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INDUSTRY PROGRAM OF THE COLLEGE OF ENGINEERING

THE HYDROGENATION OF CARBON MONOXIDE

ON A STEEL CATALYST

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STATEMENT OF THE PROBLEM

The synthesis of methane and other light hydrocarbon gases from carbon monoxide and hydrogen using a carbon steel catalyst was the subject of this research. The primary aim of the investigation was to determine the optimum conditions of temperature and feed gas composition for the production of high BTU gas. Information was desired concerning the amount of free carbon deposited on the catalyst surface under these conditions.

A secondary objective of the research was to investigate the use of air oxidation as a method for removing carbon deposition from the steel catalyst and for reactivating catalyst poisoned by sulfur compounds present in the feed gas.

INTRODUCTION

The industrial importance of the catalytic reactions of carbon monoxide with hydrogen has increased rapidly since 1897 when Sabatier and Senderens^{1,2} reported their original work on the synthesis of methane using reduced nickel and reduced cobalt catalysts.

In 1913, the Badische Anilin and Soda Fabrik³ reported the synthesis of higher hydrocarbons and oxygenated compounds in addition to methane from carbon monoxide-hydrogen mixtures at 100-200 atmospheres pressure and temperatures of 300°-400°C in the presence of alkali-activated cobalt and osmium oxides supported on asbestos.

Synthesis of Liquid Hydrocarbons

Franz Fischer and Hans Tropsch⁴ working at the Kaiser Wilhelm Institute für Kohlenforschung, Mulheim-Ruhr, Germany, reported in 1923 that alkalized iron turnings catalyzed the production of an oily liquid from carbon monoxide and hydrogen at 100-150 atmospheres and 400°-450°C. This product, which was called "synthol," contained chiefly oxygenated compounds and small quantities of hydrocarbons. At atmospheric pressure, primarily hydrocarbons were formed. Subsequent catalyst tests led to the discovery of nickel-thoria precipitated on kieselguhr in 1931,⁵ and cobalt-thoria on kieselguhr in 1932,⁶ as successful catalysts for the synthesis of liquid hydrocarbon products.

Pilot-plant tests showed that nickel catalysts were unsuitable for commercial operation, first, because of the production of high proportions of methane, and secondly, because of rapid catalyst deterioration at pres-

tures above one atmosphere through the formation of volatile nickel carbonyl. Cobalt base catalysts then received extensive study. However, the scarcity of cobalt metal prompted continuous research on iron catalysts, and a successful alkalized precipitated iron catalyst was developed in 1937.

The Fischer-Tropsch and related syntheses have been reviewed in great detail by Storch et al.,⁷ both with regard to commercial development and with regard to the fundamental thermodynamic and kinetic studies of the reactions involved.

Synthesis of Methane

A sizable amount of research on the synthesis of methane from carbon monoxide and hydrogen has paralleled this work on the production of liquid hydrocarbons and oxygenated compounds. Methanization research has been motivated primarily by a need for suitable catalysts and processes to upgrade the low heating values of gases manufactured from coal. Reports of early investigations and processes can be found in the literature.⁸⁻¹⁵

Water-gas, comprised principally of carbon monoxide and hydrogen in approximately equal proportions, is one of several gases which can be manufactured from coal. The heating value of water-gas is low, ranging from about 280 to 330 BTU per cubic foot. European countries, lacking natural gas, but with ample supplies of coal, have for years manufactured large quantities of water-gas by the steam-carbon reaction. The literature contains references to many early investigations on the synthesis of methane from water-gas as a method of increasing its heating value.¹⁶⁻¹⁹ More recently, the British Gas Research Board and the Fuel Research Board have conducted an extensive experimental program on the synthesis of methane

from water-gas and other industrial gases over a nickel catalyst as a means of enriching town gas.²⁰⁻²⁵

The use of manufactured gas is by no means unknown in the United States. Roughly 350 billion cubic feet of gas manufactured from coal have been consumed yearly for domestic and commercial heating for the last 30 years.²⁶ However, the availability of large quantities of natural gas has not yet necessitated the upgrading of manufactured gas by methane synthesis for situations where a high BTU gas is required.

The future of methanization in the United States, as a means of enriching gases manufactured from coal, is uncertain. Depletion of natural gas reserves alone will not insure its use. The potential of obtaining tremendous quantities of inexpensive useful atomic energy by fission or fusion cannot be overlooked. In fact, the advent of atomic power complicates the problem of predicting not only the future of high BTU gas from coal, but of all our present supplies of energy.

No matter how uncertain the future may be, the possibility of utilizing methanization to upgrade low BTU gas cannot be discounted. Recently, several commercial processes have been outlined in the literature.²⁷⁻³⁰ The last of these offers an economic appraisal of the production of high BTU gas from coal by methanization with regard to present-day costs.

Kinetic studies of the synthesis of methane from both carbon monoxide-hydrogen³¹⁻³⁴ and carbon dioxide-hydrogen^{35,36} mixtures on nickel catalysts have been made. The mechanism of the methanization reaction has been considered.^{37,38}

There has been much research on methanization catalysts,³⁹⁻⁴¹ particularly with regard to supported nickel catalysts.⁴²⁻⁵⁴

While most of the methanization catalyst development has been devoted

to supported catalysts, some work has been done on nonporous metal catalysts. Fischer and Jaeger⁵⁵ observed in 1925 that an electrically heated iron wire spiral brought to a red heat in a mixture of 15% CO₂, 23% CO, and 56% H₂ contained in an iron autoclave at 120-150 atmospheres catalyzed the formation of 15 to 19% methane. Gilkeson, White, and Sliepcevich⁵⁶ reported in 1953 the use of the inside wall of a stainless steel tubular reactor to catalyze the hydrogenation of carbon monoxide to methane at temperatures from 950° to 1500°F. The use of finely divided stainless steel to synthesize gasoline has been reported by Layng.⁵⁷

In the development of supported catalysts for methane synthesis, two problems arise which are not encountered with the use of nonporous catalysts. First, the carbon formation which occurs during synthesis deposits solid carbon in the pore structure of supported catalysts and eventually causes fragmentation of the catalyst pellets. Secondly, supported catalysts are often susceptible to sintering which can reduce catalyst surface area and decrease catalyst activity. Uniform temperature control, which is necessary to prevent localized overheating and catalyst sintering, is difficult to obtain, particularly in fixed catalyst beds, because of the large exothermic heat of reaction of the methane synthesis.

The report by Gilkeson, White, and Sliepcevich of the high activity of stainless steel at elevated temperatures suggests that a nonporous steel catalyst, which would not be subject to fragmentation by carbon deposition nor to loss of activity by sintering, should function well as a methanization catalyst at temperatures of 950° to 1500°F.

Recently, Smith⁵⁸ studied the hydrogenation of carbon monoxide and carbon dioxide on 1/8-inch steel particles. The effects of steel composition and various surface treatments were investigated. Ordinary un-

treated low carbon steel was superior to the other types tested from the standpoint of activity, stability, cost, and ease of preparation. Smith found the catalyst to have a threshold temperature of 925° to 1025°F with maximum stable activity obtained at approximately 1050°F. A product gas containing 25% methane was synthesized from a feed gas of 29% carbon monoxide and 70% hydrogen at 1050°F and a pressure of 30 atmospheres.

Smith's observation that increasing the reactor pressure from 5 to 30 atmospheres increased the conversion of carbon monoxide to methane, decreased carbon deposition, and increased the ratio of methane to carbon dioxide in the product gas led Lobo⁵⁹ to study the methanization reaction at pressures to 1040 atmospheres. Lobo's findings were in agreement with those of Smith at lower pressures. However, no observation with regard to the amount of carbon deposition at high pressure was made.

Virtually all of the previous work using steel catalyst has been on methanization of feed gas streams composed of approximately 30% carbon monoxide and 70% hydrogen. At 30 atmospheres and 1050°F, the product gas formed from such a feed contains roughly 33% methane, 1% ethane, 53% hydrogen and 13% carbon monoxide after the removal of water and carbon dioxide, and has a heating value of about 575 BTU/SCF. Much of the hydrogen, which has a heating value of only 325 BTU/SCF, remains unreacted and acts as a diluent, reducing the heating value of the product gas.

The use of feed gas containing higher ratios of carbon monoxide to hydrogen would reduce the amount of excess hydrogen present, and should result in an increase in the heating value of the product gas. A single experimental run by Smith at 30 atmospheres and 1070°F, which investigated the effect of feed composition on the distribution of the products from synthesis, substantiated this premise. From feed gas composed of 37.8%

carbon monoxide and 61.0% hydrogen, a product gas was synthesized which contained 46% methane, 2% ethane, 36% hydrogen, and 16% carbon monoxide after the removal of water and carbon dioxide. This gas had a heating value of approximately 675 BTU/SCF, an increase of 100 BTU/SCF over that obtained from a 30% carbon monoxide-70% hydrogen feed, which would indicate that further investigation of the effect of feed gas composition on the product distribution is warranted.

In addition to the increased heating value of the product gas, Smith observed an appreciable increase in the amount of carbon deposited on the catalyst surface when the feed gas used contained more than 30% carbon monoxide. Under conditions of carbon deposition, fixed-bed reactors would eventually become plugged with carbon, which suggests that methanization on a commercial scale might advantageously be carried out in fluidized-bed reactors where the steel catalyst, in finely divided form, could be continuously circulated to a carbon removal unit and back to the reactor. The high mechanical strength of steel catalyst should reduce the formation of catalyst "fines" and should permit severe carbon removal methods without serious effect on the catalyst structure. Information on the amount of carbon deposition to be expected under various synthesis conditions would be of value.

The present work is a study of the hydrogenation of carbon monoxide on 1/8-inch-diameter carbon steel spheres to produce methane and other light hydrocarbon gases. An integral fixed-bed reactor and experimental conditions favoring high conversions were used to investigate the effect of feed gas composition and of temperature on the distribution of the products from synthesis. The operating conditions required to produce a product gas of the highest heating value were determined. Information was ob-

tained concerning the amount of free carbon deposited on the catalyst surface under various synthesis conditions. Regeneration by air oxidation of catalyst which had been poisoned by sulfur compounds present in the feed gas was investigated. In addition, a single experimental run was made using a supported cobalt-thoria catalyst at temperatures from 500° to 840°F.

EXPERIMENTAL EQUIPMENT

The fixed-bed catalyst testing unit used in this research program was a part of a larger experimental plant which included two fluidized-bed reactors. The reactors were interconnected and operated from a central control unit. By making appropriate changes in the electrical wiring and the piping of the experimental plant, it was possible to operate any one of the three reactors. Figure 1 is a photograph of the front view of the experimental plant, and Figure 2 shows the central control unit.

In a general manner, the flow of gas through the fixed-bed system can be described as follows. Carbon monoxide and hydrogen, supplied from commercial gas cylinders, were metered in separate flow control panels. After mixing, the feed gas was admitted to an electrically heated reactor, fabricated from a 1-inch-diameter, schedule-80 stainless steel pipe. The feed gas contacted a catalyst bed of steel balls positioned in the reactor pipe, reacted to form product gas, and passed out of the reactor to a wet-test meter and a sampling system.

For purposes of a more detailed description, the fixed-bed system can be divided into six sections. These are:

1. Gas Supply System
2. Feed Gas Control Panels

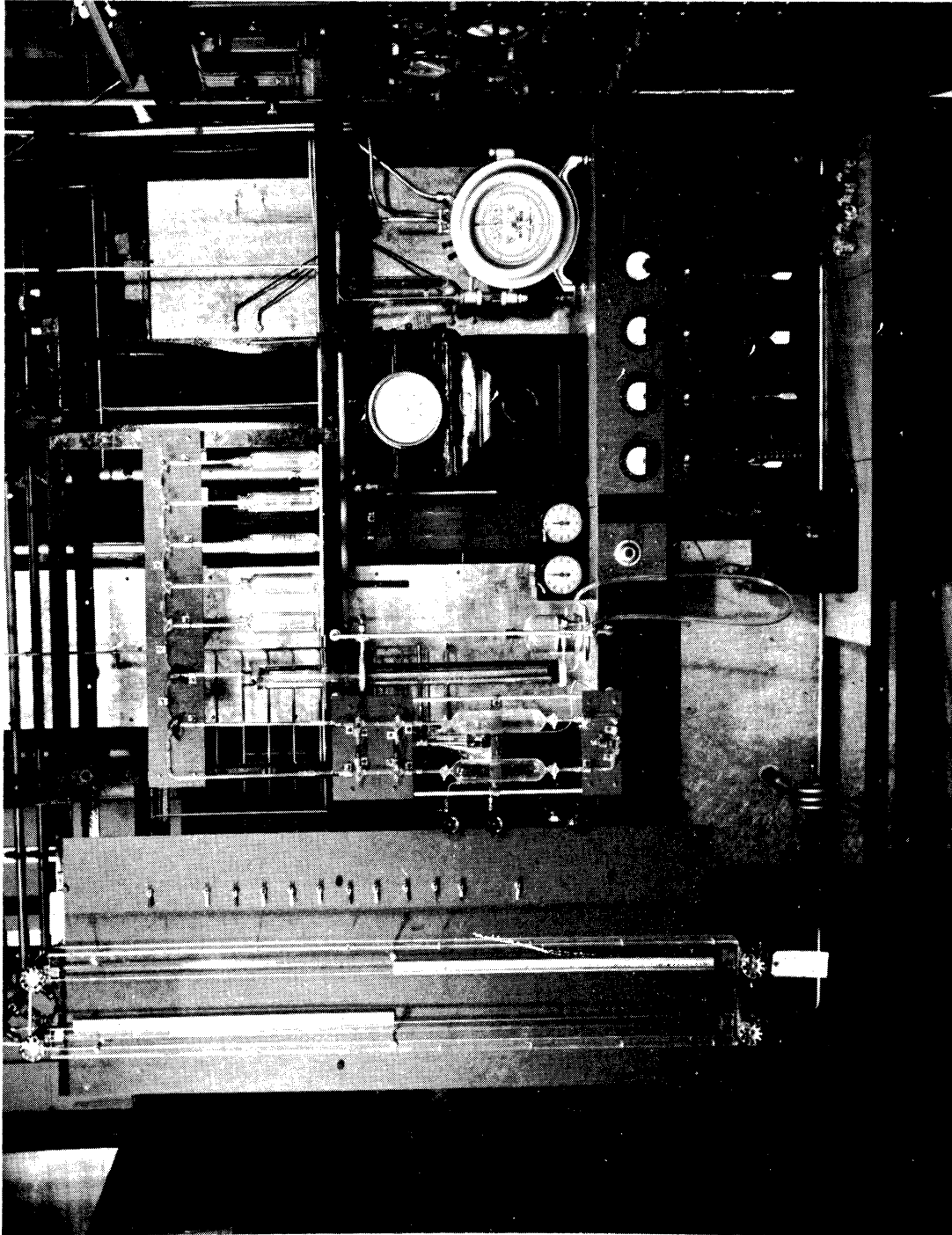


Figure 1. Front View of the Experimental Plant.

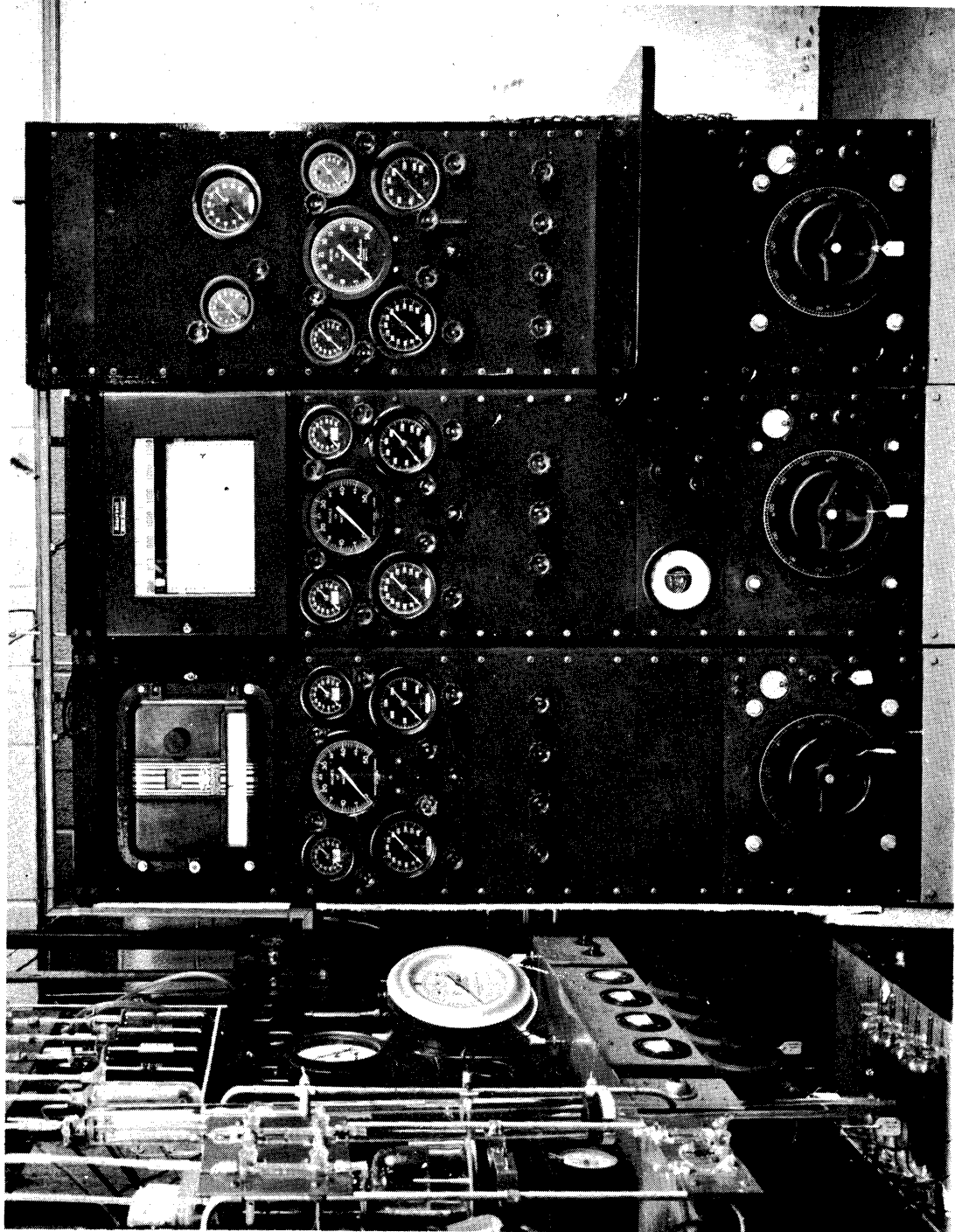


Figure 2. Front View of the Central Control Unit.

3. Fixed-Bed Reactor and Heaters
4. Gas Flow Measurement and Sampling
5. Temperature Control and Measurement
6. Auxiliary Equipment

Reference to the schematic diagram of the fixed-bed catalyst testing unit, Figure 3, should aid both in identifying the components being described and in following the flow of gases.

Gas Supply System

Feed gases were supplied to the control unit from size 1-A commercial gas cylinders. Three hydrogen cylinders were attached in parallel to the hydrogen side of a gas supply manifold, and three carbon monoxide cylinders were connected to the carbon monoxide side. The valve and piping arrangement of the manifold was designed so that empty cylinders could be replaced without interrupting the flow of gas to the control unit. A second manifold capable of accommodating eight additional gas cylinders was available for use when the fluidized bed reactors were operated.

Each side of the gas supply manifold was connected to a separate feed gas line leading to the control unit. Airco reducers mounted on the manifold reduced the cylinder pressure to the desired line pressure.

Before entry to the control unit, the carbon monoxide feed stream was passed through a trap containing a mixture of activated charcoal and silica gel to remove sulfur compounds. The trap was approximately 30 inches long and 2 inches in diameter. A by-pass line around the trap permitted operation without the removal of sulfur compounds for those runs in which catalyst poisoning was investigated.

A nitrogen cylinder attached to the hydrogen supply line provided in-

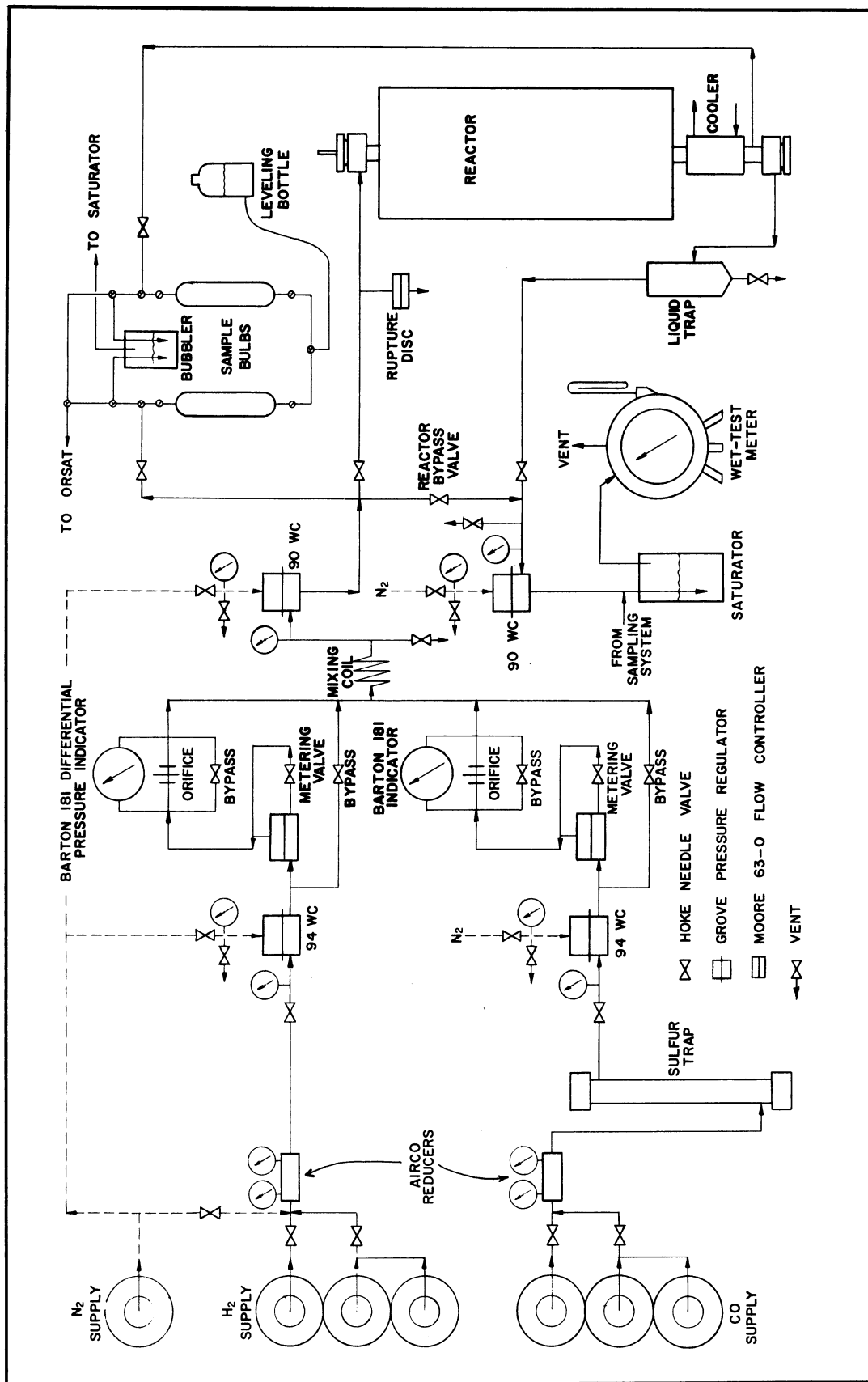


Figure 3. Schematic Flow Diagram of the Fixed-Bed Catalyst Testing Unit.

ert gas for purging the reactor. High pressure nitrogen was supplied to the Grove pressure regulators of the control unit as shown in Figure 3.

Feed Gas Control Panels

The central control unit, shown in Figure 2, was composed of three individual flow control panels. The left-hand and center panels were identically constructed and were used for controlling the flow rate of hydrogen and carbon monoxide to the fixed-bed reactor. The two gases were metered separately and mixed just before leaving the control unit. A larger capacity panel on the right was built for metering a single mixed gas stream for use with the fluidized-bed reactors. The following discussion will be concerned only with the hydrogen and carbon monoxide panels.

At the entrance to each of the panels, Hoke needle valves were provided so that the flow of feed gas could be shut off at the panels. Pressure gauges immediately downstream indicated the supply line pressure when the shut-off valves were open.

The Airco reducers at the gas supply manifold were capable only of coarse adjustment. Furthermore, they did not provide a constant supply line pressure as the pressure in the gas cylinders decreased. Consequently, the feed gases were next passed through nitrogen-loaded Grove constant downstream pressure regulators (type 94WC) which reduced the supply line pressure approximately 20 psi and provided a constant inlet pressure at the metering valves. The Grove regulators also prevented the panel pressure from becoming excessive. If the pressure of a panel ever exceeded the selected nitrogen-loading pressure, the regulator valve stopped the flow of gas to the panel.

Hoke 2RB281 metering valves controlled the flow of each feed stream.

Twenty turns were required to fully open each needle valve, which facilitated precise control of the flow rates. A Moore 63-D flow controller maintained a constant pressure drop of 3 psi across each metering valve.

The approximate feed rates were indicated by Barton 181 differential pressure indicators which measured the pressure drop across small orifices through which each feed gas flowed. The Barton gauges were not calibrated and were used primarily as a means of detecting changes in the feed rates during experimental runs. A by-pass line around each orifice was kept open whenever the flow panels were being pressurized to prevent damage to the Barton gauges by sudden full scale deflections.

Rapid pressurizing of the reactor was made possible by by-passing the feed gases around the low capacity flow control units.

After passage through their respective orifices, the hydrogen and carbon monoxide streams were combined and mixed and were then sent to the reactor. A nitrogen-loaded Grove constant back pressure regulator (type 90WC) maintained the desired panel pressure. No gas flowed through the regulator until the nitrogen-loading pressure was exceeded. The panel pressure was indicated by a gauge immediately upstream from the back pressure regulator.

Because the nitrogen pressure in the Grove regulators was sensitive to small changes in the room temperature, it was necessary to enclose the back of the control unit and to thermostatically control the temperature in order to maintain constant flow rates. The panel temperature was maintained above the maximum room temperature by a household Kenmore heater-fan. The heater-fan was wired so that the fan ran continuously, while the heating coil was turned on and off by a Fenwal temperature controller. A second fan provided rapid circulation of the panel air and made temperature

control to within 0.5°F possible.

Fixed-Bed Reactor and Heaters

The reactor used was constructed by B. J. Clark in 1951 and was used by B. D. Smith⁵⁸ in his research program. Only relocation of the reactor and machining of the closures was necessary to put it into operating condition.

The components of the reactor are shown in cross section by Figure 4. The main body of the reactor was a 58-inch length of 1-inch-diameter, schedule-80 stainless steel pipe (type SAE 304) which was fitted with pressure cone fittings on both ends for closures.

Feed gas entered the reactor pipe through an opening in the lower half of the top pressure cone fitting. The gas flowed down the pipe, through a heated reaction zone, to a cooler, and out of the reactor through two exit ports in the bottom cone fitting. A tight fitting brass liner (not shown in Figure 4) was inserted into the reactor pipe so that the feed gas would contact no steel other than the catalyst pellets while in the heated reaction zone. The liner extended from the feed gas entrance to a point below the cooler. Saureisen cement was used to seal the crack between the top of the liner and the reactor wall. This effectively prevented any gas from passing between the liner and the reactor pipe.

The reaction zone was heated by a 700-watt main heating coil of 16-gauge nichrome wire and by three smaller 400-watt coils formed from 20-gauge nichrome wire. The heating coils were wrapped around a 40-inch-long, 4-inch-diameter ceramic tube, as shown in Figure 4, and were insulated from one another with alundum cement. The ceramic tube fitted closely over a 3-1/2-inch-diameter steel pipe which surrounded the reactor pipe. Steel

balls filled the annulus formed by the heater assembly and the reactor pipe and provided a large sensible heat reservoir. The heat reservoir facilitated control of the reactor temperature at any desired value for prolonged periods, but also decreased the rate at which this temperature could be changed. Two wells were provided for the insertion of thermocouples into the mass of steel balls.

Catalyst pellets were supported in the reaction zone by a perforated brass disc which was held on to the end of the reactor thermocouple well by a ball of brazing material. The reactor thermocouple well assembly is shown in Figure 5. A 1/4-inch-diameter steel tube was fitted inside a 3/8-inch-diameter copper tube. The tubes were brazed together at the ends and machined to the designated dimensions. The inner steel tube was needed to withstand the large pressure drop across the wall of the thermocouple well, while the copper covering served to mask the steel tube from the feed gas.

The thermocouple well passed through a hole in the center of the upper pressure cone fitting and was attached to it with Ermeto fittings. When the reactor was closed, the catalyst support disc was positioned approximately two-thirds of the distance from the top of the reactor heaters to the bottom. This provided a preheating zone above the catalyst bed. A 19-inch-long brass plug was inserted into the reactor volume below the catalyst bed to reduce hold-up of the product gas.

Product gas flowed out of the reactor to a trap, where liquid products were removed, and was then returned to the flow control panels. The gas pressure was reduced to slightly above atmospheric by passage through a nitrogen-loaded Grove back pressure regulator which maintained the reactor at pressure.

