oxide on a rugged spherical support. Purchased from Girdler.	252, 255

Ni-5104	A propriatory catalyst sample from CCI containing nickel oxide on an innert support.	543-6
Houdralite-Ni	A nickel catalyst supplied by Houdry, NiO on a proprietary support.	552, 561-2, 565, 638-9
NA_2-V	2mm dia. spheres with a vacant center containing 40% NiO on Al_2O_3. Supplied from Osaka Yogyo Co., Ltd.	566-72, 578-82, 584-99
Houdralite-20Ni	Houdralite catalyst from Houdry, containing 20% nickel.	720-22, 724

CONVERSION OF COAL STEAM TO METHANE ONE INCH REACTOR DATA AVERAGE RUNS

RUN NO.	201	204	205	205A	205	207	237	223
COAL DESCRIPTION	GLENROCK COAL	GLENROCK COAL	GLENROCK COAL	GLENROCK COAL	GLENROCK OVERALL	GLENROCK COAL	GLENROCK COAL	GLENROCK COAL
COAL MASS (G)	150.0	150.0	150.0	69.0*	150.0	150.0	150.0	150.0
CATALYST DESCRIPTION	NONE	NONE	NONE	NONE	NONE	MILLSCALE	MILLSCALE	MILLSCALE
CAT. PRETREATMENT						FROM-236 2750F-24HR REDUCED	2650F FUSED	2650F-24HR
CATALYST MASS(G)	.0	.0	.0	.0	.0	155.0	150.0	150.0
ALKALI DESCRIPTION	NA2CO3	NONE	K2CO3	NONE	K2CO3	K2CO3	K2CO3	K2CO3
ALKALI MASS (G)	25.0	.0	25.0	.0	25.0	25.0	25.0	25.0
RUN TIME (HRS)	5.0	5.0	7.0	4.0	11.0	9.0	6.0	11.0
AVE. PRESSURE (PSIA)	211.4	236.4	361.4	361.4	361.4	211.4	336.4	336.4
CAT. TEMP.(DEGREES C)	456.4	454.4	482.2	482.2	482.2	492.2	621.1	398.9
COAL TEMP.(DEGREES C)	615.6	633.9	587.8	647.8	627.4	537.6	621.1	621.1
GAS PRODUCT (ACTUAL CF)	1.41	1.70	2.27	1.91	4.22	2.46	2.57	3.52
GAS PRODUCT (SCF)	1.72	1.32	1.66	1.39	3.06	1.77	1.97	2.61
LIQUID PRODUCT (ML)	.50	.50	.50	8.50	8.50	3.00	.50	.50
STEAM RATE (LB/HR)	.05	.05	.05	.00	.03	.03	.05	.02
STEAM VELOCITY (FT/SEC)	.02	.02	.01	-.00	.01	.01	.01	.01
SPACE VEL.(1/HOURS)	27.50	19.98	14.16	.00	9.01	13.70	12.19	5.05
GAS RATE (SCF/HR)	.23	.26	.24	.35	.28	.20	.31	.24
GAS VELOCITY (FT/SEC)	.00	.00	.00	.00	.00	.00	.00	.00
UNREACTED COAL (G)	55.00	50.00	69.00	44.00	19.00	9.00	35.00	35.00
OVERALL CONV. (PER CENT)	63.33	66.67	70.67	36.23	87.33	94.00	76.67	76.67
CARBON IN GAS (G)	12.86	13.48	22.81	9.22	31.22	19.70	19.90	25.32
CARBON REC.(PER CENT)								
NET WATER USED (G)	15.02	20.05	15.00	-8.00	7.00	-1.00	75.00	-16.00
HYDROGEN REC.(PER CENT)								
SCF GAS/TON COAL CHARGE	6161.05	7853.87	9979.13	18275.70	18396.57	10720.55	11302.14	15770.39
GAS COMP. (PER CENT) CO	.0	.0	.0	.0	.0	.0	.0	.0
CO2	29.2	25.4	22.9	17.7	20.1	26.4	23.6	27.1
UNSATS	.0	.0	.0	.0	.0	.0	.0	.0
H2	29.2	35.7	23.9	56.3	33.7	38.9	32.5	36.0
HYDROCARBONS C1	44.7	34.2	47.5	25.2	42.8	29.4	40.1	33.5
C2	2.8	2.4	2.9	.4	1.7	3.5	2.0	1.8
C3	1.5	1.2	1.3	.0	1.1	1.6	.8	.5
C4	.3	.2	.3	.0	.1	.2	.1	.1
C5	.5	.7	1.3	.5	.3	1.4	.8	.3
BBLS LIQ./TON CHARGE	.0	.0	.0	.7	.3	.1	.0	.0
MAX. CH4 YIELD(SCF/TON)	19581.7	19581.7		19581.7	19581.7	19581.7	19581.7	19581.7
SCF HYDROGEN/TON CHARGE	1799.0	2463.9		12099.2	6233.0	4179.3	3654.5	5803.5
SCF HYDROCARBON/TON	2930.8	2374.5		4678.6	8182.9	3527.1	4758.2	5566.9
BTU/SCF (CO2 FREE)	781.12	690.14	822.10	543.86	732.40	670.23	733.60	601.29
CAT. ACT.(CC/HR/G. CAT.)						53.12	58.90	44.75
CAT. SEL.(CC/HR/G. CAT.)						15.62	23.58	14.99
TOTAL MASS BALANCE(PCT.	75.4	74.6	75.8	123.2	95.6	75.7	67.0	90.8

* estimate

[illegible]

RUN NO.	226	227	231	237	235	242	253	255
COAL DESCRIPTION	GLENROCK	GLENROCK	GLENROCK	GLENROCK	GLENROCK	CONSOL	CONSOL	CONSOL
	COAL	COAL	COAL	COAL	COAL	LIGNITE	LIGNITE	LIGNITE
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	125.0	125.0	125.0
CATALYST DESCRIPTION	[illegible]	NI-[illegible]	NI-[illegible]	NI-3104	GIRDLER	NI-0104	NI-3104	NI-3104
		1/8-INCH	1/8-INCH	1/8-INCH	T-[illegible]	1/8-INCH	1/8-INCH	1/8-INCH
CAT. PRETREATMENT	OXID.STEAM	NONE	NONE	NONE	SINTERED	NONE	NONE	NONE
	REDUCE-H2				[illegible]	SEPARATE	SEPARATE	MIXED
CATALYST MASS(G)	[illegible]	150.0	150.0	125.0	150.0	125.0	125.0	125.0
ALKALI DESCRIPTION	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3
ALKALI MASS (G)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
RUN TIME (HRS)	9.0	12.0	14.0	8.0	5.0	7.0	7.0	7.0
AVG. PRESSURE (PSIA)	174.4	511.4	511.4	261.4	451.4	26.1	511.4	26.1
CAT. TEMP.(DEGREES C)	416.7	626.7	591.9	625.7	413.0	744.1	750.0	732.2
COAL TEMP.(DEGREES C)	537.9	591.7	515.6	573.3	575.1	751.7	752.0	732.2
GAS PRODUCT (ACTUAL CF)	2.32	3.21	5.25	2.45	3.43	6.05	5.36	5.46
GAS PRODUCT (SCF)	1.67	2.31	3.70	1.76	2.47	4.93	3.95	4.65
LIQUID PRODUCT (ML)	4.00	.50	1.50	.00	11.00	.00	.00	.00
STEAM RATE (LB/HR)	.02	.02	.21	.06	.25	.05	.06	.03
STEAM VELOCITY (FT/SEC)	.01	.00	.20	.02	.01	.29	.01	.19
SPACE VEL.(1/HOURS)	1.29	3.07	2.64	21.57	12.54	300.42	11.05	196.47
GAS RATE (SCF/HR)	.19	.19	.27	.22	.49	.70	.55	.65
GAS VELOCITY (FT/SEC)	.01	.00	.00	.00	.00	.22	.01	.20
UNREACTED COAL (G)	35.00	35.00	17.00	15.00	65.01	7.20	6.50	11.00
OVERALL CONV. (PER CENT)	75.67	76.67	88.67	88.00	143.34	94.40	94.80	91.20
CARBON IN GAS (G)	14.45	19.36	54.12	24.47	28.48	69.55	54.49	65.02
CARBON REC.(PER CENT)								
NET WATER USED (G)	46.00	69.00	5.00	20.00	40.00	66.00	107.00	54.00
HYDROGEN REC.(PER CENT)								
SCF GAS/TON COAL CHARGE	13194.96	13786.20	22083.49	12789.51	14732.97	35798.40	28042.16	33767.00
GAS COMP. (PER CENT) CO	.0	.0	.0	.0	.0	.0	.0	.0
CO2	12.4	27.5	49.9	45.0	51.6	48.7	49.0	43.4
UNSATS	.0	.0	.0	.0	.0	.0	.0	.0
H2	13.3	16.3	3.5	3.3	27.2	1.9	1.7	3.1
HYDROCARBONS C1	29.2	55.0	46.1	51.7	18.6	49.4	49.2	53.9
C2	2.9	.2	.3	.0	1.9	.0	.0	.0
C3	1.5	.0	.2	.0	.7	.0	.0	.0
C4	.3	.0	.0	.0	.3	.0	.0	.0
C5	.9	1.7	.6	.9	.6	.0	.0	.0
BBLS LIQ./TON CHARGE	.2	.0	.0	.0	.4	.0	.0	.0
MAX. CH4 YIELD(SCF/TON)	17501.7	19591.7	11591.1	.19501.7	19581.7	16423.3	16423.3	16423.3
SCF HYDROGEN/TON CHARGE	3365.0	2279.8	800.9	422.1	4001.9	680.2	476.7	1046.0
SCF HYDROCARBON/TON	3173.2	7723.4	10517.9	6612.2	3061.3	17684.4	13796.7	18200.4
BTU/SCF (CO2 FREE)	509.99	858.33	959.43	971.72	651.71	987.52	990.02	975.58
CAT. ACT.(CC/HR/G. CAT.)	35.25	36.19	51.92	49.99	93.22	159.63	125.04	150.57
CAT. SEL.(CC/HR/G. CAT.)	13.23	23.01	23.52	25.80	17.34	78.06	61.52	81.16
TOTAL MASS BALANCE REC.	73.0	71.4	97.3	35.7	63.4	97.7	81.0	95.5

CONVERSION OF COAL, STEAM TO METHANE [illegible] REACTION DATA SUMMARY [illegible]

RUN NO.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
COAL DESCRIPTION	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	CONSOL	CONSOL
	COAL	COAL	COAL	LIGNITE	COAL	COAL	LIGNITE	LIGNITE
COAL MASS (G)	125.0	125.0	150.0	125.0	100.0	100.0	95.0	100.0
CATALYST DESCRIPTION	NI-3134	NI-3134	NI-3210	NI-3210	NI-3250	NI-3250	NI-3210	NI-3210
	1/8-INCH	1/8-INCH	1/8-INCH	1/8-INCH	1/8-INCH	1/8-INCH	1/8-INCH	1/8-INCH
CAT. PRETREATMENT	REUSED	REUSED	REREDUCED	REDUCED	REDUCED	REDUCED	REREDUCED	REREDUCED
	SEPARATE	SEPARATE	SEPARATE	IN SITU	IN SITU	SEPARATE	MIXED	MIXED
CATALYST MASS(G)	125.0	123.2	127.5	150.0	100.0	100.0	173.0	113.0
ALKALI DESCRIPTION	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3
ALKALI MASS (G)	75.0	25.0	20.0	15.0	12.0	12.0	20.0	23.0
RUN TIME (HRS)	7.0	6.5	7.5	7.5	7.5	7.5	7.5	11.5
AVE. PRESSURE (PSIA)	279.2	251.2	251.6	32.1	32.1	32.2	32.2	30.3
CAT. TEMP.(DEGREES C)	665.6	626.1	733.7	657.8	762.2	775.5	648.9	660.6
COAL TEMP.(DEGREES C)	737.2	737.8	665.6	660.6	759.4	768.9	560.0	577.2
GAS PRODUCT (ACTUAL CF)	5.22	5.14	3.57	4.27	4.34	3.82	2.19	3.55
GAS PRODUCT (SCF)	3.74	3.59	2.64	3.08	3.12	2.69	1.55	2.57
LIQUID PRODUCT (ML)	5.00	5.00	.37	.00	.09	.00	.00	.00
STEAM RATE (LB/HR)	.04	.03	.03	.02	.03	.03	.01	.01
STEAM VELOCITY (FT/SEC)	.01	.01	.01	-.07	.14	.12	.04	.04
SPACE VEL.(1/HOURS)	14.93	11.46	10.99	73.22	147.46	123.09	38.92	42.17
GAS RATE (SCF/HR)	.53	.57	.34	.41	.42	.36	.21	.22
GAS VELOCITY (FT/SEC)	.01	.01	.01	.08	.09	.08	.04	.05
UNREACTED COAL (G)	12.00	18.50	34.00	32.00	24.00	30.50	33.50	39.50
OVERALL CONV. (PER CENT)	90.40	85.20	56.00	74.40	76.00	69.50	64.74	60.50
CARBON IN GAS (G)	51.86	49.34	33.59	42.09	43.77	37.48	19.01	33.17
CARBON REC.(PER CENT)				72.91	78.87	75.50	83.34	103.75
NET WATER USED (G)	54.00	49.00	10.00	17.00	65.00	66.00	-5.00	25.00
HYDROGEN REC.(PER CENT)				95.42	73.48	66.79	106.50	83.31
SCF GAS/TON COAL CHARGE	27127.96	26723.57	23035.95	22310.34	28267.94	24357.92	14831.11	23307.54
GAS COMP. (PER CENT) CO	.0	.0	.4	.4	.0	.0	2.9	1.7
CO2	51.0	46.8	43.7	44.3	39.0	37.9	39.1	41.9
UNSATS	.0	.0	.0	.0	.0	.0	.0	.0
H2	5.5	6.7	7.9	4.7	2.2	2.8	11.2	10.1
HYDROCARBONS C1	43.7	46.5	48.0	50.6	58.8	59.3	46.9	46.3
C2	.0	.0	.0	.0	.0	.0	.0	.0
C3	.0	.0	.0	.0	.0	.0	.0	.0
C4	.0	.0	.0	.0	.0	.0	.0	.0
C5	.0	.0	.0	.0	.0	.0	.0	.0
BBLS LIQ./TON CHARGE	.2	.2	.0	.0	.0	.0	.0	.0
MAX. CH4 YIELD(SCF/TON)	19591.7	19591.7	11591.1	19476.2	25456.2	25456.2	19171.1	19171.1
SCF HYDROGEN/TON CHARGE	1492.0	1603.4	1819.8	1069.0	621.9	682.0	1661.1	2354.1
SCF HYDROCARBON/TON	11854.9	12426.4	11057.2	11293.1	16521.5	14444.2	6995.8	10791.4
BTU/SCF (CO2 FREE)	936.00	934.37	911.55	949.98	980.19	981.79	854.70	873.18
CAT. ACT.(CC/HR/G. CAT.)	124.97	128.33	75.17	116.11	117.65	101.37	47.67	55.98
CAT. SEL.(CC/HR/G. CAT.)	52.86	59.67	36.39	58.75	69.18	60.11	22.36	25.92
TOTAL MASS BALANCE(REC.	93.2	93.2	102.1	97.5	87.4	83.5	96.8	98.3

[illegible]

