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LABORATORY SCALE INVESTIGATION OF CATALYTIC CONVERSION OF SYNTHESIS GAS TO METHANE

BY H. W. WAINWRIGHT, G. C. EGLESON, AND C. M. BROCK

United States Department of the Interior — April 1954

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UNITED STATES DEPARTMENT OF THE INTERIOR
Douglas McKay, Secretary
BUREAU OF MINES
J. J. Forbes, Director

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H. W. Wainwright,^{1/} G. C. Egleson,^{2/} and C. M. Brock^{3/}

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SUMMARY AND CONCLUSIONS

1. A schematic diagram and a description of the apparatus are presented.
2. Five runs were made using gas having a hydrogen-carbon monoxide ratio of about 2:1 and sulfur concentrations ranging from nil to 1.53 grains per 100 std. c.f.
3. At constant space velocity of synthesis gas the product of the sulfur concentration and days of operation, with conversion of $H_2 + CO$ above 97 percent, was constant. With a gas containing 0.04 grain of sulfur as carbonyl sulfide per 100 std. cu.ft., the conversion of $H_2 + CO$ remained over 97 percent for 40 days. During that time the heating value of the product gas (on a CO_2 -free basis) remained relatively constant at 940 B.t.u. per c.f., based on dry gas measured at $60^\circ F.$ and 30 inches Hg.
4. In all runs in which sulfur was present in the gas, catalytic activity decreased as soon as approximately 0.58 gram of sulfur had been absorbed per 100 grams of nickel.
5. An attempt was made to regenerate the spent catalyst from one run by burning off the sulfur with air at $900^\circ C.$ The catalyst, when again placed in operation, gave an initial conversion of $H_2 + CO$ of 91.8 percent.

INTRODUCTION

Until recently there has been marked lack of interest in using the synthesis of methane for the production of domestic and commercial pipeline gas. This lack undoubtedly existed because of the apparently large reserves of natural gas in the gas fields of the Southwest. Because of this indifference relatively few studies have been made in this country of catalysts whose prime function is the formation of methane from synthesis gas. The use of sulfur-resistant molybdenum catalysts for the methanation of carbon monoxide at atmospheric pressure has been investigated by J. J. S. Sebastian^{4/5/}. However, some producers and distributors of natural gas believe that eventually it will be necessary to augment deliveries of natural gas in the northern markets of this country by developing a more or less comparable synthetic gas from coal.^{6/}

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- 4/ Sebastian, J. J. S., Study of Catalysts for the Hydrogenation of Carbon Monoxide: D. Sc. thesis, Carnegie Inst. Technol., May 1935, 71 pp.
 - 5/ Sebastian, J. J. S., The Catalytic Reduction of Carbon Monoxide to Methane at Atmospheric Pressure: Coal Res. Lab. Contrib. 35, Carnegie Inst. Technol., March 1936, 8 pp.
 - 6/ Breck, C. R., The Timing of an Initial "Pipeline Gas from Coal" Enterprise; Paper pres. at annual meeting of Am. Inst. Min. and Met. Eng., New York, February 1952:

In England, increased cost and shortage of oil for enrichment of manufactured gas have forced the industry to study methanation for enrichment as a substitute for oil. Much research work on catalysts for the synthesis of methane has been done by the Gas Research Board.^{7/}

In this country, the Southern Natural Gas Co. has been actively engaged in a program of investigating the practicability and cost of producing pipeline gas from coal. In 1944 a cooperative agreement was arranged with the Bureau of Mines for performing experimental work at the Pittsburgh Station on the production of synthesis gas from coal, using the German Lurgi Process.^{8/} After the completion of this experimental program in 1950, the cooperative agreement was extended to cover pilot plant studies at the Bureau's Morgantown Station on the purification of synthesis gas. Included in this purification program was the investigation of processes for removing organic sulfur compounds, hydrogen sulfide, and carbon dioxide from the synthesis gas which is produced directly from coal. Some of the results from this work are described in an earlier Bureau of Mines report.^{9/}

To make its cost estimates as realistic as possible, the Southern Natural Gas Co. (later joined by the Tennessee Gas Transmission Corp.) extended further its agreement with the Morgantown Station to determine the economic factors involved in the methane-synthesis step, using a catalyst that had already been developed for such a process. After a literature survey, the most promising catalyst appeared to be that developed and tested in England by the Gas Research Board.^{10/}

It was desired to maintain a conversion of not less than 97 percent of the hydrogen and carbon monoxide in the raw gas, using a reasonably high space velocity and feed gas containing varying concentrations of carbonyl sulfide. The specific object was to confirm the theory that a nickel catalyst would give the desired conversion for a long enough time so that catalyst cost would not be a prohibitive factor in connection with the practicability of the methanation step.