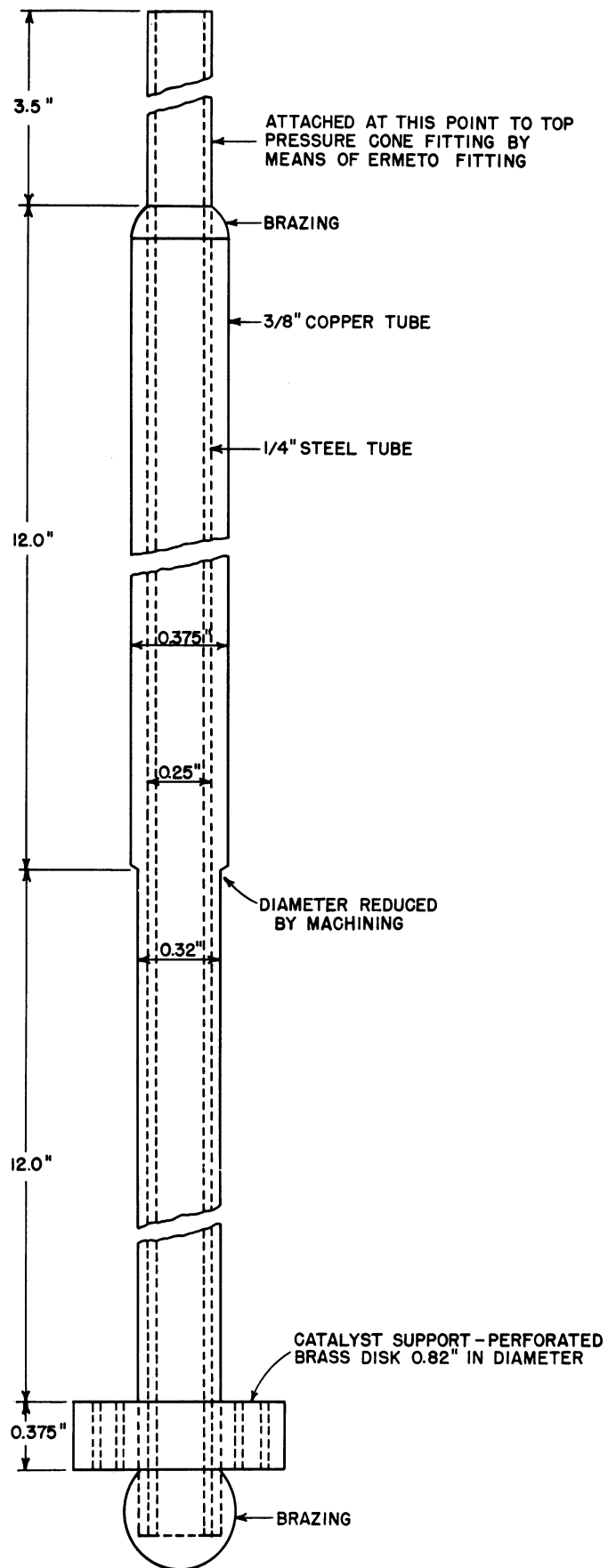


Figure 5. Thermocouple Well and Catalyst Support.

A by-pass line was provided around the reactor. By closing valves at the entrance and exit of the reactor unit, it was possible to divert the feed gas stream directly to the gas metering system after pressure reduction.

Gas Flow Measurement and Sampling

A Precision Scientific wet-test meter was used to measure the flow rate of the feed and product gases. Product gas (or feed gas if the reactor was by-passed) flowed from the control panels after pressure reduction, through a water saturator, to the wet-test meter. The time required for one-tenth of a cubic foot of gas to flow through the meter was measured by two stop clocks. The clocks were wired so that at the end of each revolution of the meter, one clock was automatically stopped and the other started. Exhaust gas from the wet-test meter was vented to the out-of-doors.

Feed gas samples could be withdrawn from the feed stream at the exit from the control panels. Product gas samples were removed from the reactor through a sample tap below the reactor cooler. The sampling lines were arranged so that the sample streams flowed through the sampling system and returned to the main gas stream before it entered the wet-test meter. This permitted the measurement of flow rates while the sample lines were being purged.

The sample streams passed through a bubbler which permitted visual observation of the sample flow rate. An arrangement of three-way glass stopcocks made it possible to divert the sample stream to the burette of a conventional Orsat apparatus or to sample bulbs for mass spectrometer analysis.

Samples were collected by displacing liquid from the sample bulbs under a slight head, which prevented air from leaking into the sample bulbs during sampling. The liquid which was used for filling the sample bulbs, the Orsat burette, and the bubbler, was a 20% solution of sodium sulfate in water with enough sulfuric acid and methyl orange indicator to color it red.

Temperature Control and Measurement

The amount of heat generated by the three small reactor heaters was controlled by varying the voltage to each heating coil with a manually operated Powerstat variable-voltage transformer. The line voltage to the transformer was 115 volts and the maximum current output to the heater windings was approximately 4 amperes.

The power input to the main heater was regulated by a V-50 Variac. A 220 line voltage to the Variac yielded a maximum current output to the heater winding of about 3 amperes. The input to the heater could be controlled either manually or by a Leeds and Northrup Micromax temperature controller. A potentiometer circuit in the controller, actuated by a control thermocouple inserted into the mass of steel balls surrounding the reactor, opened and closed a mercury switch through which the input current to the main heater flowed. The Micromax controller was used for approximate control whenever the operator was absent, and maintained the reactor temperature within a 15°F cycle of the desired value. For more accurate temperature control during periods of data-taking, manual operation was necessary.

Temperature measurements were made with 24-gauge iron-constantan thermocouples. Three such thermocouples were used. Two control thermocouples

were placed into the thermocouple wells provided in the mass of steel balls around the reactor pipe. One of these actuated the Micromax temperature controller and the other was connected to a temperature recorder. A third thermocouple, inserted into the reactor thermocouple well, measured the catalyst-bed temperature.

A Brown six-point Elektronik recorder provided continuous temperature recordings. Three points of the recorder were used to record the catalyst-bed temperature, and the other three points were connected to the control thermocouple.

Auxiliary Equipment

A gas recompression and mixing manifold was used to prepare gas mixtures and also to refill the carbon monoxide supply cylinders whenever the cylinder pressure dropped below the desired supply line pressure. A schematic diagram of the recompression and mixing manifold is presented in Figure 6.

When used for recompression, low pressure gas from cylinders attached to an Airco gas cylinder manifold was allowed to displace oil from a gas compression cylinder to an oil storage tank. The low pressure gas cylinders were shut off, and the gas pressure in the compression cylinder was increased by pumping oil from the storage tank back into the cylinder with a Simplex high pressure pump. After compression, gas was allowed to flow from the compression cylinder into the cylinder being refilled.

For gas mixing, only the cylinder manifold section was used. The compression cylinder, pump, and oil storage tank were closed off with a Hoke needle valve. Gas was transferred during mixing by the pressure drop between cylinders. A pressure gauge indicated the gas pressure in the

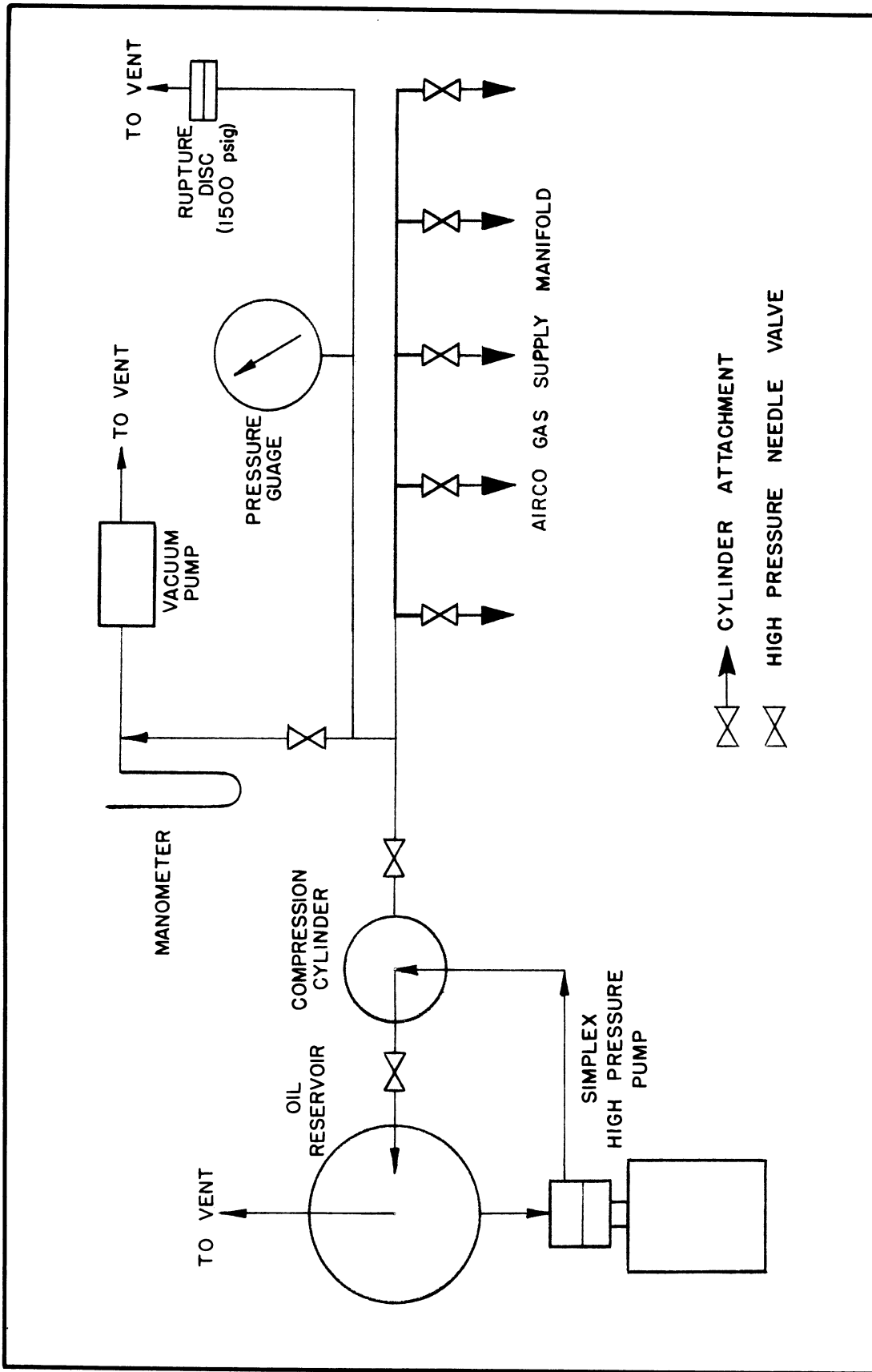


Figure 6. Schematic Diagram of the Gas Compression and Mixing Manifold.

manifold, and a vacuum pump was provided for evacuating gas cylinders.

Aluminum tubing (52S-0) was used for piping throughout the experimental plant. The tubing had good bending characteristics and would hold a pressure of 2000 psia at room temperature.

All valves used were stainless steel Hoke needle valves, except for the metering valves which had brass bodies and steel stems. All elbows, tees, unions, etc., were steel Ermeto fittings.

The feed gas line to the reactor was attached to a Black, Sivalis, and Bryson rupture disc fitting. An aluminum disc, which had a rupture pressure of 600 psia at 72°F, released the reactor pressure to a vent line upon bursting.

MATERIALS

Gases

The composition of the gases used in this experimental program, determined by mass spectrometer analysis, are presented in Table I. Carbon monoxide and hydrogen were used as feed gases. Nitrogen was used to pressurize the Grove regulators of the control unit and also to purge the reactor when necessary.

TABLE I
GAS COMPOSITIONS

Gases	Supplier	Purity %	Impurities, %					Sulfur mg/l
			O ₂	N ₂	CO ₂	H ₂	Hydro- carbons	
CO	Matheson	97.7	-	0.6	0.5	1.0	0.2	0.32*
H ₂	Bird	99.9	0.1	-	-	-	-	-
N ₂	Bird	99.6	0.4	-	-	-	-	-

*From Matheson specifications.

Catalysts

One-eighth-inch-diameter SAE C-1013 steel balls were used as catalyst in all but one of the experimental runs. The composition of the steel catalyst balls is listed in Table II. The balls were obtained from Hoover Ball and Bearing Company and had received only enough grinding to remove the equatorial rim produced when the metal was compressed from wire into spheres.

TABLE II
STEEL CATALYST COMPOSITION

Constituent	Weight % Present in SAE C-1013 Steel
Carbon	0.13 - 0.18
Manganese	0.50 - 0.80
Sulfur	0.05 max
Phosphorus	0.04 max

A single catalyst run was made using a supported cobalt-thoria catalyst, Co-Th-268 Tablets 1/8", which was obtained from the Harshaw Chemical Company. The chemical analysis of the catalyst is listed in Table III. The catalyst base was kieselguhr. Approximately 4% graphite was added as a tableting lubricant.

TABLE III
COBALT-THORIA CATALYST COMPOSITION

Component	Weight %
Co	32.8
ThO ₂	6.0
K ₂ O	1.5
HCl insolubles	29.0

Catalyst-Bed Diluent

Three times as many 1/8-inch-diameter brass balls as steel balls were mixed with the catalyst charge to facilitate the removal of the heat of reaction and to provide space in the catalyst bed for carbon deposition.

Sulfur Trap Charge

Activated coconut charcoal (size 6 to 14 mesh) was mixed with an equal amount of silica gel and was used to remove the sulfur compounds present in the carbon monoxide.

EXPERIMENTAL PROCEDURE

The procedure used in conducting an experimental run can be described briefly as follows. The fixed-bed reactor was heated to temperature, the catalyst charge was introduced, and a flow of feed gas to the reactor was established. After steady-state operation was obtained at the desired reaction conditions, various experimental data were recorded, and samples of the feed and product gas were collected. Generally, several sets of data and samples were collected during a run. At the end of most of the runs, the catalyst was removed from the reactor, and the carbon which had deposited during the run was weighed.

For purposes of a more detailed discussion, the experimental procedure can be divided into five subtopics.

1. Catalyst Pretreatment
2. Catalyst Charging and Reactor Heat-up
3. Setting Flow Rates
4. Data-Taking and Sampling
5. Measuring Carbon Deposition

Any deviation from normal operation will be discussed under the appropriate subheading.

Catalyst Pretreatment

When received from the supplier, the steel catalyst balls were coated with a film of oil for protection against corrosion. All the steel balls used were washed three times with thiophene-free benzene to remove this protective coating.

Two experimental runs, designated Pro-A and Pro-B, were made to investigate the promoting effect of potassium carbonate on the steel catalyst for the formation of hydrocarbons higher than methane. After washing with benzene, the steel balls used in these runs were moistened with a solution of 90 grams of potassium carbonate in 200 grams of water and dried at 200°C. No other forms of pretreatment were used.

The catalyst charge for the reactor was prepared by counting out the desired number of catalyst pellets and mixing them with three times as many inert brass balls.

Catalyst Charging and Reactor Heat-up

In all of the experimental runs, except the first six runs and the cobalt-thoria catalyst run, the empty reactor was heated to the desired run temperature before the catalyst was introduced. (The experimental runs are listed in chronological order in Table VIII.) The normal operating procedure was as follows.

Before a run was to be made, the brass liner was inserted into the open reactor, and the crack between the top of the liner and the reactor pipe was sealed with Saureisen cement. The brass plug, which reduced hold-up of the product gas, was inserted into the bottom of the reactor,

and the lower pressure cone fitting was bolted into place. Closure of the reactor was completed by bolting the upper pressure cone fitting and the attached reactor thermocouple well into position. The thermocouple which measured the catalyst-bed temperature was inserted into the reactor thermocouple well.

The valves on the supply cylinders were opened and gas was allowed to flow to the control unit. The nitrogen-loading domes of the Grove regulators were filled to the desired pressures. With the orifice by-pass valves open to protect the Barton gauges, the feed gas shut-off valves on each flow control panel were opened. Gas was by-passed around the low capacity flow control units and the panels were pressurized. Once the panels were at operating pressure, all by-pass valves were closed, and the gas flow rates were controlled by the metering valves.

The closed reactor was purged with nitrogen and then tested for leaks by pressurizing to about 350 psig with hydrogen. If no drop in the reactor pressure was observed in two hours, the reactor heaters were turned on, and the Micromax controller was set at the desired control temperature. Because of the large exothermic heat of reaction of the methane synthesis, the maximum temperature of the catalyst bed during an experimental run was 100° to 130°F hotter than the control temperature, depending upon the composition of the feed gas used. Consequently, the empty reactor was heated to a temperature below the expected run temperature to allow for the increase in the catalyst-bed temperature when feed gas flow was established.

It was possible to heat the reactor from room temperature to 1000°F in five hours using the maximum heat output of the reactor heaters. However, the reactor was usually heated to temperature overnight using the full 220 line voltage on the main heater, but only 50 volts on each of the

three smaller heaters.

Once the reactor reached temperature, the catalyst charging procedure was begun. The reactor pressure was reduced to atmospheric, and the system was flushed with nitrogen to remove any remaining hydrogen. The catalyst was introduced into the reactor by lifting the top pressure cone fitting and pouring in the catalyst charge. Two hundred brass balls were added first, followed by the steel catalyst balls mixed with brass balls, and then by another two hundred brass balls. The layers of brass balls, which were about an inch deep, were added above and below the catalyst bed to minimize entrance and exit effects. The catalyst-bed thermocouple indicated that in less than 15 minutes the catalyst charge was heated to within a few degrees of the control temperature.

After charging with catalyst, the reactor was closed and was purged with nitrogen to remove any air which entered while the reactor was open. Flow of carbon monoxide and hydrogen to the reactor was started. The Barton gauges were used to set the composition of this gas at about 20% carbon monoxide and 80% hydrogen. Gas was allowed to flow into the reactor until the pressure exceeded the nitrogen-loading of the Grove regulator which maintained the reactor at pressure. The reactor was then by-passed, and the desired hydrogen and carbon monoxide flow rates were set.

The procedure of pressurizing the reactor before the flow rates were established was adopted when it was found that introduction of feed gas to the reactor at atmospheric pressure caused a small change in the flow rates. A gas containing a high ratio of hydrogen to carbon monoxide was used so that no carbon would be deposited on the catalyst surface while the reactor was by-passed.

In only seven runs, the first six experimental runs and the cobalt-

thoria catalyst run, was there deviation from this procedure for heating the reactor and charging the catalyst. In these seven runs, the catalyst was introduced into the cold reactor, the feed rates were accurately set, and the reactor was then heated to the desired temperature.

Setting Flow Rates

The first step in setting the feed gas flow rates was to calculate the time necessary for 0.1 cubic foot of gas to flow through the wet-test meter at the desired feed rates. With the reactor by-passed, the feed gas metering valves were adjusted until the wet-test meter times agreed with the calculated values. The hydrogen feed rate was established first, and then enough carbon monoxide was added to bring the total flow of feed gas to the desired value.

Once the flow rates were established, the reactor by-pass line was closed, and the flow of feed gas was directed to the reactor. The catalyst was now considered to be at age zero.

Data-Taking and Sampling

Introduction of feed gas to the reactor caused a rapid increase in the catalyst-bed temperature because of the exothermic heat of reaction. However, after a period of from 20 to 30 minutes, the maximum catalyst-bed temperature leveled off to a constant value. During the run, this temperature was maintained by manual adjustment of the power input to the main heater winding. The three smaller heaters were used only when gross adjustments were made in the reactor temperature.

Once the catalyst-bed temperature had become constant, a period of at least 30 minutes was allowed to elapse before any experimental data or gas samples were taken. The data of Smith⁵⁸ showed that this was suffi-

cient time to reach steady-state conditions in the reactor. The following list is a summary of the data which were recorded and the gas samples which were collected for each set of experimental conditions.

1. Run designation
2. Date and hour
3. Catalyst and pretreatment
4. Number of catalyst pellets and brass balls
5. Pressures
 - a. Grove regulator nitrogen loadings
 - b. Exit-panel pressure
 - c. Hydrogen and carbon monoxide supply line pressure
 - d. Exit-reactor pressure
 - e. Barometric pressure
6. Pressure drop across the Barton gauge orifices
7. Input voltages to the reactor heaters
8. Wet-test meter readings
 - a. Time per revolution for the product and the feed gas
 - b. Pressure differential between the atmosphere and the gas in the meter
 - c. Gas temperature in the wet-test meter
 - d. Hour at which the flow rates were measured
9. Temperatures
 - a. Catalyst-bed temperature
 - b. Control temperature (temperature in the mass of steel balls around the reactor)
 - c. Control unit temperature
 - d. Room temperature
10. Orsat sample for CO₂ analysis
 - a. Original sample volume
 - b. Final sample volume
 - c. Percent absorbed
11. Mass spectrometer samples
 - a. Feed gas sample
 - b. Product gas sample
 - c. Time at which each sample was collected
12. Any remarks concerning the experimental data recorded

The procedure used in collecting these data and gas samples was as follows.

The product gas sample valve was opened, and the sample stream was allowed to flow through the sampling system and back to the main gas stream entering the wet-test meter. While the product sample line was being purged, the product flow rate was measured with the wet-test meter, and the data listed in the tabulation as numbers 1 through 7 were recorded. After the sample line was flushed, gas was diverted to a 300-cc sample bulb and to the burette of the Orsat apparatus. The product sample for mass spectrometer analysis and the Orsat sample were collected simultaneously. The temperatures listed opposite number 9 were recorded.

Next, the reactor was by-passed, and the feed gas sampling valve was opened. The feed gas flow rate was measured, while the sample line was being flushed. A feed sample was collected, the reactor by-pass line was closed, and flow of feed gas to the reactor was resumed.

By-passing the reactor to sample and to measure the flow rate of the feed gas, resulted in an immediate decrease in the temperature of the catalyst bed. By the end of the sampling period, this temperature was approaching the control temperature. Resumption of gas flow to the reactor, returned the maximum catalyst-bed temperature to within several degrees of the previous run temperature, and the usual procedure was to take a second complete set of data and samples about an hour later.

Measuring Carbon Deposition

At the completion of an experimental run, the flow of feed gas was stopped, and the reactor was cooled to room temperature. To make certain that no leaks had developed during the run, the reactor system was again pressure tested.

In order to measure the carbon deposition in the catalyst bed, the

reactor was opened, and the brass liner holding the reactor thermocouple well and the catalyst charge was removed. Because the steel and brass balls resting on the catalyst support disc locked themselves against the reactor thermocouple well and the inside of the brass liner, it was impossible to pull the thermocouple well and catalyst charge from the reactor pipe without also removing the liner. The most satisfactory method was to insert a plug, which had the same outside diameter as the brass liner, into the bottom of the reactor pipe and to drive the liner from the reactor with several hammer blows.

The liner was inverted, and the catalyst balls, brass balls, and any loose carbon were poured out. After separating the catalyst pellets and carbon from the brass balls with a magnet, they were weighed against an equal number of unused catalyst pellets. The difference in weight was equal to the weight of carbon deposited on the catalyst during the experimental run.

METHODS OF ANALYSIS

The feed and product gas analyses were obtained by use of a Consolidated Engineering Corporation Analytical Mass Spectrometer, Model 21-103B.

In addition, the carbon dioxide content of the product gas was checked during each run by a conventional Orsat apparatus using a 33% potassium hydroxide solution.

The mass spectrometer analyses of the product gas were on a water-free basis, since the water produced by the reaction was condensed out before the product samples were collected. The quantity of water formed was determined by material balance, since no provision was made to collect and

measure the amount of water condensed.

The Consolidated Engineering Corporation Analytical Mass Spectrometer,
Model 21-103B

The CEC Analytical Mass Spectrometer is an instrument in which gaseous molecules, admitted at low pressure to an analyzer section from an inlet sample volume, are fragmented and ionized by a stream of electrons. The ions formed are accelerated by an adjustable voltage, and are passed through a magnetic field where they are deflected in a circular path. The radius of this path is dependent upon the mass-to-charge ratio (m/e) of the ion, the magnetic field strength, and the accelerating voltage. With a constant magnetic field strength, it is possible to focus ions of a particular m/e upon a collector at the far end of a semi-circular analyzer tube by changing the accelerating voltage. Ions striking the collector deposit a charge which is amplified and recorded. The current produced is a measure of the abundance of ions of the particular m/e for which the instrument is focused.

By scanning the range of possible accelerating voltages, the CEC Analytical Mass Spectrometer produces a continuous photographic record of abundance of ions, shown by peaks on the chart, versus m/e for a sample from mass numbers 1 to 750.

Mass Spectra of Pure Compounds

Under the same conditions of ionization, a given compound will fragment and ionize in a fixed pattern. This pattern, which is called the mass spectrum, is unique for any compound. The largest peak in the spectrum of a pure compound is called the major peak, and the peak at the m/e corresponding to the molecular weight is the parent peak. Figure 7 is the

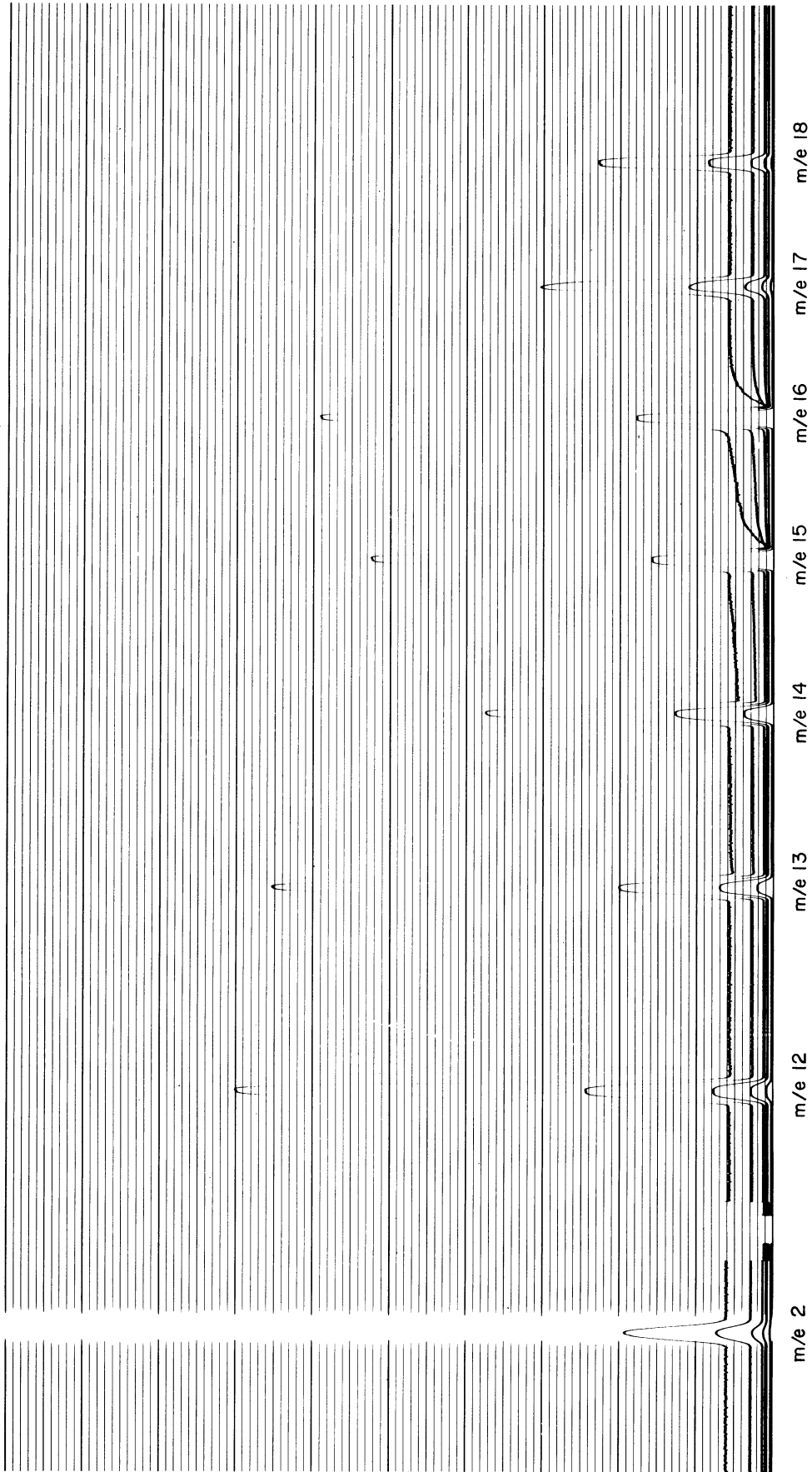


Figure 7. Mass Spectrum of Methane .

mass spectrum of methane with a parent peak at m/e 16 and ion fragment peaks at m/e 's 15, 14, 13, 12, and 2. The relative heights of the peaks compared to any one of the peaks selected as reference, usually the major peak, is called the cracking pattern of a compound. The reference peak used for calculating the cracking pattern is known as the base peak. Table IV shows the cracking pattern of methane computed with reference to the m/e 16 base peak.

TABLE IV
CRACKING PATTERN OF METHANE

m/e	Peak Height in Scale Units	Cracking Pattern Coefficients
2	13.2	0.0075
12	64.1	0.0365
13	187.2	0.1068
14	361.0	0.2061
15	1551.0	0.8852
16	1752.0	1.0000

The height of any peak in the mass spectrum of a compound is proportional to the pressure of that compound in the inlet volume of the instrument. If the mass spectrum of methane, shown in Figure 7, were determined at double the pressure, each of the peaks of the spectrum would be twice as large. The cracking pattern, however, is independent of the sample inlet pressure and would not be changed.

The relationship between the height of any peak in the spectrum and the pressure of the compound in the inlet volume is expressed as a sensitivity.

$$\text{Sensitivity} = \frac{\text{Peak height in scale units at a specific } m/e}{\text{Microns pressure in the inlet volume}}$$

A determination of the cracking pattern and a sensitivity referred to some base peak is required for each of the pure components of a mixture before the mixture analysis can be computed. These cracking patterns and sensitivities are obtained by running calibration standards for pure components before a series of mixture spectra are obtained from the mass spectrometer.

Mass Spectra of Mixtures

In a mixture, the peak heights of a compound spectrum are proportional to the partial pressure of the compound in the sample inlet volume. Thus, the spectrum of a mixture is the linear superposition, or simple sum of the spectra of all the components.

Given the composition of a mixture and the mass spectra of each of its components, the mixture spectrum can be computed. Conversely, given the mixture spectrum and the calibrating spectra for all components present, the composition can be determined.

Computation of Mixture Analyses

The heart of the analysis process is the fact that when one peak of a component spectrum is known, the entire component spectrum and the partial pressure can be computed using the cracking pattern and the sensitivity determined from the pure component calibration spectrum.