RUN NO.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
COAL (TYPE)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible] COAL [illegible]	GLEN[illegible] COAL
COAL MASS (G)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	15.[illegible]	[illegible].5	100.0
CATALYST DESCRIPTION	NI-3210 179-1504	NI-3210 179-1504	NI-3210 179-1504	NI-3210 179-1050	NI-3210 179-1504	NI-3210 179-1504	NI-3210 179-1504	NI-3210 178-1504
CAT. PRETREATMENT	REDUCED MIXED	REDUCED MIXED	REDUCED MIXED	FROM 725	FROM 725	FROM 725	FOR [illegible]2	COMP. RUN MIXED
CATALYST MASS(G)	115.2	11[illegible].0	1[illegible]	1[illegible].0	105.0	105.0	105.0	105.0
ALKALI DESCRIPTION	[illegible]	[illegible]	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3
ALKALI MASS (G)	[illegible]	22.0	[illegible]	[illegible]	22.0	2[illegible].0	25.0	20.0
RUN TIME (HRS)	11.2	7.6	7.5	17.0	12.0	4.0	25.0	33.5
AVG. PRESSURE (PSIA)	30.5	3[illegible].6	3[illegible].6	30.6	33.5	30.3	33.6	30.4
CAT. TEMP.(DEGREES C)	6[illegible].6	65[illegible].3	[illegible].5	565.6	566.1	566.7	5[illegible].1	584.4
COAL TEMP.(DEGREES C)	552.2	[illegible]	[illegible].1	520.6	562.9	563.2	550.6	55[illegible].4
GAS PRODUCT (ACTUAL CF)	3.59	1.99	2.59	3.78	4.66	.83	9.24	11.32
GAS PRODUCT (SCF)	2.61	1.41	1.51	2.75	3.37	.50	6.70	8.20
LIQUID PRODUCT (ML)	.00	.00	.00	.00	.00	.00	.00	.00
STEAM RATE (LB/HR)	.01	.01	.01	.12	.11	.1[illegible]	.12	.09
STEAM VELOCITY (FT/SEC)	.36	.33	.33	.51	.50	.82	.54	.42
SPACE VEL.(1/HOURS)	37.68	33.22	34.37	547.10	51[illegible].61	838.36	550.46	434.91
GAS RATE (SCF/HR)	.23	.19	.20	.29	.29	.14	.26	.24
GAS VELOCITY (FT/SEC)	.35	.34	.36	.05	.06	.03	.05	.05
UNREACTED COAL (G)	36.00	43.50	50.00*	30.00*	15.00*	8.50*	6.50	6.50
OVERALL CONV. (PER CENT)	64.00	56.50	50.00	50.00	50.00	43.33	23.53	93.50
CARBON IN GAS (G)	32.83	17.93	18.06	15.63	10.47	3.03	37.06	55.36
CARBON REC.(PER CENT)	1[illegible].68	1[illegible].26						98.22
NET WATER USED (G)	[illegible].03	7.93	8.00	61.00	107.00	71.00	92.00	100.00
HYDROGEN REC.(PER CENT)	1[illegible].23	81.41						76.13
SCF GAS/TON COAL CHARGE	23551.49	12035.12	13556.23	41667.50	101806.81	34971.41	714930.19	14693.75
GAS COMP. (PER CENT) CO	2.7	4.9	10.4	1.9	2.0	1.1	1.9	3.4
CO2	39.5	39.6	35.9	37.5	36.1	35.1	36.6	36.5
UNSATS	.0	.0	.0	.0	.0	.0	.0	.0
H2	12.4	11.9	12.1	60.5	61.8	63.4	61.4	53.0
HYDROCARBONS C1	45.4	47.8	41.4	.1	.1	.1	.0	7.1
C2	.0	.0	.0	.0	.0	.0	.0	.0
C3	.0	.0	.0	.0	.0	.0	.0	.0
C4	.0	.0	.0	.0	.0	.0	.0	.0
C5	.0	.0	.0	.0	.0	.0	.0	.0
BBLS LIQ./TON CHARGE	.0	.0	.0	.0	.0	.0	.0	.0
MAX. CH4 YIELD(SCF/TON)	16664.4	16664.4	19323.7					18023.7
SCF HYDROGEN/TON CHARGE	2937.9	1527.4	1579.7					39434.0
SCF HYDROCARBONS/TON	1[illegible]74.3	6135.2	5553.7					5282.7
BTU/SCF (CO2 FREE)	463.94	933.05	769.87	326.01	325.99	326.00	324.91	401.77
CAT. ACT.(CC/HR/G. CAT.)	55.02	45.27	54.13	74.32	75.66	30.93	69.40	56.02
CAT. SEL.(CC/HR/G. CAT.)	24.70	21.64	22.41	.07	.08	.04	.30	4.69
TOTAL MASS BALANCE REC.	98.4	91.9	99.3	96.1	94.3	86.2	103.7	100.1

* estimate

[illegible]

RUN NO.	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
COAL DESCRIPTION	GLENROCK COAL	GLENROCK COAL CHAR	GLENROCK COAL CHAR	GLENROCK COAL CHAR	GLENROCK COAL CHAR	GLENROCK COAL
COAL MASS (G)	[illegible]	60.3*	43.5*	33.0*	22.0*	[illegible]
CATALYST DESCRIPTION	91-3210 [illegible]	91-3210 [illegible]	91-3210 [illegible]	91-3210 [illegible]	91-3210 [illegible]	91-3210 [illegible]
CAT. PRETREATMENT	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
CATALYST MASS (G)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
ALKALI DESCRIPTION	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3	K2CO3
ALKALI MASS (G)	[illegible]	[illegible]	20.0	20.0	25.0	20.0
RUN TIME (HRS)	7.5	5.0	1.0	6.5	21.0	28.5
AVE. PRESSURE (PSIA)	33.4	32.4	32.2	39.3	32.3	30.3
CAT. TEMP. (DEGREES C)	543.6	554.4	554.6	559.6	556.1	557.2
COAL TEMP. (DEGREES C)	497.8	557.8	565.6	564.4	546.1	549.9
GAS PRODUCT (ACTUAL CF)	2.63	1.87	2.86	1.89	6.59	8.39
GAS PRODUCT (SCF)	1.73	1.36	2.65	1.36	4.16	6.49
LIQUID PRODUCT (ML)	.00	.00	.07	.00	.00	.00
STEAM RATE (L/HR)	.01	.04	.06	.09	.06	.05
STEAM VELOCITY (FT/SEC)	.03	.17	.25	.17	.29	.22
SPACE VEL. (1/HOURS)	31.64	199.11	250.32	380.94	288.91	221.21
GAS RATE (SCF/HR)	.23	.27	.20	.21	.23	.23
GAS VELOCITY (FT/SEC)	.05	.05	.04	.04	.04	.04
UNREACTED COAL (G)	61.00*	41.00*	31.09*	23.59*	19.00	19.00
OVERALL CONV. (PER CENT)	[illegible]	31.67	22.59	21.67	13.64	76.20
CARBON IN GAS (G)	27.31	8.36	11.69	7.50	26.07	49.67
CARBON REC. (PER CENT)						107.20
NET WATER USED (G)	3.00	26.00	43.00	35.00	194.00	107.00
HYDROGEN REC. (PER CENT)						63.49
SCF GAS/TON COAL CHARGE	15971.62	20524.43	46436.12	41148.09	195474.12	58861.00
GAS COMP. (PER CENT) CO	6.9	3.8	3.9	2.6	3.5	4.4
CO2	37.7	35.5	35.4	35.7	33.5	36.1
UNSATS	.0	.0	.0	.0	.0	.0
H2	11.2	57.1	60.4	61.7	59.8	46.7
HYDROCARBONS C1	44.2	3.6	.4	.1	1.3	12.8
C2	.0	.0	.0	.0	.0	.0
C3	.0	.0	.0	.0	.0	.0
C4	.0	.0	.0	.0	.0	.0
C5	.0	.0	.0	.0	.0	.0
BBLS LIQ./TON CHARGE	.0	.0	.0	.0	.0	.0
MAX. CH4 YIELD (SCF/TON)	10823.7					10823.7
SCF HYDROGEN/TON CHARGE	1777.6					27488.1
SCF HYDROCARBON/TON	7015.2					7534.2
BTU/SCF (CO2 FREE)	812.78	363.22	329.07	325.95	338.60	462.61
CAT. ACT. (CC/HR/G. CAT.)	61.21	72.87	54.59	55.14	58.64	61.63
CAT. SEL. (CC/HR/G. CAT.)	27.94	2.62	.22	.36	.76	7.90
TOTAL MASS BALANCE % REC.	104.9	94.8	98.4	97.1	99.1	97.1

* estimate

203. A charge was made up of coal and $Na_2CO_3 \cdot H_2O$, without catalyst.

The reactor pressured up readily enough, but condensation of steam in the bottom of the reactor was suspected. The off-gas averaged 800 Btu on a CO_2-free basis. The best sample was 60% C_1 and 880 Btu.

About 100 ml of water were used up or unaccounted for. This is equivalent to:

$$\frac{100}{454}\ \frac{1}{18}\ (359) = 4.38 \text{ cu. ft. as } H_2O$$

$$\text{or } 2.19 \text{ cu. ft. as } CH_4$$

This is way over the 1.6 cu. ft. total recovered. Hence either steam is condensing out at the bottom of the reactor or there is a leak. The wet-test meter also reads low at low rates.

If 70 grams of coal reacted,

$$2C + 2H_2O = CH_4 + CO_2$$

$$\frac{70}{454}\ \frac{1}{12}\ (359) = 4.6 \text{ cu. ft. (total)}$$

$$\text{or } 2.3 \text{ cu. ft. of } C_1$$

$$C + 2H_2O = 2H_2 + CO_2$$

$$\frac{70}{454}\ \frac{1}{12}\ (359)\ (3) = 13.8 \text{ cu. ft. total}$$

$$\text{or } 9.2 \text{ cu. ft. of } H_2$$

The volume of water reacted would be, in the first case

$$\frac{70}{12}\ (18) = 105 \quad \text{ml}$$

In the second,

$$\frac{70}{12}\ (18)\ (2) = 210 \quad \text{ml}$$

There is some agreement between the water and carbon balance, but none for the gas produced. We are simply not metering all the gas produced (as also indicated by a rotameter in the line) and will require a more accurate volumetric meter.

This emphasizes that the gas (and liquid) production so far has been much more favorable than reported -- at least in many instances.

204. A charge of coal only was reacted with steam. The charge pressured up satisfactorily, indicating no leaks.

The best sample showed 50% C_1, but went to H_2 after that.

205. A charge of Glenrock coal and K_2CO_3 was made up without the catalyst. The system was reactive, pressuring up to 350 psi.

The average was 785 Btu, with the best sample showing 64% C_1 and 890 Btu on a CO_2-free basis.

205A. Continuation at a higher steam rate. About 8 ml of liquid showed up. This could be carryover of holdup by steam distillation. As more water was condensed, the layer seemed to form a black emulsion.

On continuing hydrogen was produced preferentially to methane.

205 (overall) Using the recorded gas volumes, 0.57, barrels/ton of liquid were measured plus about 15,000 SCF of an approximately 50-50 mixture of C_1 and H_2.

There is a large discrepancy on the carbon balance. Only 28 g of carbon showed up in the gas while 106 g of coal reacted (of which about 10 g were water). The liquids could account for only

$$8(0.7)\ (\frac{12}{14}) \sim 5 \text{ grams}$$

assuming the C/H ratio = 1/2. Either (or both) liquids are carried in suspension or the gas metered is too low.

207. The catalyst from 206 was mixed with Glenrock coal and K_2CO_3.

About 9000 SCF of a 50-50 mixture hydrocarbon and H_2 was produced. Hydrocarbon liquids in the amount of 0.36 bbls/ton. Again the material balance is off for reasons noted in Run 205.

209. Millscale + 25% K_2CO_3 was taken to 2650°F in a thinner walled crucible. Fusion took place (and fluxed the crucible).

The result was ground and sized and mixed with Glenrock coal and K_2CO_3.

The gas was relatively high in hydrocarbons but only a trace of condensed liquids was noted. The condensed water was coal-black. Of 125 ml of water introduced, 26 were recovered during the run.

209B. Continuation adding CO caused 24 ml more of water to condense out (presumably forced from the reactor bottom).

The gas was higher in H_2.

209B. The bottom of the reactor was wrapped with heating tape and the run continued.

The off-gas tended to be H_2, about 20 ml more of water were introduced.

209. Overall, 145 ml of water were introduced and 42 ml recovered. 125 ml of coal (10% water) reacted, which would tend to agree with the water reacted.

This does not check with gases (or liquids) produced for reasons previously noted (in Runs 205 and 207).

223. A run similar to 222 was repeated. This time the results were encouraging.

About 0.5 bbl/ton of heavies were produced and 12,000 SCF/ton of H_2 and C_1, in about equimolal proportions.

Still had trouble with water holdup. When pressure is reduced, all the water comes over.

About 30 ml of water were produced from coal at the start. This is high -- water may be in part holdup or leaky check-valve in pump.

224. It is suspected that the iron catalyst is in part oxidized by steam. So millscale catalyst was first reacted with steam, then used with a charge. The oxidized catalyst was mostly magnetite. H_2 was produced during the steam-oxidation.

The run wasn't too bad, producing some liquids and gases.

Apparently all the coal reacted.

239. The catalyst from 238 was placed at the top of a Glenrock coal-K_2CO_3 charge.

The run was very successful. A wild, translucent liquid product was obtained. It has a reddish cast, and has been sent out for analysis.

Even after flashing down from 400 psi the liquid product amounted to 0.4 bbls/ton. From other tests, half of the liquid may be lost -- thus up to 0.8 bbls/ton may have been present. If so, the total heavies could have been over one bbl/ton.

Additionally there may have been a leak on the gas side; an odor was noticed.

Due to the difficulty of flashing, a high-pressure gauge glass will be installed.

The condensed hydrocarbons had an unusual, pronounced odor. In odor and appearance they were very much similar to those produced by the Fischer-Tropsch synthesis of H_2 and CO.

All in all, this run indicates strikingly that the system will work with the proper iron catalyst. Unfortunately, this catalyst disintegrated and eventually plugged the reactor.

282. An excellent run using the North Dakota lignite from the Consolidation Coal Company at Stanton.

The Ni-0104 catalyst from Girdler was used, and placed at the top of the coal-K_2CO_3 charge.

Reaction rates were high, the conversion was high, the yield high, and the CO_2-free product had a high-Btu rating.

The reaction temperature was increased to nearly 1400°F. Reaction pressure was atmospheric.

The catalyst breakup was 10%.

283. The conditions of Run 282 were repeated, only at 500 psi rather than atmospheric pressure.

It was noted that the higher pressure required a slightly higher temperature (about 50°F higher). The difficulty may be in part due to condensation of water at the top of the reactor -- the saturation temperature being higher at the higher pressure.

Excellent gas compositions were obtained, but the yield fell off. This may have been caused by a leak (at the higher pressure), since a high conversion was effected. It was noted the carbon balance was deficient.

285. Another run with lignite at atmospheric pressure, only the Ni-0104 catalyst was mixed with the coal-K_2CO_3 charge -- as compared to Run 282.

The gas composition was a little higher in H_2, but still above 900 Btu/SCF on a CO_2-free basis.

The gas yield was acceptable -- though conversion could have been higher.

288. The conditions of Run 287 were repeated.

Some liquids were again produced, possibly due to slow initial heating of the charge.

The hydrogen rose somewhat but the CO_2-free gas still stayed above 900 Btu/SCF.

Yields and conversion were acceptable.

Catalyst breakup was 10%.

289. Reused Ni-0104 catalyst from previous runs was placed at the top of a Glenrock coal-K_2CO_3 charge. Conditions were the same as 289.

While yields and conversion were acceptable, the catalyst breakup was higher for the used catalyst: 23%.

Again some liquids were produced, and it was noted that higher temperatures were required to keep the H_2 concentration down.

Runs 491-495 utilized a high-sulfur eastern coal (Old Ben). Initially, there was some trouble with caking, but this was resolved. The attempts at making a sulfur mass balance were unsatisfactory, but high yields of high-Btu gas were obtained.

Runs 693-701 were runs made using the optimum ratio of alkali to coal (20%) with ~ 110g of rereduced Ni-3210 and 100g of coal. In all runs the charge was made in a glove box. These series of runs were made to determine the reactivity of a commercial lignite, Consol. lignite, (runs 693-697) versus a Wyoming, high volatile subbituminous coal, Glenrock coal, (runs 698-701). As is evidenced from the runs, both behaved nearly identically. In prolonged runs both yielded over 10MSCF CH_4/ton coal and both produced a gas over 800 Btu/SCF (CO_2-free) per ton of coal. The mass balances, with the exceptions of run 696 (in which the reactor plugged) and 701, were all above 95%. It was anticipated that the reactivity of the two coals would be nearly the same since on a dry basis they had nearly the same analyses as shown by Table I.

For runs 725 A-D the usual charge of Glenrock coal K_2CO_3 and reduced Ni-3210 was used. The run was made over a period of several days. The first day's run 725A was made at ~ 580°C, with a steam rate of ~ .03 lb/hr in an attempt to produce gas with a high heating value. The heating value obtained was ~ 770 Btu. The charge was not removed, therefore no carbon recovery data is relevant.