The Bureau of Mines was especially interested in such a program, as this afforded it the opportunity of studying the applicability and efficiency of its gas-purification system in rendering synthesis gas suitable for methanation processes. The tests were made using carbonyl sulfide, as experience had shown it to be the organic sulfur compound most likely to be present in purified synthesis gas produced from coal, oxygen, and steam. It is believed, however, that most sulfur compounds, organic and inorganic, would affect the catalyst to about the same degree.

^{7/} Dent, F. J., and Hedden, D., The Catalytic Synthesis of Methane as a Method of Enrichment in Town-Gas Manufacture: Gas Res. Board Comm. GRB 51, 1949, 41 pp.

^{8/} Cooperman, J., Davis, J. D., Seymour, W., and Ruckes, W. L., Lurgi Process: Use for Complete Gasification of Coals With Steam and Oxygen Under Pressure: Bureau of Mines Bull. 498, 1951, 38 pp.

^{9/} Wainwright, H. W., Egleson, G. C., Brock, C. M., Fisher, J., and Sands, A. E., Removal of Hydrogen Sulfide and Carbon Dioxide from Synthesis Gas, Using Di- and Tri-ethanolamine: Bureau of Mines Rept. of Investigations 4891, 1952, 19 pp.

^{10/} Work cited in footnote 7.

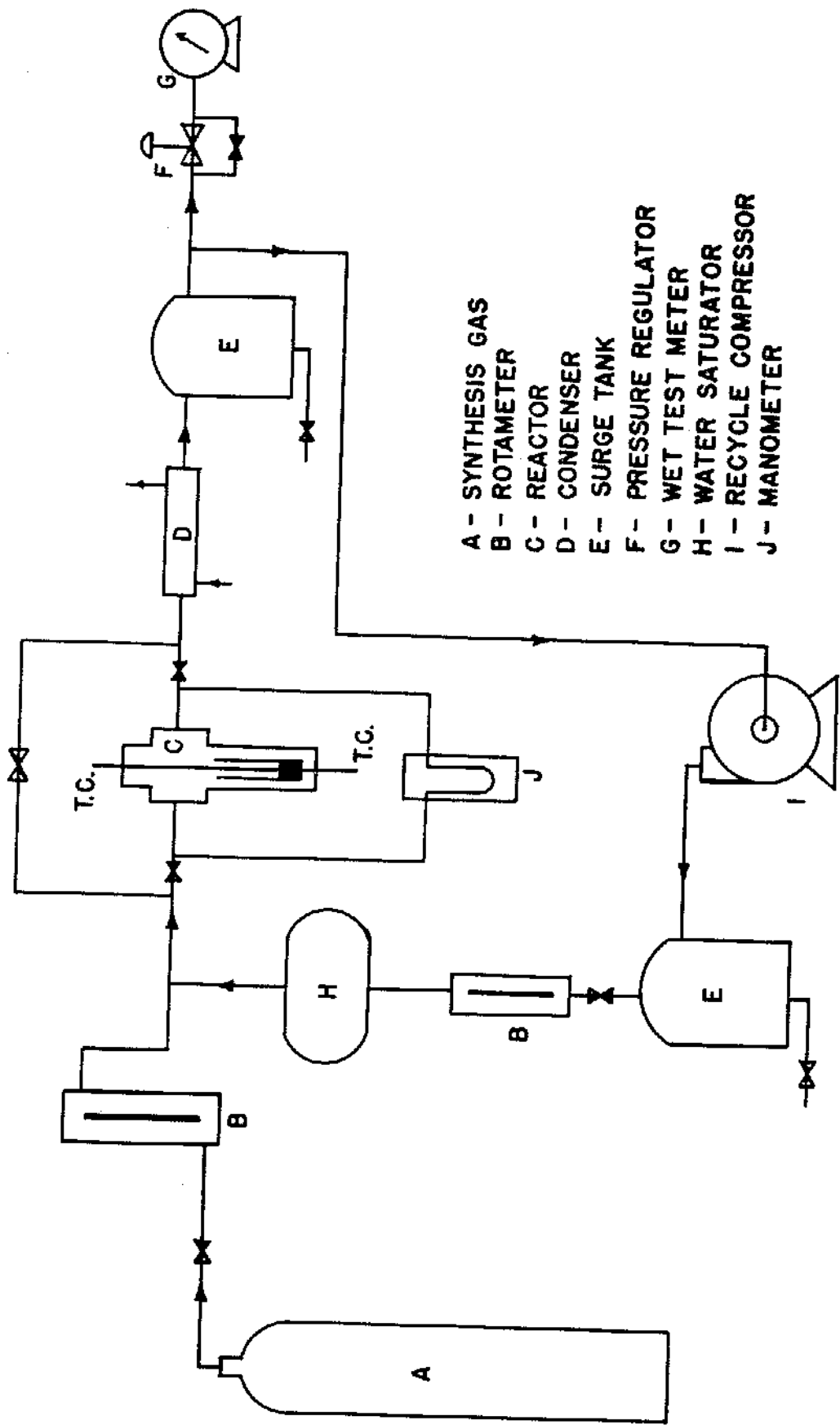


Figure 1. - Schematic diagram of apparatus used in methanation experiments.