In many mixture spectra, peaks appear which are caused by only one component. Such peaks are called unicomponent peaks. For example, the feed gas used in the experimental runs was comprised of hydrogen, carbon monoxide, and a small amount of carbon dioxide impurity. The mass spectrum of a feed gas sample contains peaks at m/e 's of 2, 12, 16, 28, and 44. The m/e 2 peak and the m/e 44 peak are unicomponent peaks caused by hydrogen and carbon dioxide, respectively. Partial pressures of hydrogen and car-

bon dioxide can be calculated immediately from these peaks.

$$\text{p.p. of H}_2 = \frac{\text{Height of the m/e 2 peak}}{\text{Sensitivity of m/e 2 peak from the H}_2 \text{ calibrating spectrum}}$$

$$\text{p.p. of CO}_2 = \frac{\text{Height of the m/e 44 peak}}{\text{Sensitivity of m/e 44 peak from the CO}_2 \text{ calibrating spectrum}}$$

The partial pressure of carbon monoxide, however, cannot be calculated directly because there is no unicomponent peak in the mixture spectrum from carbon monoxide. Every peak in the mixture spectrum resulting from carbon monoxide (m/e's 12, 16, and 28) also receives a contribution from carbon dioxide. By use of the unicomponent peaks at m/e 2 and m/e 44, and the cracking patterns and sensitivities for hydrogen and carbon dioxide, it is possible to compute and to subtract the spectra for hydrogen and carbon dioxide from the mixture spectrum. The resulting residual spectrum is that of carbon monoxide alone. Its partial pressure can be computed from the m/e 28 peak which is now a Δ -unicomponent peak.

$$\text{p.p. of CO} = \frac{\text{Height of the residual 28 peak}}{\text{Sensitivity of the m/e 28 peak from the CO calibrating spectrum}}$$

Frequently, mixtures do not permit the successive peeling off of all components on the basis of unicomponent or Δ -unicomponent peaks. In most cases a residual spectrum is obtained at some point in the analysis in which every peak has contributions from two or more components. It then becomes necessary to set up and solve a set of n simultaneous linear equations in n unknowns. The coefficients of the equations are the cracking pattern coefficients; the constant terms are the mixture peak heights; and the unknowns are the heights of the base peaks of the respective components.

As an example, consider the computation of the analysis of a mixture containing only propane and propene on the basis of the m/e 29 and m/e 41 peaks of the mixture spectrum. Table V contains the cracking pattern coefficients and the sensitivities for propane and propene obtained from calibration runs.

TABLE V
CRACKING PATTERN COEFFICIENTS AND
SENSITIVITIES FOR PROPANE AND PROPENE

m/e	Propane	Propene
29	1.0000	.0254
41	.1480	1.0000
base peak sens.	70.84 $\frac{\text{div.}}{\mu}$	53.58 $\frac{\text{div.}}{\mu}$

Let x_1 = number of divisions of m/e 29 peak in mixture spectrum due to propane.

x_2 = number of divisions of m/e 41 peak in mixture spectrum due to propene.

Then from the cracking pattern coefficients:

$$.1480 x_1 = \text{divisions of m/e 41 peak due to propane}$$

$$.0254 x_2 = \text{divisions of m/e 29 peak due to propene}$$

The mixture spectrum is the sum of its components:

$$x_1 + .0254 x_2 = \text{height of m/e 29 peak in the mixture spectrum}$$

$$x_2 + .1480 x_1 = \text{height of m/e 41 peak in the mixture spectrum}$$

The values of x_1 and x_2 determined from these two linear simultaneous equations are the portion of the respective base peaks due to only one component. Finally, the partial pressure of each component can be computed.

$$\text{p.p. of propane} = \frac{x_1}{70.84}$$

$$\text{p.p. of propene} = \frac{x_2}{53.58}$$

In general form for \underline{n} unknown components, the set of linear simultaneous equations may be expressed as follows:

Let a_{ij} = the cracking pattern coefficient at $m/e = i$,
for component j .

Then $a_{ij}x_j$ = the number of divisions of mixture peak at $m/e = i$,
due to component j .

Summing the contributions from all j components to the mixture peak height at $m/e = i$,

$$m_i = \sum_{j=1}^{j=n} a_{ij}x_j \quad (1)$$

By assigning values from 1 to \underline{n} for i , the entire set of \underline{n} linear simultaneous equations is described. It is important that every component which contributes to the mixture spectrum be included in this set of equations.

Analysis of the Feed and Product Gas Samples

Portions of the feed and product gas samples, which had been collected in 300-cc sample bulbs during the experimental runs, were transferred through a drying tube containing calcium sulfate to evacuated 40-cc tubes suitable for attachment to the inlet cabinet of the mass spectrometer. The samples were introduced into the mass spectrometer, and their mass spectra were obtained.

Product Gas Analysis.---From the mass spectra of the product gas samples, peaks caused by the presence of hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, propane, propylene, and traces of C₄ compounds were identified. In order to determine the composition of product gas samples from their mass spectra, calibration standards were run for each of the components present. Sensitivities and cracking patterns with respect to the major peak of each of the standards were computed.

Because the condition of the mass spectrometer shifted from day to day, it was necessary to recalibrate frequently. Cracking patterns remained relatively constant for prolonged periods, but pure component sensitivities changed considerably over a period of a few days and had to be determined each time a set of mixture spectra were obtained.

Nine components were present in the product samples and nine peaks were selected from the product gas mass spectrum as a basis for the nine linear simultaneous equations required to determine the composition of the product gas. These peaks along with the component determined are tabulated in Table VI.

TABLE VI
SPECTRUM PEAKS USED FOR THE DETERMINATION
OF THE PRODUCT GAS COMPOSITION

Component Determined	m/e of Peak Used
H ₂	2
CH ₄	15
C ₂ H ₄	27
CO	28
C ₂ H ₆	30
C ₃ H ₈	39
C ₃ H ₆	41
CO ₂	44
C ₄ ⁺	56

The nine simultaneous equations were written in accordance with equation (1). Three additional equations were used. Two, based on the m/e 16 and m/e 26 peaks, were used as checks on the analysis. The third, based on the m/e 32 peak, provided a means of determining the small quantity of air which leaked into the sample bulbs. Table VII presents the matrix of the coefficients, a_{ij} , of this set of twelve equations. The m_i terms of the equations are the respective heights of the selected peaks read from the product gas mass spectra.

Solution of the set of equations by use of a Consolidated Engineering Corporation Electrical Computer, Model 30-103 yielded the base peak height of each mixture component. Partial pressures were computed by dividing the base peak height by the pure component sensitivity.

Feed Gas Analysis.--The compositions of the feed gas samples were determined from their mass spectra in the manner described in the discussion of unicomponent peaks.

EXPERIMENTAL DATA

The objectives of this research, as established in the Statement of the Problem, were first, to determine the optimum conditions of temperature and feed gas composition for the production of high BTU gas by methane synthesis; secondly, to determine the amount of carbon deposited on the steel catalyst under these conditions; and thirdly, to investigate regeneration by air oxidation of catalyst poisoned by sulfur compounds present in the feed gas.

In order to accomplish these objectives, six series of experimental

runs were made. The data obtained from these runs are summarized in Table VIII.

The first series of runs, designated Pro, explored the possibility of promoting the formation of hydrocarbons higher than methane during synthesis by treating the steel catalyst with potassium carbonate.

The next four series of runs were made to determine the effect of temperature and of feed gas composition on the distribution of the products from synthesis. These series were given the designations 30, 40, 50, and 55, respectively. Feed gas of the same composition was used in all of the runs of a particular series, and the series designation corresponds to the percentage of carbon monoxide in this feed gas. The runs of a given series were made at different temperatures in order to determine the product composition as a function of temperature. Experimental runs were also made to investigate the use of air oxidation to remove carbon deposited on the catalyst surface and to regenerate catalyst which had been poisoned by sulfur compounds.

The final series of runs, designated Co-Th, was an exploratory investigation of a supported cobalt-thoria catalyst which was active for the synthesis of methane from carbon monoxide and hydrogen over a temperature range of 500° to 900°F.

Referring to Table VIII, in which the experimental data are summarized, columns (1) and (2) list the date and designation of each experimental run in chronological order. Experimental runs of a given series are designated by a capital letter, and each complete set of data and gas samples collected during a run (hereafter known as a data point) are indicated by arabic numerals. Thus, the designation 40-F3 would refer to the third data point taken during the sixth experimental run of series 40 in which the feed gas

contained approximately 40% carbon monoxide.

Column (3) indicates the catalyst age in hours. For those runs in which the catalyst was dropped into the hot reactor, age zero was considered to be the moment when the flow of feed gas was established over the catalyst. In the first six experimental runs in which the catalyst was introduced into the cold reactor, the catalyst was considered to be at age zero when the reactor temperature reached 700°F.

The catalyst-bed temperature and the reactor pressure are listed in columns (4) and (5). Column (6) is the ratio of column (12) to column (10), and column (7) reports the space velocity defined as the total moles of feed gas per hour per square foot of catalyst surface. The space velocity is obtained by dividing column (8), the feed gas flow rate, by the surface area of the catalyst and by 379 standard cubic feet per mol. Column (9) reports the product gas flow rate on a water-free basis.

The composition of the feed gas used is given by columns (10) through (13), and the product composition, including water, is presented in columns (14) through (23). Components which range from 0.01 to 0.05 volume percent of the product gas are listed as traces (T).

The percentage conversions of carbon monoxide to carbon dioxide and to methane are shown in columns (24) and (25), while the total carbon monoxide conversion to products is given by column (26).

The carbon balances which appear in column (27) were calculated by determining the difference between the amount of carbon which entered the reactor in the feed gas and that which left in the product gas, and by dividing this result by the amount of entrance carbon. A negative carbon balance, which indicates that more carbon entered than left the reactor, would be expected because deposition of carbon on the catalyst surface

TABLE VIII. EXPERIMENTAL DATA

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)	
Date	Run	Catalyst Age, hr	Temp., °F	Pres., atm	Feed H ₂ /CO Ratio	Space Velocity H ₂ /CO mols/hr-ft ²	Gas Flow Rate SFPH	Feed Product	Feed Composition volume percent	CO	CO ₂	H ₂	N ₂	CO	CO ₂	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	CH ₄	H ₂ O	Conversion of CO to Products, %	Total CO Converter, %	Carbon Balance, %	
Catalyst bed: 194 steel balls promoted with K ₂ CO ₃ (0.0661 ft ² of surface) - 194 brass balls.																											
6-10-55	Pro-A1*	0.3	723	31.0	2.32	0.197	4.93	4.76	30.0	0.2	69.6	0.2	29.1	68.1	0.8	0.4	T	T	T	T	T	T	1.0	2.6	1.4	5.4	+ 0.1
	2	0.8	768	31.1	2.40	0.194	4.86	4.64	29.3	0.1	70.3	0.2	27.3	69.1	1.6	0.5	T	0.4	0.1	0.1	0.1	0.1	1.0	5.1	1.5	10.7	- 0.4
	3	1.5	810	31.1	2.49	0.187	4.67	4.30	28.6	0.1	71.3	0.2	22.9	70.0	3.8	1.1	T	0.4	0.1	0.3	0.1	1.2	12.4	3.5	29.5	- 2.2	
	4	3.3	841	31.1	2.58	0.175	4.38	3.81	27.8	0.1	71.9	0.2	16.1	71.1	7.6	2.2	0.2	0.7	-	0.5	0.2	1.1	24.1	7.1	49.1	- 5.6	
	5	5.3	877	31.2	2.64	0.164	4.11	3.45	27.4	0.1	72.5	0.2	13.3	70.2	8.7	4.0	0.3	1.1	-	0.8	0.3	1.1	27.0	12.4	58.7	+ 0.7	
	6	4.8	891	31.0	2.27	0.165	4.12	3.43	30.4	0.2	69.2	0.2	17.1	69.8	8.6	4.4	0.4	1.1	0.2	0.7	0.5	1.4	23.8	12.2	58.0	+ 0.5	
	7	8.2	1000	31.1	2.27	0.208	5.22	3.61	30.4	0.2	69.2	0.2	11.9	47.7	10.1	15.3	1.5	0.5	0.4	0.2	0.1	12.5	25.6	35.7	72.5	- 1.4	
	8	8.5	1002	31.1	2.46	0.208	5.22	3.39	28.8	0.2	70.7	0.2	9.6	46.3	10.3	17.5	1.5	0.5	0.4	0.2	0.1	15.6	24.4	41.7	77.2	+ 1.0	
Leak in the feed gas panel forced discontinuance of this run. The reactor was cooled to room temperature but the catalyst was not removed.																											
Catalyst bed: Catalyst of run 30-Pro A was reused.																											
8-10-55	Pro-B1*	16.3	825	31.0	2.41	0.205	5.14	4.03	29.3	0.1	70.5	0.2	20.9	61.2	4.3	5.3	0.6	0.4	0.2	0.2	0.1	6.8	12.4	15.1	39.6	- 3.8	
	2	17.3	857	31.0	2.74	0.183	4.76	3.71	26.6	0.1	73.1	0.2	18.3	62.5	4.3	7.0	0.7	0.2	0.1	0.2	-	6.5	13.4	21.9	42.8	+ 0.6	
	3	19.3	909	31.1	2.56	0.196	4.91	3.65	28.4	0.1	71.3	0.2	17.7	58.3	5.5	9.5	0.8	0.1	0.1	0.1	-	7.5	15.5	26.8	50.1	0	
	4	20.7	967	31.0	2.46	0.194	4.85	3.30	28.8	0.1	70.9	0.2	14.0	54.8	6.3	13.1	1.0	0.3	0.2	0.1	-	9.8	16.6	34.3	53.5	- 3.1	
	5	22.2	1049	31.0	2.46	0.197	4.94	2.79	28.8	0.1	70.9	0.2	9.6	42.8	9.1	20.2	1.5	0.4	0.2	0.2	-	15.7	21.3	47.0	77.7	+ 1.5	
	6	25.4	1116	30.9	2.57	0.197	4.94	2.58	29.6	0.1	70.1	0.2	9.5	36.2	9.7	23.3	1.6	0.1	0.3	0.1	-	18.9	21.6	50.5	79.3	+ 1.2	
	7	27.8	1046	31.0	2.64	0.195	4.87	2.58	27.3	0.2	70.3	0.2	6.8	41.4	8.8	21.6	1.5	0.4	0.5	0.1	-	18.8	21.1	51.6	83.7	+ 0.1	
Catalyst bed: 194 steel balls (0.0661 ft ² of surface) - 382 brass balls.																											
8-24-55	30-A1*	6.1	823	31.0	2.46	0.200	5.03	4.34	28.8	0.1	70.9	0.2	21.9	67.2	3.0	2.2	0.2	0.4	0.1	0.3	0.1	4.3	9.5	6.9	31.7	- 7.2	
	2	8.5	889	31.0	2.92	0.195	4.84	2.66	25.4	0.1	74.3	0.2	5.7	48.7	7.3	19.4	1.4	0.2	0.3	0.2	T	16.6	19.4	51.8	84.9	- 1.8	
	3	11.3	1035	31.0	2.52	0.202	5.08	2.71	28.3	0.1	71.4	0.2	7.5	39.8	9.4	23.5	1.0	0.1	0.2	0.1	T	18.1	21.7	53.9	82.7	- 0.6	
	4	14.2	1132	31.0	2.62	0.200	5.02	2.76	27.5	0.1	72.2	0.2	8.7	41.5	8.1	23.4	0.5	T	T	T	-	17.4	19.5	56.8	79.0	+ 0.2	
	5	17.5	1096	31.0	2.47	0.208	5.23	2.92	28.7	0.1	71.0	0.2	8.1	41.8	9.6	22.4	0.9	0.1	0.2	0.1	-	15.9	22.3	52.0	79.8	+ 0.2	
	6	19.9	1002	31.0	2.57	0.202	5.07	2.79	29.6	0.1	70.1	0.2	8.1	40.9	10.6	22.3	1.2	0.2	0.2	0.1	T	16.2	23.4	49.3	82.1	- 1.1	
	7	22.0	933	31.0	2.49	0.198	4.96	2.78	28.6	0.1	71.1	0.2	7.4	45.2	10.4	18.1	1.6	0.3	0.3	0.3	0.1	16.1	24.4	42.4	82.7	- 2.8	
Catalyst bed: Catalyst of run 30-A was cooled to room temperature and allowed to remain in the reactor for 19 days.																											
Catalyst was heated to 1030°F and oxidized with 2.5 SFPH of air to 1150°F for 46 minutes.																											
9-13-55	30-Ox-A1*	19.5	1066	31.0	2.22	0.204	5.11	2.75	30.9	0.2	68.7	0.2	8.1	37.0	11.7	25.4	0.9	0.1	0.1	T	-	16.3	24.4	52.9	83.2	- 1.3	
	2	22.0	1068	30.9	2.25	0.202	5.06	2.69	30.7	0.2	68.9	0.2	7.8	36.8	11.2	25.8	0.8	0.1	0.1	T	-	17.1	23.4	53.9	83.7	- 2.4	
	3	24.5	1069	31.0	2.36	0.201	5.04	2.71	29.7	0.2	69.9	0.2	7.1	38.5	10.3	25.3	0.8	0.1	0.1	T	-	17.7	22.3	54.9	84.7	- 3.4	
	4	27.7	1066	31.0	2.36	0.210	5.25	2.76	29.7	0.2	69.9	0.2	8.2	36.9	10.0	24.9	0.8	0.1	T	-	18.8	21.7	54.1	82.1	- 2.8		

*"Cold charging method" used.

TABLE VIII (Continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)
Date	Run	Catalyst Age, hr	Temp., °F	Pres., atm	Feed Ratio, H ₂ /CO	Space Velocity, mols/hr-ft ²	Gas Flow Rate, SCFH	Feed Product	CO	CO ₂	H ₂	CO	H ₂	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	CO ₂	CH ₄	Total CO Converter, %	Carbon Balance, %	
10-14-55	40-A1*	3	1060	31.1	2.16	0.165	5.08	2.66	31.5	0.2	68.0	0.2	7.9	35.3	12.2	25.0	1.3	0.2	0.1	0.1	-	17.4	23.5	50.3	84.1	-2.5
		2	1080	31.1	1.44	0.160	4.99	2.56	40.8	0.3	58.6	0.2	12.0	20.1	22.7	29.9	1.3	0.1	0.2	0.1	-	13.2	32.8	43.4	82.6	-1.5
		3	1077	31.0	1.44	0.160	5.00	2.56	40.8	0.3	58.6	0.2	12.1	20.3	22.7	29.3	1.3	0.1	0.2	0.1	-	13.6	32.8	42.5	82.5	-2.2
10-17-55	40-B1*	7	1120	30.9	2.12	0.159	4.98	2.64	31.9	0.2	67.7	0.2	8.9	34.0	12.7	26.4	0.8	0.1	0.1	T	-	16.6	25.4	52.7	82.4	-0.7
		2	1042	31.0	1.44	0.158	4.93	2.54	40.8	0.3	58.7	0.2	13.4	20.4	21.1	30.2	0.9	0.1	0.1	T	-	13.4	31.0	44.5	80.3	-2.1
		3	1143	31.0	1.45	0.159	4.97	2.59	40.7	0.3	58.8	0.2	13.9	19.6	21.5	30.1	1.0	0.1	0.1	T	-	13.3	31.6	44.3	79.6	-0.4
12-14-55	40-C1	1	816	31.2	1.50	0.162	5.07	4.81	39.9	0.3	59.6	0.2	39.2	56.8	0.7	1.0	T	0.1	0.1	T	-	1.7	1.7	2.5	5.1	0
		2	958	31.1	1.44	0.159	4.97	3.48	40.8	0.3	58.6	0.2	27.1	44.5	8.5	8.6	0.8	0.4	0.3	0.4	0.1	0.1	16.1	16.2	48.8	-8.4
		3	1092	31.0	1.44	0.159	4.97	2.52	40.8	0.3	58.6	0.2	13.1	24.6	19.7	24.7	1.6	0.3	0.3	0.2	T	15.1	29.5	37.0	80.3	-7.1
		4	1028	31.0	1.46	0.162	5.05	2.68	40.5	0.3	59.0	0.2	13.2	23.7	19.8	25.8	1.6	0.2	0.3	0.2	T	14.9	29.7	38.8	80.1	-4.9
1-17-56	40-D1	2	1104	31.1	1.51	0.162	5.05	2.49	39.7	0.3	59.7	0.2	10.2	18.8	21.4	32.7	0.8	T	T	-	-	15.6	31.3	47.7	85.1	-3.4
		3	1106	30.9	1.54	0.160	5.00	2.50	39.1	0.3	60.4	0.2	10.0	19.2	21.1	33.0	0.6	-	-	-	-	15.7	31.3	48.9	85.2	-2.9
		3	1248	31.0	1.75	0.167	5.22	2.78	21.0	0.2	78.7	0.1	4.0	48.2	3.1	22.9	0.1	T	-	-	-	21.6	9.8	73.2	87.3	-3.6
1-18-56	40-E1	2	1266	31.0	1.48	0.168	5.22	2.94	19.6	0.2	80.1	0.1	3.8	53.3	2.2	20.9	0.1	T	-	-	-	19.6	7.7	74.1	86.4	-4.1
		3	1105	31.0	1.54	0.160	4.99	2.50	39.3	0.3	60.2	0.2	10.5	20.0	20.2	32.9	0.5	0.1	-	-	-	15.4	30.3	49.3	84.2	-3.0
		3	271.5	31.0	1.48	0.165	5.11	2.56	40.1	0.3	59.4	0.2	11.6	19.1	20.6	32.6	0.5	T	-	-	-	15.3	30.2	47.7	83.0	-3.6
1-20-56	40-F1	2	1093	30.9	1.54	0.161	5.03	2.47	39.3	0.2	60.3	0.2	9.5	20.0	21.0	32.1	0.9	0.1	0.1	T	-	15.9	31.1	47.5	85.9	-4.0
		2	1092	30.9	1.54	0.161	5.03	2.47	39.2	0.2	60.4	0.2	9.5	19.4	21.1	32.9	0.6	T	0.1	-	-	16.0	31.4	48.9	85.8	-3.5
		3	1096	31.0	1.53	0.256	8.00	4.03	39.4	0.2	60.2	0.2	10.6	20.4	20.4	32.1	0.6	0.1	0.1	-	-	15.3	30.8	48.2	84.0	-2.7
		4	1098	31.0	1.56	0.257	8.04	4.06	39.0	0.2	60.6	0.2	10.9	21.2	19.8	31.7	0.7	T	0.1	T	-	15.3	30.0	48.1	83.5	-2.7
1-24-56	40-G1	2	1155	31.0	1.52	0.161	5.04	2.59	39.5	0.2	60.1	0.2	12.4	20.4	19.9	32.3	0.4	T	-	-	-	14.2	30.1	48.8	81.3	-1.1
		3	1151	31.0	1.51	0.161	5.04	2.57	39.8	0.1	59.8	0.2	11.9	20.0	20.1	32.9	0.4	T	-	-	-	14.4	29.9	49.0	82.3	-2.1
		3	1198	31.0	1.53	0.162	5.04	2.64	40.0	0.1	59.7	0.2	14.1	21.7	18.4	31.5	0.3	-	-	-	-	13.6	27.7	47.4	78.8	-2.7
1-26-56	40-H1	2	1055	31.0	1.48	0.162	5.07	2.50	40.2	0.1	59.4	0.2	9.5	19.9	21.9	31.1	1.4	T	0.2	T	-	15.6	31.5	44.8	86.3	-4.9
		3	1049	31.0	1.48	0.163	5.09	2.51	40.2	0.1	59.4	0.2	9.6	19.8	22.0	31.2	1.3	0.1	0.2	T	-	15.6	31.7	45.0	86.2	-4.8
2-2-56	50-A1	1	1092	31.1	.98	0.101	5.04	2.57	50.2	0.2	49.3	0.3	13.0	9.1	34.0	33.3	1.0	T	0.1	T	-	9.1	37.9	37.2	85.5	-8.2
		2	1085	31.0	.98	0.101	5.05	2.60	50.1	0.2	49.4	0.3	13.5	9.0	33.8	33.4	1.0	T	0.1	T	-	8.6	37.9	37.4	84.9	-7.3
2-6-56	50-B1	1	1227	31.0	1.01	0.101	5.06	2.71	49.6	0.3	49.8	0.3	18.1	9.0	30.0	34.2	0.2	-	-	-	-	8.0	35.1	40.0	78.8	-3.7
		2	1219	31.0	1.00	0.102	5.10	2.72	49.8	0.3	49.6	0.3	18.3	9.1	29.8	33.8	0.2	-	-	-	-	8.3	34.8	39.4	78.6	-4.3
2-8-56	50-C1	1	1153	31.0	.99	0.100	5.00	2.61	50.0	0.3	49.4	0.3	15.1	8.5	32.8	34.4	0.5	0.1	-	-	-	8.1	37.3	40.1	82.9	-5.7
2-14-56	50-D1	1	880	31.0	.96	0.099	4.98	4.40	50.7	0.3	48.7	0.3	48.3	42.7	2.3	2.3	0.5	0.2	0.1	0.2	0.1	3.0	4.2	4.1	13.0	-0.3
2-17-56	50-E1	2	1051	31.1	.97	0.100	5.00	2.69	50.4	0.3	49.0	0.3	15.7	16.3	31.0	24.5	1.8	0.2	0.6	0.2	0.1	9.2	36.1	28.6	81.8	-10.0
		2	1070	31.0	.97	0.101	5.06	2.71	50.4	0.3	49.0	0.3	16.6	16.4	30.1	24.3	1.8	0.3	0.5	0.1	0.1	9.3	35.3	28.5	80.5	-10.0

TABLE VIII (Concluded)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)	(21)	(22)	(23)	(24)	(25)	(26)	(27)		
Date	Run	Catalyst Age, hr	Temp., °F	Pres., atm	Feed Ratio H ₂ /CO	Space Velocity mols/hr-ft ²	Space Velocity mols/hr-ft ²	Gas Flow Rate SCFH	Feed Product	CO	CO ₂	H ₂	N ₂	CO	H ₂	CO ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂	C ₂ H ₆	C ₃ H ₈	C ₄	H ₂ O	Conversion of CO to Products, %	Total CO Conver., %	Carbon Balance, %	
3-6-56	55-A1	1.6	1151	31.0	0.78	0.100	5.02	2.68	55.7	0.2	43.8	0.3	17.5	6.4	37.1	31.7	0.5	-	0.1	-	-	-	-	6.2	37.8	36.4	82.2	-11.2
Catalyst bed: 388 steel balls (0.1532 ft ² of surface) - 1164 brass balls.																												
3-7-56	55-B1	1.5	1210	31.0	0.78	0.099	4.98	2.72	55.8	0.2	43.6	0.3	21.1	7.0	35.2	31.0	0.2	-	-	-	-	-	-	5.9	36.7	36.3	79.1	-10.1
2	2.2	1208	31.0	0.78	0.099	4.98	2.74	55.8	0.2	43.6	0.3	20.3	6.8	35.2	31.6	0.2	-	-	-	-	-	-	-	5.3	36.6	36.8	78.9	-9.3
3-10-56	55-C1	1.4	1074	31.0	0.78	0.100	5.00	2.67	55.9	0.2	43.6	0.3	17.4	11.5	35.2	26.0	1.0	0.1	0.1	0.1	-	-	-	8.2	36.7	27.1	81.9	-15.6
Catalyst bed: 200 cobalt-thoria catalyst pellets (1/8-in. diam. x 1/8-in. long cylinders) - 400 copper cylinders (same dimensions).																												
2-22-56	CO-Th1	3.8	505	30.0	2.35	0.148	4.90	29.7	0.2	69.8	0.2	29.5	68.3	0.4	0.3	0.1	-	-	-	-	-	-	-	1.1	1.3	1.1	2.4	0
2	4.8	543	30.0	2.35	0.165	5.08	29.7	0.2	69.8	0.2	27.0	66.2	0.9	1.8	0.1	0.1	-	-	-	-	-	-	-	3.4	2.9	5.6	14.8	-3.6
3	5.5	645	30.0	2.44	0.165	5.08	29.7	0.2	70.6	0.2	0.4	10.2	10.5	43.5	0.3	0.1	-	-	-	-	-	-	-	34.7	19.2	79.3	99.2	-0.1
4	6.0	702	30.0	2.44	0.165	5.10	1.81	29.0	0.2	70.6	0.2	0.4	11.9	10.5	42.9	0.4	0.1	-	-	-	-	-	-	35.4	19.4	79.0	99.3	+0.4
5	9.1	838	30.0	2.42	0.166	5.15	1.88	29.2	0.2	70.5	0.2	1.1	13.0	10.6	42.1	0.4	-	-	-	-	-	-	-	32.5	19.6	77.7	97.9	+0.2
3-20-56	30-B1	1.1	878	31.0	2.48	0.159	4.96	4.84	28.7	0.1	71.0	0.2	27.9	70.1	0.3	0.7	-	-	-	-	-	-	-	0.6	1.2	2.6	4.8	0
2	3.9	1064	31.0	2.36	0.165	5.08	2.60	30.0	0.1	69.7	0.2	6.7	34.7	11.9	27.3	1.0	0.1	-	-	-	-	-	-	18.0	24.9	57.0	86.4	+1.0
3	4.3	1065	31.0	2.36	0.165	5.08	2.61	30.0	0.1	69.7	0.2	6.7	34.7	11.5	27.4	1.0	0.1	-	-	-	-	-	-	18.3	24.1	57.1	86.0	+0.2
4	6.2	1130	31.0	2.35	0.166	5.07	2.59	29.8	0.1	69.9	0.2	7.1	34.2	10.9	28.4	0.5	0.1	-	-	-	-	-	-	18.7	22.9	60.0	85.1	0
5	6.6	1131	31.0	2.35	0.166	5.07	2.59	29.8	0.1	69.9	0.2	7.1	34.3	10.9	28.3	0.5	0.1	-	-	-	-	-	-	18.6	23.0	59.8	85.1	-0.2
6	10.5	1202	31.0	2.43	0.160	5.02	2.76	29.1	0.1	70.7	0.2	9.5	38.9	9.2	29.5	0.5	-	-	-	-	-	-	-	16.4	20.9	57.8	78.5	+1.5
3-21-56	30-Ox-B1	24.5	1083	31.0	2.29	0.161	5.04	2.65	30.6	0.2	69.0	0.2	7.7	35.3	11.6	26.8	0.7	0.1	-	-	-	-	-	17.4	24.0	55.8	83.9	-1.3
Catalyst bed: Used catalyst from run 30-B which was cooled overnight from 1204° to 1100°F. Sulfur trap by-passed at 25.2 hours.																												
3-22-56	2	33.4	1083	31.0	2.31	0.160	5.00	2.98	30.1	0.2	69.5	0.2	7.0	34.7	11.6	27.4	0.8	0.1	-	-	-	-	-	18.1	24.3	57.2	85.4	-0.4
3	60.7	1078	31.0	2.35	0.159	4.98	2.74	29.8	0.2	69.9	0.2	9.2	40.0	10.1	22.8	1.2	0.1	0.2	-	-	-	-	-	16.3	22.4	50.4	79.7	-0.8
3-23-56	4	72.7	1093	31.0	2.18	0.164	5.12	2.77	31.3	0.1	68.4	0.2	9.8	36.5	11.1	24.5	1.1	0.1	0.1	-	-	-	-	16.4	23.0	50.7	79.8	-0.5
Catalyst oxidized with 3.3 SCFH of air to 1070°F for 50 minutes (0.3% CO ₂ in off-gas when oxidation stopped).																												
5	76.5	1077	31.0	2.33	0.160	5.02	2.59	29.9	0.1	69.7	0.2	6.8	35.5	10.9	26.8	1.1	0.1	0.1	-	-	-	-	-	18.4	23.0	56.5	85.6	-0.9

TABLE IX

CARBON DEPOSITION

Run	Average Temperature, °F	Minutes at Temperature	Average % CO + CO ₂ in Feed Gas	Carbon in CO + CO ₂ Feed, grams	Carbon Deposited on Catalyst, grams	Wt. % of C Fed Deposited as Solid Carbon
40-A	1078	228	40.2	112.7	1.45	1.3
40-B	1142	326	41.0	160.4	1.4	0.9
40-C	1030	140	40.8	68.6	3.6	5.3
40-D and E	1108	300	39.8	143.0	2.3	1.6
40-E	1093	305	39.4	144.3	2.7	1.9
40-G	1175	359	39.8	171.5	1.9	1.1
40-H	1053	136	40.3	65.8	2.45	3.7
50-A	1088	150	50.4	90.7	7.7	8.5
50-B	1223	141	50.0	84.6	4.1	4.9
50-C	1153	163	50.4	98.6	5.9	6.0
50-E	1031	108	50.7	65.2	8.4	12.9
55-A	1151	77	56.4	52.1	6.85	13.2
55-B	1209	72	56.2	48.7	5.6	11.5
55-C	1074	50	56.1	33.7	6.0	17.8

was observed in every run.