The charge was left in place for the subsequent runs 725 B-D in an attempt to ash the coal as completely as possible, with the production of a low Btu gas. These runs employed temperatures on the coal of ~ 560°C and steam rates of ~ .50 lb/hr. Run 725 H is a summary for the runs aimed at high H_2 production. The gas composition was 61.4% H_2, 1.9% CO, .0% CH_4 and 36.6% CO_2. This gave the best H_2 production and lowest amount of CO production yet obtained. The residue consisted of only 26g of ash and alkali (and 105g Ni-3210) of which approximately 20g are the K_2CO_3 indicating the coal was nearly completely ashed in the 26 hour run. Assuming that only 40 - 50g of char remained after the initial run, 725A, the H_2 production could be extrapolated to between 80 - 100 MSCF H_2/ton of coal.

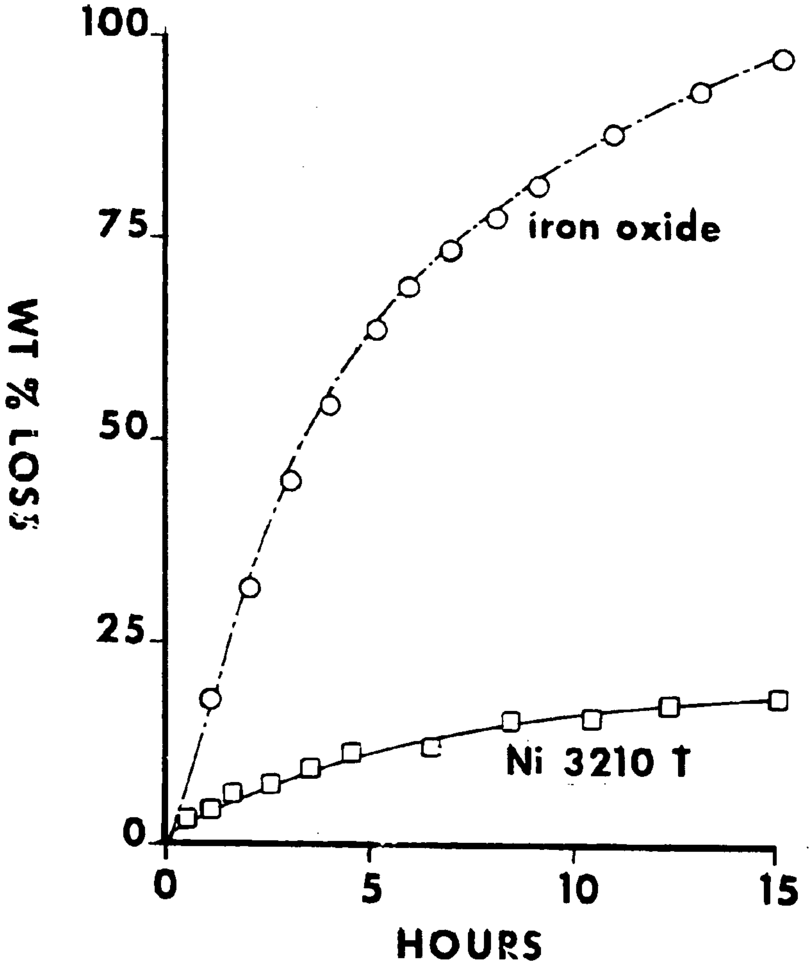
Run 725F is the entire summary of runs 725 A-D which gave an excellent overall mass balance for the 33.5 hr run of 100.1%.

Runs 728 A-D were made as a repeat of runs 725 with the exception that a lower steam rate was employed. The steam rate in the last three runs was ~ .25 lb/hr which was the rate used in 726 and 727. The first run 728A produced a gas with a heating value of over 800 Btu/SCF and over 7MSCF CH_4/ton of coal.

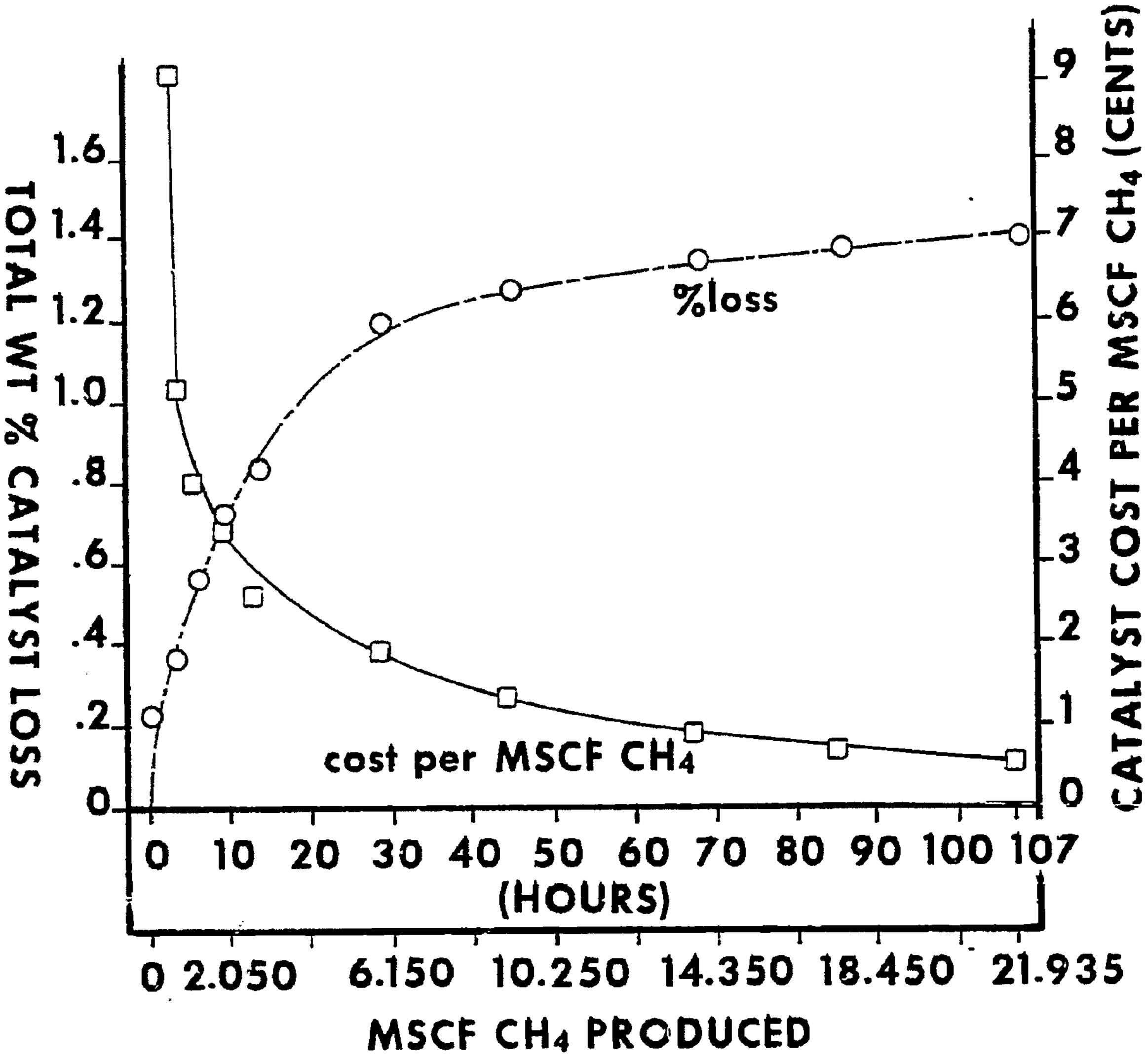
The next three runs 728 B-D were aimed at ashing the charge at a lower steam rate (~ .25 lb/hr) than used in run 725. The temperature on the coal was ~ 560°C. These runs aimed at H_2 production are summarized in 728H. The average composition of the gas was H_2 59.8%, CO 3.5%, CH_4 1.3%, and CO_2 33.5% This run produced only slightly more CO and CH_4, than run 725 which used a steam rate of over twice that employed here. It appears that the lower temperature is more important in increasing H_2 production than steam rates.

Run 728 A-D was carried out for a shorter time period (21 hr.) than 725 as evidenced by the increased residue, 36g, and lower H_2 production (between 55 and 70MSCF H_2/ton coal).

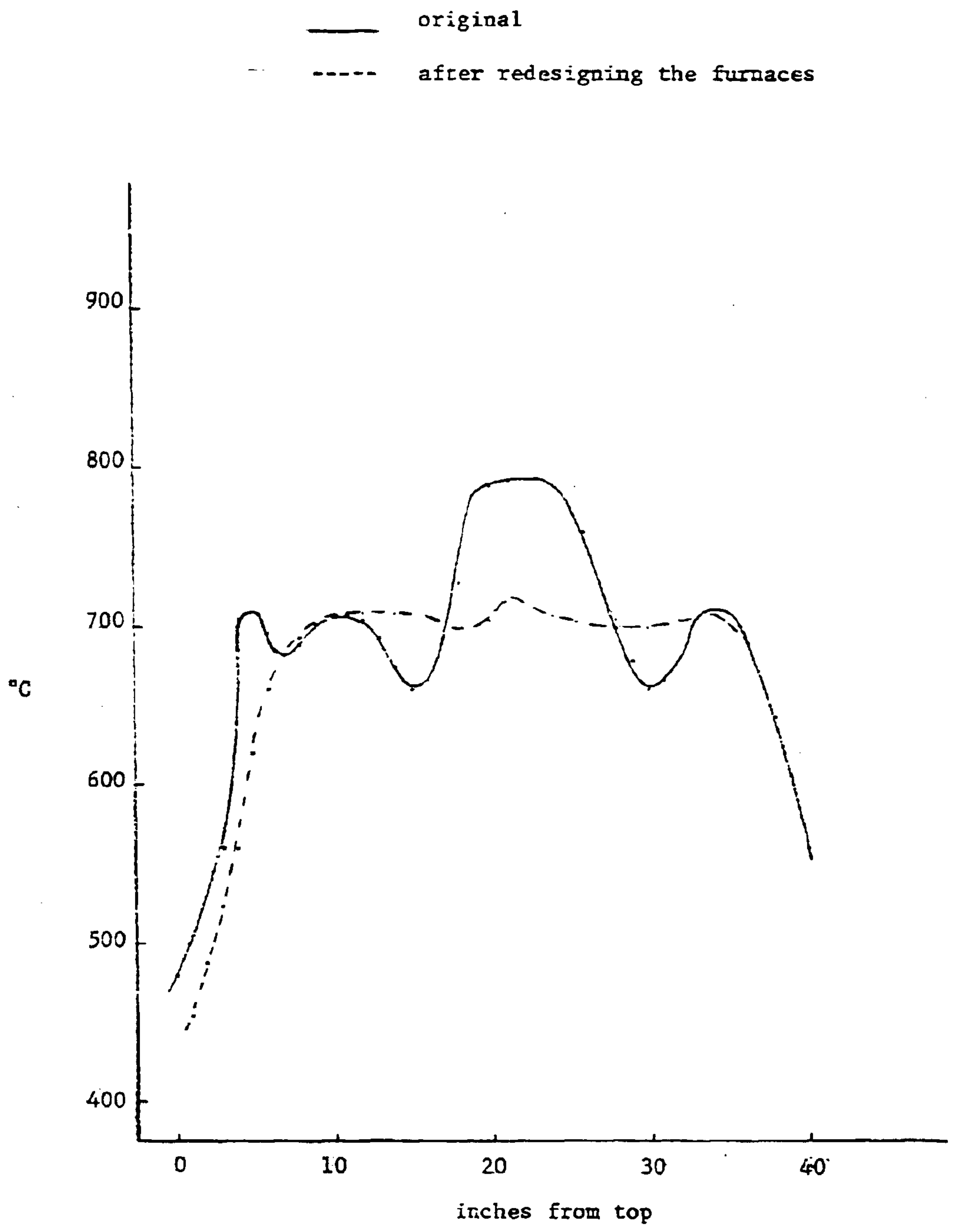
Run 728F is a summary of the four proceeding runs covering 28.5 hours. The mass balance was again very satisfactory at over 97%.



Comparison of weight % loss due to attrition of Girdler G-47 ammonia dissociation catalyst (iron oxide) to Harshaw Ni-3210 T vs. time at flow rates higher than are needed for fluidization.



Plot of weight % loss of Ni-3210T catalyst and catalyst cost per MSCF CH_4 due to attrition vs. time and MSCF CH_4 produced.



TEMPERATURE PROFILES

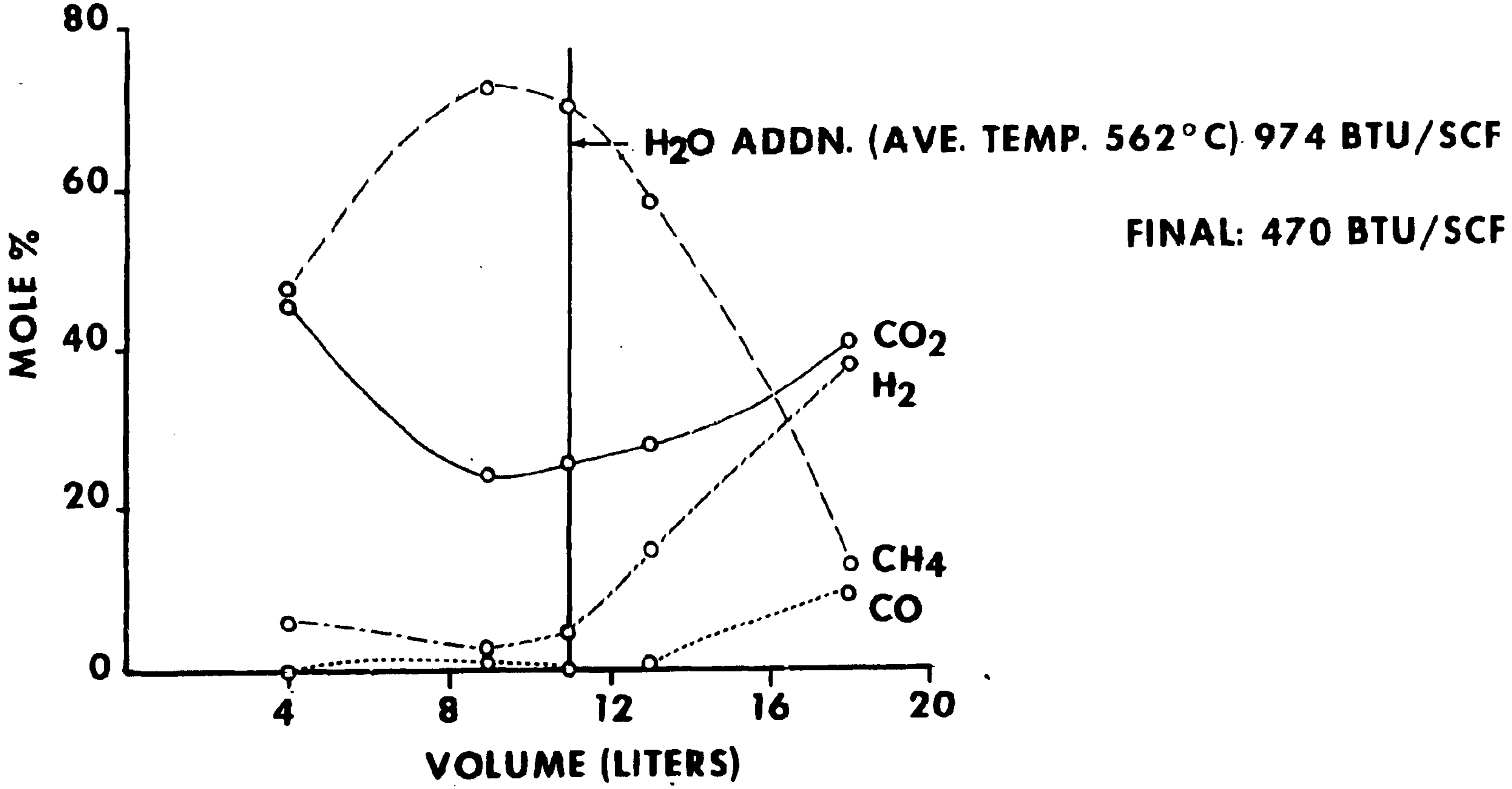
In run 668 lower temperatures were employed in an attempt to see if the rapid loss of activity upon steam addition was due to crystal growth in the new 150 lb. supply of Ni-3210 at 650°C. In these runs the temperature was held between 520 and 560°C and the mass of K_2CO_3 charged was increased to 25g. Although the total mass balances were less than satisfactory, being only ~ 94%, it is felt that any leakage was constant and that the volume rated composition is a true reflection of the gas produced. On page 52 is a graph of the gas composition versus gas production from run 668, which demonstrates the serious problem of steam addition. The methane production although decreasing slightly before the addition of steam, drops rapidly after steam addition. Even though the quality of the gas for a five hour run on a volume rated basis was 830 Btu/SCF, the important change is noted by examining the heating value before and after the addition of steam. Before steam addition the heating value was excellent at 974 Btu/SCF whereas at the termination of the run the value had decreased to only 470 Btu/SCF. These results tend to support the x-ray data which does not show any significant difference between the Ni-3210 used previously and the new 150 lb. sample.