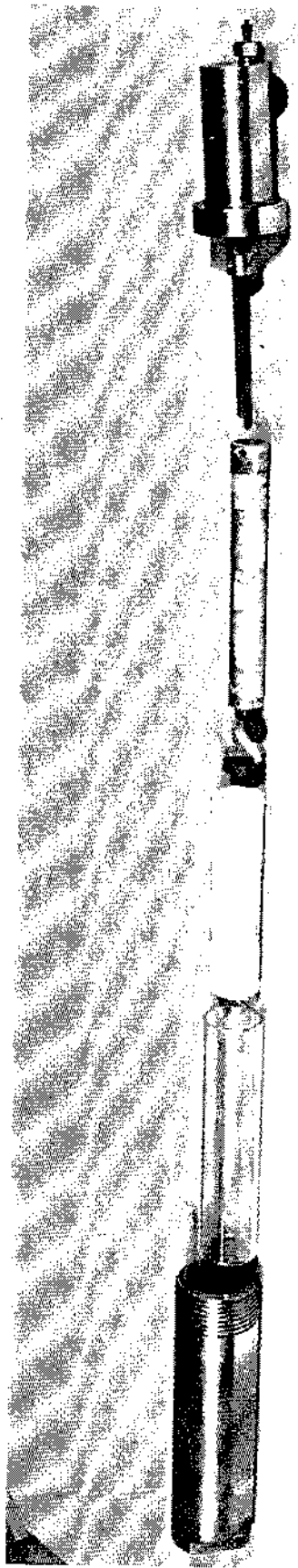


Figure 2. - Reactor parts before assembly. The outer shell is shown on extreme left and pressure head with cap on extreme right; between these are shown, from left to right: Glass jacket, aluminum-tube heater, meshed wire disk with threaded supporting flange, and catalyst container-tube.



Figure 3. - Partly assembled reactor; pyrex-glass jacket and outer shell not shown.

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The authors wish to express their appreciation to the members of the Synthesis Gas Branch, especially those of the Gas Treating and Testing Section, whose cooperation was most helpful. Special thanks are due to Dr. J. J. S. Sebastian of the branch for the valuable suggestions made in his review of the manuscript.

The authors wish to acknowledge the assistance and cooperation received from C. R. Breck of Southern Natural Gas Co. and J. J. King of Tennessee Gas Transmission Corp.

EXPERIMENTAL APPARATUS

Figure 1 is a schematic diagram of the apparatus used in the methanation experiments. Synthesis gas from a manifold of five cylinders flows through a rotameter that measures the fresh feed flow to the system and joins the recycle gas that contains 18 to 20 percent steam. (This amount of steam, as explained later, is added to simulate plant-scale conditions). The total gas stream then flows through a short length of tubing, heated and insulated to prevent condensation of the steam, and passes into the synthesis reactor. Thermocouples are placed close to the top and bottom of the catalyst bed to measure the temperature of the gas as it enters and leaves the catalyst. Pressure taps are installed before and after the reactor to measure the pressure drop through the catalyst bed.

Figure 2 is a photograph of the reactor parts before assembly. The various individual parts fit into each other in the sequence shown. The outer shell of the reactor, on the extreme left, is closed by means of a pressure head and an outside cap closure, shown on the extreme right. A spiral-wound stainless-steel gasket effects a gastight seal between them. Within the reactor is a 3/4-inch-diameter and 6-inch-long stainless-steel catalyst container having a stainless-steel meshed-wire support for the catalyst at its bottom. An aluminum tube with an embedded heating coil surrounds the catalyst container, and a Pyrex tube forms an insulating outer jacket. The partly assembled reactor is shown in figure 3.

In operation, the gas enters the reactor at the top through an inlet tube inserted in the hole shown on the curved side of the cap (fig. 3) and passes through the catalyst bed. As the catalyst occupies only part of the reactor volume, the remaining space is used for preheating the incoming gas. The gas leaving the catalyst bed in the reactor passes through a water-cooled condenser, where the steam from the reaction condenses and flows to a trap. After leaving the condenser, a portion of the product gas flows through a pressure-reducing regulator, through a wet test meter, and is discharged from the system.

A greater part of the product gas leaving the condenser is recirculated through the system by means of a controlled proportioning pump. It would have been desirable to recirculate the gas while hot, but this was not feasible. Before the recycle gas mixes with fresh raw-feed gas, it is measured with a rotameter and then passes through a water saturator, where a quantity of steam, equal to that removed by condensation, is added to the gas. The recycle gas leaving the saturator joins the raw input gas and passes to the reactor.