The manner in which the data summarized in Table VIII were calculated from the original experimental data is illustrated in detail in a sample calculation included in the Appendix.

A determination of the amount of carbon deposited on the catalyst surface during synthesis was one of the primary objectives of this research. While the carbon balance, column (27) of Table VIII, provides a measure of the amount of carbon deposition, the accuracy of the carbon balance is affected by any errors which occur in the determination of the feed and product gas compositions or flow rates.

A more accurate method of determining the amount of carbon deposition was used in the experimental runs of series 40, 50, and 55. Each run was started with a fresh batch of catalyst, and operating conditions were maintained constant throughout the course of a run. Removal of the catalyst bed from the reactor at the end of each run made it possible to weigh the amount of deposited carbon. A summary of the data on carbon deposition is presented in Table IX.

DISCUSSION OF EXPERIMENTAL ERRORS

Temperature Measurement and Control

The scale of the Brown Electronik temperature recorder was graduated for the temperature range 700° to 1300°F when using iron-constantan thermocouples. The recorder was checked against a calibrated portable potentiometer and was found to be accurate within $\pm 1^\circ\text{F}$ over the temperature range of the instrument.

A 24-gauge iron-constantan thermocouple was used to measure the catalyst-

bed temperature. Four such thermocouples were fabricated from matched iron-constantan wire and were checked against each other at a temperature of 1100°F. The temperatures indicated by the couples agreed to within 2°F. It was standard procedure to change couples at least once during each experimental run to guard against the possibility of couple failure.

Because of the large exothermic heat of reaction of the methane synthesis, an appreciable temperature gradient existed in the catalyst bed. Typical temperature profiles of the catalyst bed during synthesis are shown in Figures 8 and 9. A vertical temperature traverse of the catalyst bed was made for each data point of an experimental run, and the maximum temperature observed was reported as the catalyst-bed temperature.

During a period of data-taking, the maximum catalyst-bed temperature never varied more than 1°F. At any temperature not in the reaction threshold region (900° to 1040°F), a 1°F temperature change had negligible effect on the product composition.

Pressure Measurement and Control

The pressure gauge used to measure the reactor pressure was checked against a dead-weight tester. The maximum error over the pressure range 0 to 450 psig was 2 psi. However, at 441 psig, the pressure at which the experimental runs were made, no error was observed.

Careful control of the nitrogen loading in the dome of the reactor back pressure regulator made it possible to maintain the reactor pressure within 2 psi of the desired value. The change in the product composition caused by a 2-psi deviation from the desired reactor pressure was imperceptible.

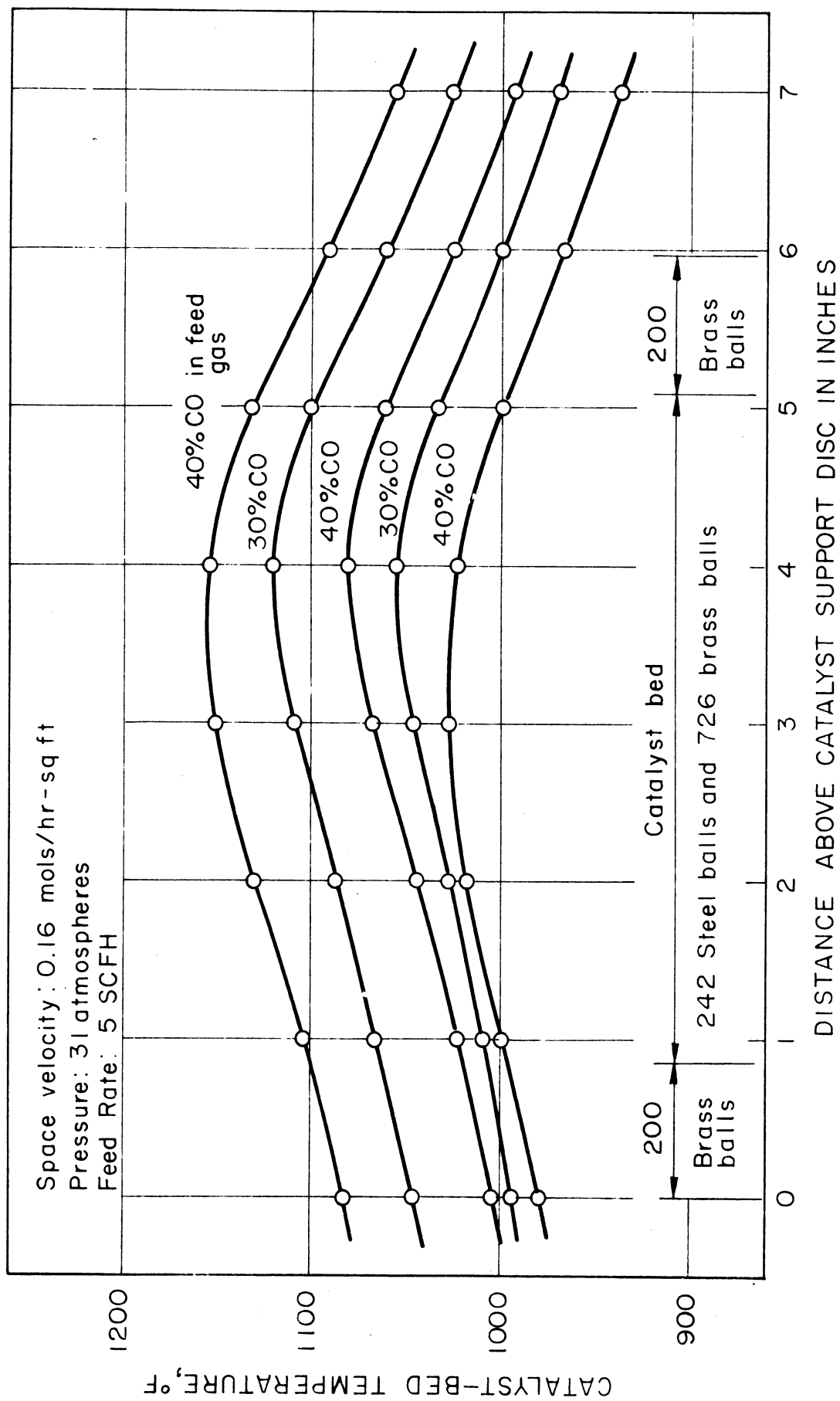


Figure 8. Temperature Profiles of the Catalyst Bed Containing 242 Steel Balls.

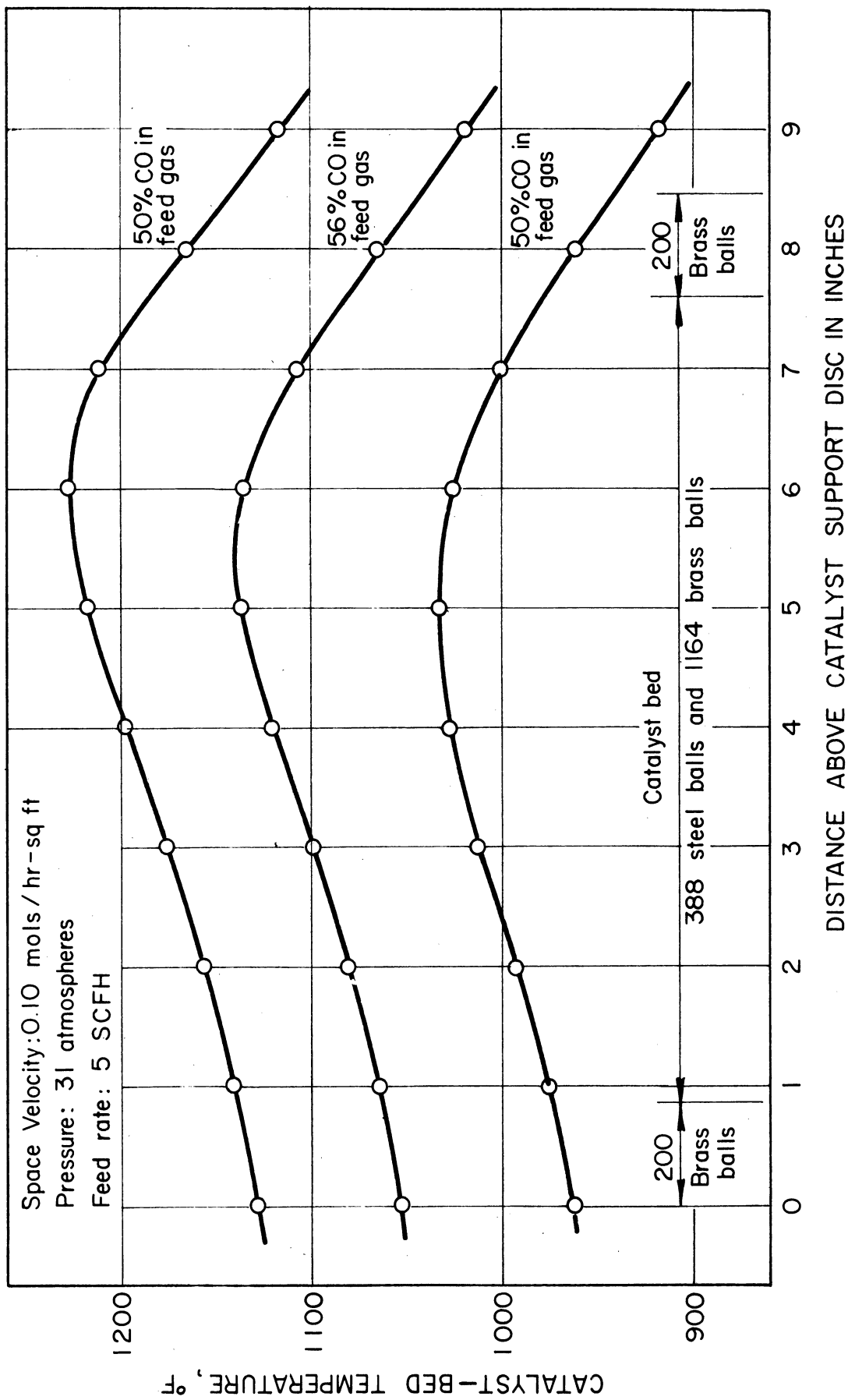


Figure 9. Temperature Profiles of the Catalyst Bed Containing 388 Steel Balls.

Flow Rate Measurement and Control

Flow rates were measured and were set by timing one complete revolution of the wet-test meter (0.1 SCF of gas). The wet-test meter was checked against a 0.1 cubic foot bottle, and no error could be detected. The maximum error in timing a revolution of the meter was less than 1/2 second. Three observations were made consecutively and the results averaged. Using the smallest time reading taken, 62 seconds, the maximum timing error is calculated to be $0.5 \times 100/3 \times 62 = 0.27\%$.

For each data point, the product and feed gas flow rates were measured immediately prior to collecting the respective gas samples for mass spectrometer analysis. A period of less than 30 minutes elapsed between the collection of the product and the feed gas samples, and during this interval all operating conditions were maintained constant.

The maintenance of constant feed gas flow rates for prolonged periods was not difficult. Any variation in either the hydrogen or the carbon monoxide flow rate was indicated by a change in the position of the pointers of the Barton gauges. Adjustment of the metering valves so as to return the pointers to their original position, usually returned the flow rates of the gas streams to their desired values. Reference to column (8) of Table VIII shows that seldom did the total feed gas flow rate vary by more than 3% from 5.0 SCFH. The resultant change in the space velocity had little effect on the product gas composition (see Figure 16).

More important, however, was a change in the feed gas composition (see Figures 17 through 20). In several of the early runs of the research program, appreciable changes in the carbon monoxide content of the feed gas occurred. However, as experience in operating the experimental equipment was gained, it was possible to maintain the feed gas at a desired composi-

tion for the duration of a run. In the experimental runs of series 40, 50, 55, and Co-Th, the carbon monoxide concentration of the feed gas deviated by less than $\pm 2\%$ from the average. While such a variation produced a measurable change in the product composition, this change was not appreciable.

Mass Spectrometer Analysis

The accuracy obtainable in the analysis of gas mixtures using the CEC Mass Spectrometer is dependent upon the stability of the instrument and the purity of the gas standards. The maximum accuracy of the instrument has been calculated to be 0.2% of component composition by the manufacturer, but in practice a prohibitive amount of work may be required to obtain such accuracy.

Care was taken in obtaining the gas analyses for this research, because it was hoped that an accurate determination of the feed and product gas composition in conjunction with careful measurements of the gas flow rates would make possible the calculation of a carbon balance around the reactor which would give a good indication of the quantity of carbon deposited in the catalyst bed.

Pure component sensitivities and cracking patterns were determined for each group of gas samples analyzed. Two standard mixtures containing hydrogen, carbon monoxide, methane, and carbon dioxide (these four components constitute approximately 98% of the product gas) were made up and were analyzed periodically as a check on the accuracy of the analyses obtained from the mass spectrometer. Typical analyses of the standard mixtures are presented in Table X. On the basis of these periodic checks, it is believed that throughout the course of the research, the product and feed gas analyses were correct to within 1.5% of component composition.

TABLE X
ANALYSES OF THE STANDARD MIXTURES

	Actual Composition mol %	Composition by Mass Spec. mol %
<u>Mixture I</u>		
H ₂	48.74	48.66
CH ₄	25.96	26.00
CO	10.16	10.22
CO ₂	15.14	15.12
<u>Mixture II</u>		
H ₂	22.07	21.96
CH ₄	28.62	28.84
CO	20.01	19.84
CO ₂	29.30	29.36

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental runs of this research constitute a further evaluation of carbon steel (Cl013) as a catalyst for the methanization of carbon monoxide and hydrogen. Of particular interest was the determination of the optimum conditions of temperature and feed gas composition required for the synthesis of a high BTU gas. Information concerning the amount of carbon deposition on the catalyst and also a study of catalyst regeneration was of primary importance. A discussion of the six series of experimental runs, which investigated these and other relevant subjects, follows a section concerning some of the thermodynamic aspects of methane synthesis.

Methane Synthesis

The predominant reaction in the synthesis of methane from carbon monoxide and hydrogen is usually represented by the equation



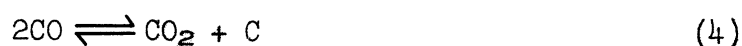
and is rapid in the presence of active catalysts at temperatures above 250°C. Catalysts used for the synthesis also promote the water-gas shift reaction



which produces carbon dioxide by interaction of water vapor, formed according to equation (2), and unconverted carbon monoxide. Both reactions are reversible, and from known equilibrium constants it is possible to calculate the composition of the gas which would be produced if various mixtures of carbon monoxide and hydrogen were allowed to come to equilibrium at constant pressure and temperature. The results of such calculations²⁴ are shown in Figure 10 to illustrate the effect of temperature, pressure, and H₂/CO ratio of the feed gas on the composition of a product gas which satisfies both the methane and the water-gas equilibria.

It can be seen from Figure 10 that the equilibrium concentration of methane is greater at low temperatures and high pressures. This would be expected in view of the decrease in volume and the evolution of heat which occur in the methane reaction. As the H₂/CO ratio of the feed gas is reduced, much larger percentages of carbon dioxide appear in the product gas, while the amount of unused hydrogen is decreased.

During synthesis at high temperatures and low H₂/CO ratios, free carbon can be deposited on the catalyst according to the equation



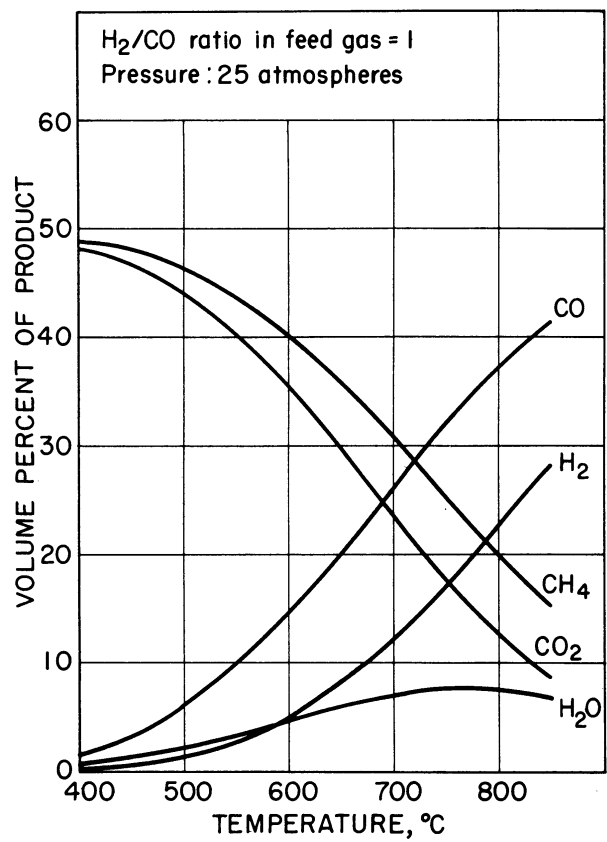
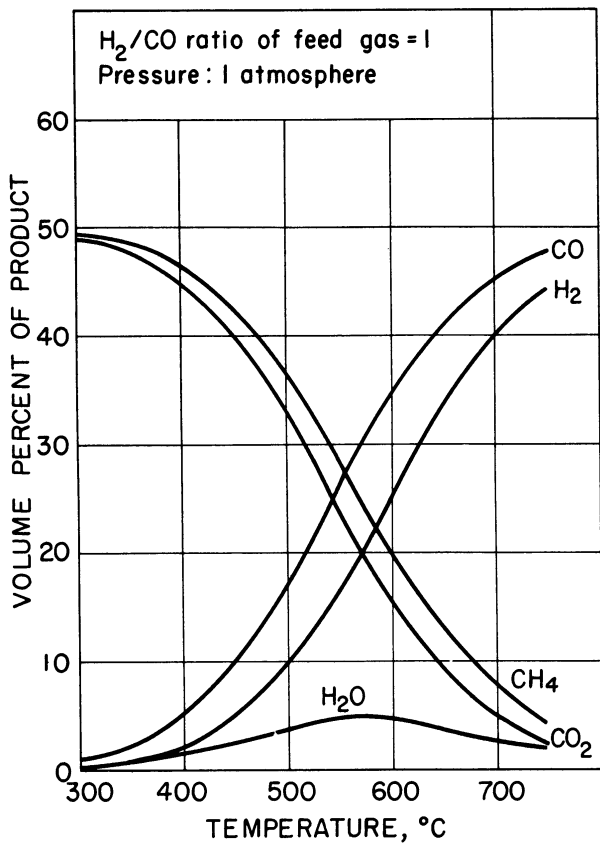
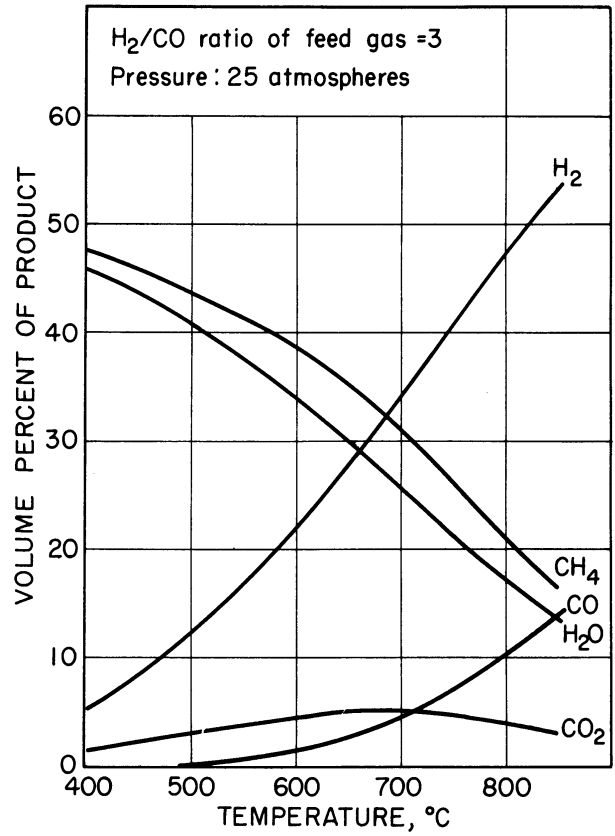
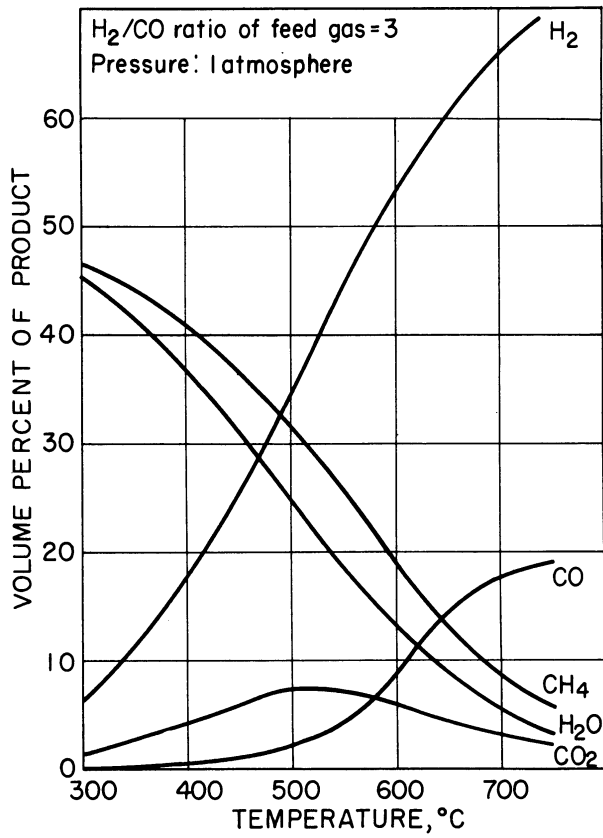


Figure 10. Effect of Temperature, Pressure, and Feed H₂/CO Ratio on the Composition of the Product Gas Which Satisfies Both the Methane and the Water-Gas Equilibria.

[Other equations may be used to describe the appearance of carbon, but all of them can be obtained by various combinations of equations (2), (3), and (4).] In experimental runs with steel catalyst, deposition of free carbon has been observed whenever the H_2/CO ratio of the feed gas used was lower than three.

For synthesis conditions at which carbon deposition would be expected, it is possible to determine the theoretical product gas composition which simultaneously satisfies the methane, the water-gas shift and the carbon equilibria, provided equilibrium constants for equation (4) are known. Values for the carbon equilibrium constants depend upon the nature of the carbon formed, and it makes considerable difference in the calculated equilibrium product composition whether the equilibrium form of the carbon is graphite, a more active metastable carbon, or perhaps a metal carbide.

Equilibrium calculations predict only the composition of the product gas which is theoretically possible from the standpoint of thermodynamics. The composition of the product which actually would be formed under a given set of reaction conditions is dependent upon many factors; the rates of reaction on the catalyst surface, the temperature distribution through the catalyst bed, the rates of mass transfer to and from the catalyst surface; and must necessarily be determined by experiment.

Promotion of the Steel Catalyst with Potassium Carbonate

The use of alkali as a promoter for the production of higher-molecular-weight hydrocarbons in the Fischer-Tropsch synthesis of liquid fuels is well known.⁷ Smith⁵⁸ studied the effect of composition and of surface treatments such as carburizing and nitriding on the activity of the steel catalyst for methane synthesis. However, the use of alkali as a promoter for the produc-

tion of higher hydrocarbons with the steel methanization catalyst had not been investigated. Consequently, before the main research was begun, two exploratory runs (Pro-A, Pro-B) were made to investigate the effect of potassium carbonate as a catalyst promoter. An increase in the yield of ethane and other light hydrocarbons, without a reduction in the conversion of carbon monoxide to methane, would result in a direct increase in the heating value of the product gas.

The steel catalyst of run Pro-A was promoted with potassium carbonate, introduced into the reactor, and heated to temperature overnight with feed gas flowing over the catalyst. A series of data points were taken at increasing temperature until a leak in the feed gas panel forced termination of the run. The reactor was allowed to cool to room temperature, and the catalyst bed was left in place. Run Pro-B was a duplication of run Pro-A to determine the effect of reheating the promoted catalyst.

During heat-up of the reactor for run Pro-A, liquid hydrocarbons were formed at temperatures below 700°F. However, at higher temperatures the formation of liquid hydrocarbons was not observed.

A comparison of the amount of methane formed in runs Pro-A, Pro-B, and 30-A is presented in Figure 11. Run 30-A was conducted in the same manner as runs Pro-A and Pro-B except that the steel catalyst used was not promoted. Figure 11 shows that smaller amounts of methane were produced in runs Pro-A and Pro-B with promoted catalyst than in run 30-A using unpromoted catalyst at temperatures above 1000°F where steel is most active as a methanization catalyst.

The amount of C₂⁺ hydrocarbons formed in runs Pro-A, Pro-B, and 30-A are compared in Table XI. This comparison shows that the quantity of C₂⁺ hydrocarbons produced during synthesis are not appreciably increased by

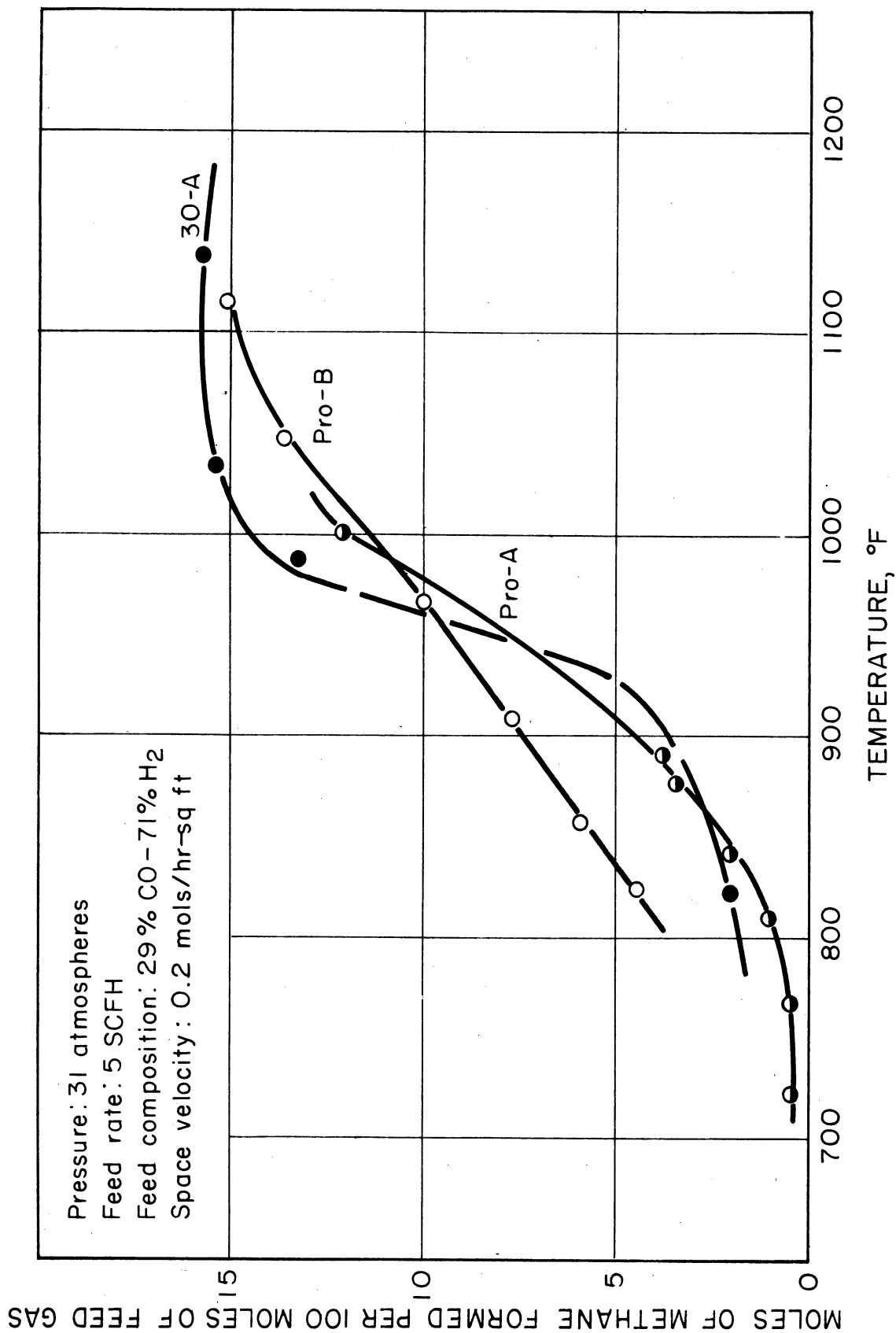


Figure 11. Comparison of the Amount of Methane Formed in Runs Pro-A, Pro-B, and 30-A.