A graph of the average, moisture free, mole percents of the products versus the volume of gas produced for run 674 is shown on page Although the methanation began to drop even before the addition of steam, its activity continued its usual decrease until the temperature on the superheater and the lowest section was increased to ~ 700°C. It was found during the course of this run, with a thermocouple inserted in the superheater near the flange, that the temperature of the steam leaving the superheater was only about 540°C or 110°C below that of the rest of the reactor. In addition a group of runs reported in a previous quarterly were examined and it was found that temperature (T_4) in the lowest section of the reactor was maintained approximately 50°C (at 700°C) higher than the rest of the reactor. At this time the superheater's temperature was increased to give a steam temperature upon exit of 650°C and furnace #4 was increased until a temperature of 700°C was obtained. This figure shows for the first time in the quarter a significant increase in the methane production and a resultant decrease in hydrogen near the end of the run. The increase in the heating value of the gas of 58 Btu/SCF occurred in only one hour after the temperatures were increased. It is realized that this additional heat caused some additional ashing that would not occur at 650°C. In order to correct this situation the configuration of the furnaces around the reactor was changed.

The total volume of the reaction is 300 cm^3 and the volume occupied by 100g. of coal, 20g. of K_2CO_3 and 110g. Ni-3210 is 235 cm^3. This leaves an unoccupied volume of 95 cm^3 and since the volume of one inch of the reactor is approximately 7.5 cm^3, there is about 12 inches of empty reactor space. For this reason it was decided to place the four inch furnace at the bottom of the configuration and raise the three larger furnaces up four inches. This enabled us to keep the temperature on the incoming steam at about 650°-700°C and, by placing a steel wool plug four inches into the reactor to hold the charge in place prevented the formation of excess product due to excess heat on certain portions of the charge. This still leaves about eight inches of empty reactor to insure that little if any catalyst is in the cool zone.

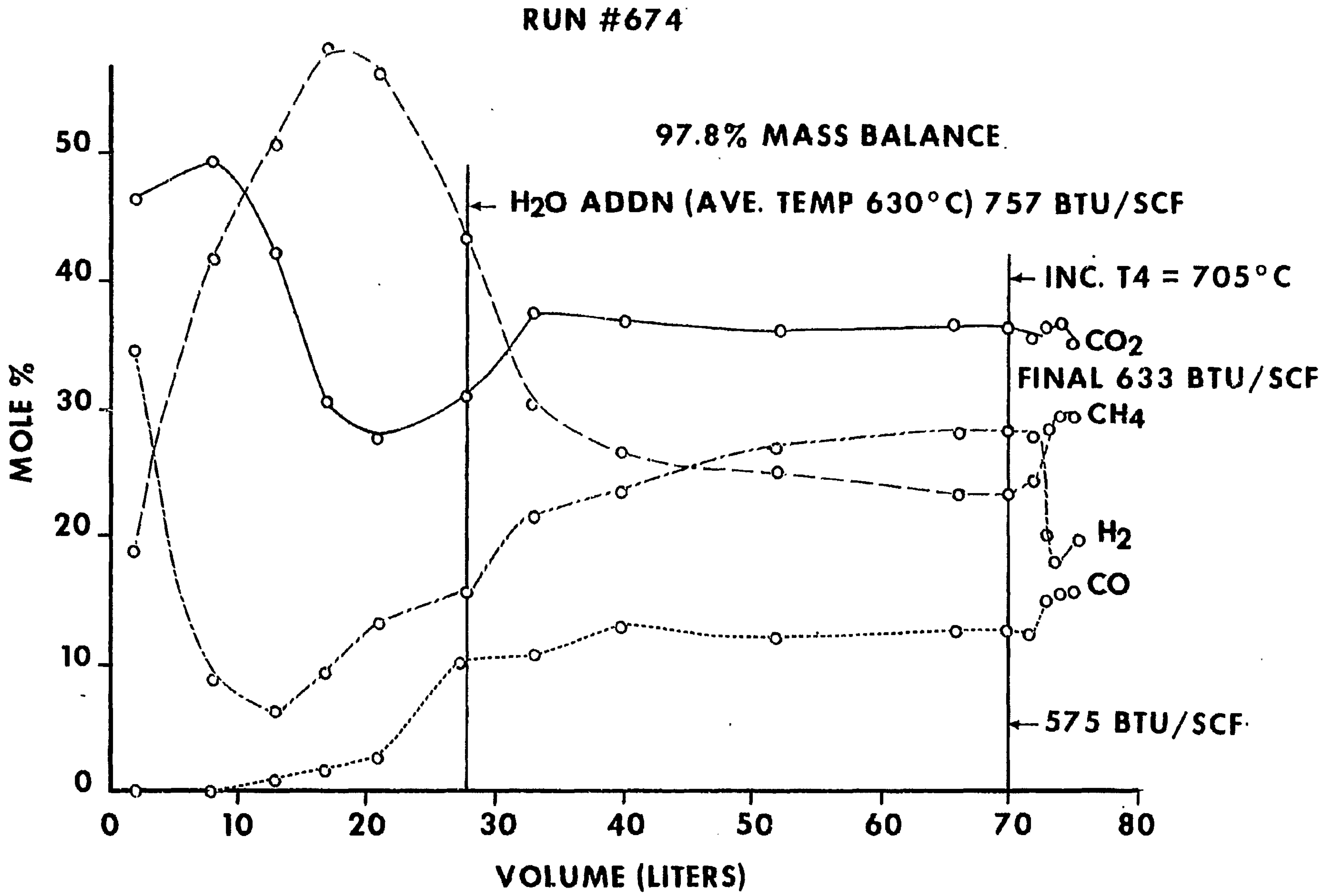
RUN #668

94.1% MASS BAL.

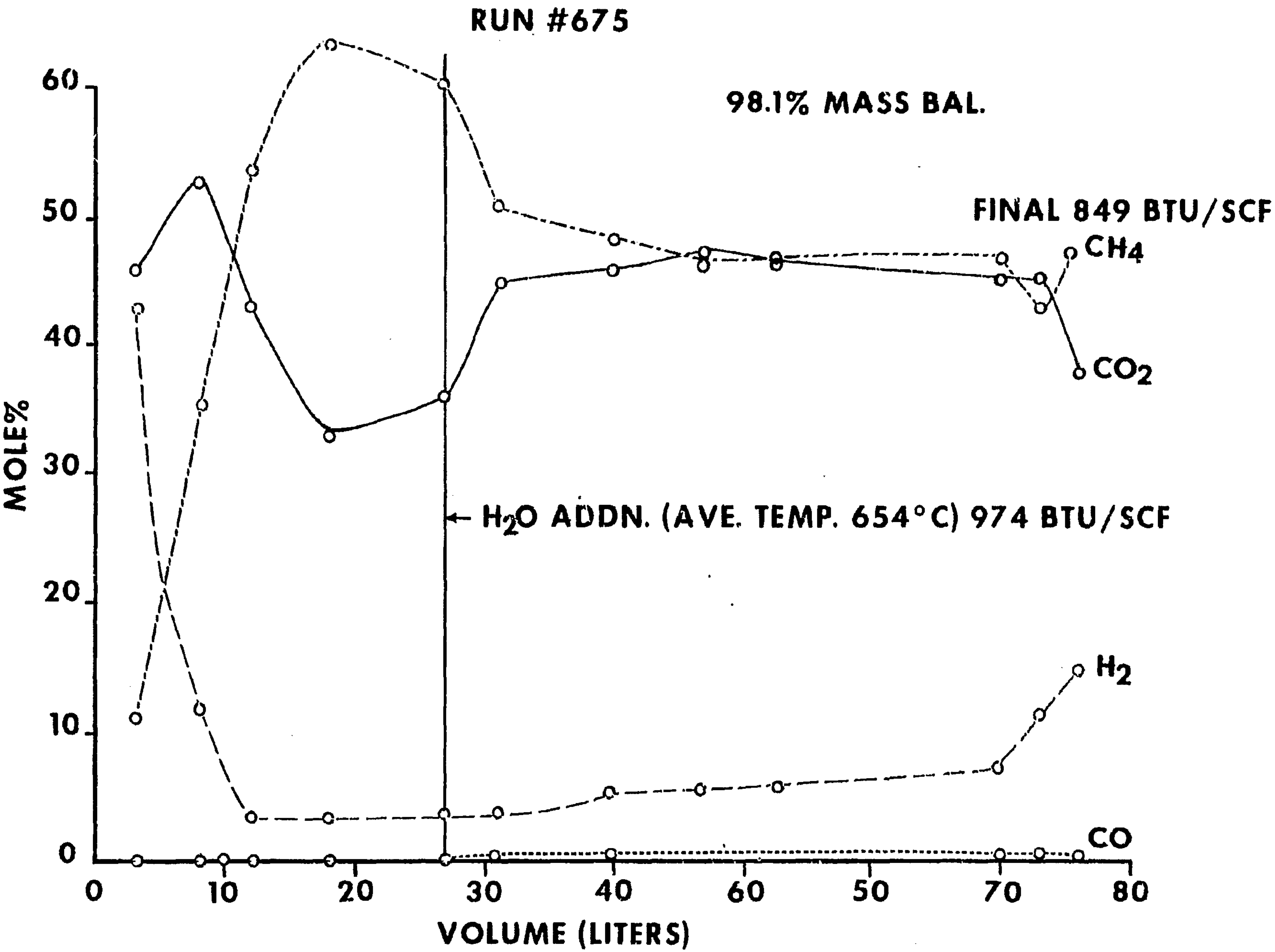


H_2O ADDN. (AVE. TEMP. 562° C) 974 BTU/SCF

FINAL: 470 BTU/SCF


RUN #674
97.8% MASS BALANCE
← H2O ADDN (AVE. TEMP 630°C) 757 BTU/SCF
← INC. T4 = 705°C
CO2
FINAL 633 BTU/SCF
CH4
H2
CO
← 575 BTU/SCF
MOLE %
0
10
20
30
40
50
0
10
20
30
40
50
60
70
80
VOLUME (LITERS)

Run 675 is displayed graphically on the next page. This run demonstrates the effect of added energy to the steam. Although there was a drop in activity of the catalyst towards methanation during the initial introduction of steam, the drop was not nearly as severe as in the previously illustrated runs and held quite constant (with one unexplained dip) after the initial decrease. The total mass recovery was excellent at over 98%. The volume rated average gas composition was 8.8% H_2, 0.3% CO, 48.3% CH_4 and 43.7% CO_2 for a heating value (CO_2-free) of 914 Btu/SCF.


RUN #675
98.1% MASS BAL.
FINAL 849 BTU/SCF
CH_4
CO_2
← H_2O ADDN. (AVE. TEMP. 654°C) 974 BTU/SCF
H_2
CO
MOLE%
60
50
40
30
20
10
0
0
10
20
30
40
60
50
70
80
VOLUME (LITERS)

Influence of Alkali on Coal Gasification

The Table on page 58 contains a summary of the runs selected to determine the optimum amount of potassium carbonate to be mixed with the coal and nickel catalyst. Observations obtained with the single-stage reactor indicate that the initial reaction involved is devolatilization of the coal, followed by cracking and hydrogenation of unsaturated compounds in the presence of the nickel catalyst. This is followed by the carbon-steam reaction.

The first run in the Table was made using only coal and steam, and in this run the gas contained about 0.5% ethylene, 0.7% ethane as well as 4 ml of heavy liquids. In all the remaining runs the nickel catalyst was present, and in no case was any hydrocarbon heavier than methane detected. Methane and carbon dioxide were the major components, with hydrogen averaging between 10-14% and the carbon monoxide usually below 2.0% in the product gas. In run No. 2 only the nickel catalyst was employed. It more than tripled the methane production, while it only increased the total gas product by about 20%. This tends to indicate that a substantial quantity of the methane produced is derived from cracking and hydrogenating unsaturated compounds.

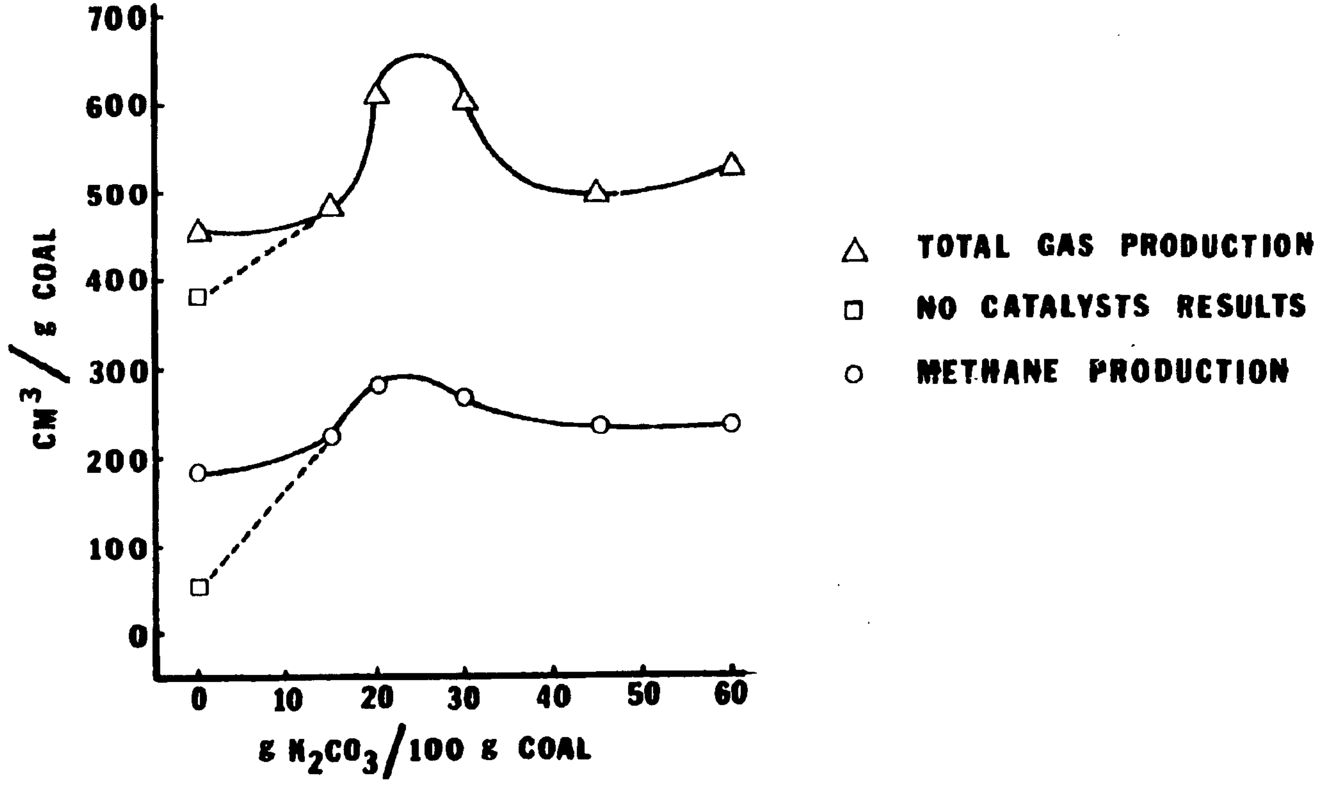
The Table also contains the analytical results for potassium recovery and carbonate recovery. The total potassium recovery by the ignition method was satisfactory, giving deviations of ±6%. Potassium recovered in the wash solution varied from about 66 to 90%. This shows that between 2.3-3.4g of potassium are forming compounds that are insoluble in water at ambient temperatures. It is of interest to note that the least amount of insoluble potassium was obtained when the optimum amount of potassium carbonate was used. The carbonate recovered from the ash was good, giving a deviation of only ±5%.

The Figure on page 59 shows a plot of total gas production, as well as the methane production versus mass of potassium carbonate charged per 100g of coal. In both cases the dashed line indicates the runs were neither alkali or nickel catalyst were present. These figures show that for the single-stage reactor, using a sub-bituminous coal at about 640°C, the optimum methane as well as gas production is obtained using between 20-25g of potassium carbonate per 100g of coal. Addition of more than 30g of potassium carbonate is detrimental to the methane production as well as total gas production. This decrease in production is readily apparent when the potassium carbonate has been increased to 45g.