The saturator is equipped with a liquid-level gage. Whenever additional water is needed in the saturator, a valve connecting the saturator with a water-makeup container is opened; and water, pressurized with hydrogen gas, flows slowly from it into the saturator.

Sample connections are placed before and after the reactor for sampling the "input" (mixture of fresh inlet and recycle gas) and product gases. Another sample connection is placed in the line leaving the manifold for determining the sulfur content as well as the composition of the fresh "inlet" gas.

ANALYTICAL METHODS

The composition of the inlet and outlet gases was determined by using standard volumetric procedures. The total sulfur content of the fresh feed gas was determined by employing a hot platinum spiral as a catalyst and utilizing the hydrogen content of the gas to effect conversion of organic sulfur compounds to hydrogen sulfide.^{11/} The hydrogen sulfide then was determined colorimetrically using the methylene blue method.^{12/} Standard gravimetric methods were used for determining sulfur in the spent catalyst.

OPERATING PROCEDURE

The catalyst was made by precipitating aluminum-manganese-promoted nickel salts on china clay with potassium carbonate solution from a solution containing nickel, manganese, and aluminum nitrates, with china-clay particles added. The weight proportions of these materials were: 100 parts of nickel nitrate, 20 parts of manganese nitrate, 13.6 parts of aluminum nitrate, 25 parts of china clay, and 97 parts of potassium carbonate. After drying, the raw catalyst was crushed to 8- by 10-mesh. No analysis was made of the exact catalyst composition either after preparation or reduction. The catalyst reactor was charged with 30 cc. (approximately 29 grams) of catalyst, and the system was purged with hydrogen.

Several preliminary tests in which the hydrogen remaining in the system after reduction was replaced by either nitrogen or methane were totally unsuccessful. Catalyst activity dropped to virtually zero at the end of only 12 hours of operation. For successful operation it was essential that the system be filled with hydrogen when the flow of fresh feed gas was started. The best conditions were as follows: The pressure in the system was raised to 300 p.s.i.g. with hydrogen, and the recycle-gas flow was adjusted to give a space velocity of approximately 2,000 std. cu. ft. per cu. ft. per hr. Enough fresh hydrogen was fed into the system to maintain the pressure. The external heater around the catalyst was then turned on, and the temperature of the catalyst was brought up to 400° to 425° C., as measured by the thermocouples at the top

^{11/} Sands, A. E., Wainwright, H. W., and Egleson, G. C., Organic Sulfur in Synthesis Gas: Occurrence, Determination, and Removal: Bureau of Mines Rept. of Investigations 4699, 1950, 51 pp.

^{12/} Sands, A. E., Grafius, M. A., Wainwright, H. W., and Wilson, M. W., The Determination of Low Concentrations of Hydrogen Sulfide in Gas by the Methylene Blue Method: Bureau of Mines Rept. of Investigations 4547, 1949, 19 pp.

and bottom of the bed. The system was kept at this temperature for 4 hours, after which the temperature was lowered to 300° C., the hydrogen was shut off, and the addition of fresh simulated Lurgi gas was started at a rate of 2.1 std. cu.ft. per hr. (30 inches Hg, 60° F., dry). This gas flow gave the desired space velocity of 2,000 std. cu.ft. per cu.ft. per hr.

The simulated synthesis gas (a volumetric mixture of approximately 2H₂:CO) used in the experiments was prepared by the Mathieson Co. and was delivered in carbon-steel cylinders compressed to 1,400 p.s.i.g. pressure. The gas, as purchased, conformed closely to specifications.

Owing to initial catalyst activity, all of the carbon monoxide, as well as the carbon dioxide in the feed gas, was converted to methane. After about 6 hours, as the activity of the catalyst decreased, a small amount of carbon monoxide appeared in the product gas along with carbon dioxide from the feed gas and the water-gas shift reaction.

As the synthesis reaction is strongly exothermic, temperature control of the catalyst bed was maintained by recycling part of the outlet gas. The recycle gas, before mixing with the fresh gas, was bubbled through the water saturator with the water temperature so controlled as to give a gas containing 18 to 20 percent steam. The space velocity of dry gas plus water vapor was 26,000 std. cu.ft. per cu.ft. per hr., resulting in the predetermined recycle ratio of 12:1 over the catalyst.

The cylinder gas generally contained more carbonyl sulfide than was specified for the tests. The desired sulfur content was obtained by passing a portion of the fresh feed gas through activated carbon, and then mixing this gas, free of sulfur, with gas that had bypassed the carbon.