TABLE XI

COMPARISON OF THE AMOUNT OF C₂⁺ HYDROCARBONS
FORMED IN RUNS PRO-A, PRO-B, AND 30-A

Temperature, °F	Moles of C ₂ ⁺ Hydrocarbons Produced per 100 Moles of Feed Gas		
	Pro-A	Pro-B	30-A (Catalyst Not Promoted)
723	0.2		0
768	0.4		
810	0.9		
823			1.0
825		1.1	
841	1.4		
857		1.0	
877	2.1		
891	2.1		
909		1.0	
967		1.3	
989			1.4
1002	1.6		
1035			0.9
1049		1.5	
1116		1.5	
1139			0.4

promoting the steel catalyst with potassium carbonate. The slight increase in C₂⁺ yield observed in runs Pro-A and Pro-B would not compensate for the reduced amount of methane formed in these runs.

No effort was made in these exploratory runs to determine the amount of potassium carbonate on the catalyst surface, though the surface appeared well coated. The use of smaller or larger amounts of potassium carbonate might possibly prove to be more advantageous. However, the results of runs Pro-A and Pro-B did not appear sufficiently promising to warrant further work on the subject, and all subsequent runs were made with unpromoted steel catalyst.

Effect of Reaction Conditions on the Product Composition

Four series of experimental runs (series 30, 40, 50, 55) were made to

investigate the effect of various reaction conditions on the composition of the product gas from synthesis. The results of these runs served as the basis for evaluating the optimum operating conditions for the synthesis of a high BTU gas from carbon monoxide-hydrogen mixtures using carbon steel (C1013) as catalyst.

Effect of Temperature.—The effect of temperature on the composition of the product gas from synthesis was determined for four different compositions of feed gas in the experimental runs of series 30, 40, 50, and 55. The results of these series of runs which covered the temperature range 800° to 1250°F are presented in Figures 12 through 15 according to the following schedule.

<u>Series</u>	<u>Runs Used</u>	<u>Approximate Feed Gas Composition</u>	<u>Presented in Figure</u>
30	30-B	30% CO - 70% H ₂	12
40	40-C,D,F,G,H	40% CO - 60% H ₂	13
50	50-A,B,C,D,E	50% CO - 50% H ₂	14
55	55-A,B,C	56% CO - 44% H ₂	15

With a feed gas of 30% carbon monoxide and 70% hydrogen the amount of carbon deposited on the catalyst during synthesis was not appreciable. Operation for periods of over 100 hours was possible without plugging the catalyst bed with carbon. All of the data shown in Figure 12 were collected in a single extended run, 30-B. After the first data points were taken at the lowest temperature of the run, steady-state conditions were re-established at a higher temperature, and the next set of data was obtained. This procedure was repeated until the desired temperature range was traversed.

The temperature traverses shown in Figures 13, 14, and 15 were obtained in a somewhat different manner. An increased amount of carbon deposition

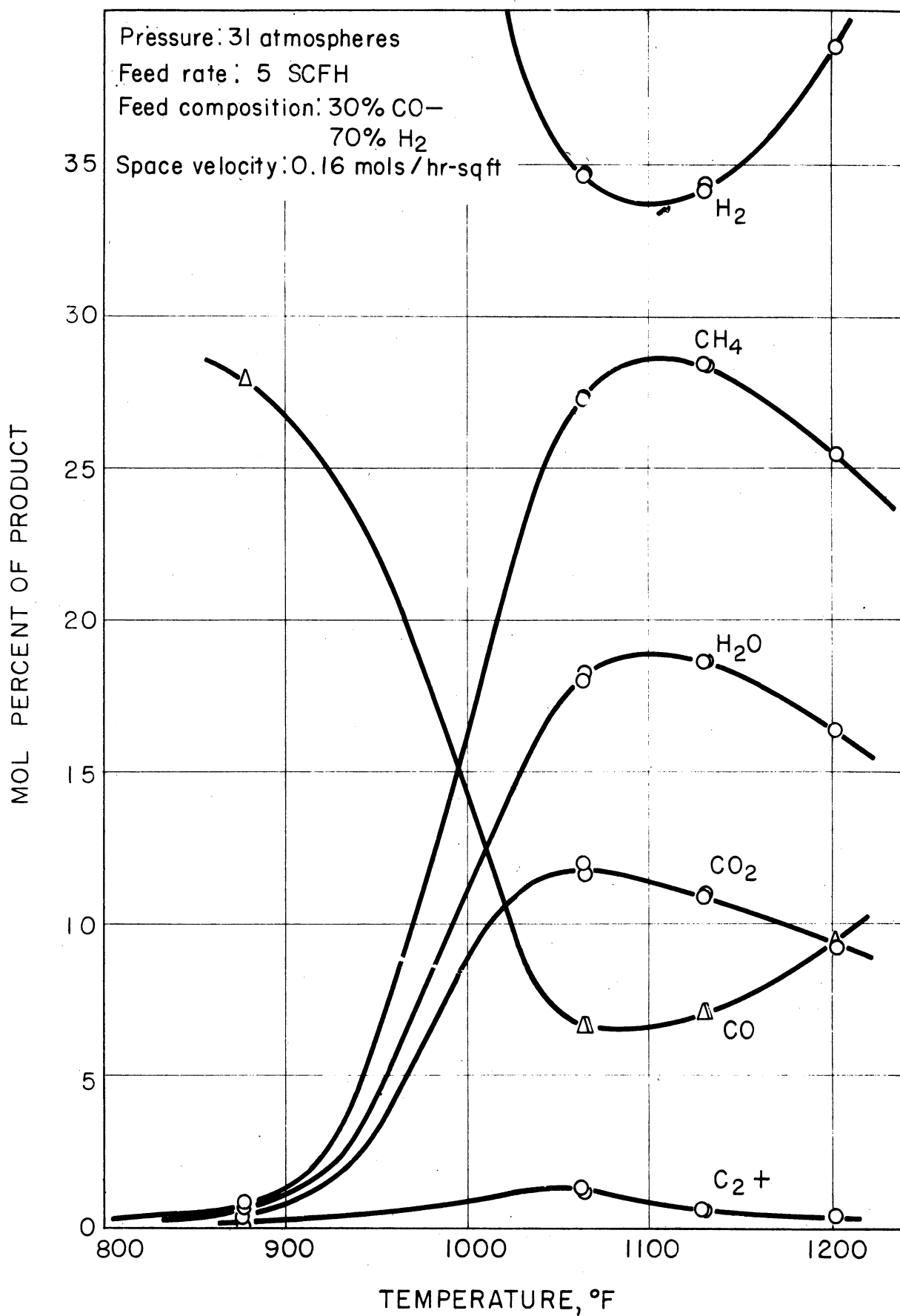


Figure 12. Effect of Temperature on the Composition of the Product Gas Obtained from a Feed of 30% CO - 70% H₂.

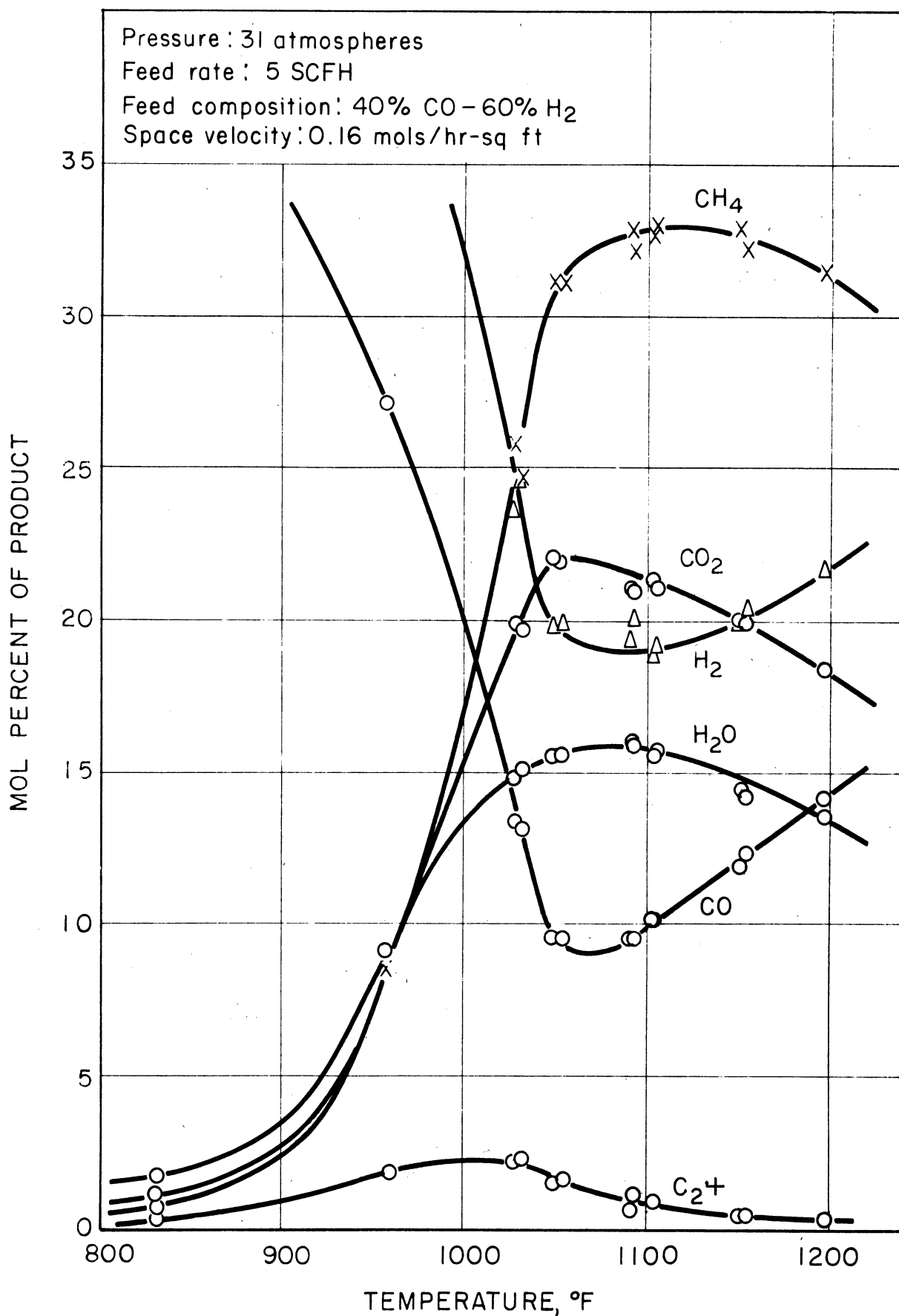


Figure 13. Effect of Temperature on the Composition of the Product Gas Obtained from a Feed of 40% CO - 60% H₂.

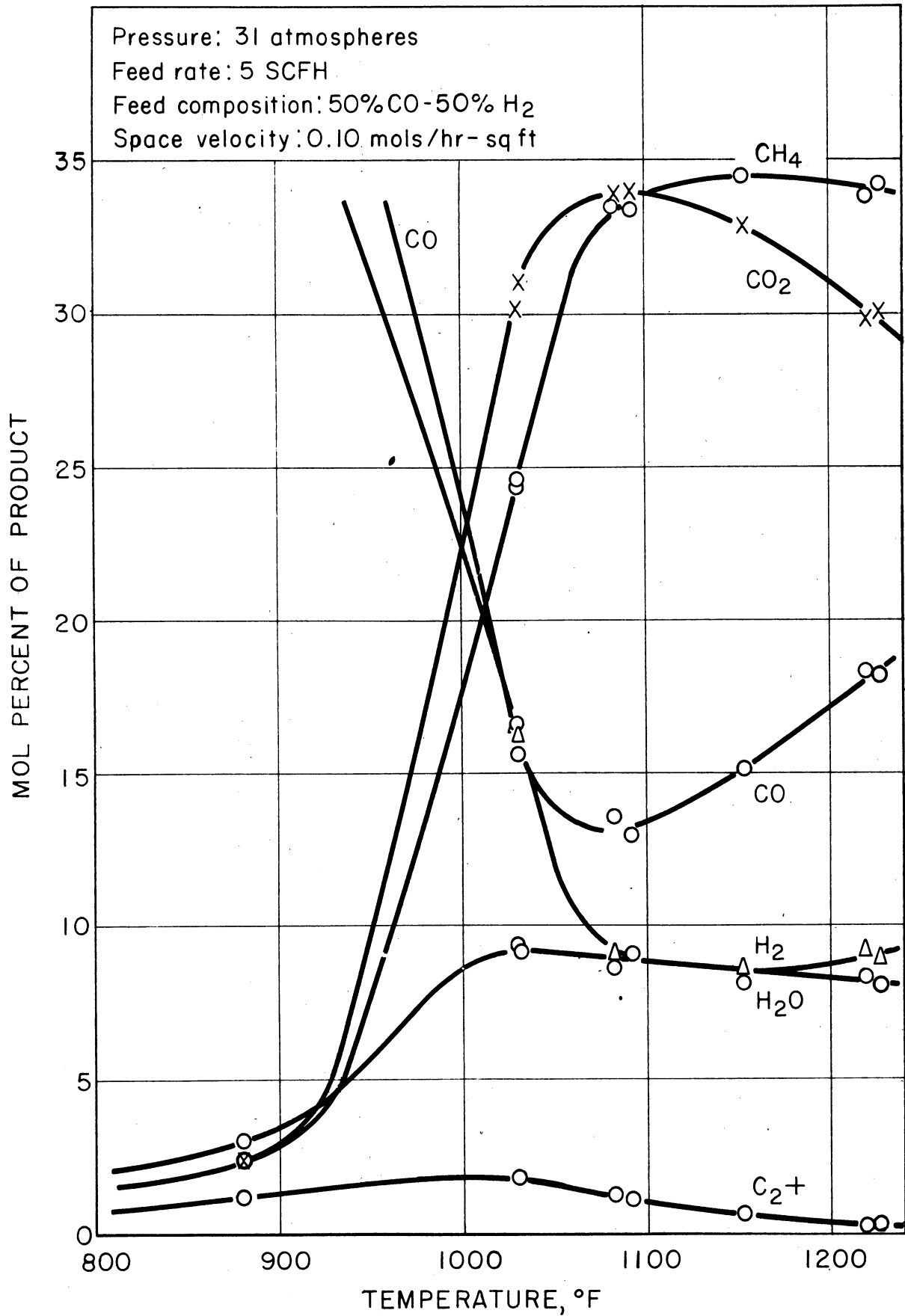


Figure 14. Effect of Temperature on the Composition of the Product Gas Obtained from a Feed of 50% CO - 50% H₂.

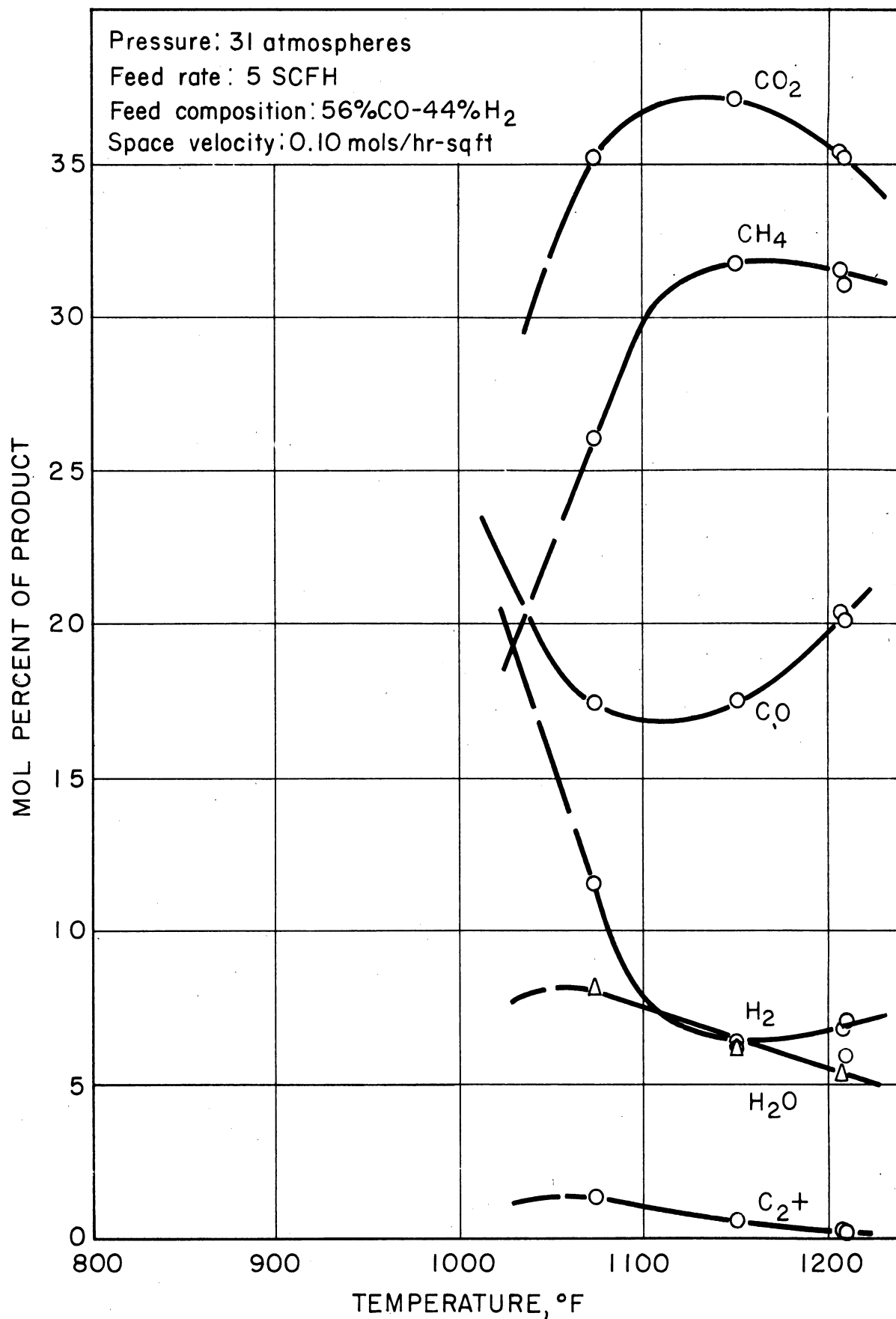


Figure 15. Effect of Temperature on the Composition of the Product Gas Obtained from a Feed of 56% CO - 44% H₂.

accompanied the use of feed gas containing more than 30% carbon monoxide. In order to measure the amount of deposited carbon, the data at each temperature of the traverses were obtained in separate runs. At the end of each run, the catalyst bed was removed from the reactor, and any carbon which had deposited on the catalyst was weighed.

From Figures 12 through 15, it can be seen that the steel catalyst exhibits a large increase in its ability to catalyze the reaction between carbon monoxide and hydrogen to form methane, water, and carbon dioxide as the temperature is increased from 900° to 1040°F. The catalyst activity, as measured by the conversion of carbon monoxide and hydrogen to products, reaches a maximum at 1100° to 1150°F, depending upon the feed gas composition, and then declines with a further increase in temperature.

It has been shown previously (see Figure 10) that from a thermodynamic standpoint the production of methane from hydrogen and carbon monoxide is favored by low temperatures and high pressures. On this basis, it would be expected that 700°F should be a better reaction temperature than 1100°F. At 700°F, however, reaction rates are so slow on the steel catalyst that the conversion of carbon monoxide and hydrogen to methane is only a small fraction of that obtained at 1100°F.

Reproducibility of Experimental Data.—As a check on the reproducibility of the experimental data obtained for the temperature traverses, two data points were taken at approximately the same catalyst-bed temperature in many of the runs of series, 40, 50, and 55. Measurement of the feed gas flow rate for the first of these points by by-passing the reactor interrupted synthesis on the catalyst and caused a drop of over 100°F in the catalyst-bed temperature. Resumption of feed gas flow to the reactor returned the catalyst bed to within a few degrees of the previous temperature, and the

second set of data was collected after an hour interval. In every case, as shown by the experimental data in Table VIII and by the points plotted in Figures 12 through 15, agreement was obtained between the compositions of the product gas for the two data points.

As a further check on the reproducibility of the experimental data, two separate runs (40-D and 40-F) were made at approximately the same reaction conditions. A comparison of the product gas composition and other relevant data for these runs is presented in Table XII. This comparison shows that the percentage of each component in the product gases from these two runs deviates by less than $\pm 0.6\%$ from the average component concentration, demonstrating that the data used to develop the temperature traverses can be reproduced.

TABLE XII

COMPARISON OF THE COMPOSITION OF THE PRODUCT GAS
FROM RUNS 40-D AND 40-F TO DEMONSTRATE THE
REPRODUCIBILITY OF DATA

	Runs			
	40-D1	40-D2	40-F1	40-F2
Temperature, °F	1104	1106	1093	1092
Feed Gas Composition				
%CO	39.7	39.1	39.3	39.2
H ₂	59.7	60.4	60.3	60.4
Product Gas Composition				
%CH ₄	32.7	33.0	32.1	32.9
CO ₂	21.4	21.1	21.0	21.1
H ₂ O	15.6	15.7	15.9	16.0
CO	10.2	10.0	9.5	9.5
H ₂	18.8	19.2	20.0	19.4

Effect of Space Velocity.—Space velocity is defined in this research as the total moles of feed gas per hour per square foot of gross catalyst surface. The effect of changes in space velocity upon the composition of the products from synthesis was investigated in run 40-F using a feed gas of 39.8% carbon monoxide and 60.4% hydrogen. Changes in space velocity can be accomplished either by varying the feed gas rate or by changing the number of catalyst pellets used in an experimental run. Run 40-F was conducted at 1092° to 1098°F using 242 steel catalyst balls. Data were collected at space velocities of 0.16 and 0.26 mole/hr-sq ft by using feed rates of 5.0 and 8.0 SCFH, respectively.

The percentages of methane, carbon dioxide, and water present in the product gas at the space velocities of run 40-F and also similar data from run 40-D at a space velocity of 0.16 mole/hr-sq ft are shown in Figure 16. The slopes of the lines drawn through these data are quite gradual, indicating that product composition is not appreciably affected by changing the space velocity over the range studied.

Smith⁵⁸ investigated the effect of space velocity on product composition more extensively for a feed gas of 70% hydrogen and 29% carbon monoxide. The range of space velocities from 0.1 to 0.4 mole/hr-sq ft was covered by varying the space velocity in two ways; by changing the amount of gas flowing over a given number of steel balls and by changing the number of balls while maintaining the feed rate constant. The slopes of the methane, carbon dioxide, and water lines of Figure 16 are approximately the same as those found by Smith for the corresponding components using a feed gas of 29% carbon monoxide and 70% hydrogen.

Effect of Feed Gas Composition.—Each of the four temperature traverses, shown in Figures 12 through 15, were made with a different composition

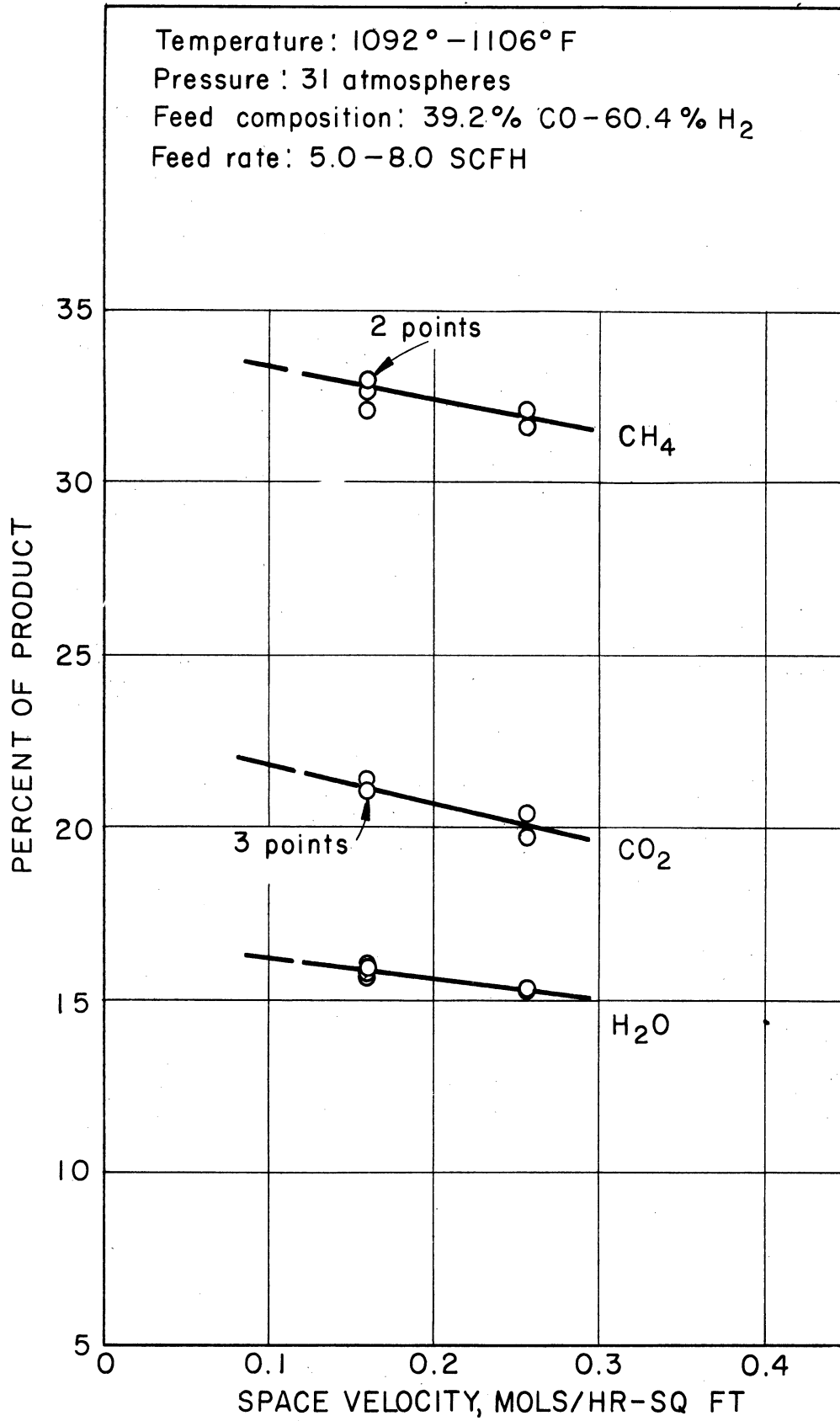


Figure 16. Effect of Space Velocity on the Composition of the Product Gas.

of feed gas. Therefore, in order to evaluate the effect of feed gas composition on the composition of the product gas from synthesis, it was necessary only to cross-plot composition values read from the curves of the four traverses for parameters of constant temperature. The results of this cross-plotting procedure at temperatures of 1050°, 1100°, 1150°, and 1200°F are given in Figures 17, 18, 19, and 20, respectively, which show product gas composition as a function of the percentage of carbon monoxide in the feed gas.

Data obtained from experimental runs conducted at two different space velocities, 0.10 and 0.16 mole/hr-sq ft, have been used to define the curves of Figures 17 through 20. (In the experimental runs of series 50 and 55, 388 catalyst balls were used rather than the usual 242 to provide additional surface for carbon deposition.) It can be seen from Figure 16 that the difference in the product composition resulting from a change in space velocity from 0.16 to 0.10 mole/hr-sq ft is small. Consequently, no significant error should be introduced into Figures 17 through 20 by the use of data obtained at these two space velocities.