Experimental Data for the Gasification Runs *

Run Number	1	2	3	4	5	6	7
K_2CO_3 (g)	0.	0.	15.	20.	30.	45.	60.
Ni-3210 (g)	0.	115.	111.	111.	111.	113.	114.
cm^3 CH_4/g Coal	51.	185.	225.	281.	266.	232.	234.
cm^3 Gas/g Coal	382.	453.	481.	612.	603.	493.	524.
Total Mass Recovery (wt %)	103.1	97.9	98.9	103.0	98.9	96.0	97.9
Total K Recovery (wt %)	—	—	94.2	105.7	105.9	95.0	98.7
K Recovery by Wash (wt %)	—	—	66.2	79.9	85.8	89.0	90.0
K Insoluble in Wash (g)	—	—	2.9	2.3	2.4	2.8	3.4
CO_3 Recovery (%)	—	—	97.7	101.2	104.1	101.8	104.8

*All runs were made at ~30 PSIA and an average temperature of ~650°C.



THE INFLUENCE OF VARYING AMOUNTS OF K_2CO_3 ON METHANE AND TOTAL GAS PRODUCTION

APPENDIX B

CATALYST STUDIES - HALF-INCH FLOW REACTOR

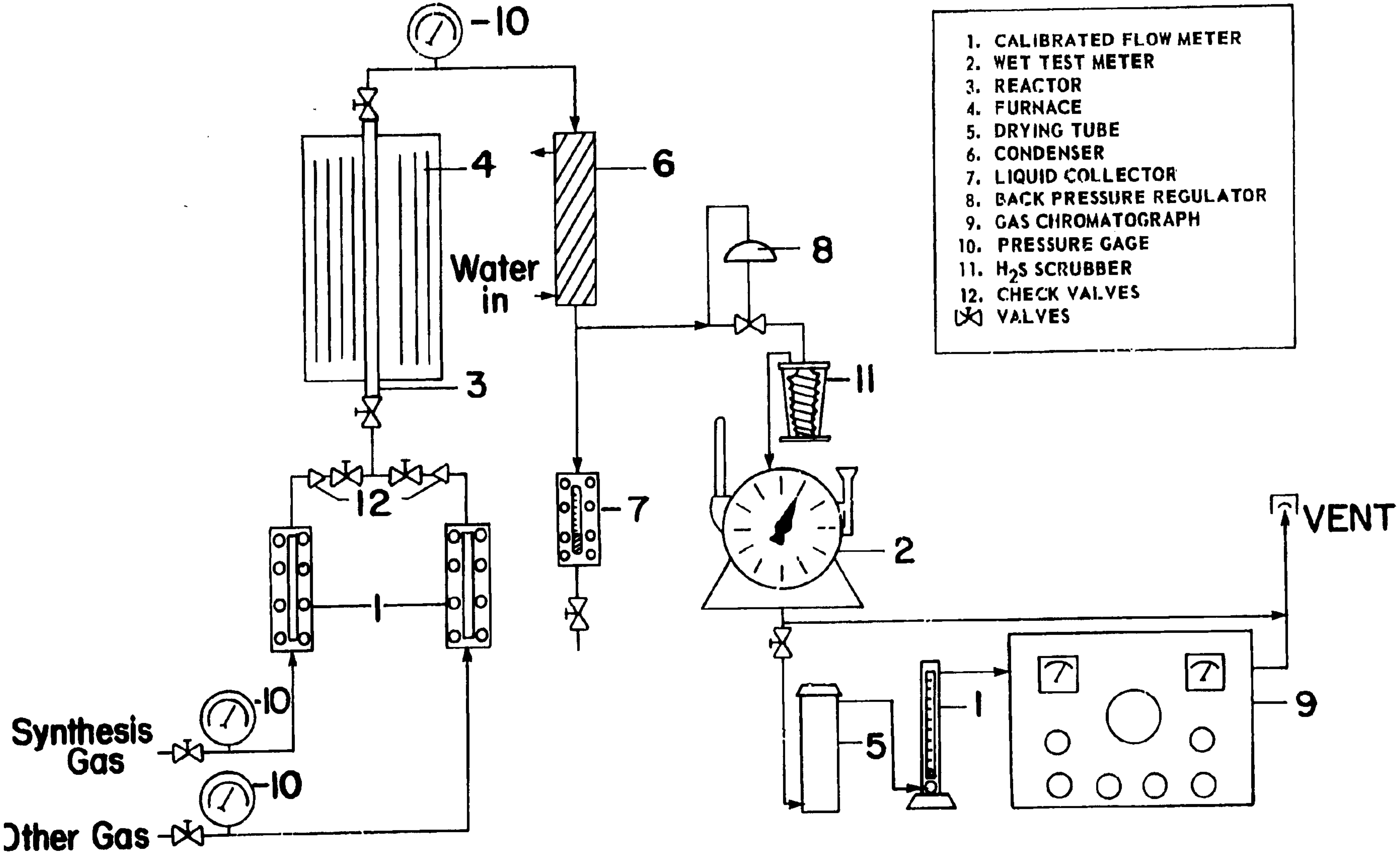


FIGURE 2. SCHEMATIC FLOW DIAGRAM 1/2" FLOW REACTOR

Appendix B. Catalyst Studies, $\frac{1}{2}$-inch Flow Reactor

Part I. Catalyst Formulations

Ferric Oxide Catalyst

Composition:
2000g Fe_2O_3
200g $K_2CO_3 \cdot 1\frac{1}{2}H_2O$
20g Acacia
5g Tragacanth

The materials were mixed dry, then made into a paste with water, extruded as $\frac{1}{4}$" lengths and finally dried overnight @ 500°C.

H_2 reduction at 600°C and 50 psig for 14 hrs. designated FeOKR-1.

Mill Scale Catalyst

Composed of 90 wt %, < 40 mesh, CF&I mill scale and 10 wt % $K_2CO_3 \cdot 1\frac{1}{2}H_2O$.

Ingredients were mixed and heated overnight @ 1500°C. Catalyst has been designated as MSK-2.

Mixed Fe-Ni Catalysts

The ingredients in the amount shown below were dry mixed, pasted with water, extruded and then heat treated @ 500°C for 12 hrs. Catalysts -1U, -2U and -3U were physically strong but -4U and -5U were weak and crumbled easily. However, heating these latter two catalysts to 1000°C made a considerable improvement in their crush strength.

Cat. design	wt % Fe_2O_3	wt % $NiCO_3$	wt % $K_2CO_3 \cdot 1\frac{1}{2}H_2O$	wt % Acacia	wt % Tragacanth
FeOKNi-1U	86	5	5	3	1
FeOKNi-2U	81	10	5	3	1
FeOKNi-3U	71	20	5	3	1
FeOKNi-4U	61	30	5	3	1
FeOKNi-5U	51	40	5	3	1

Nickel - Alumina Catalyst

The catalyst which contained 14 wt % Ni, was prepared by adding 75g $Ni(NO_3)_2 \cdot H_2O$ in 300 ml H_2O to a slurry prepared by adding 50g NaOH/250 ml H_2O. The catalyst was collected by filtration, dried for 16 hours at 105°C and finally reduced in H_2 for 16 hours at 350°C.

Metal Impregnated Molecular Sieves

Conditions were examined for obtaining high concentrations of transition metal ions in spherical molecular sieves. Solution impregnation was the approach used. Of the transition elements Cr, Fe, Ni and Co, the latter two were found to give the best results. Catalysts designated as 544MS-Ni and 655MS Co were prepared which contained about 12 wt % and 5 wt % of the metal on a dry basis, respectively.

Commercial Catalyst

Several commercial catalysts or materials used directly as catalysts were employed with the catalyst test unit. These include Harshaw's Ni-3210, Ni-0104, Co-0101 and Co-0401 Girdler's G-47, G-61RS and T-1845, Davison Chemical's molecular sieves and DMS-Ni and steel wool and mill scale from CF&I. Further information concerning the composition of these catalysts has been presented in conjunction with the results from the 1-inch integrated batch charge reactor.

Appendix B. Catalyst Studies, 1/2-inch Flow Reactor

Part II. Synthesis Gas Compositions

Although the initial observations concerning catalyzed carbon deposition were qualitative in nature, they nevertheless serve to emphasize the seriousness of the problem. Catalyst test run #1, with $2H_2/CO$ and FeOKNi-1U and reaction conditions of 70 psig and 500°C, began to experience plugging about one hour after initiating the run. Shortly thereafter a 250 psig pressure drop across the catalyst bed with zero flow was noted. In runs #2 and #3, under similar conditions and the same synthesis gas with Ni-3210 catalyst, it was about 1-1/2 hours before reactor plugging was observed. The carbon content in the catalysts upon completion of runs #2 and #3 was found to be 48.0 wt % and 39.7 wt %, respectively. Employing the $2H_2/CO$ synthesis gas, reactor plugging was observed for every catalyst employed including Ni-0104, G-61RS, Co-0101, T-1845, steel wool, mill scale (CF&I) 544 molecular sieves and 544 MS-Ni. Even thermally induced carbon monoxide decomposition, although at a much slower rate, was observed in run #11 where an empty reactor was employed.

The carbon deposition of synthesis gas composed of $4H_2/CO_2$ was in sharp contrast to that of $2H_2/CO$. Thus, using 544 MS-Ni catalyst at 100 psig and 1020°F (run #17-6) the reactor plugged in about one hour with the $2H_2/CO$ mixture. At the same operating conditions with a fresh batch of the same catalyst and $4H_2/CO_2$ (runs #18-1, -2, -3) the reactor was run for twenty-five hours with no evidence of plugging.

Carbon deposition accompanying catalytic methanation with $3H_2/CO$ was observed to be between that for $4H_2/CO_2$ and $2H_2/CO$. Although no pressure drop across the reactor was observed in run #50, which covered a 17-1/2 hour period of time using 29.3% CO and 70.7% H_2, there was noticeable carbon deposit removed from the reactor.

Catalytic methanation with sulfided Ni-3210 was attempted in run #4 using $2H_2/CO$. The objective of the catalyst sulfidation was to inhibit carbon formation which readily occurs with $2H_2/CO$ synthesis gas. The catalyst was sulfided by soaking in 500 ml of an aqueous solution containing 50g Na_2S. A couple of days running without plugging at atmospheric pressure and temperatures of 500-900 was followed by a day at pressures of 100 psig and temperatures of 1050-1150°F. Still no plugging was observed. However, upon disassembling the reactor the catalyst was observed to have undergone considerable breakup and indicated some carbon formation. At both the low and high pressures the methanation activity of the catalyst was low, producing a product which contained about 0.5% CH_4 in the former and 2% CH_4 in the latter case. In contrast to the low pressure runs (#4-1, -2, -3) the high pressure run (#4-4) evolved a detectable amount of H_2S in the product gas. It also appeared that the methanation activity of the catalyst was showing a slight improvement with run time.

Another approach to the prevention of carbon deposition while using synthesis gas of $2H_2/CO$ involved the addition of steam. This approach was based upon the prediction that the use of steam would promote the following two reactions and consequently decrease the rate of carbon formation. In runs #13 and #14 this was the case. When considerable carbon deposition had

$$CO + H_2O = H_2 + CO_2$$

$$C + H_2O = H_2 + CO$$

occurred as evidenced from the increase in the pressure drop across the reactor steam was added to the system. The pressure drop across the reactor decreased and the runs were continued without need for termination because of plugging. Although the steam benefitted the carbon removal it was detrimental to methanation. As water was added along with the synthesis gas a decrease in methane production and an increase of hydrogen and carbon dioxide was observed. Upon returning the synthesis to its normal mode of operation (absence of externally added steam) the methanation activity increased to near its original level.

Yet an alternate approach to alleviating carbon deposition during catalytic methanation over a nickel catalyst with $2H_2/CO$ employed H_2S-N_2 mixture (5.15 mole % H_2S) which was added with the synthesis gas in runs #22 and #23. As in the other approaches the rate of carbon deposition was drastically reduced, but there was also an accompanying reduction in catalytic methanation. The methane production decreased from about 35% to less than 5% by introducing the sulfur gas at high space velocities. At lower space velocities the decrease in methanation was not so drastic.

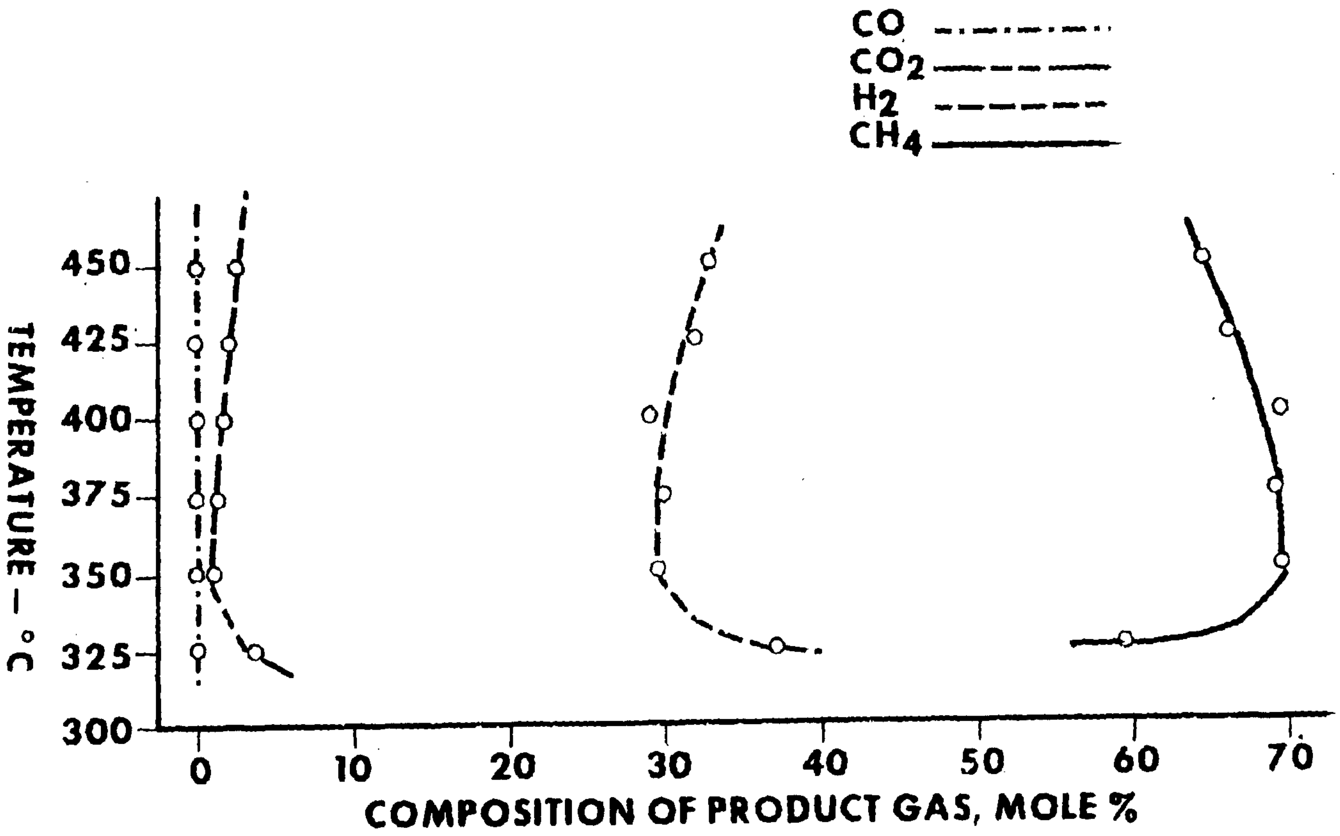
Appendix B. Catalyst Studies, 1/2-inch Flow Reactor