RESULTS

In addition to preliminary tests, five separate experimental runs were made. Table 1 lists those operating conditions that were held constant throughout the five runs, and the sulfur content of the fresh feed gas (inlet gas) in each run.

TABLE 1. - Operating conditions for methane synthesis tests

| | |
|---|--------|
| Space velocity, fresh feed gas.....std. cu.ft./cu.ft./hr. | 2,000 |
| Space velocity, fresh feed plus recycle gas plus steam..... | |
|std. cu.ft./cu.ft./hr. | 26,000 |
| Gas temperature entering catalyst.....°C. | 300 |
| Gas temperature leaving catalyst.....°C. | 400 |
| Sulfur in inlet gas, gr./100 std. cu.ft.: | |
| Run 1..... | 0.12 |
| Run 2..... | Nil |
| Run 3..... | .04 |
| Run 4..... | 1.53 |
| Run 5..... | .19 |

Figure 4 summarizes the results of four runs by showing, from day to day, the percentage conversion of hydrogen and carbon monoxide and the calorific value of the product gas. It must be understood that percentage conversion indicates conversion to methane and carbon dioxide. For this reason, the calorific value has also been plotted as an indication of catalyst activity. The calorific value shown is the gross heating value based on dry gas measured at 60° F. and 30 inches of mercury, assuming a carbon dioxide-free gas containing 3 percent nitrogen.

The fifth run (run 2), made with no sulfur in the feed gas, was discontinued after 23 days. Throughout this period no deterioration in catalytic activity was observed, with 98 percent conversion continually maintained. It was assumed that the high activity of the catalyst would have continued for a long period.

Feed-gas analyses for the entire series of five runs are given, along with typical product-gas analyses, in table 2. The reader's attention is called to the definition of "inlet" gas as fresh feed gas, as was stated previously.

TABLE 2. - Gas analyses

Run 1
Days from start

| Percent | 1-7 | 7 | 8-12 | 12 | 13-18 | 18 |
|-----------------------|-------|--------|-------|--------|-------|--------|
| | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet |
| CO ₂ | 4.9 | 20.5 | 5.0 | 19.8 | 5.7 | 21.7 |
| O ₂ | .6 | .2 | .7 | .6 | .4 | .1 |
| Ill. ... | .2 | .4 | .1 | .5 | .0 | .2 |
| H ₂ | 52.6 | 2.7 | 52.6 | 4.0 | 53.0 | 8.4 |
| CO..... | 23.9 | .9 | 24.1 | 1.5 | 24.9 | 2.5 |
| CH ₄ | 12.9 | 67.1 | 12.8 | 64.8 | 12.4 | 61.4 |
| N ₂ | 4.9 | 8.2 | 4.7 | 8.8 | 3.6 | 5.7 |

Run 2
Days from start

| Percent | 1-6 | 6 | 7-13 | 13 | 14-21 | 21 | 22-23 | 23 |
|-----------------------|-------|--------|-------|--------|-------|--------|-------|--------|
| | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet |
| CO ₂ | 5.0 | 23.1 | 5.0 | 25.0 | 4.6 | 23.7 | 4.5 | 23.7 |
| O ₂ | .3 | .3 | .2 | .3 | .2 | .3 | .2 | .2 |
| Ill. | .3 | .4 | .1 | .5 | .4 | .5 | .1 | .3 |
| H ₂ | 53.3 | 3.9 | 52.8 | 3.2 | 53.5 | 3.1 | 53.3 | 3.2 |
| CO..... | 24.0 | 1.0 | 27.1 | .5 | 26.3 | .4 | 26.9 | .5 |
| CH ₄ | 14.7 | 64.6 | 13.7 | 65.6 | 13.6 | 69.3 | 13.5 | 69.1 |
| N ₂ | 2.4 | 6.7 | 1.1 | 4.9 | 1.4 | 2.7 | 1.5 | 3.0 |