Figures 17 through 20 show that as higher and higher concentrations of carbon monoxide are used in the feed gas, the amount of unreacted hydrogen in the product gas declines rapidly. While this rapid decrease in product dilution by unused hydrogen is partially offset by an increased amount of unconverted carbon monoxide, the total sum of unreacted hydrogen and carbon monoxide is reduced by decreasing the H₂/CO ratio of the feed gas. Eventually, the sum of the product gas diluents levels off to a relatively constant value when feed gases containing from 50% to 55% carbon monoxide are used. As even higher feed gas concentrations of carbon monoxide are used, the sum of the unused hydrogen and carbon monoxide present in the product

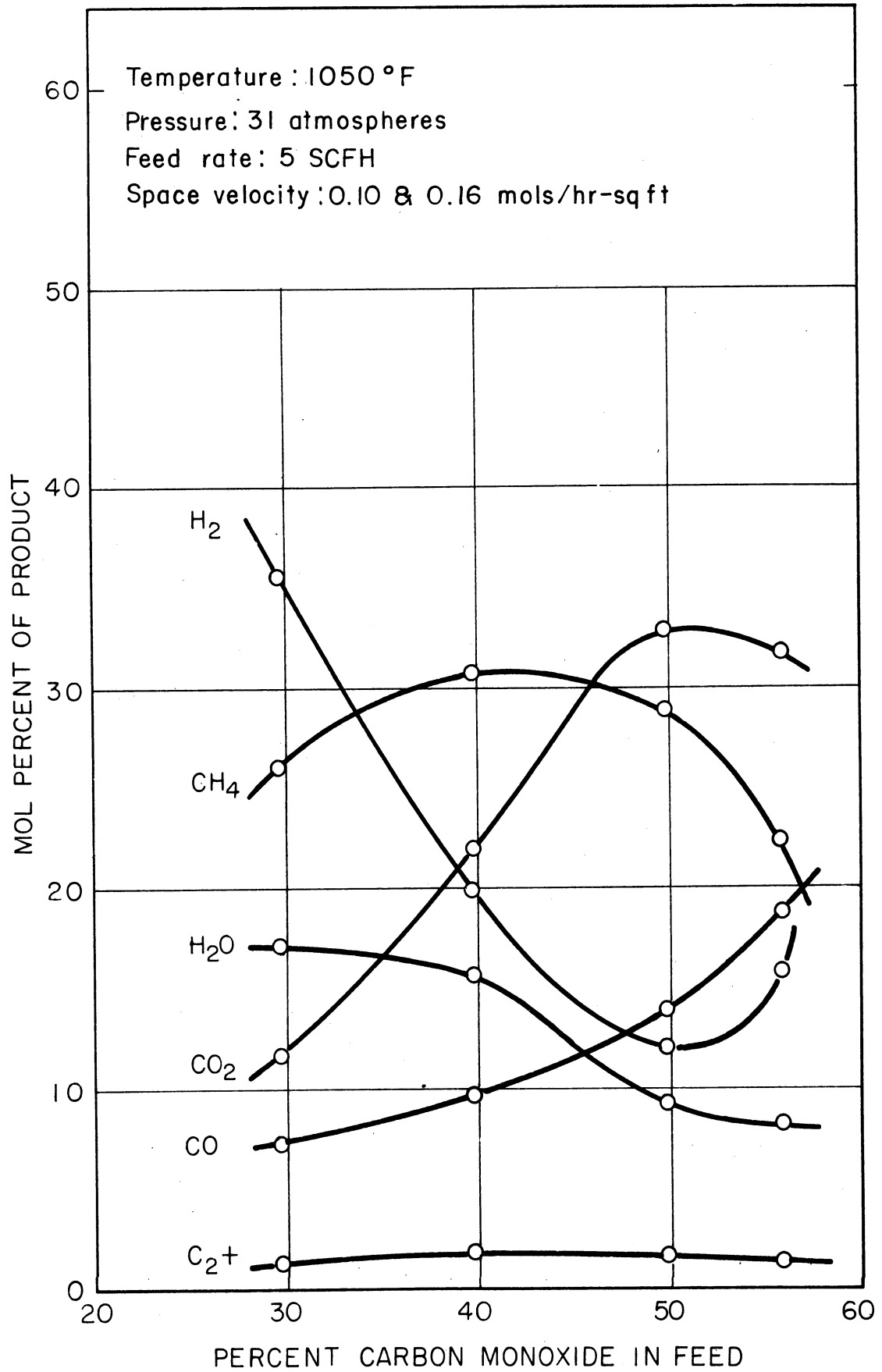


Figure 17. Effect of Varying the Composition of the Feed Gas on the Product Obtained at 1050°F.

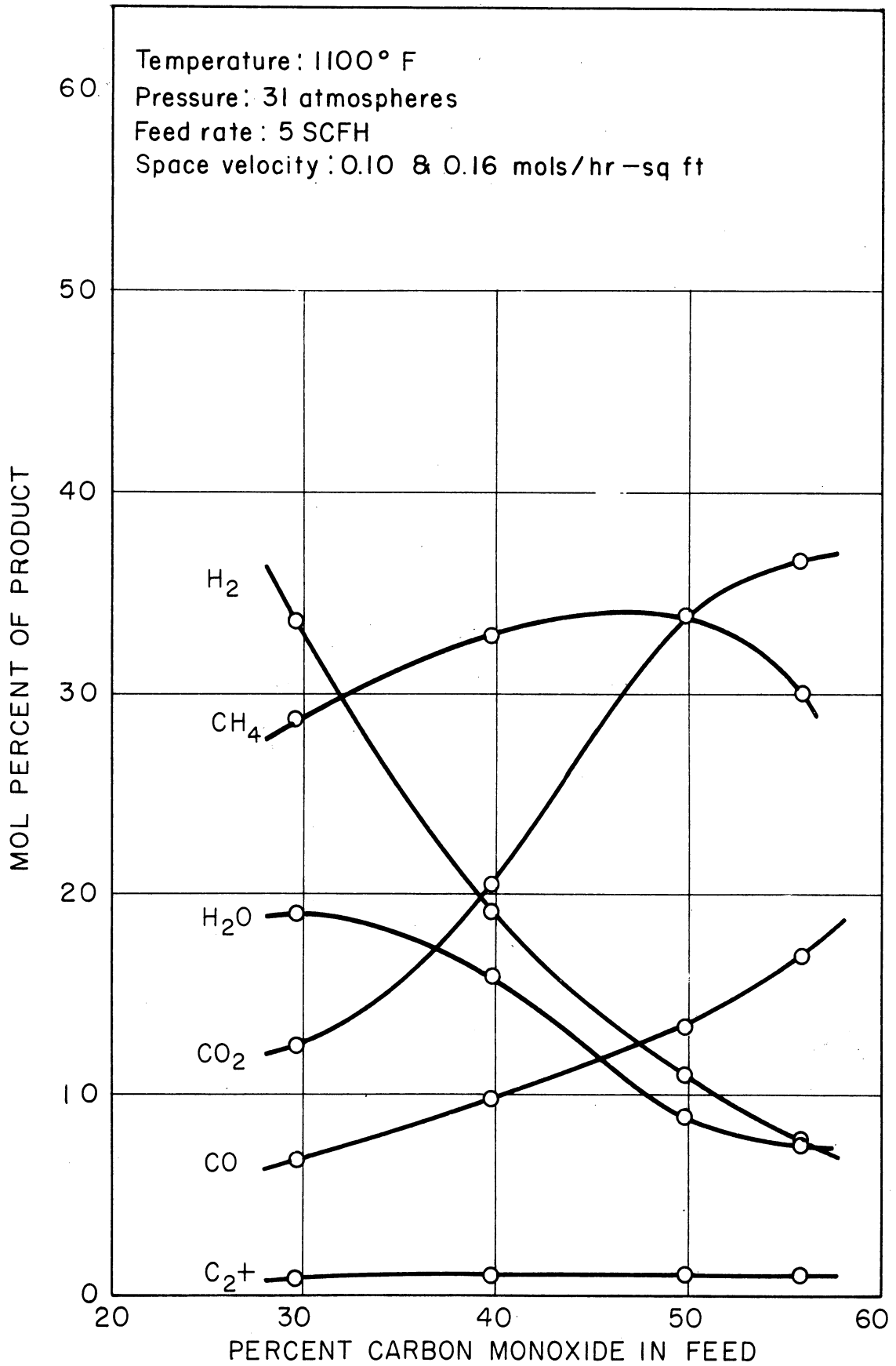


Figure 18. Effect of Varying the Composition of the Feed Gas on the Product Obtained at 1100° F

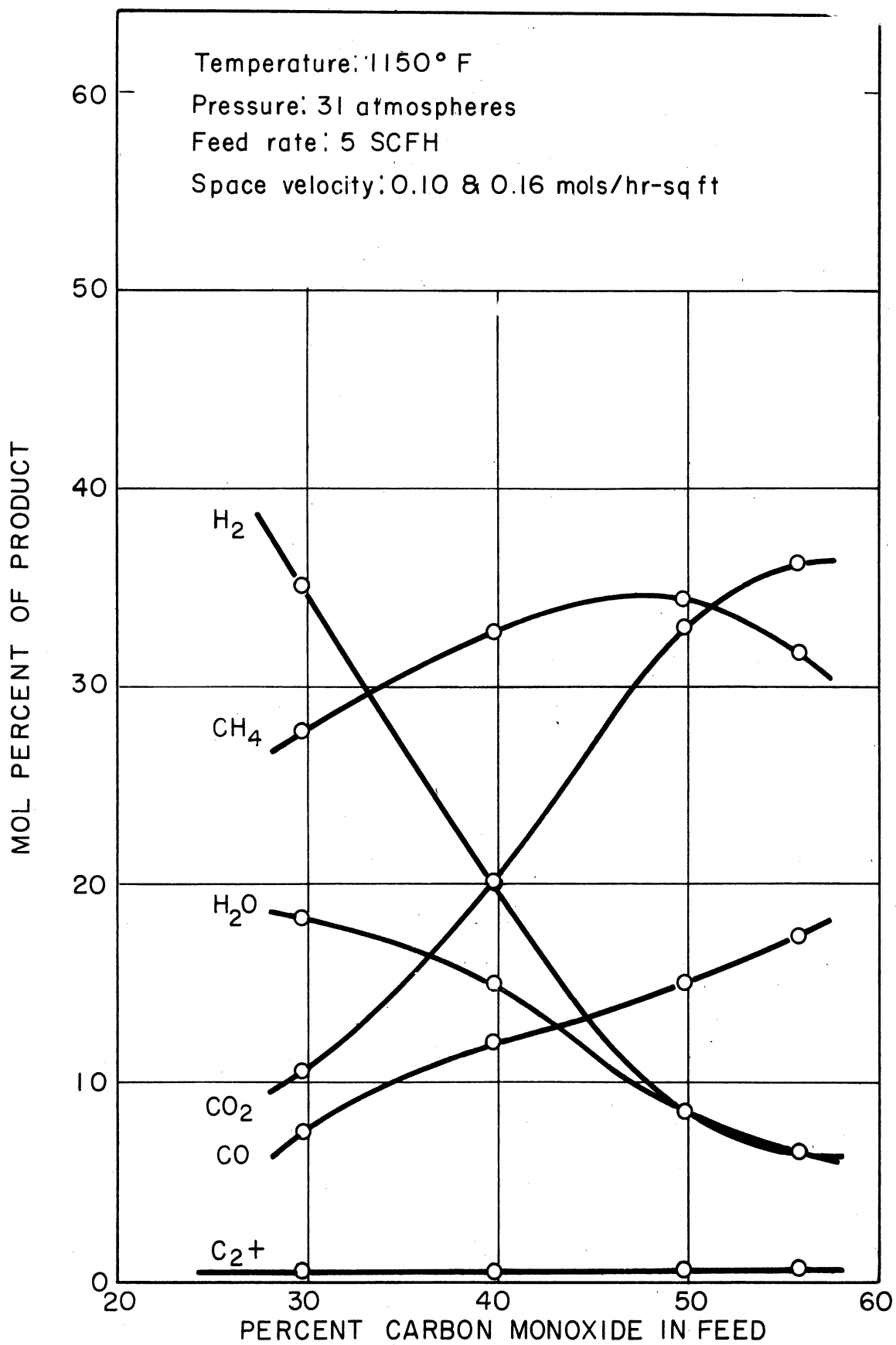


Figure 19. Effect of Varying the Composition of the Feed Gas on the Product Obtained at 1150°F.

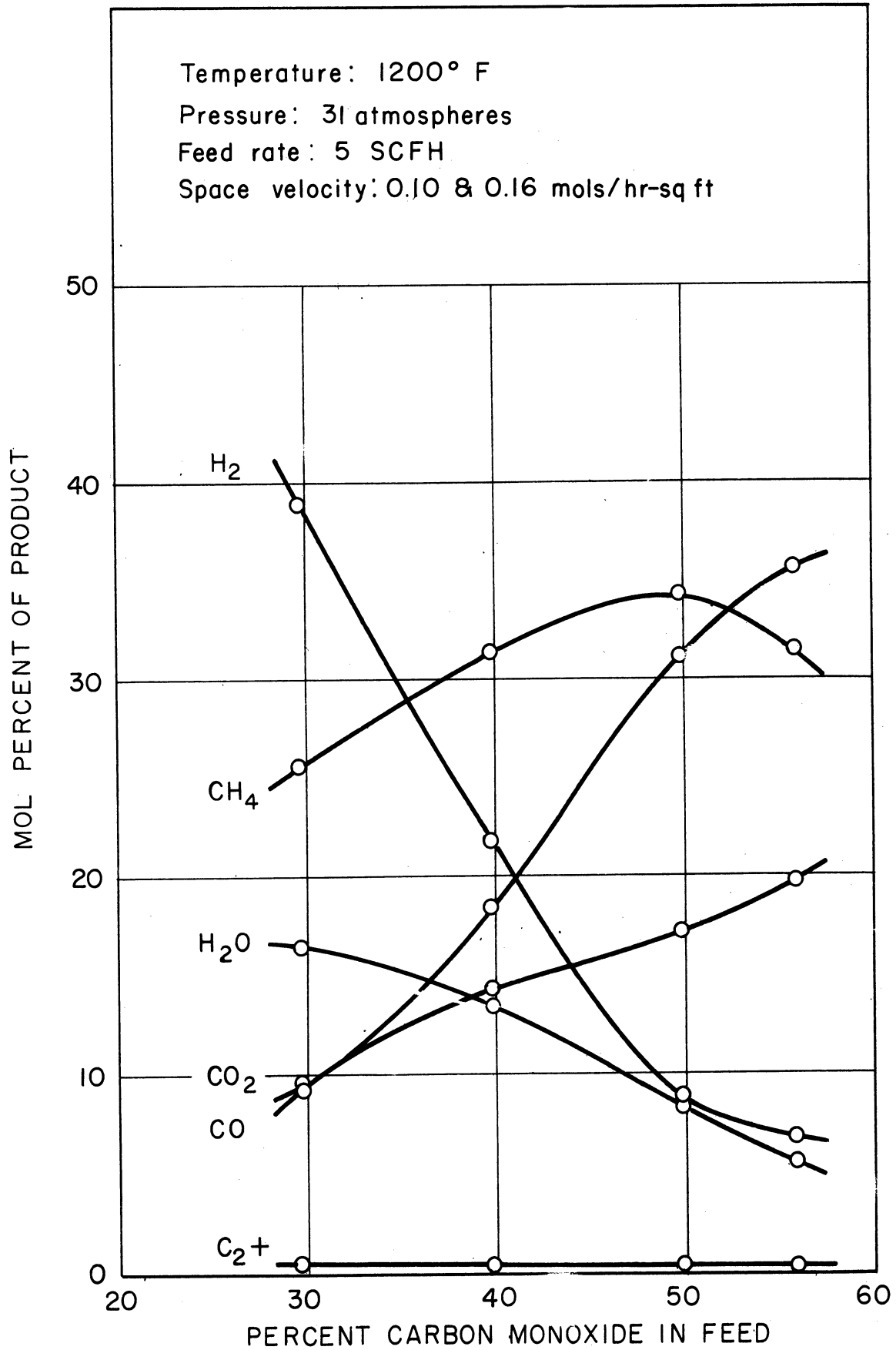


Figure 20. Effect of Varying the Composition of the Feed Gas on the Product Obtained at 1200°F.

gas begins to slowly increase.

A reduction in the dilution of the product by two gases which have low heating values results in an overall increase in the product gas heating value after water and carbon dioxide have been removed. However, it can be seen from Figures 17 through 20 that increases in the product heating value, resulting from reduced dilution, are eventually limited by a decline in methane formation when feed gas containing more than 50% carbon monoxide is used.

Decreasing the H_2/CO ratio of the feed gas used for synthesis results in the formation of increased amounts of carbon dioxide. The conversion of carbon monoxide to carbon dioxide, rather than to methane, constitutes a loss in potential heating value, since carbon dioxide, not being combustible, would be scrubbed from a product gas prior to its use as a heating gas. The percentage of the carbon monoxide in the feed gas which is converted to methane and to carbon dioxide during synthesis at temperatures from 800° to 1250° is shown in Figures 21 and 22, respectively. As feed gases of lower and lower H_2/CO ratio are used, these figures show that the conversion of carbon monoxide to methane is decreased, while the conversion to carbon dioxide is increased. Eventually, a larger portion of the carbon monoxide in the feed is converted to carbon dioxide than to methane, as illustrated in Figure 23 for a synthesis temperature of $1120^\circ F$.

Carbon Deposition.—At temperatures at which the steel catalyst is active for methane synthesis, deposition of carbon on the catalyst surface is observed whenever the H_2/CO ratio of the feed gas used is less than three. Furthermore, as the percentage of carbon monoxide in the feed gas is increased, larger and larger percentages of the carbon fed to the reactor in the form of carbon monoxide are deposited on the catalyst as free carbon.

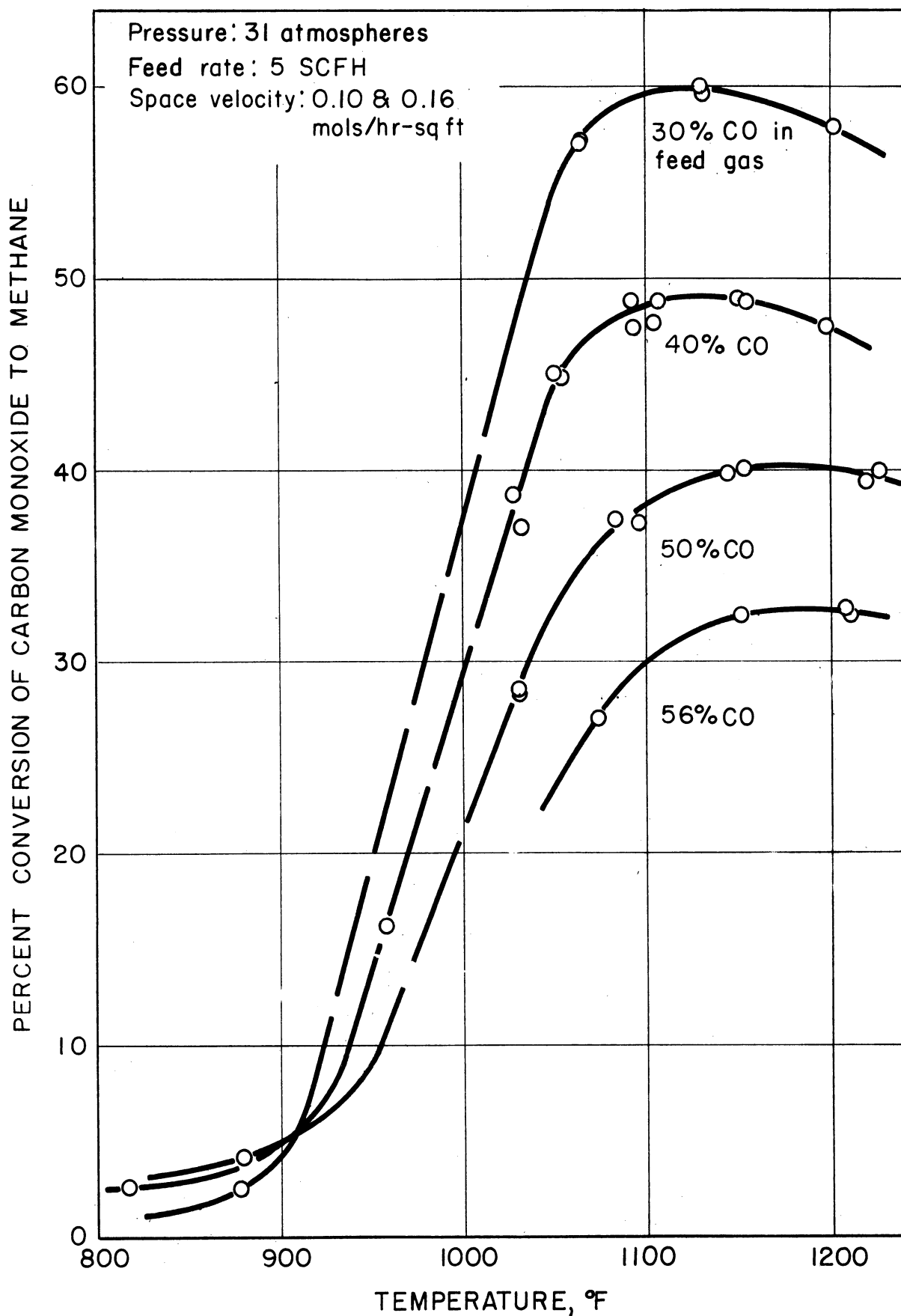


Figure 21. Effect of Temperature on the Percent Conversion of the Feed Carbon Monoxide to Methane.

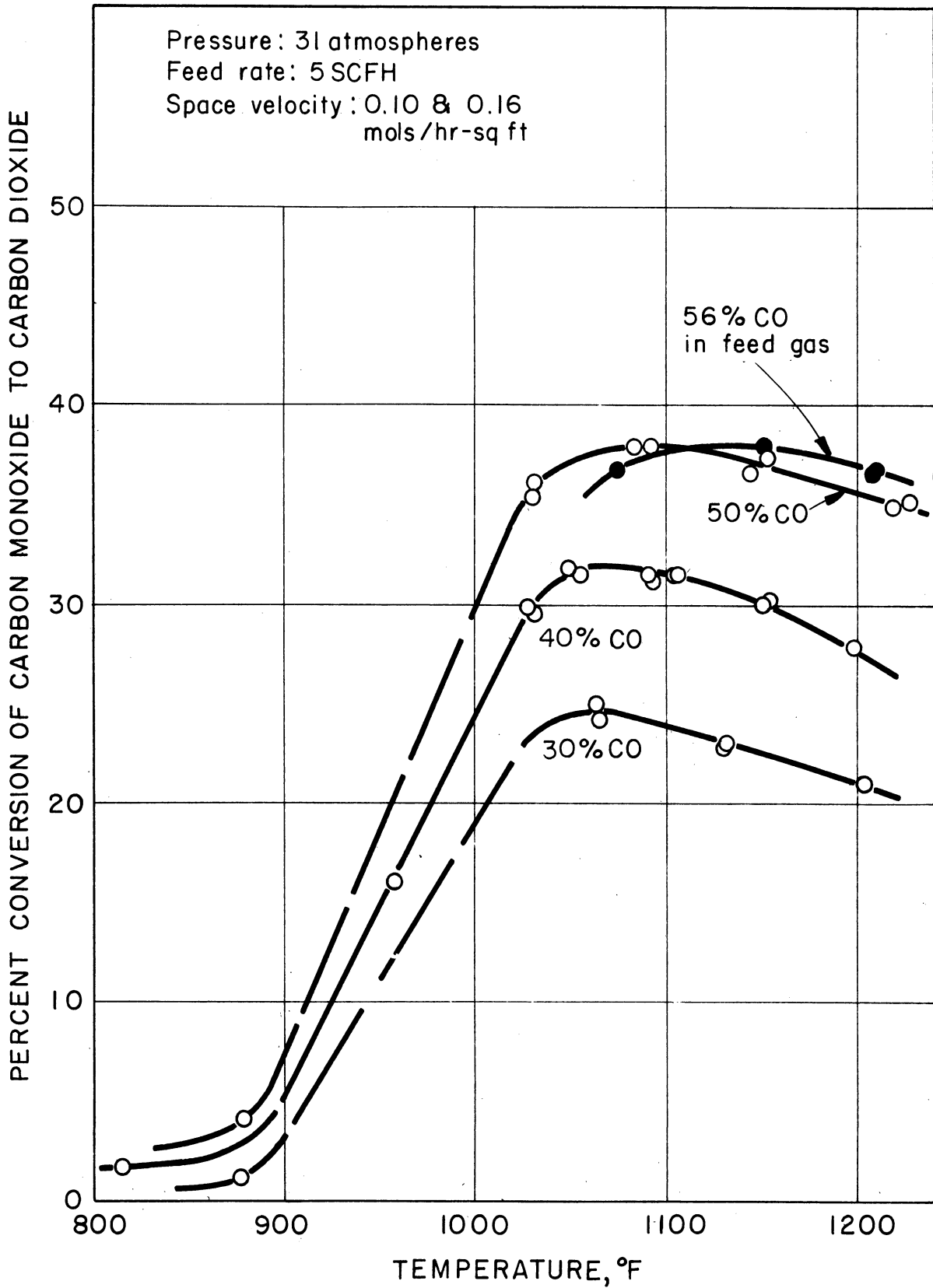


Figure 22. Effect of Temperature on the Percent Conversion of the Feed Carbon Monoxide to Carbon Dioxide.

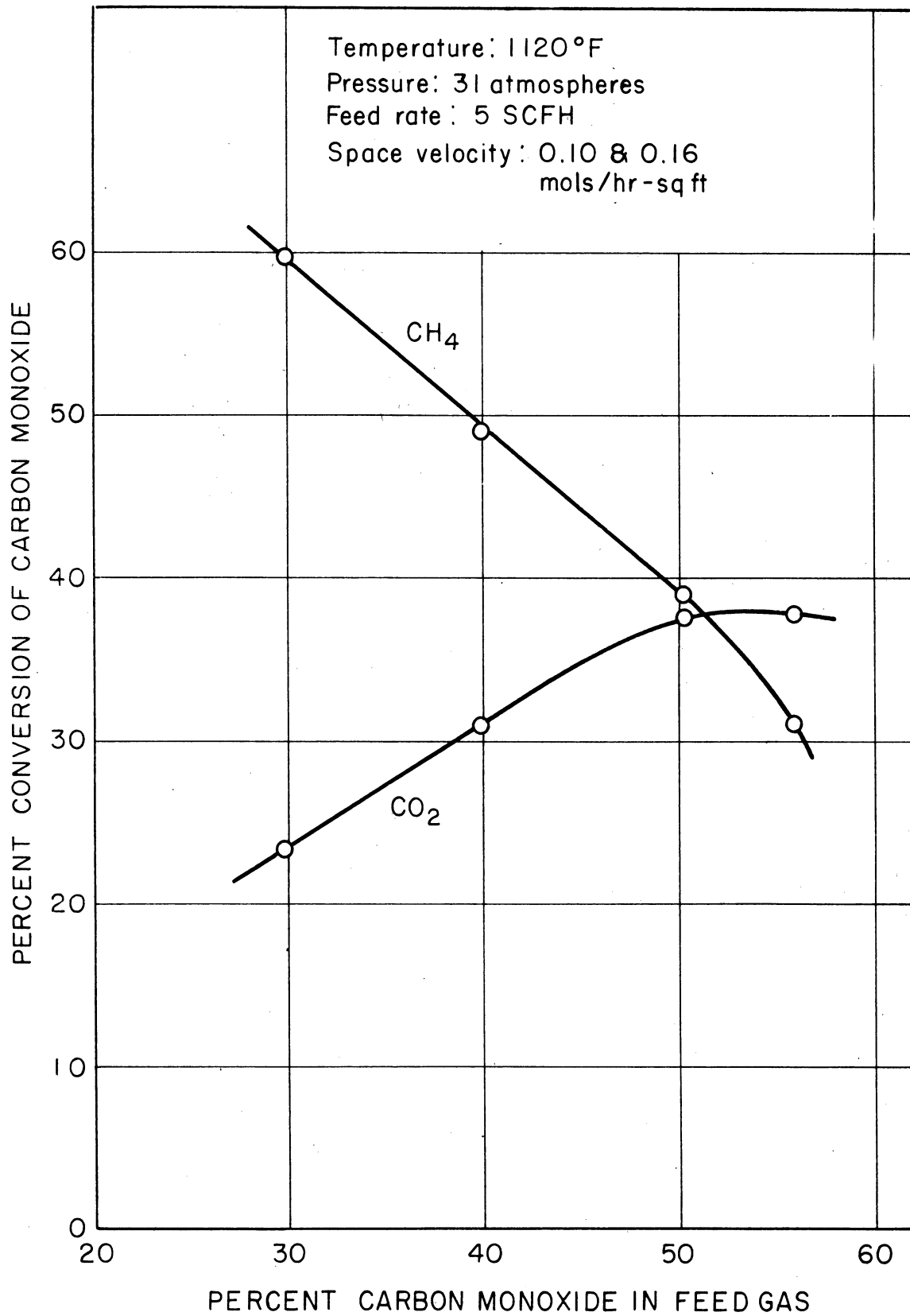


Figure 23. Effect of Varying the Feed Carbon Monoxide Concentration on the Percent Conversion of the Carbon Monoxide to Methane and Carbon Dioxide at 1120°F.

In the experimental runs of series 40, 50, and 55, the amount of carbon deposition which occurred at various catalyst temperatures was investigated for three different compositions of feed gas. After the termination of each experimental run, the catalyst bed was removed from the reactor, and the quantity of deposited carbon was weighed. Data concerning carbon deposition, which were obtained in this manner, are summarized in Table IX.

On the basis of accurate determinations of the feed and product gas compositions and flow rates, it was possible to make a carbon balance around the reactor for each data point of the experimental runs. Calculating the difference between the amount of carbon entering and leaving the reactor provided a second method for determining the amount of carbon deposited in the catalyst bed. These data are given in column (27) of Table VIII.

The amount of carbon deposition at temperatures from 1000° to 1220°F, described in terms of weight percent of the carbon fed to the reactor in the form of carbon monoxide and carbon dioxide which is deposited as free carbon, for parameters of constant feed gas composition is shown in Figure 24. Curves have been drawn through the data obtained by weighing the deposited carbon. These points represent a direct measurement of the carbon deposition, and therefore should be more reliable than the carbon balances, which are subject to any errors which occur in the determination of the feed and product gas compositions and flow rates. Actually, the points determined by carbon balance lie close to the curves drawn through the "weighed carbon" points.