Part III. Methanating Variables

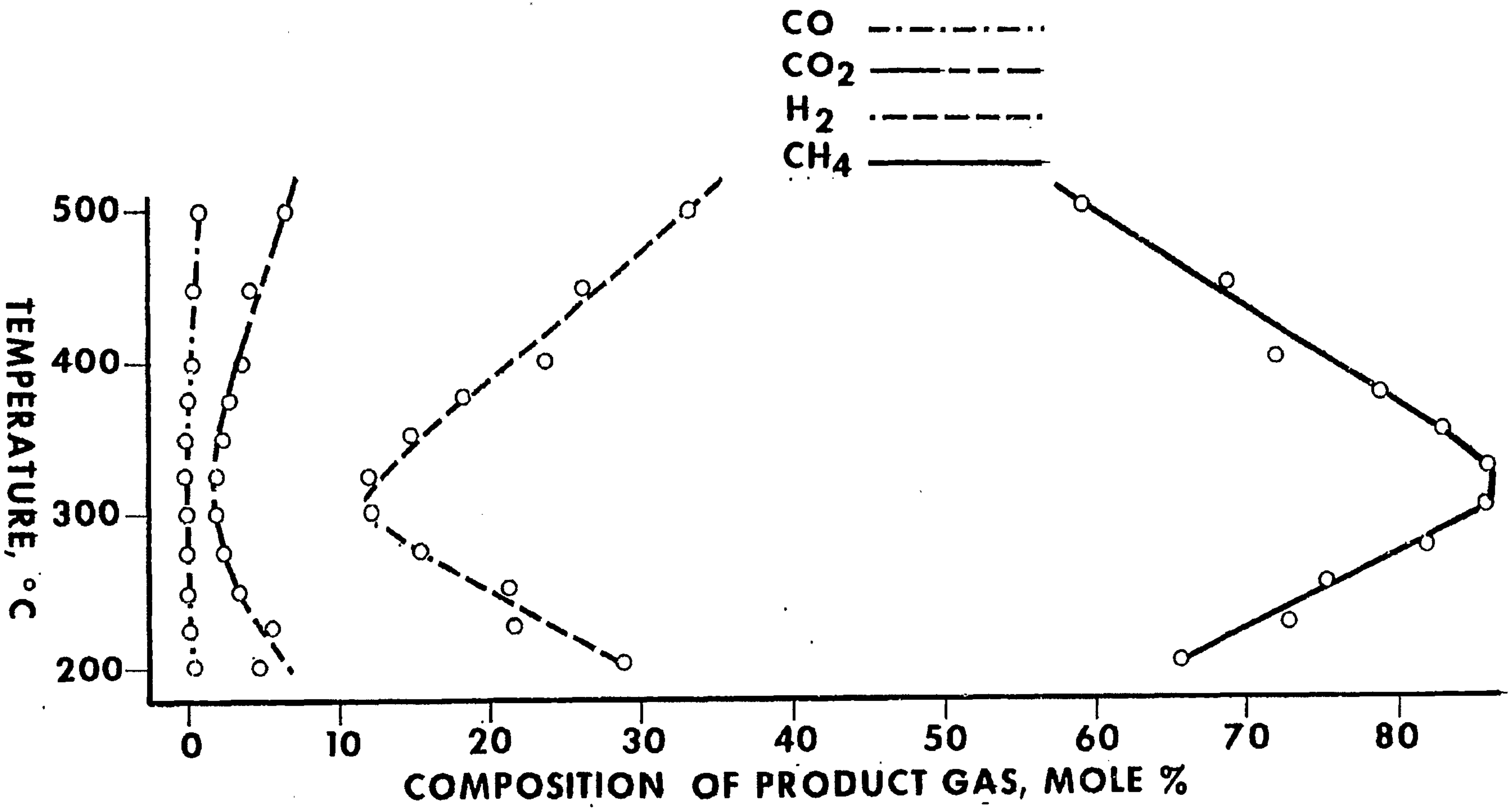
In the following table are contained catalytic methanation results with different synthesis gas compositions under similar synthesis conditions.

Run No.	17-5B	38-1E	19-2A
Catalyst	544MS-Ni	544MS-Ni	544MS-Ni
Syn. Gas Comp.	$\sim 2H_2/CO$	$\sim 3H_2/CO$	$\sim 4H_2/CO_2$
Avg. Reactor Temp.	450°C	500°C	500°C
Reactor Press, (psia)	112	107	112
Comp. Gas Product (mole %)*			
H_2	5.3	32.9	25.3
CO	11.7	0.9	3.7
C_1	37.6	59.8	43.0
CO_2	45.4	6.4	28.1

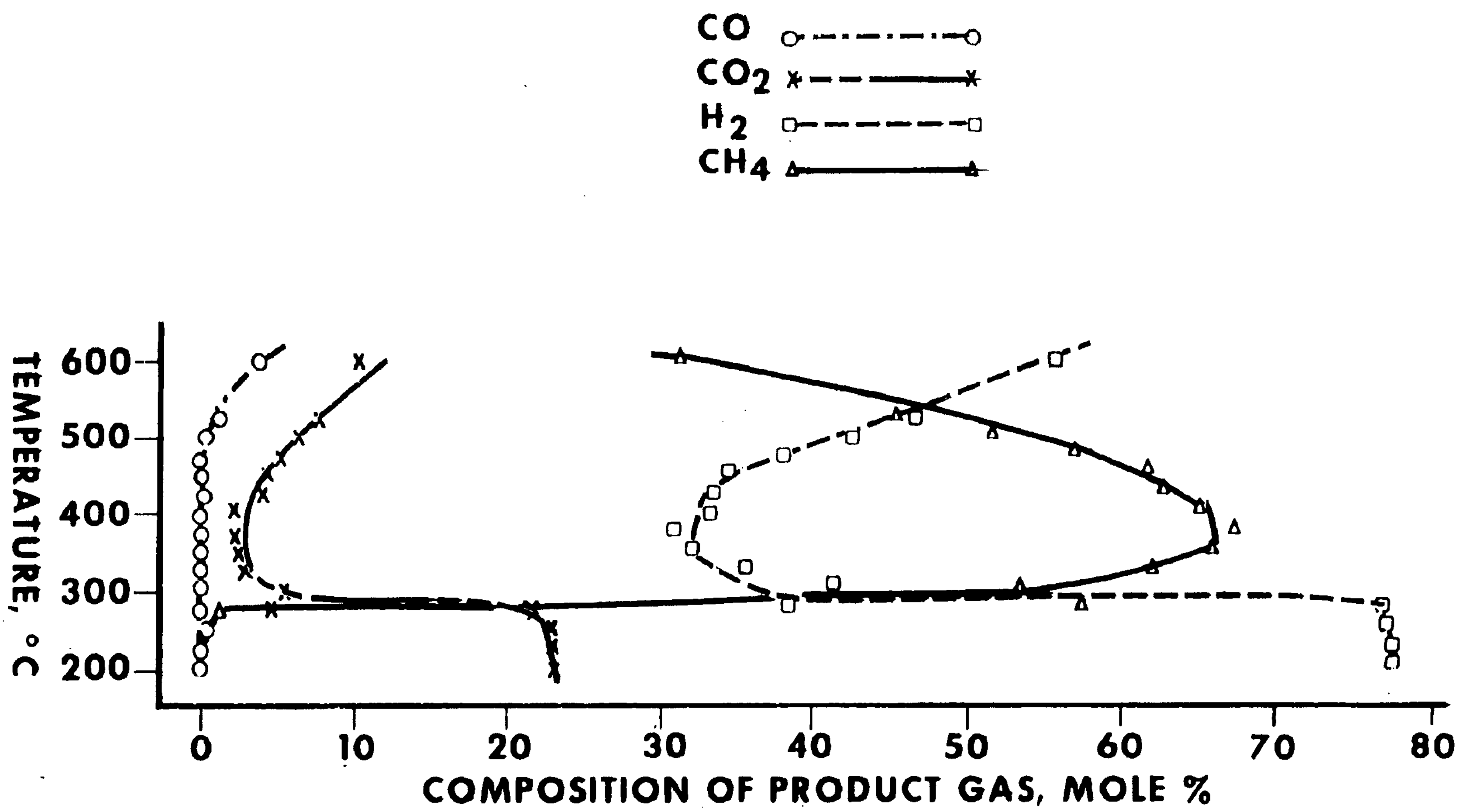
*H_2O-free basis.



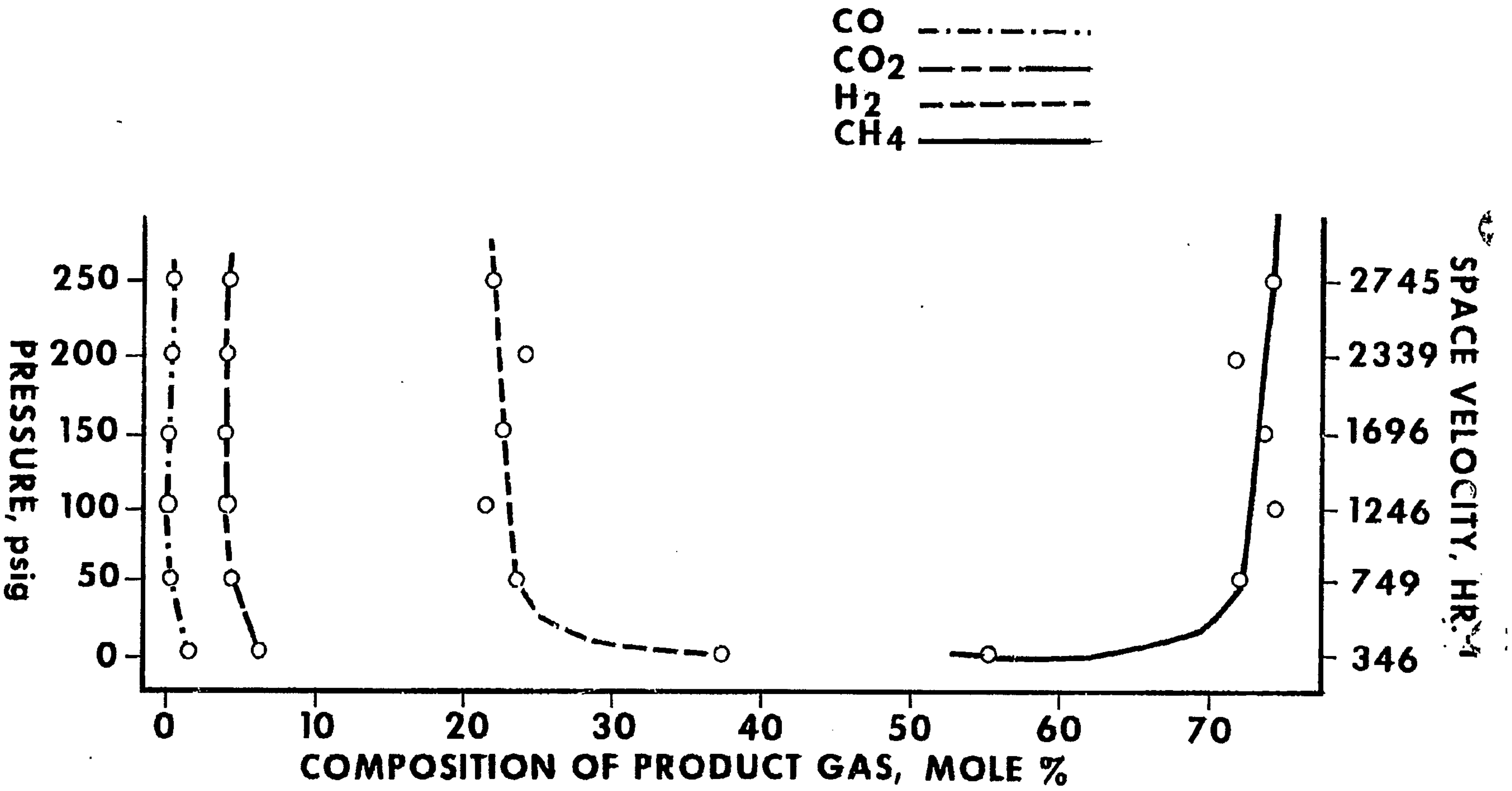
Temperature Dependence of Methanability of $4H_2:1CO_2$ Synthesis Gas Over Ni-3210 Catalyst. Runs #31-1 @ 100 psig and 1395 $hr.^{-1}$ Space Velocity.



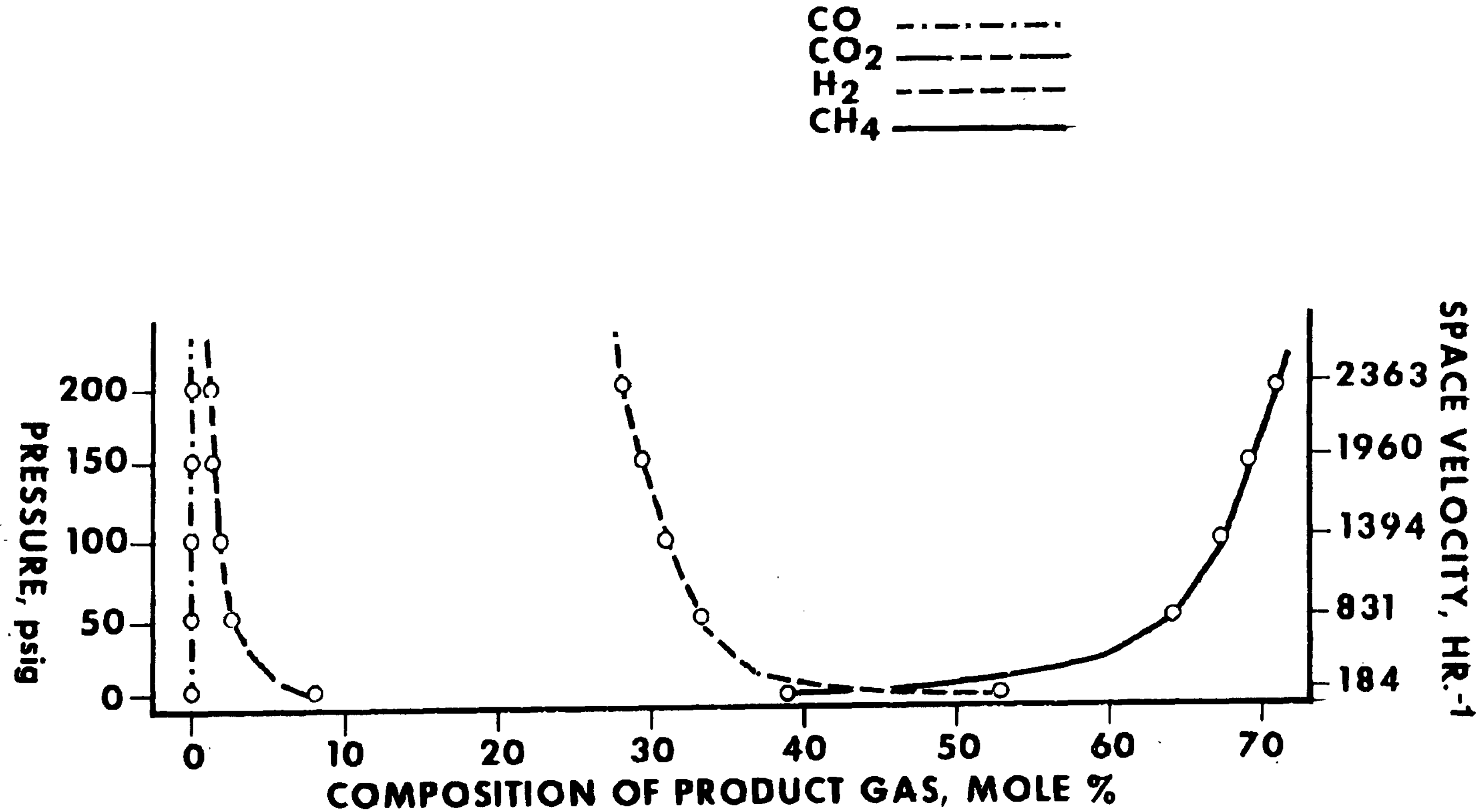
Temperature Dependence of Methanability of $3H_2$:1CO Synthesis Gas Over Ni-3210 Catalyst. Runs #34-1, -2 @ 100 psig and 1235 $hr.^{-1}$ Space Velocity.