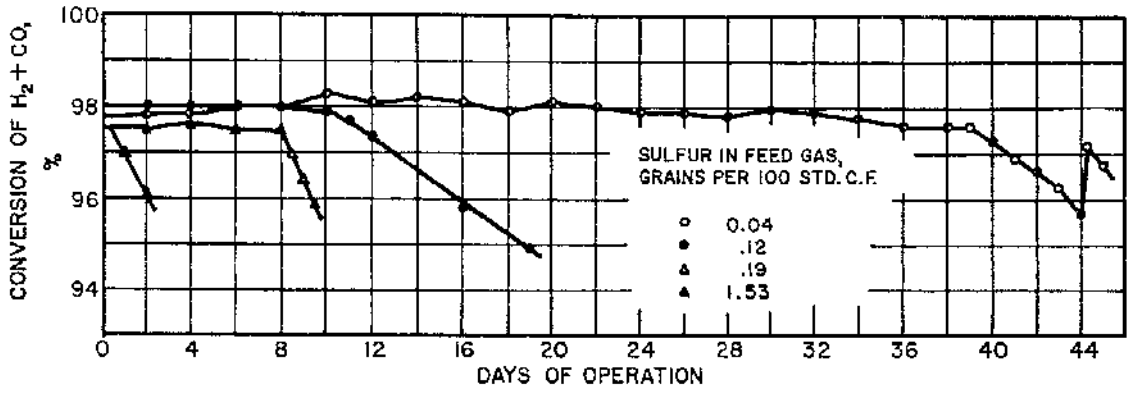
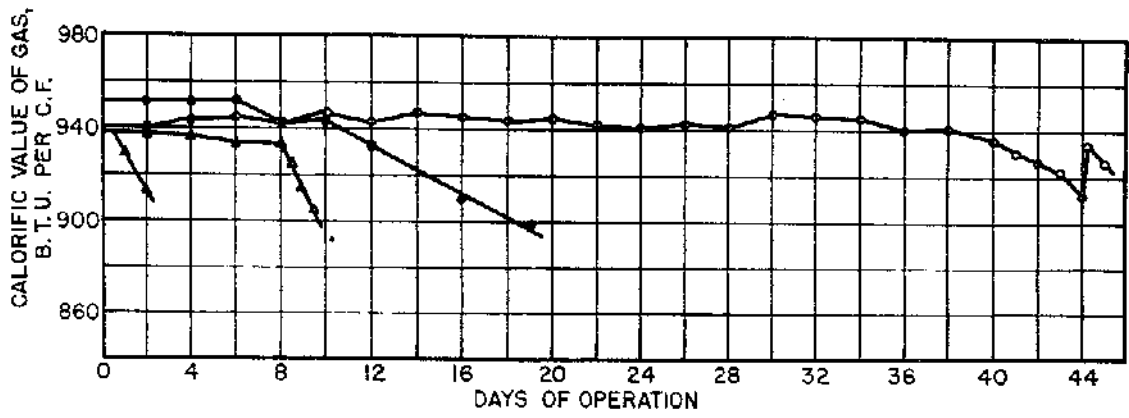


Figure 4. - Daily variations in H₂ + CO conversion and calorific value of product gas.

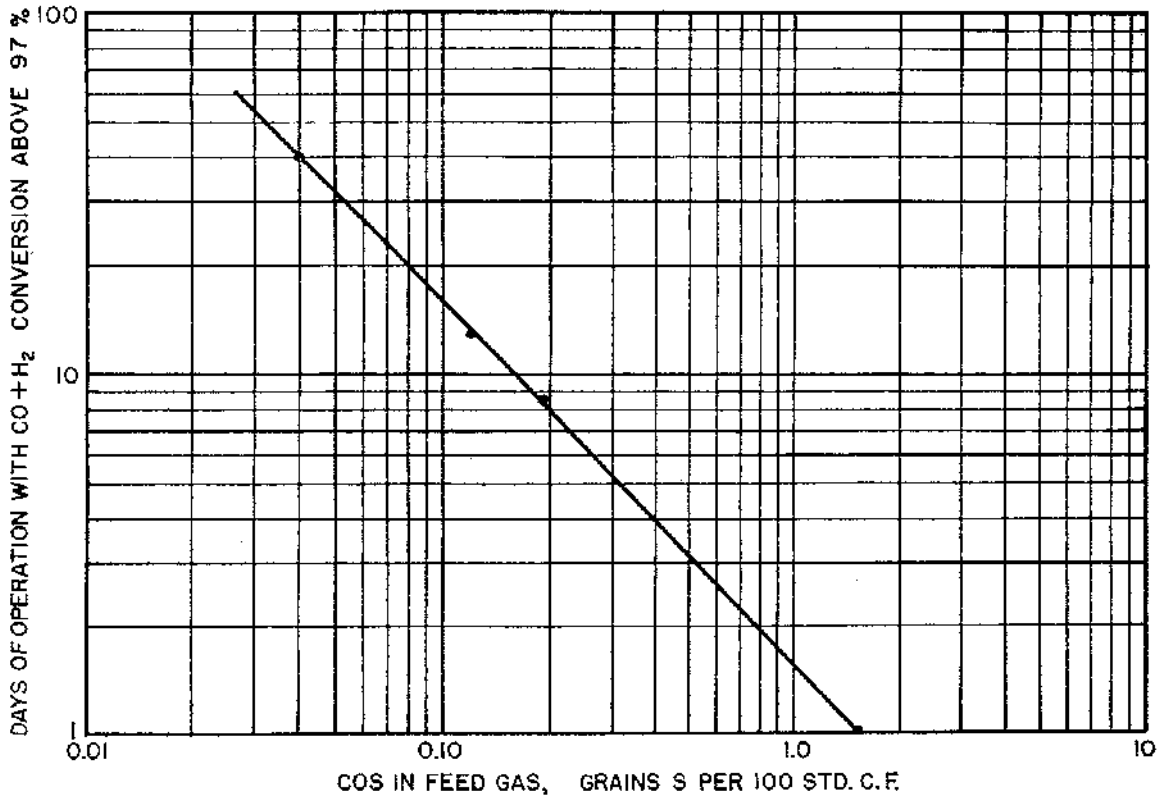


Figure 5. - Effect of sulfur content of feed gas on catalyst activity.