Figure 24 shows that as the synthesis temperature is increased, the amount of carbon deposited increases to a maximum at 980° to 1020°F and

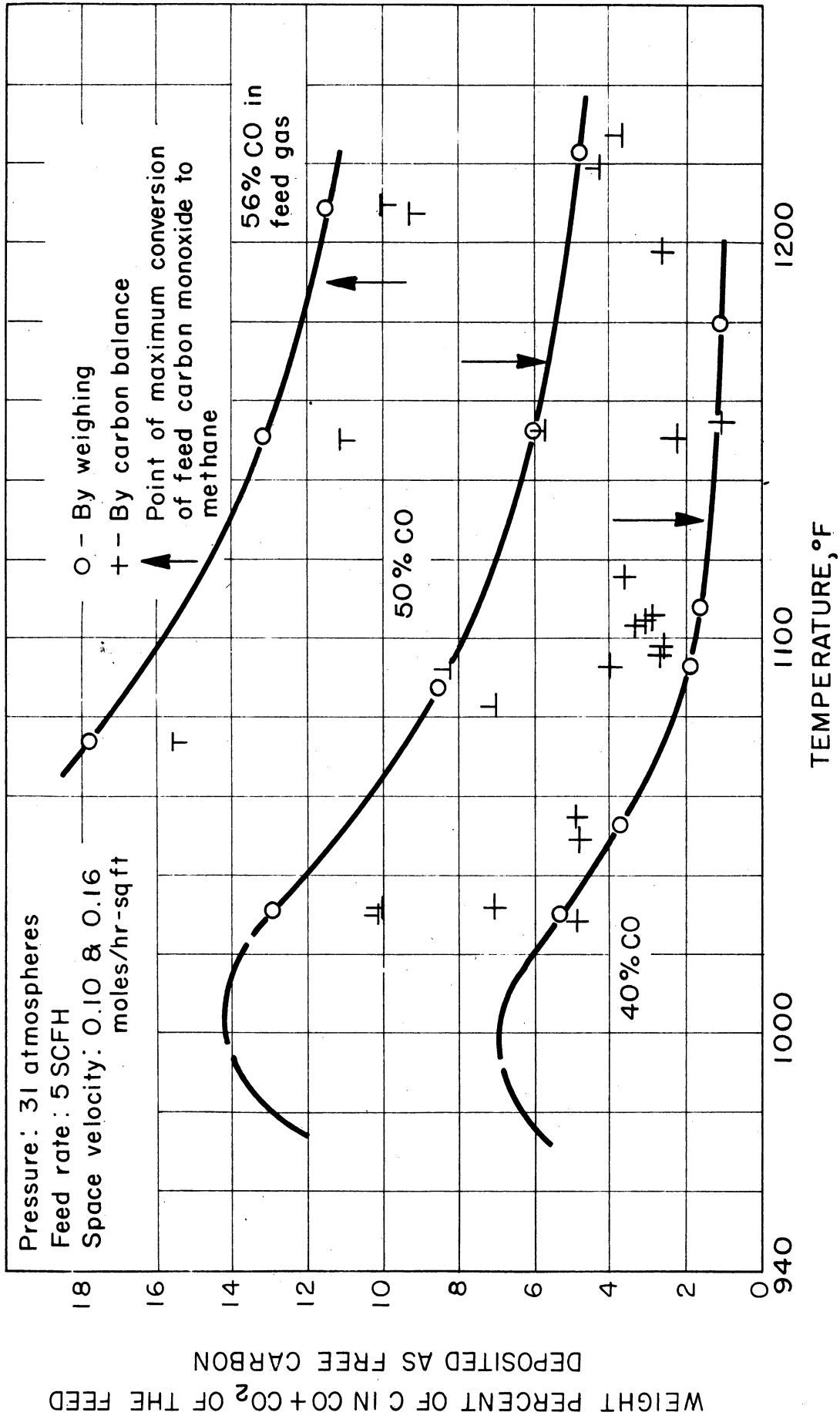


Figure 24. Effect of Temperature and Feed Carbon Monoxide Concentration on the Amount of Carbon Deposition Which Occurs During Synthesis.

then decreases with further increases in temperature. Considerably less carbon is deposited at a temperature corresponding to the point of maximum conversion of carbon monoxide to methane for a particular feed gas composition (indicated by arrows in Figure 24) than in the region of heaviest carbon deposition at 980° to 1020°F.

The temperature region of maximum carbon deposition coincides with the upper portion of the reaction threshold temperature range. This fact, coupled with the observation that little or no carbon deposition occurs at temperatures below 900°F, indicates that the mechanism which accounts for carbon deposition on the steel catalyst experiences a rapid increase in rate over the same temperature range as do the mechanisms by which methane, carbon dioxide, and water are formed.

Samples of the carbon deposited during synthesis have been examined with an electron microscope. Several electron micrographs of the carbon at a magnification of approximately 20,000 diameters are shown in Figure 25. Two distinct types of particles are evident; one a porous fluffy looking mass, the other a more solid plate-like structure. Both forms are magnetic, indicating that they have picked up iron from the catalyst surface. The fluffy type particles appear to be an amorphous type carbon containing iron in solution, while the plate-like particles resemble iron carbides or iron oxides.

Evaluation of the Optimum Reaction Conditions

From the previous discussion concerning the effect of reaction conditions on the composition of the product gas from synthesis, it is apparent that certain ranges of temperature and feed gas composition exist which are most favorable for the synthesis of methane from carbon monoxide and hydrogen.

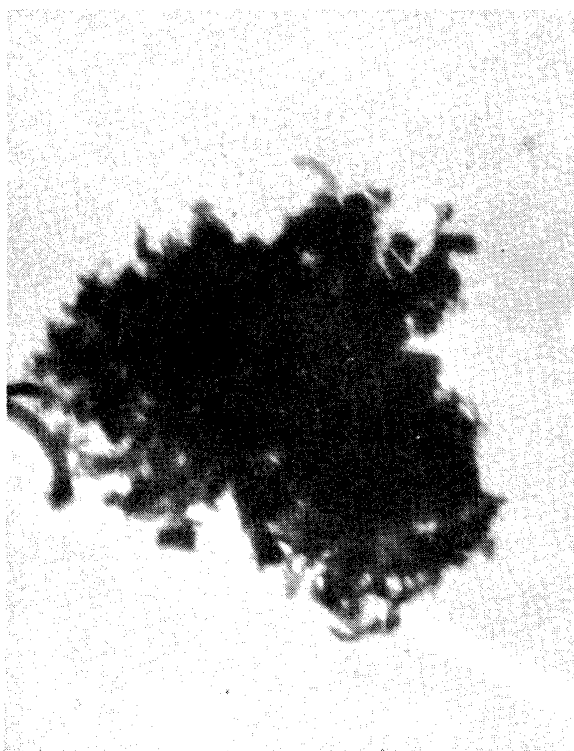
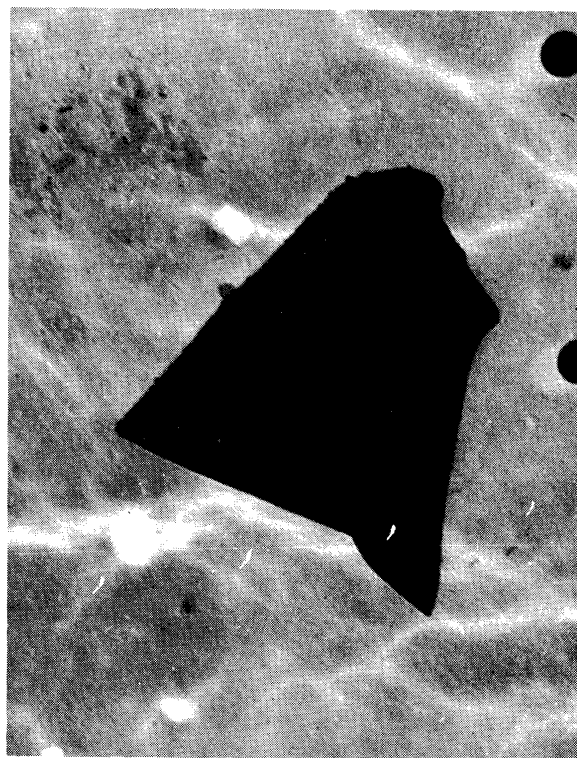


Figure 25. Electron Micrographs of Carbon Particles Deposited During Synthesis at a Magnification of 20,000 Diameters.

It has been noted that the activity of the catalyst reaches a maximum at a temperature of 1100° to 1150°F, depending upon the composition of the feed gas, and then declines with further increases in temperature. Furthermore, it has been shown that less carbon is deposited on the catalyst from a given composition of feed gas as the synthesis temperature is increased. In the discussion of the effect of feed gas composition on the composition of the product gas from synthesis, it has been pointed out that increases in the product heating value, because of reduced dilution with unused hydrogen, are eventually limited by a decline in the methane formation when the H₂/CO ratio of the feed gas is reduced to values lower than one.

In order to determine the optimum reaction conditions for the synthesis of a product gas of the highest heating value, the gross heating values of the product gases obtained from synthesis at 1050°, 1100°, 1150°, and 1200°F using feed gases containing 30%, 35%, 40%, 45%, 50%, and 55% carbon monoxide have been calculated from the product composition curves of Figures 17 through 20. A summary of the results of these calculations is presented in Table XIII. Heating values used for the components of the product gas are tabulated below.

<u>Component</u>	<u>Gross Heating Value BTU/SCF</u>
H ₂	325
CO	321
CH ₄	1011
C ₂ +	2000 (avg value)

The product gases were assumed to be scrubbed free of carbon dioxide and water.

In order to offer a pictorial representation of the effect of temperature and of feed gas composition on the gross heating value of the product

TABLE XIII
GROSS HEATING VALUE OF THE
SCRUBBED PRODUCT GAS, BTU/SCF

Percent CO in Feed Gas	Temperature, °F			
	1050	1100	1150	1200
30	613	629	605	573
35	667	666	637	608
40	712	700	678	650
45	733	734	724	695
50	722	743	742	720
55	647	730	733	706

gas, the heating value data of Table XIII, plotted versus temperature for parameters of percent carbon monoxide in the feed gas, are shown in Figure 26. In Figure 27, the same data are presented versus percent carbon monoxide in the feed gas for parameters of temperature. While these two figures indicate the heating value of the scrubbed product gas which can be produced by methanization of carbon monoxide and hydrogen mixtures, they offer no information concerning the amount of scrubbed product gas (containing only methane, C₂⁺ hydrocarbons, hydrogen, and carbon monoxide) which can be synthesized from one cubic foot of feed gas at various conditions of temperature and feed gas composition. Such information is presented in Figure 28.

Figures 26 and 27, in conjunction with Figure 28 and with Figure 24 concerning the amount of carbon deposition at various reaction conditions, offer operating data which can be used to determine (1) the heating value of a scrubbed product gas formed by methanization of a particular carbon

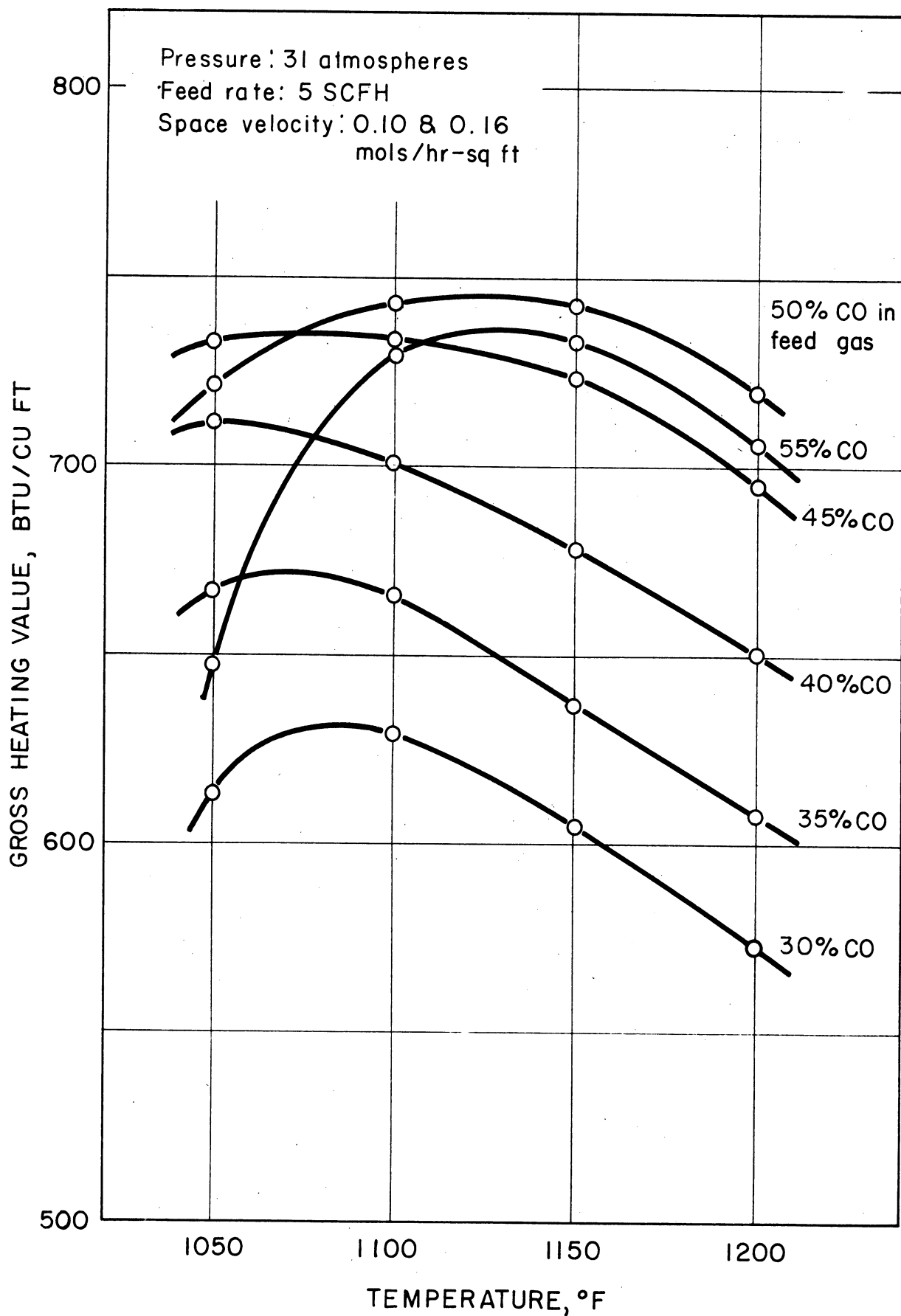


Figure 26. Gross Heating Value of the Scrubbed Product Gas as a Function of the Synthesis Temperature.

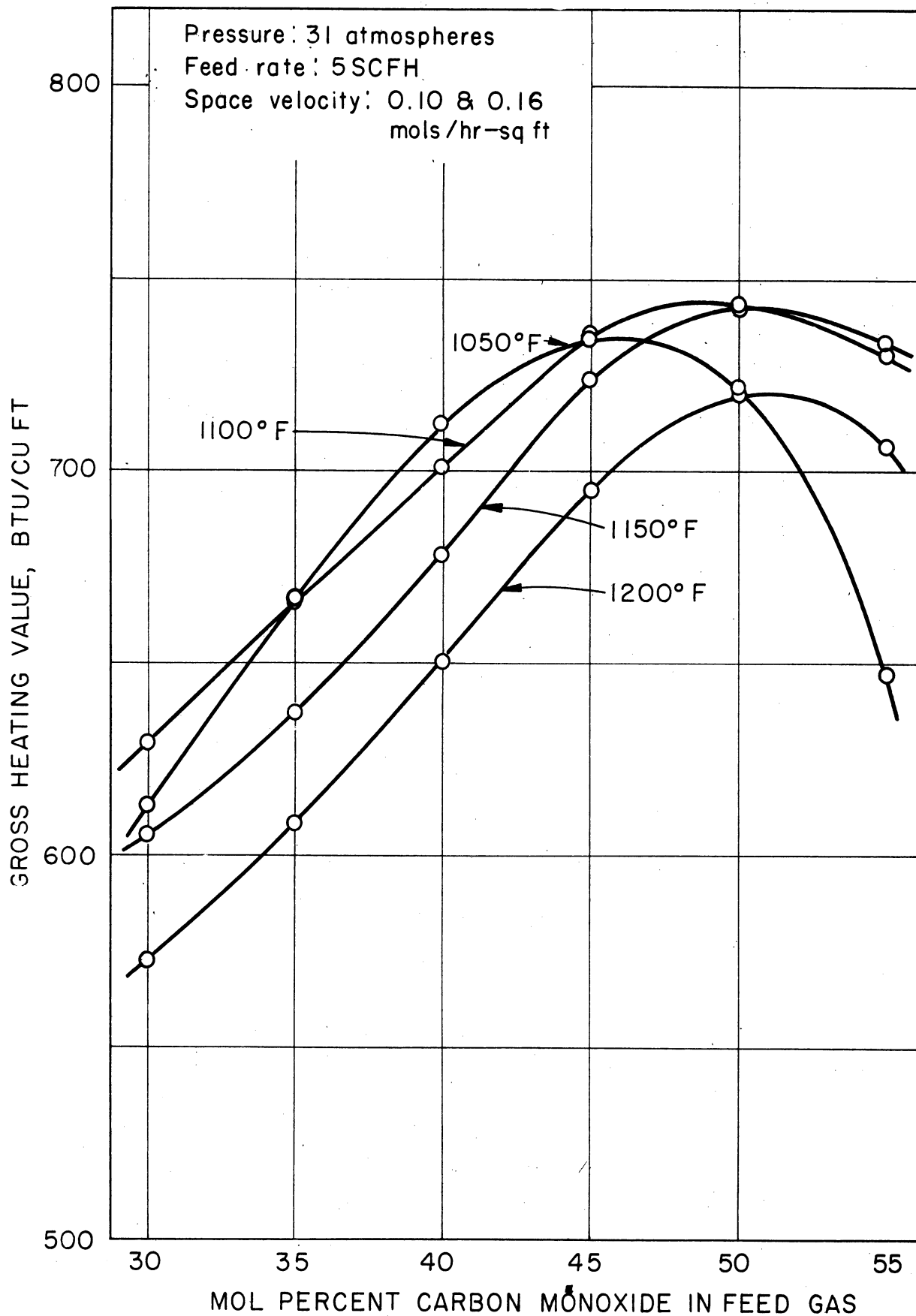


Figure 27. Gross Heating Value of the Scrubbed Product Gas as a Function of the Feed Gas Composition.

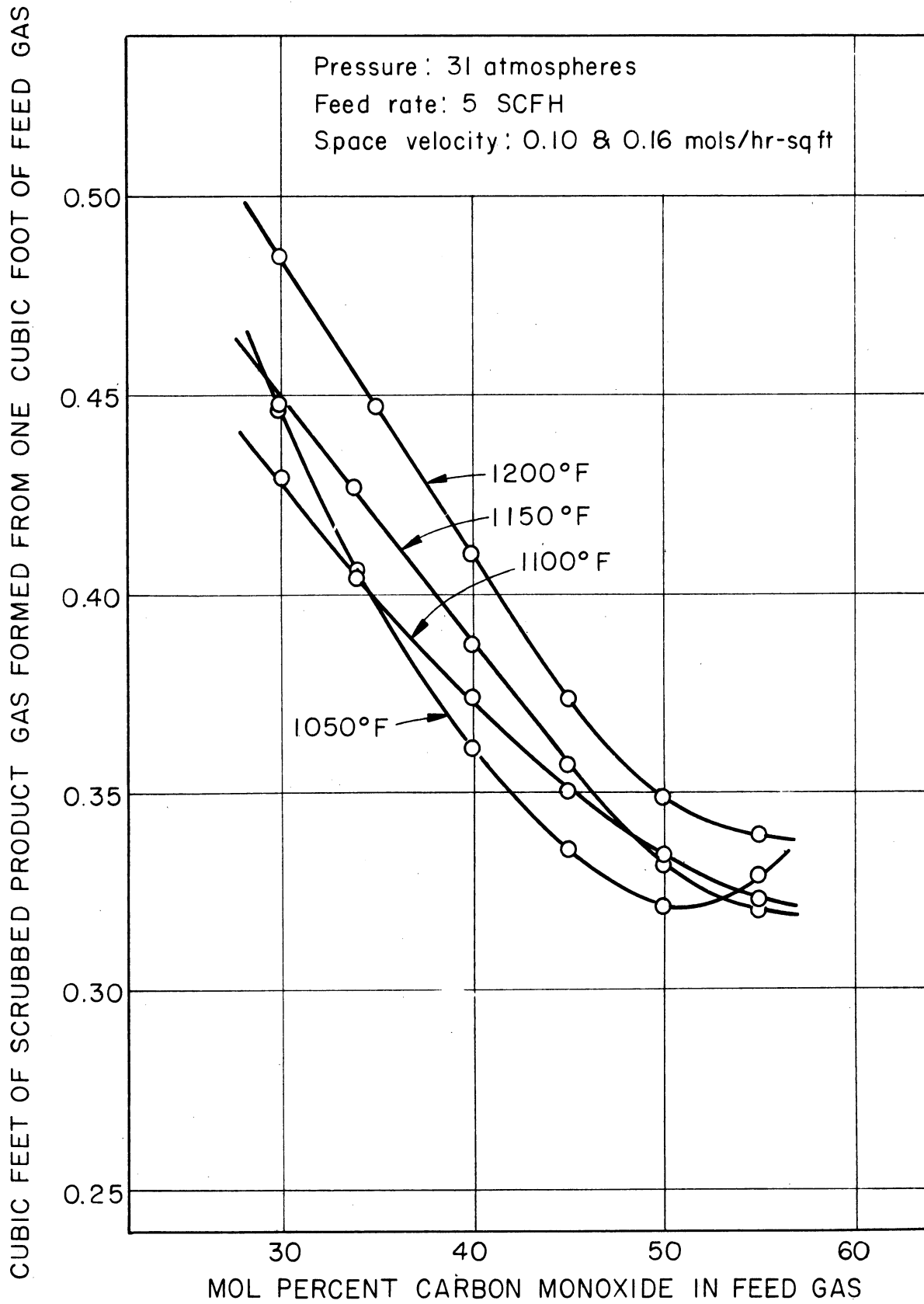


Figure 28. Effect of the Feed Gas Composition and Temperature on the Amount of Product Gas Formed from One Cubic Foot of Feed Gas.

monoxide-hydrogen mixture at a given temperature, (2) the amount of free carbon deposited on the steel catalyst at these conditions, and (3) the cubic feet of scrubbed product gas obtainable from one cubic foot of feed gas.

The ranges of temperature and feed gas composition which yield product gas of the highest heating value using a steel catalyst have been determined from Figures 26 and 27 and are listed below.

<u>Optimum Reaction Conditions</u>	<u>Range</u>
Temperature	1090° to 1150°F
Percent CO in the feed gas	47% to 52%

Appreciable carbon deposition is encountered throughout this range of reaction conditions.

For situations which do not require the production of gas of the highest heating value, carbon deposition can be minimized by operating at high temperatures and low concentrations of carbon monoxide in the feed gas. The following comparison is offered in tabular form to illustrate the large reduction in carbon deposition which can be obtained for a small sacrifice in heating value.

	<u>Case A</u>	<u>Case B</u>
Feed composition	40% CO - 60% H ₂	50% CO - 50% H ₂
Temperature, °F	1150	1150
Pressure, atm	31	31
Space velocity, mols/hr-sq ft	0.10	0.10
Gross heating value of scrubbed product gas, BTU/SCF	678	742
Cubic feet of scrubbed product gas per one cubic foot of feed gas	0.377	0.331
Weight % of carbon fed deposited as free carbon	1.2	6.1
Gross heating value of scrubbed product gas per one cubic foot of feed, BTU/SCF	256	246

Less than one-sixth as much carbon is deposited from the feed gas of Case A as from the feed of Case B. While this reduced carbon deposition is accompanied by a lower gross heating value, more scrubbed product gas is formed in Case A, resulting in a greater recovery of the energy available in the feed gas than for Case B.

The point to be made in the above discussion is that although optimum operating conditions have been determined for the synthesis of product gas of the highest heating value, these conditions do not necessarily constitute the best set of reaction conditions for every methanization situation.

The conversion of carbon monoxide and hydrogen to methane is favored by high pressure, as predicted by equilibrium calculations (see Figure 10) and as reported by Lobo.⁵⁹ However, it is unlikely that the methanization step of any process to enrich low heating value gas manufactured from coal would be conducted above the pipe line pressure used to transmit the product gas to consumers. Normal pipe line pressures average about 1000 psig, limiting methane synthesis pressures to less than 70 atmospheres.

The experiments of the present work were limited to a pressure of 31 atmospheres because of the design of the fixed-bed reactor. However it has been estimated from the report of Lobo, with regard to the effect of pressures from 30 to 1040 atmospheres on the product composition, that increasing the synthesis pressure from 31 to 70 atmospheres would result in an increase of only 30 to 40 BTU/SCF in the heating value of the product gas formed at the optimum reaction conditions of temperature and feed gas composition determined in this research.

Regeneration of the Steel Catalyst by Air Oxidation

Oxidation of the steel catalyst with air, as a means of removing de-

posited carbon from the catalyst bed and as a method for reactivating catalyst poisoned by sulfur compounds present in the feed gas, has been investigated in the course of this research.

Removal of Deposited Carbon.—Appreciable amounts of carbon are deposited on the steel catalyst when feed gas containing more than 40% carbon monoxide is used. Unless the carbon is periodically removed from the catalyst bed, heavy depositions accumulate resulting in an increased pressure drop and eventual plugging in a fixed bed reactor or in loss of fluidization in a fluidized bed reactor. Run 30-Ox-A was made to investigate the effect on the catalyst activity of oxidizing the carbon with air.

In the course of run 30-A, which preceded run 30-Ox-A, quantities of carbon were deposited on the steel catalyst. At the completion of the run, the reactor was cooled to room temperature and the catalyst was left in place. Run 30-Ox-A was started 19 days later. The catalyst was slowly heated to 1050°F, at which temperature the oxidation procedure was begun. The reactor pressure was reduced to atmospheric and any remaining synthesis gas was flushed from the reactor with a flow of nitrogen. Air was then passed over the catalyst at a rate of 2.5 SCFH for a period of 46 minutes. At the end of this time, the off-gas from the reactor contained less than 0.5% carbon dioxide, as measured by Orsat analysis, indicating almost complete removal of carbon. During the oxidation period, the catalyst temperature increased rapidly from 1030°F to a maximum temperature of 1150°F and then decreased slowly as the carbon was removed from the catalyst. The reactor was again flushed with nitrogen and the flow of feed gas was re-established.

Four sets of experimental data were collected at a temperature of 1066° to 1069°F over an 18-hour period from the time of oxidation. The

percentage of methane in the product gas at these four points is compared in Figure 29 to the percentage of methane obtained in the product gas of run 30-A at a temperature of 1066° to 1069°F. Unfortunately, in the course of these runs, the composition of the feed gas varied somewhat from the desired composition of 30.0% carbon monoxide and 69.6% hydrogen. Consequently, the data presented in Figure 29 have been corrected for deviations from the desired feed composition by multiplying the (percentage conversion of carbon monoxide to methane observed for the actual feed gas composition) by the (moles of carbon monoxide present in 5.0 SCFH of feed gas containing 30.0% carbon monoxide) and dividing by the (moles of product gas obtained from 5.0 SCFH of feed gas). While this procedure does not provide an exact correction, it does offer an improvement.

Figure 29 shows that 18 hours after the oxidation procedure the amount of methane in the product gas is still greater than the amount obtained before oxidation, demonstrating that carbon can be removed from the catalyst by oxidation with air without a deleterious effect on the catalyst activity. Furthermore, the high mechanical strength of the steel catalyst should permit many such oxidations without adverse effect on the structure of the catalyst.

Reactivation of Poisoned Catalyst.—It is well known that supported nickel and cobalt base methanization catalysts are poisoned by carbonyl sulfide present in carbon monoxide-hydrogen mixtures manufactured from coal. Runs 30-B and 30-Ox-B were made to determine whether the steel catalyst was susceptible to poisoning by sulfur, and if so, whether the catalyst could be reactivated by oxidation with air.

Sulfur, in the form of carbonyl sulfide, was present in the carbon monoxide obtained from the Matheson Company. During experimental runs, car-

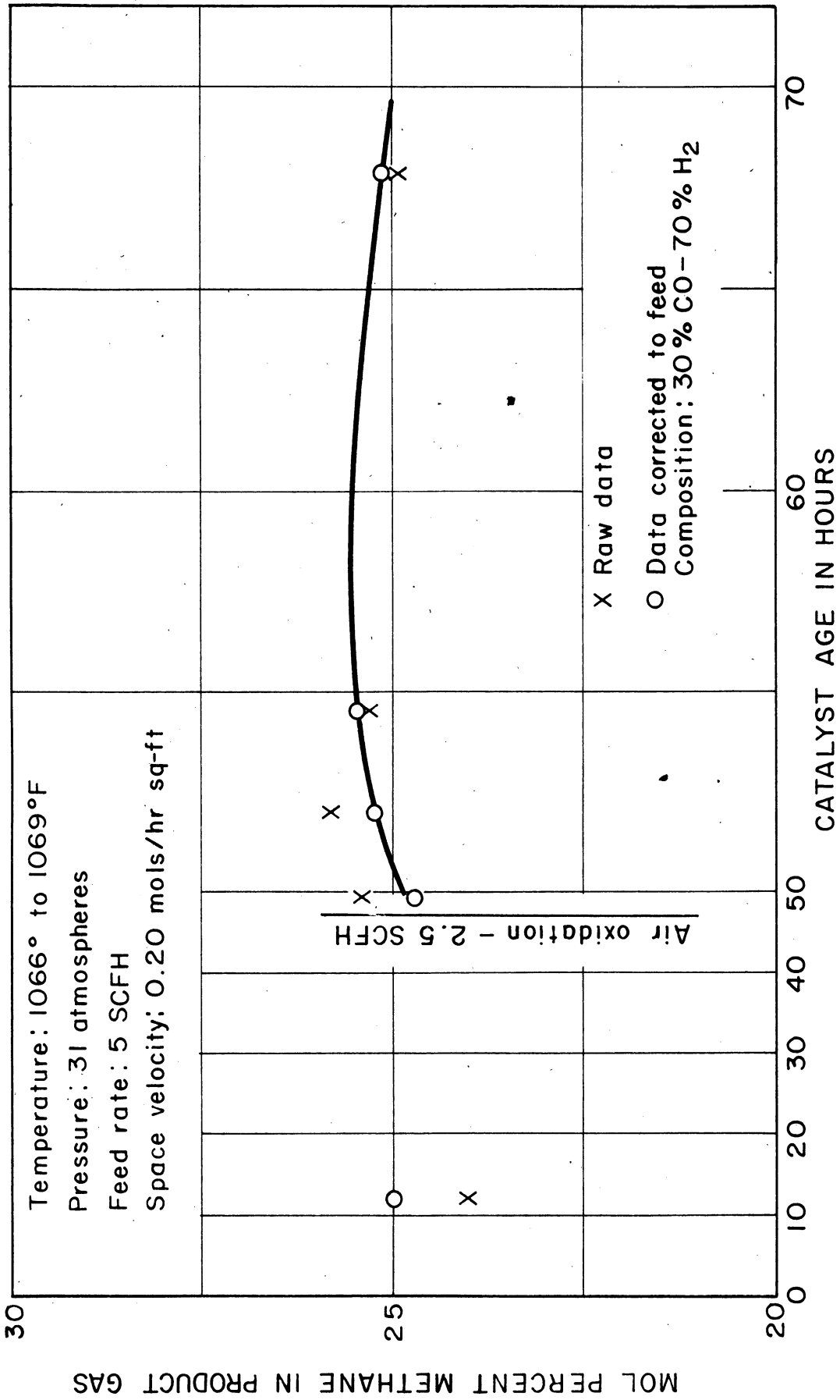


Figure 29. Effect of the Use of Air Oxidation to Remove Carbon on the Methane Concentration of the Product Gas.

bonyl sulfide was removed by passing the carbon monoxide feed stream through a trap containing a mixture of activated charcoal and silica gel. An analysis by mass spectrometer of a sample of the carbon monoxide before entry to the sulfur trap indicated the presence of 0.004 mol percent carbonyl sulfide. However, no carbonyl sulfide could be detected in the carbon monoxide leaving the sulfur trap.