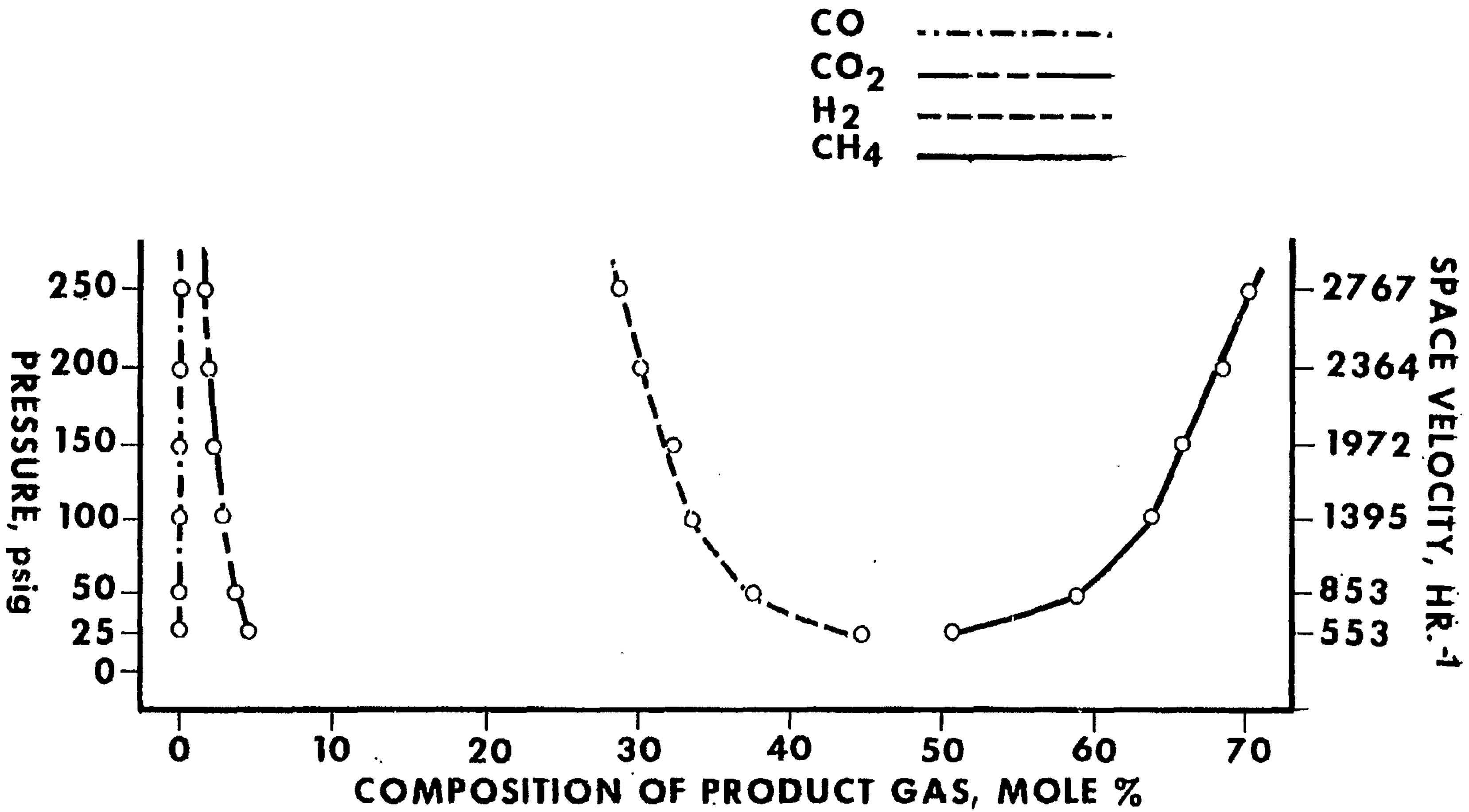
Temperature Dependence of Methanability of 4H$_2$:CO$_2$ Synthesis Gas Over DMS-Ni Catalyst. Runs #33-1, -2 @ 100 psig and 1395 hr.$^{-1}$ Space Velocity.



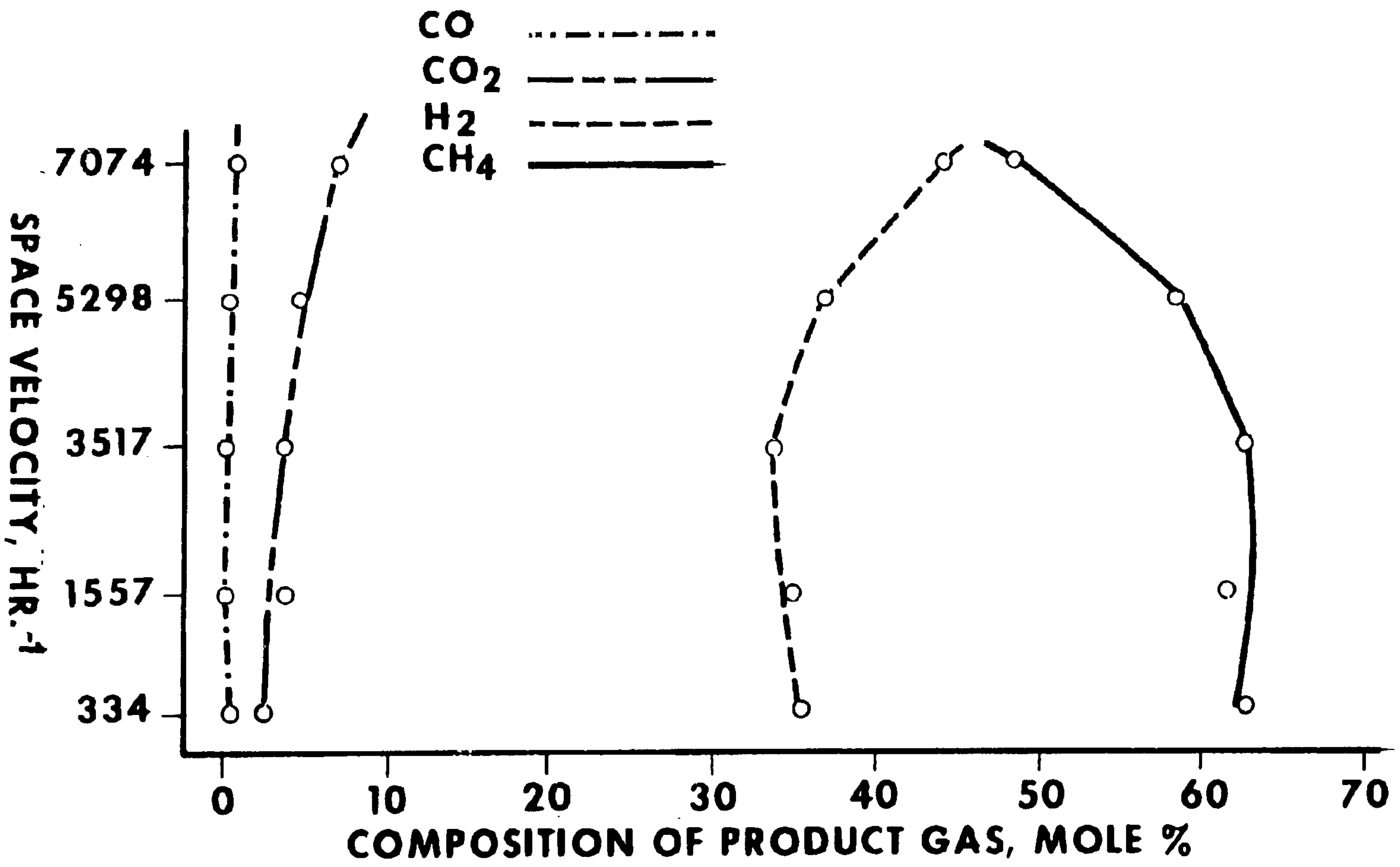
Pressure Dependence of Methanability of $3H_2$:1CO Synthesis Gas Over Ni-3210 Catalyst. Runs #34-3 @ 325°C.



Pressure Dependence of Methanability of $4H_2:1CO_2$ Synthesis Gas Over Ni-3210 Catalyst. Runs #31-2 @ 350°C.



Pressure Dependence of Methanability of $4H_2$:$1CO_2$ Synthesis Gas Over DMS-Ni Catalyst. Runs #33-3 @ 375°C.



Space Velocity Dependence of Methanability of $4H_2:1CO_2$ Synthesis Gas Over DMS-Ni Catalyst. Runs #33-4 @ 375°C and 100 psig.

The following table contains catalytic methanation data illustrating the influence of space velocity and temperature. The catalyst was Ni-3210 and the synthesis gas was composed of 26.2% CO and 73.8% H_2. Synthesis pressure was 0 psig.

Cat. Temp. °C	Space Vel. $hr.^{-1}$	%CO Conv.	Product Gas Comp. (mole %) H_2	CO	CH_4	CO_2
449	9000	95.4	34.0	1.2	56.2	8.7
528	9000	77.1	53.0	6.0	31.9	9.1
610	9000	42.4	65.6	15.1	14.1	5.2
185	10200	89.3	87.6	2.8	9.6	0.0
327	10200	100.0	12.2	0.0	87.6	0.1
459	10200	96.6	38.0	0.9	53.2	8.0
534	10200	77.9	55.5	5.8	30.1	8.6
615	10200	41.2	65.6	15.4	13.9	5.2
373	14200	100	22.3	0.0	77.3	0.4
403	14200	100	17.6	0.0	82.0	0.3
436	14200	100	23.3	0.0	76.2	0.5
498	14200	99.6	43.7	0.1	55.3	0.9
562	14200	77.1	53.8	6.0	31.4	8.8
630	14200	39.1	65.2	15.8	13.5	5.4

Appendix B. Catalyst Studies, 1/2-inch Flow Reactor

Part IV. Catalyst Poisoning and Regeneration Studies

The following graphs and data are included for the purpose of demonstrating catalyst poisoning by hydrogen sulfide. This coupled with thermodynamic data indicates the severity of the catalyst poisoning by sulfur gases in methanation units.

The graphical display of the Ni-H_2S equilibrium was obtained by extrapolating Kirkpatric's data. The graphical interpretation is that if at any given temperature you exceed the equilibrium H_2S/H_2 value then nickel sulfide will be formed until the H_2S/H_2 value is reestablished in the system or all of the nickel has been converted to nickel sulfide.

Some results of both low and high temperature sulfur poisoning experiments are shown in the following figures. The results indicate that sulfur poisoning is more serious for low than high temperature catalytic methanation.

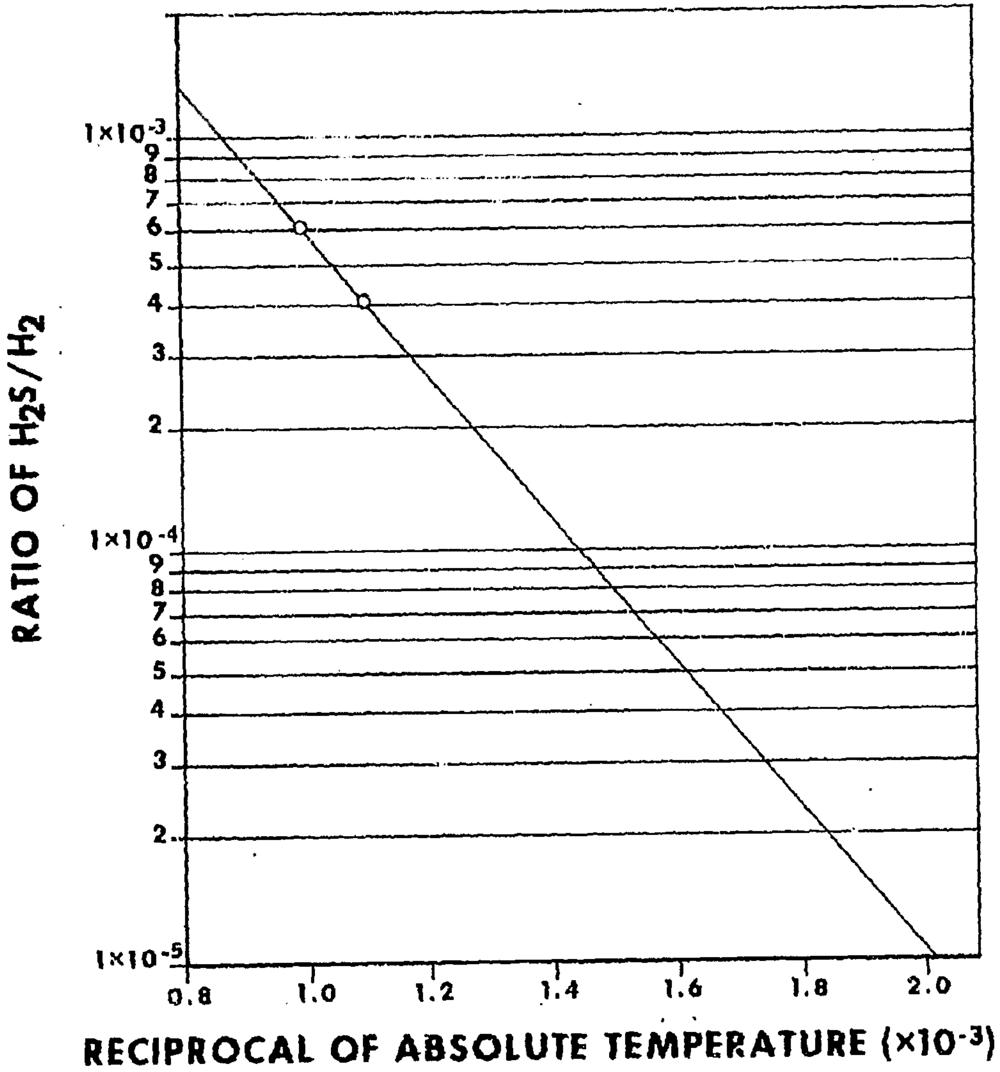
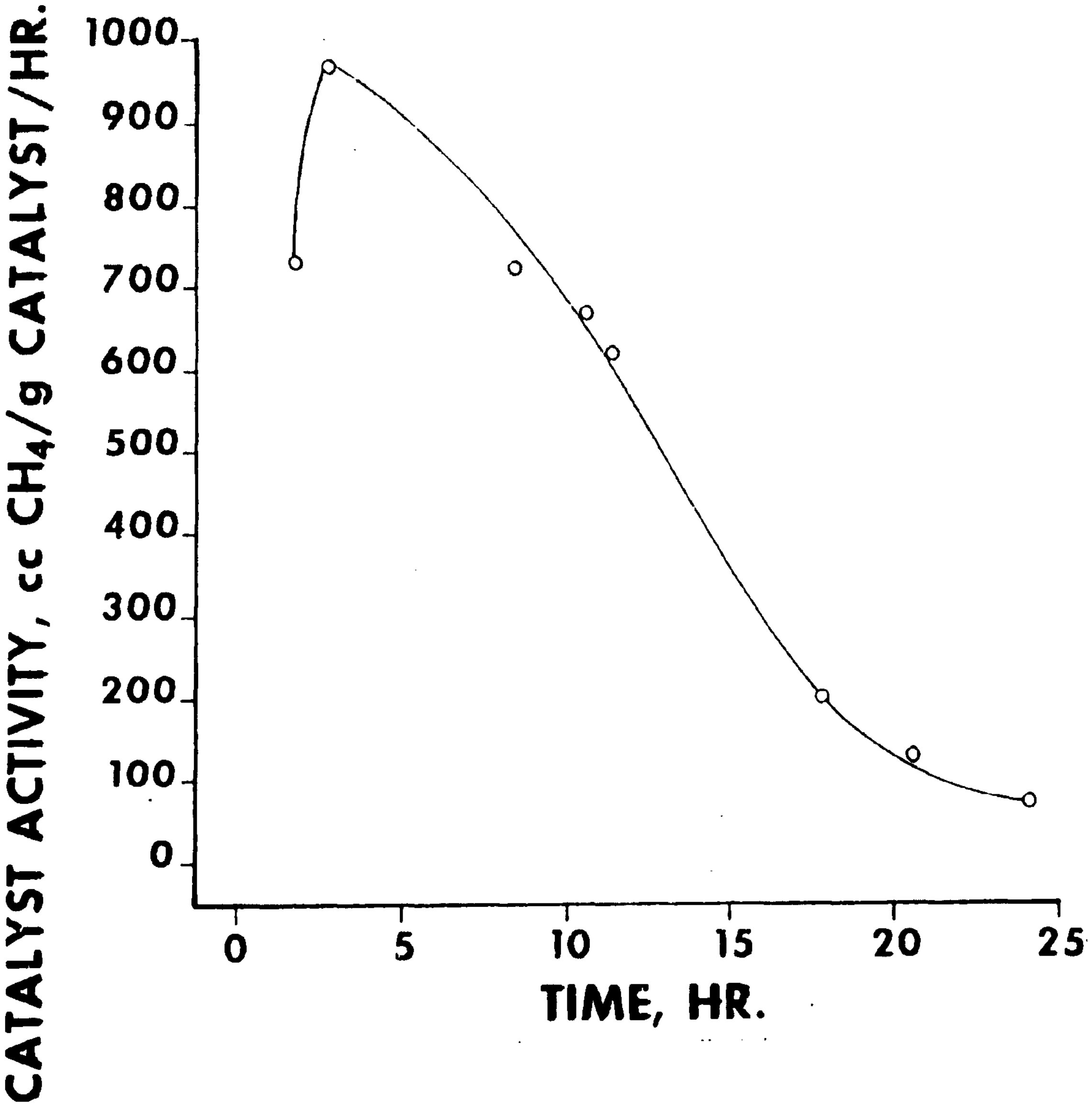
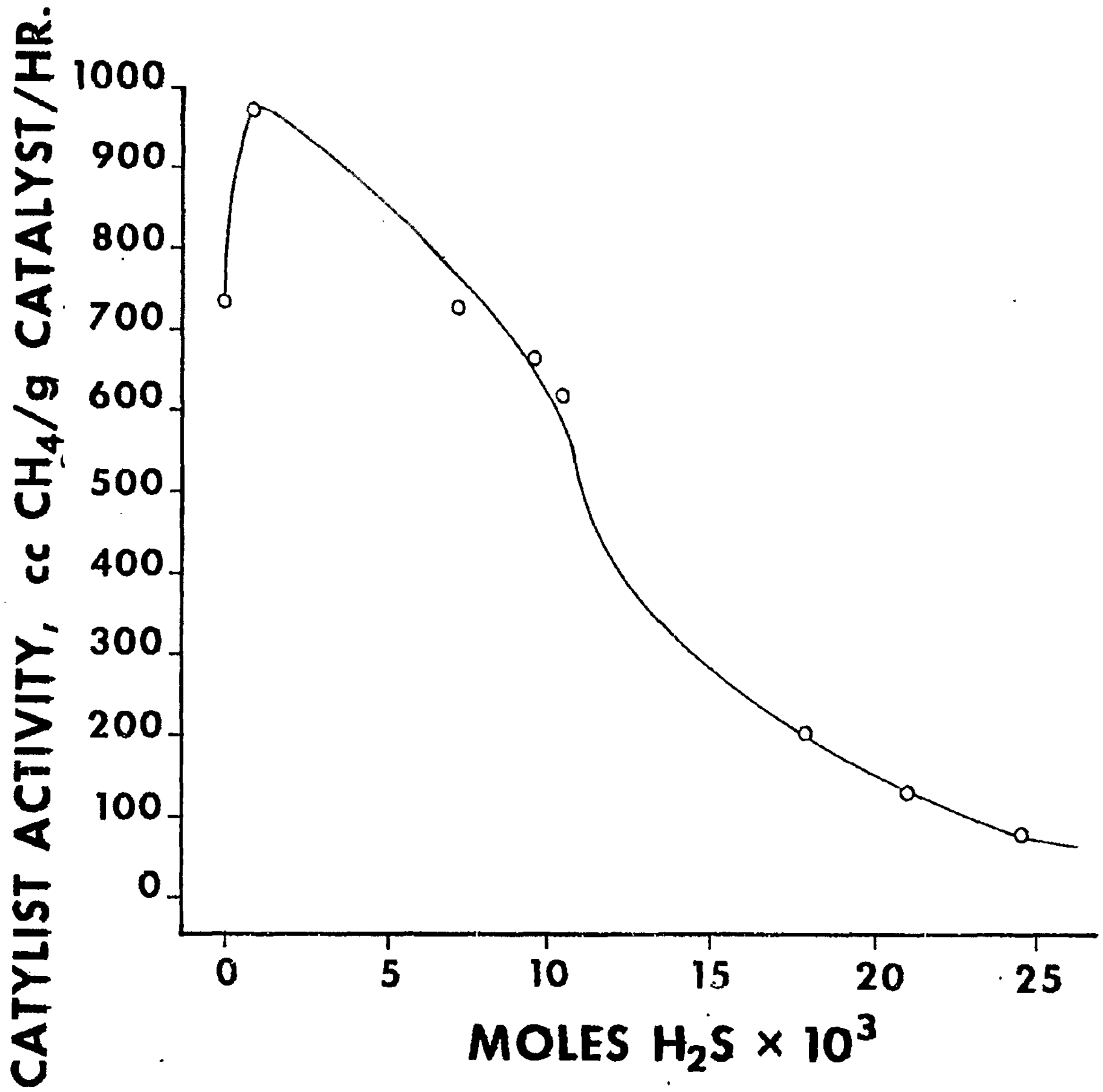