TABLE 2. - Gas analyses (con.)

Run 3
Days from start

| Percent | 1-5 | 5 | 6-11 | 11 | 12-18 | 18 | 19-23 | 23 |
|-----------------------|-------|--------|-------|--------|-------|--------|-------|--------|
| | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet |
| CO ₂ | 4.5 | 24.0 | 4.6 | 23.3 | 4.5 | 23.4 | 4.7 | 25.3 |
| O ₂ | .2 | .1 | .3 | .3 | .2 | .4 | .2 | .3 |
| Ill. | .1 | .3 | .1 | .3 | .1 | .3 | .0 | .1 |
| H ₂ | 53.3 | 3.2 | 53.1 | 2.6 | 53.3 | 3.0 | 52.0 | 3.1 |
| CO..... | 26.9 | .5 | 26.6 | .4 | 26.9 | .4 | 28.0 | .4 |
| CH ₄ | 13.5 | 68.2 | 12.7 | 68.7 | 13.3 | 69.1 | 13.2 | 67.4 |
| N ₂ | 1.5 | 3.7 | 2.6 | 4.4 | 1.7 | 3.4 | 1.9 | 3.4 |

| Percent | 24-29 | 29 | 30-37 | 37 | 38-45 | 44 |
|-----------------------|-------|--------|-------|--------|-------|--------|
| | Inlet | Outlet | Inlet | Outlet | Inlet | Outlet |
| CO ₂ | 4.5 | 23.7 | 4.1 | 21.9 | 4.5 | 22.7 |
| O ₂ | .4 | .4 | .5 | .1 | .3 | .3 |
| Ill. | .0 | .3 | .1 | .3 | .0 | .3 |
| H ₂ | 52.5 | 2.4 | 53.0 | 3.1 | 53.3 | 4.6 |
| CO..... | 27.3 | .6 | 25.4 | .7 | 26.3 | 2.3 |
| CH ₄ | 13.6 | 68.6 | 15.3 | 70.7 | 15.1 | 66.8 |
| N ₂ | 1.7 | 4.0 | 1.6 | 3.2 | .5 | 3.0 |

Run 4
Days from start

| Percent | 1-2 | 2 |
|-----------------------|-------|--------|
| | Inlet | Outlet |
| CO ₂ | 4.2 | 25.2 |
| O ₂ | .1 | .3 |
| Ill. | .1 | .4 |
| H ₂ | 52.3 | 4.3 |
| CO..... | 27.8 | 2.3 |
| CH ₄ | 12.2 | 64.5 |
| N ₂ | 3.3 | 3.0 |

Run 5
Days from start

| Percent | 1-8 | 8 | 9 | 9 |
|-----------------------|-------|--------|-------|--------|
| | Inlet | Outlet | Inlet | Outlet |
| CO ₂ | 4.1 | 27.0 | 4.3 | 24.7 |
| O ₂ | .0 | .2 | .1 | .3 |
| Ill. | .7 | .3 | .1 | .4 |
| H ₂ | 51.0 | 3.1 | 52.1 | 4.3 |
| CO..... | 27.8 | 1.0 | 27.7 | 2.3 |
| CH ₄ | 14.2 | 64.1 | 13.0 | 64.0 |
| N ₂ | 2.2 | 4.3 | 2.7 | 4.0 |

During each run operation was continuous and, before the catalyst failed, a 97-to 98-percent conversion of the hydrogen and carbon monoxide in the feed gas was obtained in all instances. Figure 5 correlates the results of the runs by showing catalyst life as a function of the sulfur content of the feed gas. It is felt that extrapolations of the curve to sulfur concentrations as low as 0.01 grain of sulfur per 100 std. cu. ft. are justifiable.

At the conclusion of each of the tests, the catalyst was removed and examined. The catalyst particles were quite hard, and there was no evidence of disintegration. Chemical analysis of the used catalyst showed not more than 0.15 percent carbon.