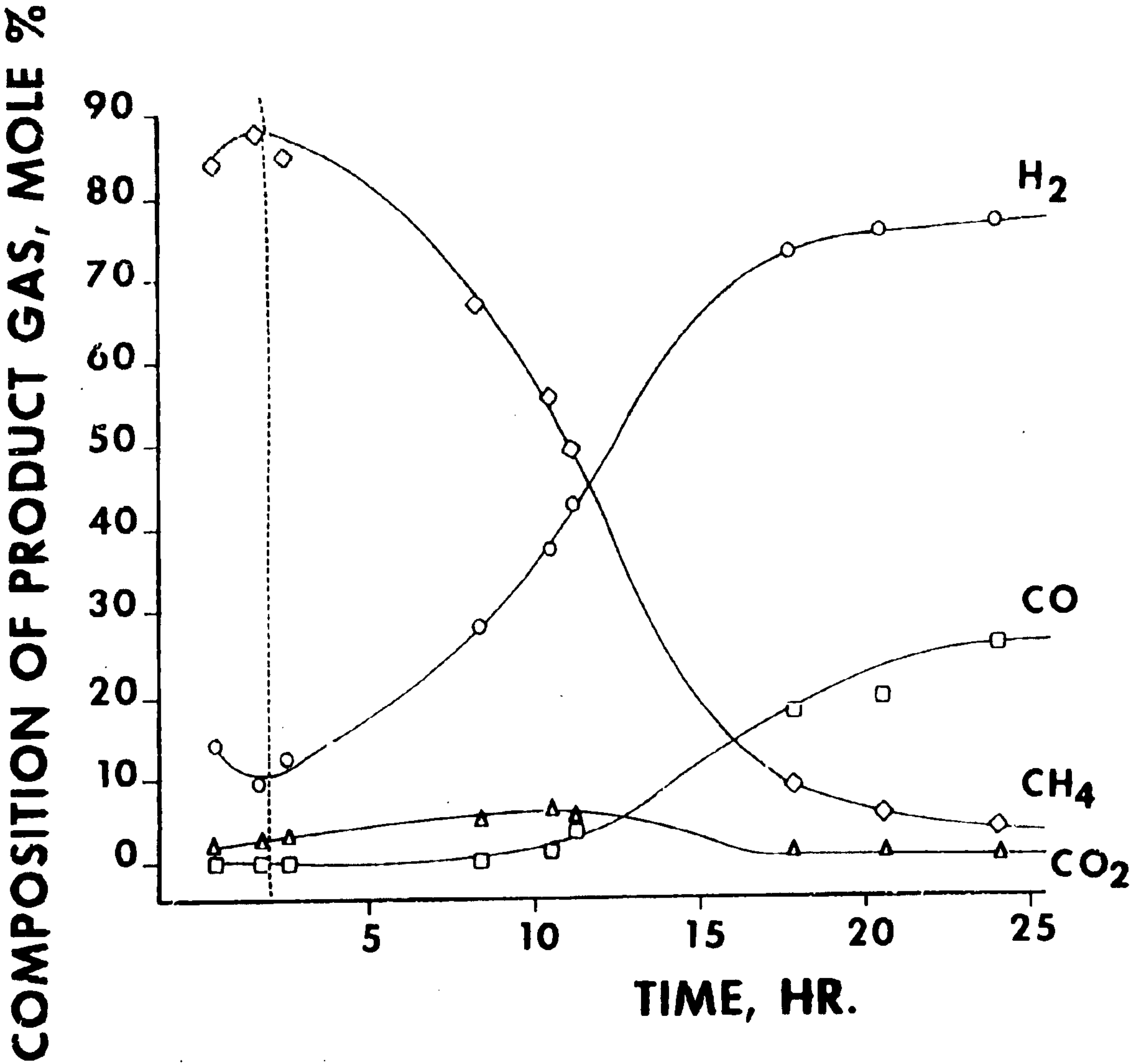
FIGURE 3 THE Ni-H_2S EQUILIBRIUM. $1/2\ Ni_3S_2 + H_2 = 3/2\ Ni + H_2S$



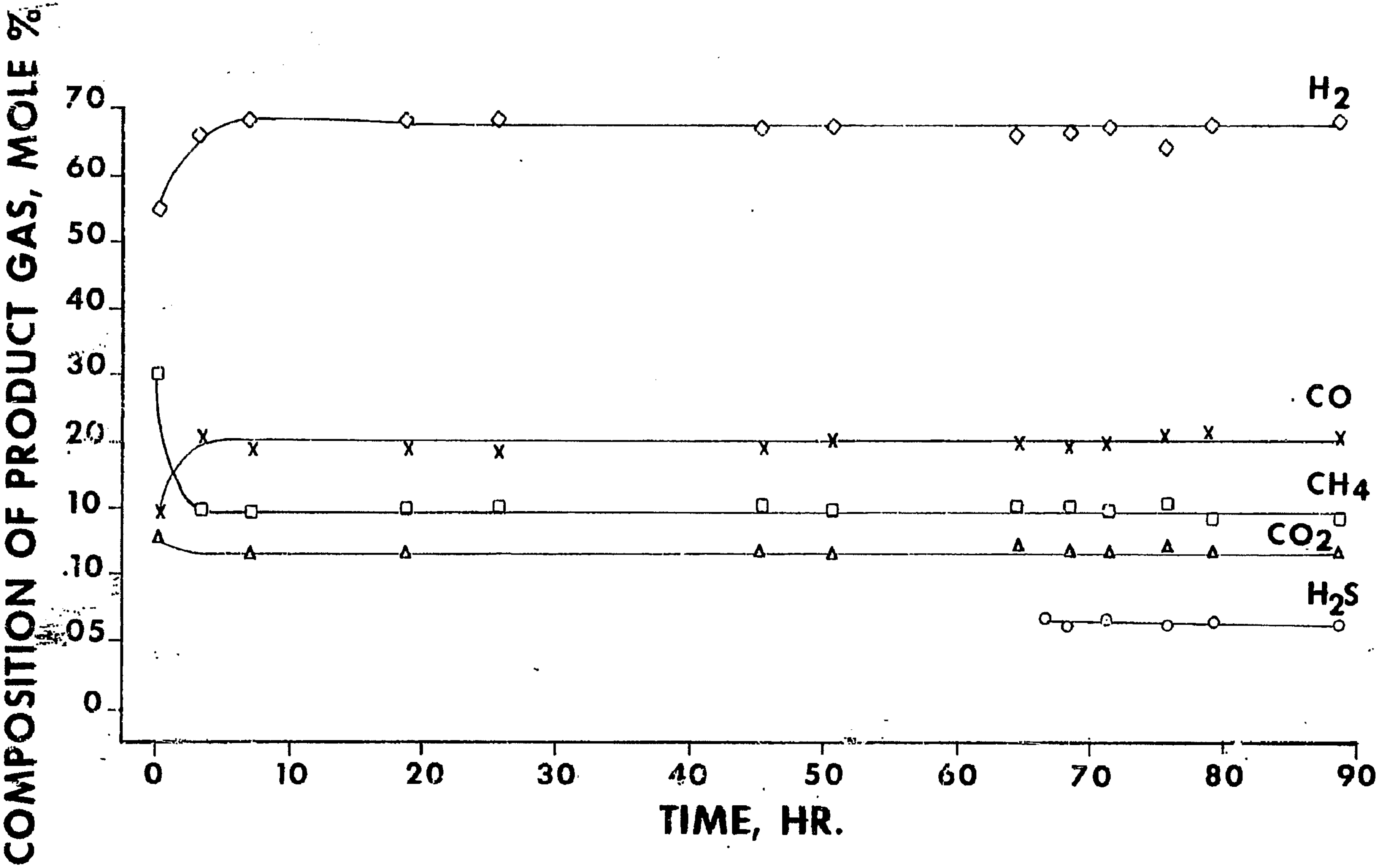
Catalyst Poisoning Experiment with Ni-3210 Catalyst
0.06% H_2S, 4.3% He, 77% H_2 and 19% CO @ 325°C.



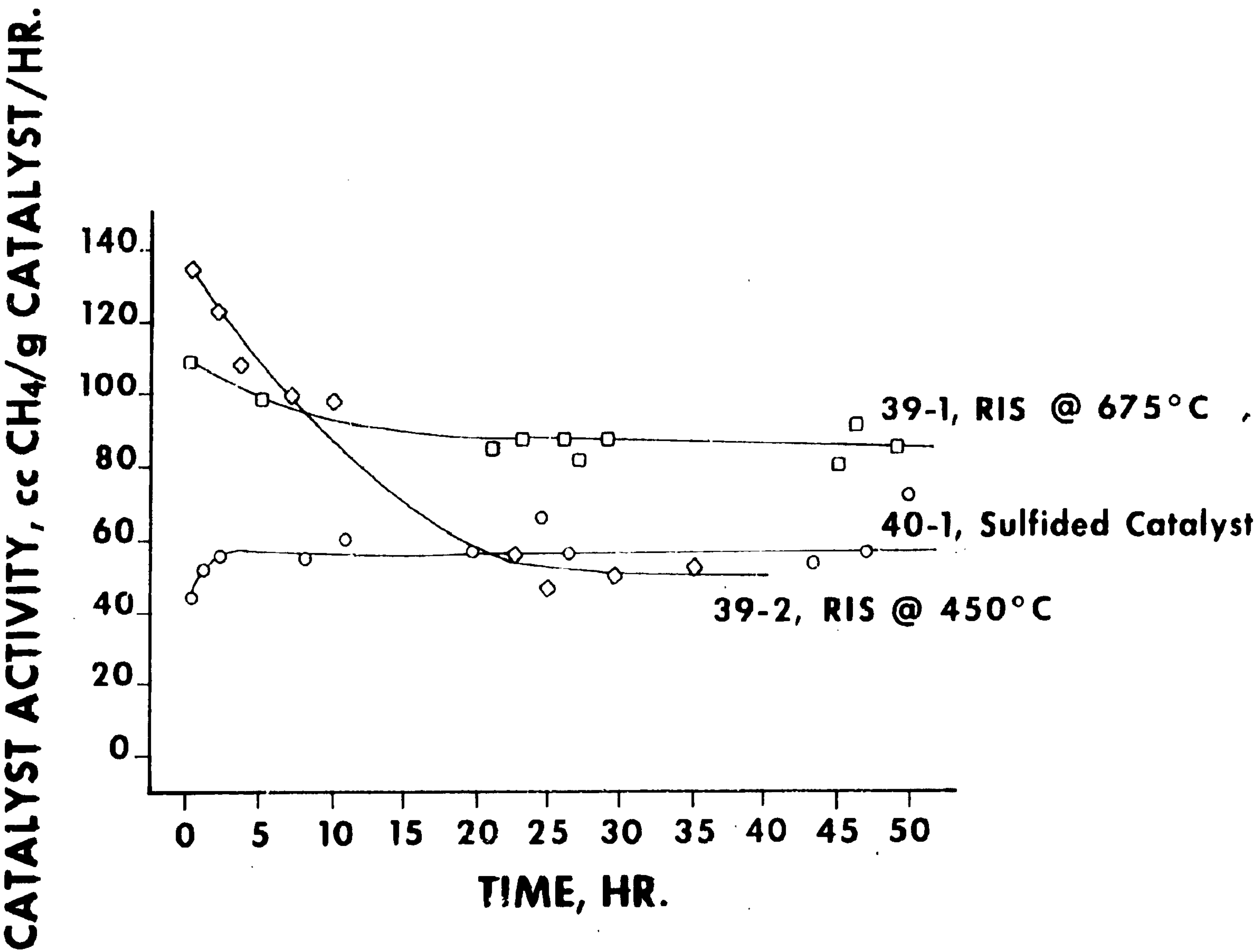
Poisoning of Ni–3210 Catalyst with Cummulative Addition of H_2S.
0.06% H_2S, 4.3% He, 77% H_2 and 19% CO @ 325°C



Catalyst Poisoning Experiment with Ni-3210 Catalyst
0.06% H_2S, 4.3% He, 77% H_2 and 19% CO @ 325°C.



Catalyst Poisoning Experiment with Split Catalyst Bed of Sulfided Catalyst (Ni-3210) and G-65RS. Run #42-1 $3H_2/1CO$, 25 psig and 750 hr^{-1} space velocity.



Comparative Catalyst Activity. $3H_2/1CO$ Synthesis Gas @ 675°C.

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