Role of Sulfur

It was planned to make the first run with approximately 0.03 to 0.05 grain of sulfur as carbonyl sulfide per 100 std. cu. ft. of fresh feed gas and to maintain this concentration throughout the run. However, at the conclusion of the run, an analysis of the catalyst showed that it contained about three times the amount of sulfur anticipated from the inlet-gas analysis. To ascertain the source of the excess sulfur, the tap water added to the saturator for imparting steam to the recycle gas was analyzed. This water was found to contain, in the form of sulfates, 10 times the amount of sulfur required to complete the sulfur balance. Accordingly, it was assumed that entrained water from the saturator was carried by the recycle gas to the heated tube, where it was vaporized and thence carried to the catalyst. This resulted in an excessive sulfur concentration in the input gas, expressed on fresh inlet-gas basis as 0.12 grain of sulfur per 100 std. cu. ft., instead of the intended 0.03 to 0.05 grain. To eliminate this source of contaminating sulfur, all subsequent runs were made by injecting sulfur-free, triply distilled water into the saturator.

Table 3 gives the length of each run and shows the results of sulfur analyses. The activity of the catalyst decreased in all instances when about 0.58 gram of sulfur per 100 grams of nickel had been absorbed.

The second run was made with the feed gas as nearly sulfur-free as possible. Before entering the apparatus all gas was passed through active carbon. The main purpose of this run was to establish that the loss of catalytic activity after the 13 days' operation of the previous run was directly attributable to sulfur poisoning. After 23 days of operation with no loss in activity, this run was discontinued.

Effect of Shutdown on Catalyst Activity

In view of the necessity of maintaining certain conditions during reduction and the early stages of methanation, as explained under "Operating Procedure," there was some question as to whether a catalyst, once on stream, might not lose activity during a shutdown. Accordingly, at the end of this second run the gas in the system was purged out with hydrogen, after which the pressure was reduced and the catalyst cooled. Five days later the same catalyst was again employed as previously described. Methanation was then continued 2 days more. During this period the catalyst behaved in all respects exactly as it had before the shutdown, giving a conversion of 97.8 percent of the hydrogen and carbon monoxide and a product gas having a calorific value of 944 B.t.u. per cu. ft.

TABLE 3. - Results of sulfur analyses

Sulfur absorbed by catalyst, gm. sulfur per 100 gm. nickel

| Run No. | Duration of run, days | | Total | | | Conversion above 97 percent | | Average sulfur in feed gas, gr./100 std. cu.ft. |
|---------|-----------------------------|-------|----------------------|-------------------------------|----------------------|--|---------|---|
| | Conversion above 97 percent | 1/ | By feed-gas analysis | By analysis of spent catalyst | By feed-gas analysis | By calc. from analysis of spent catalyst ^{2/} | Average | |
| 1 | 13 | 19 | 0.25 | 0.86 | 0.173/ | 0.58 | 0.58 | 0.12 |
| 2 | 23 | 23 | .003 | | | | | .0004 |
| 3 | 40 | 45 | .63 | .64/ | .57 | .56 | .56 | .04 |
| 4 | 1 | 2-1/6 | 1.18 | 1.21 | .55 | .56 | .56 | 1.53 |
| 5 | 8-1/2 | 9-1/3 | .66 | .67 | .58 | .62 | .60 | .19 |

1/ Number of days of run during which the conversion was 97 percent or higher.

2/ Calculated by prorating the total sulfur absorption for the number of days during which the conversion was minimum 97 percent.

3/ Not used as part of average; see discussion.

4/ By determination of SO₂ in effluent regeneration air.

Variation of Space Velocity and Temperature

A sulfur concentration of 0.04 grain per 100 std. cu.ft. was used for run 3. The hydrogen and carbon monoxide conversion dropped below 97 percent between the fortieth and forty-first days. On the forty-third day the inlet-gas temperature was increased 25° C. in an attempt to increase the activity of the catalyst. This failing (see fig. 4), the space velocity was reduced 50 percent on the forty-fourth day. As expected, this reduction of space velocity was followed immediately by a period of increased conversion of hydrogen and carbon monoxide, after which, however, the percent conversion continued to fall.

Catalyst Regeneration

Following the third run, an attempt was made to regenerate the catalyst. Air at atmospheric pressure was passed over the catalyst while its temperature was gradually increased. Negligible sulfur dioxide was evolved until 800° C. was reached at the top of the catalyst bed; it was necessary to increase the temperature to 900° C. to burn off the major portion of the sulfur. This catalyst, when again placed in operation, gave an initial conversion of hydrogen and carbon monoxide of only 91.8 percent, not enough for producing a 900-B.t.u. gas.

Further work in this direction may be indicated when cost calculations are completed. Even if no better activity can be obtained after regeneration, the possibility of using two beds in series might merit consideration. The first bed, while not active enough to produce 900-B.t.u. gas, would remove sulfur compounds and provide protection for the second bed. However, if enough catalyst life is obtained in single-stage operation, so that catalyst cost per unit of gas is small, it may be more expedient to discard the catalyst.