At the end of run 30-B, which was a temperature traverse for a feed gas of 30% carbon monoxide and 70% hydrogen (see Figure 12), the catalyst temperature was reduced to 1080°, and the sulfur trap was by-passed. Feed gas containing carbonyl sulfide was passed over the catalyst for 48 hours. During this interval, several sets of experimental data were taken to determine the extent of catalyst deactivation. At the end of the 48-hour period, the flow of feed gas was stopped, and the reactor pressure was reduced to atmospheric. The reactor was flushed with nitrogen, and then air at the rate of 3.3 SCFH was passed over the catalyst. After 50 minutes of oxidation, the off-gas from the reactor contained 0.32% carbon dioxide, indicating almost complete removal of the carbon which had deposited on the catalyst during the run. The catalyst temperature did not exceed 1070°F during the oxidation procedure. Air was purged from the reactor with nitrogen, and the flow of feed gas was resumed. Two hours later a final set of experimental data was collected.

A comparison of the percentage of methane present in the product gas at four points during the course of runs 30-B and 30-Ox-B is presented in Figure 30 to illustrate the deactivation of the catalyst by carbonyl sulfide and to show the effect of air oxidation on the activity of the poisoned catalyst. It can be concluded from Figure 30 that steel catalyst, like nickel and cobalt catalysts, is poisoned by carbonyl sulfide. Before carbonyl

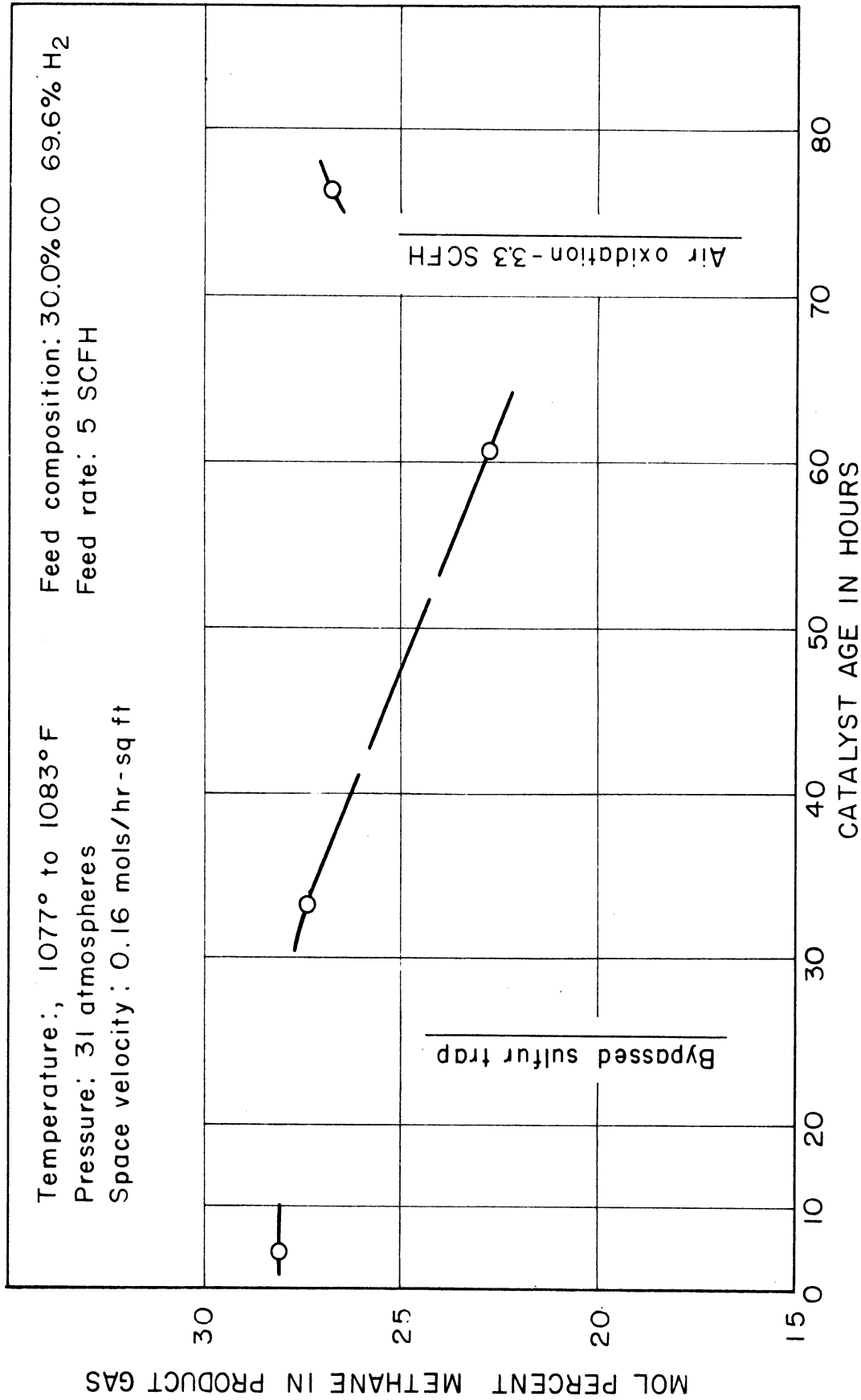


Figure 30. Effect of the Use of Air Oxidation to Reactivate Catalyst Poisoned by Carbonyl Sulfide on the Methane Concentration of the Product Gas.

sulfide was allowed to contact the catalyst, the product gas from run 30-B at 1077° to 1083°F contained 28.1% methane. However, after the sulfur trap was by-passed, the catalyst suffered a gradual decline in activity as indicated by the decreasing amount of methane in the product gas.

Oxidation of the poisoned catalyst with air, in addition to removing deposited carbon, restored the catalyst activity to a level almost equal to that observed before the catalyst was poisoned. Figure 29 indicates that over a period of roughly 10 hours from the time of oxidation with air, the activity of the steel catalyst slowly increased with time. This suggests that if the test period of run 30-Ox-B had been extended, the activity of the oxidized catalyst might eventually have equaled or exceeded the activity of the unpoisoned catalyst.

Summarizing the results of the experiments on catalyst regeneration; oxidation with air provides (1) a satisfactory method for removing deposited carbon from steel catalyst without adversely affecting the catalyst activity and (2) a means of reactivating steel catalyst poisoned by sulfur compounds. Furthermore, both operations can be accomplished in a single step.

Effect of Extended Periods of Synthesis at Temperatures Above 1200°F on the Activity of the Catalyst

In the course of the series of experimental runs which were made to determine the effect of temperature on product gas composition, several runs were made to further investigate some interesting phenomena observed by Smith⁵⁸ in his research with steel catalyst.

Smith made a temperature traverse (similar to that shown in Figure 12) using a feed gas of 70% hydrogen and 29% carbon monoxide. Data taken at increasing temperatures showed that a maximum catalyst activity was reached

at a temperature of about 1070°F, at which point the product gas contained 25% methane. Upon completion of the upward temperature traverse, the catalyst temperature was raised to 1250°F and held at this level overnight. Smith observed that a period of synthesis above 1200°F served to enhance the activity of the steel catalyst. The downward temperature traverse not only yielded higher concentrations of methane in the product gas (28% methane at 1050° to 1000°F), but the catalyst activity did not decline in the threshold temperature range as rapidly as it rose on the upward temperature traverse.

To investigate more fully the increased activity as a result of extended periods of synthesis at temperatures above 1200°F, Smith made a double traverse, using a feed gas of 75% hydrogen and 24% carbon monoxide, in which the catalyst was heated and cooled twice. The results of the double traverse were much the same as the previous traverse; increased catalyst activity after prolonged synthesis at temperatures above 1200°F. In addition, considerable instability in the activity of the catalyst was observed while operating in the temperature region 1200° to 1270°F.

Runs 40-D and 40-E of the present work were made to examine the effect of high temperature synthesis on catalyst activity using a feed gas of approximately 40% carbon monoxide and 60% hydrogen. The usual procedure of heating the reactor to temperature, dropping in the catalyst charge, and then commencing the flow of feed gas over the catalyst was used in initiating run 40-D. (This was not the procedure used by Smith.) Two data points were taken at 1104° and 1106°F, respectively, and the catalyst-bed temperature was then raised to 1250°F. Because of the increased carbon deposition encountered with the use of feed gas containing 40% carbon monoxide, it would not have been possible to operate for the duration of runs 40-D and

40-E at this feed composition without plugging the catalyst bed with carbon. Consequently, after the first two data points were obtained, the composition of the feed gas was changed to roughly 20% carbon monoxide and 80% hydrogen, at which composition negligible amounts of free carbon were formed. After fourteen hours of synthesis at temperatures of 1248° to 1270°F, the original feed gas composition was re-established. The reactor was allowed to cool to about 1100°F and two additional sets of data were collected. All data collected on the downward traverse from 1266° to 1100°F were considered to be part of run 40-E.

A comparison of the composition of the product gas from runs 40-D and 40-E is presented in Table XIV. Contrary to the observations made by Smith for lower concentrations of carbon monoxide in the feed gas, the data of Table XIV indicate that extended periods of synthesis at temperatures above 1200°F have no apparent effect on the catalyst activity. Furthermore, the data show that approximately the same composition of product gas is formed

TABLE XIV

COMPARISON OF THE PRODUCT GAS COMPOSITION BEFORE AND AFTER
EXTENDED SYNTHESIS AT TEMPERATURES ABOVE 1250°F

	Run 40-D		Run 40-E	
	(before high temp)		(after high temp)	
	40-D1	40-D2	40-E2	40-E3
Temperature, °F	1104	1106	1105	1116
Feed Gas Composition				
%CO	39.7	39.1	39.3	40.1
H ₂	59.7	60.4	60.2	59.4
Product Gas Composition				
%CH ₄	32.7	33.0	32.9	32.6
CO ₂	21.4	21.1	20.2	20.6
H ₂ O	15.6	15.7	15.4	15.3
CO	10.2	10.0	10.5	11.6
H ₂	18.8	19.2	20.0	19.1

regardless of whether the desired catalyst temperature is approached from a higher or from a lower temperature.

Effect of the Catalyst Charging Procedure on the Activity of the Catalyst

A suggested explanation for the contradictory results of runs 40-D and 40-E and the data reported by Smith is based upon an observation made early in this research with regard to the procedure for starting a run. The usual method for charging the reactor with catalyst, as described in detail in the section on Experimental Procedure, was to heat the empty reactor to temperature before adding the catalyst charge and commencing the flow of feed gas. In this way the catalyst was heated from room temperature to within a few degrees of the control temperature in less than 15 minutes. In subsequent discussion this catalyst charging procedure will be referred to as the "hot charging method."

An alternate catalyst charging procedure, hereafter known as the "cold charging method," was to introduce the catalyst into the cold reactor, to establish flow of feed gas over the catalyst, and then to heat the reactor to the desired operating temperature. (This was the method used by Smith.)

It has been observed in this research that the steel catalyst is more active for methane synthesis when the "hot charging method" rather than the "cold charging method" is used to initiate an experimental run. The data from runs 40-A and 40-B, in which the catalyst was introduced into the reactor using the "cold charging method," serve to illustrate the reduced catalyst activity obtained when using this procedure. The product gas composition data from runs 40-A and 40-B have been compared in Figures 31 to the methane, carbon dioxide, and water curves of the temperature traverse for a 40% carbon monoxide—60% hydrogen feed gas. The dashed curves drawn

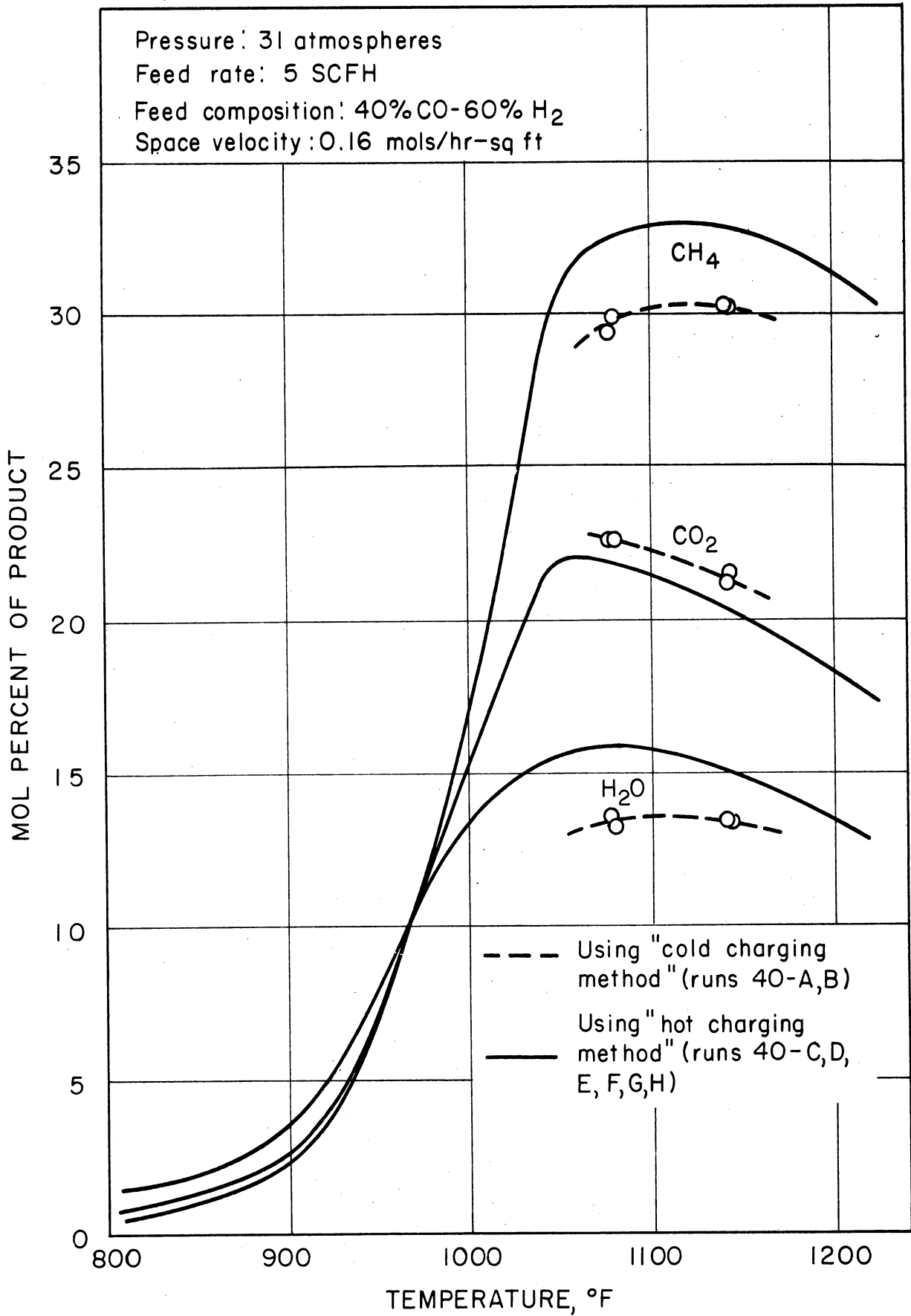


Figure 31. Effect of Using the "Cold Catalyst Charging Method" on the Composition of the Product Gas Obtained from a Feed of 40% CO - 60% H₂.

through the data points of runs 40-A and 40-B indicate that the activity of the catalyst for methane synthesis was lower in these runs than in the experimental runs which defined the curves of the temperature traverse.

Runs 30-A and 30-B offer a further example of the reduced catalyst activity obtained when the "cold charging method" is used. In run 30-B (see Figure 12), in which the "hot charging method" was used, for a feed gas composition of 30% carbon monoxide and 70% hydrogen the catalyst attained a maximum activity at about 1100°F. At this temperature, the product gas contained 28.6% methane. However, in run 30-A, which was begun with the "cold charging method," the product gas contained a maximum concentration of approximately 25% methane (after making allowance for the lower carbon monoxide content of the feed gas used in this run) at 1100°F.

Lobo⁵⁹ observed that the conditions of flow of synthesis gas over a steel catalyst, during heatup to an operating temperature of 1050°F, had a marked effect on the final catalyst activity obtained. The effect of heating the catalyst through the reaction threshold temperature region at low synthesis gas flow rates (less than 1 SCFH compared to the usual flow rate of 5 SCFH) was to lower severely the activity of the catalyst.

The results of the above-mentioned experimental runs and the report by Lobo indicate that during the period when the catalyst is slowly heated from room temperature to operating temperature in contact with feed gas, the steel catalyst is susceptible to some form of deactivation which renders it less active for methane synthesis. However, when the catalyst is rapidly heated to temperature before contacting feed gas using the "hot charging method," a more active catalyst is obtained. It is believed by this author that extended periods of synthesis at temperatures above 1200°F do not result in enhanced catalyst activity as suggested by Smith, but ra-

ther they allow the catalyst to recover in some manner from deactivation resulting from the use of the "cold charging method" in initiating an experimental run.

The above premise is substantiated by a review of some previously discussed data concerning the maximum percentage of methane present in the product gas from runs 30-A and 30-B and from the temperature traverse made by Smith.

	<u>Maximum Percent CH₄ in Product Gas</u>
<u>Temperature Traverse Made by Smith</u>	
Upward traverse	25.0
Downward traverse (after extended period of synthesis at temperatures above 1200°F)	28.4
<u>Temperature Traverses of This Research</u>	
Run 30-A (using "cold charging method")	25 (approx)
Run 30-B (using "hot charging method")	28.6

Approximately the same maximum percentage of methane was present in the product gas from Smith's upward temperature traverse as in the product from run 30-A. This would be expected, since both runs were started with the "cold charging method" and were conducted in a similar manner. The fact that the same maximum percentage of methane was obtained in the product gas of Smith's downward temperature traverse as in the product gas of run 30-B suggests that during the extended period of synthesis above 1200°F the activity of the catalyst was merely restored to the level of activity which would have been obtained on the upward traverse had the "hot charging method" been used.

Exploratory Investigation of a Cobalt-Thoria Catalyst for Methane Synthesis

On the basis of thermodynamic equilibrium considerations, it has been pointed out previously that low temperatures and high pressures are most favorable for the conversion of carbon monoxide and hydrogen to methane. Unfortunately, the steel catalyst studied is not active for methane synthesis at temperatures much below 1000°F. Thus, while steel possesses many attributes that make it an attractive methanization catalyst, it is necessary to operate at temperatures which are not the most favorable for methane synthesis. As a result, it is not possible to approach complete conversion of the carbon monoxide and hydrogen of the feed gas to methane. Even at the optimum reaction conditions determined for the steel catalyst, appreciable quantities of carbon monoxide and hydrogen remain unreacted, thus limiting the maximum gross heating value of the product gas obtained at 31 atmospheres pressure to approximately 745 BTU/SCF.

Supported nickel and cobalt base catalysts, on the other hand, are known to be active for methane synthesis at temperatures at which almost complete conversion of carbon monoxide and hydrogen to methane is thermodynamically possible. While such porous type catalysts are subject to sintering and to fragmentation by carbon deposition making them less desirable from a structural standpoint, potentially they are capable of producing a product of higher heating value than is obtainable with a steel catalyst.

A single experimental run, designated Co-Th, was made near the end of the research to evaluate in a cursory manner the use of a supported cobalt-thoria catalyst for methane synthesis. Two hundred 1/8-inch-diameter by 1/8-inch-long catalyst pellets were mixed with twice as many inert brass cylinders of the same dimensions. The catalyst charge was introduced into the reactor, and a flow of 5 SCFH of feed gas containing 29.0% carbon mo-

noxide and 70.6% hydrogen was established. Since the exact temperatures at which the cobalt-thoria catalyst was active were not known, the reactor was heated slowly. Data were collected at temperatures of 505° and 543°F. At about 560°F, the rate of methanization increased rapidly. The heat of reaction was so great that control of the reaction temperature was not possible. A third set of data was collected in the region of 645°F; however, the reaction temperature was still rising rapidly. Finally at 702°F the reaction temperature leveled off. Data were taken at this temperature and at 838°F.

The effect of temperature on the composition of the product gas from run Co-Th is shown in Figure 32. It can be noted that a larger percentage of methane is present in the product gas than is observed in the product from an active steel catalyst. Only a small amount of carbon monoxide remains unreacted in the product gas. Some hydrogen is present in the product gas, and in view of the nearly complete conversion of carbon monoxide, it appears likely that the use of a feed gas of 33% carbon monoxide and 67% hydrogen would result in virtually complete conversion to methane, water, and carbon dioxide.

The gross heating values of the product gas, free of water and carbon dioxide, have been determined at three temperatures of run Co-Th and are tabulated below.

Temperature, °F	Gross Heating Value, BTU/SCF
645	885
702	868
838	846

These values exceed the heating values of product gases synthesized on

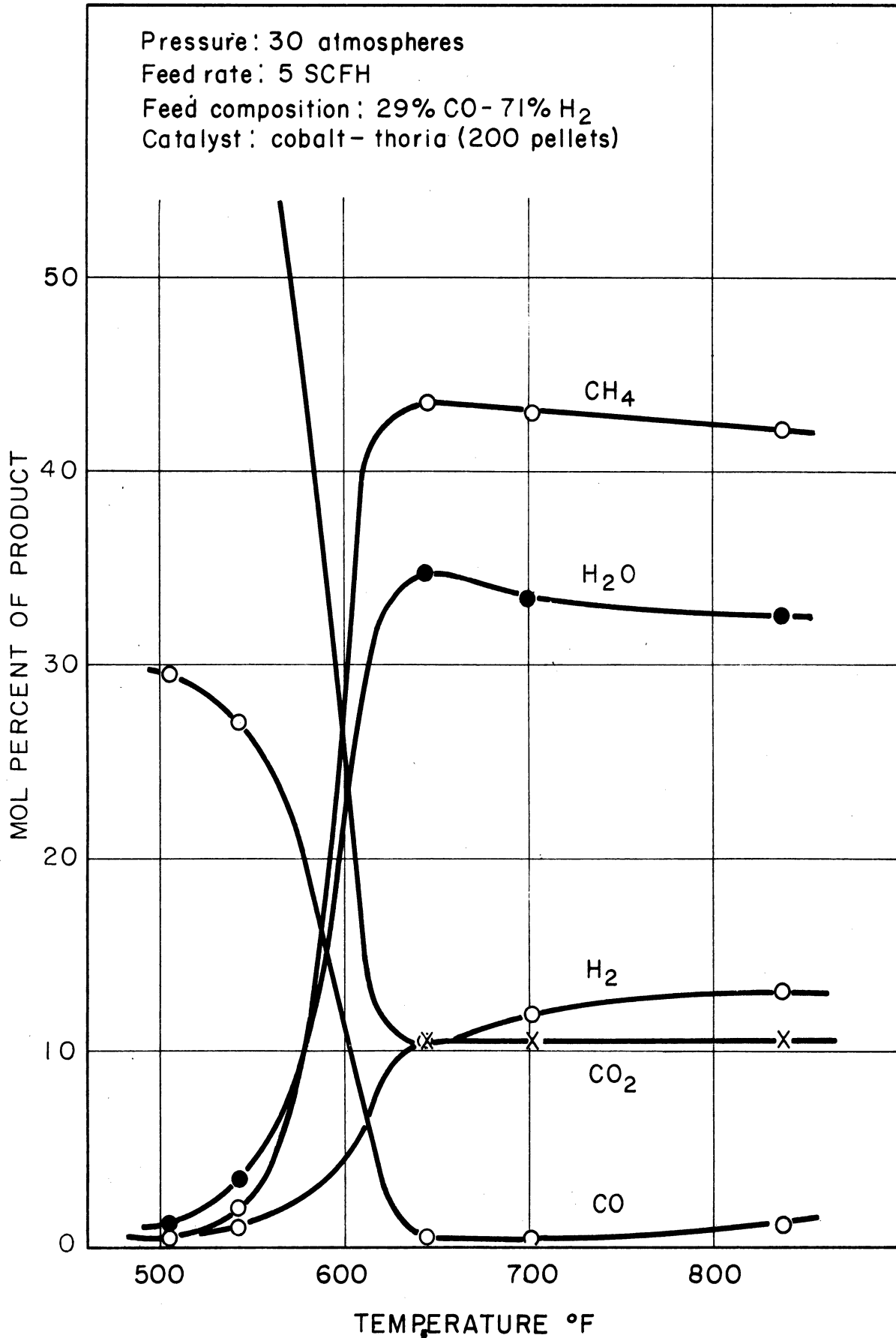


Figure 32. Effect of Temperature on the Product Gas Composition Using a Cobalt-Thoria Catalyst.

Steel catalyst, demonstrating the advantage of synthesis at lower temperatures and indicating, moreover, that the use of cobalt-thoria type catalysts for methanization is worthy of further study.

CONCLUSIONS

It is concluded that:

1. Carbon steel (C1013) is an effective methanization catalyst, exhibiting a large increase in its ability to catalyze the reaction between carbon monoxide and hydrogen to form methane, water, and carbon dioxide as the temperature is raised from 900° to 1040°F.
2. The catalyst activity reaches a maximum at 1100° to 1150°F, depending upon the feed composition, and then declines with a further increase in temperature.
3. The product gas composition is not appreciably affected by changes in space velocity over the range 0.10 to 0.26 mole/hr-sq ft.
4. Dilution of the product gas with unused reactants is reduced by increasing the carbon monoxide concentration of the feed gas, up to a value of 50%. At higher carbon monoxide concentrations, the sum of the unreacted hydrogen and carbon monoxide in the product gas begins to slowly increase.
5. Increases in the heating value of the product gas, resulting from reduced dilution by unconverted reactants, are limited by a decline in methane formation when feed gases containing more than 50% carbon monoxide are used.
6. Increasing the feed gas carbon monoxide concentration results in an increase in the percentage of the carbon monoxide converted to carbon dioxide and a decrease in the percentage converted to methane. When the

feed gas contains more than 50% carbon monoxide, the conversion of carbon monoxide to carbon dioxide exceeds the conversion to methane.

7. The optimum conditions of temperature and feed gas composition for the synthesis of a product of the highest heating value at 31 atmospheres pressure and a space velocity of 0.10 mole/hr-sq ft using a steel catalyst are as follows:

Temperature: 1090° to 1150°F

Percent CO in feed gas: 47% to 52%

The heating value of the scrubbed product gas ranges from 735 to 745 BTU/SCF. Considerable carbon deposition is encountered over this range of reaction conditions.

8. The amount of carbon deposition increases as the carbon monoxide content of the feed gas is increased.

9. The rate of carbon deposition increases rapidly as the temperature is raised from 900° to 1000°F. For a particular feed gas composition, the region of heaviest carbon deposition occurs over the temperature range 980° to 1020°F. As the temperature is further increased, the amount of carbon deposition decreases substantially.

10. Carbon can be removed from the catalyst by oxidation with air without a deleterious effect on the catalyst activity.

11. Steel catalyst is poisoned by carbonyl sulfide present in the feed gas.

12. Catalyst poisoned by carbonyl sulfide can be reactivated by oxidation with air.

13. Extended periods of synthesis at temperatures above 1200°F have no apparent effect on the composition of the product gas obtained from a feed of 40% carbon monoxide and 60% hydrogen at the optimum operating tem-

perature of 1100°F.

14. Steel catalyst is more active for methane synthesis when it is introduced into a hot reactor and rapidly heated to temperature before contacting feed gas, than when introduced into a cold reactor and heated slowly to temperature in contact with feed gas.

15. Promotion of the steel catalyst with potassium carbonate results in a slight increase in the production of C₂+ hydrocarbons, but in a decrease in the amount of methane formed.

16. Supported cobalt-thoria catalyst shows promise as a methanization catalyst. Synthesis at a temperature of 645°F resulted in almost complete conversion of the feed carbon monoxide to products, which had a heating value of 885 BTU/SCF after water and carbon dioxide were removed.

APPENDIX

SAMPLE CALCULATIONS

Experimental Data

Run: 50-A2

Catalyst: Carbon steel (C1013)

Number of Catalyst Balls: 388

Catalyst Surface Area: 0.132 sq ft

Reactor Pressure: 31 atmospheres

Catalyst Bed Temperature: 1092°F

Wet-Test Meter Data:

	Feed	Product
Temperature, °F	77	77
Pressure, in. Hg	29.17	29.17
Correction factor*	0.912	0.912
Seconds/0.10 cu ft	65.2	127.8

Mass Spectrometer Analyses of the Feed and Product Gas:

The methods used to obtain the feed and product gas analyses have been described in the section titled Methods of Analysis.

	Feed, %	Product Gas (water free), %
CO	50.25	14.27
H ₂	49.24	9.96
CO ₂	0.20	37.37
CH ₄	-	36.59
C ₂ H ₆	-	1.08
C ₂ H ₄	-	0.02
C ₃ H ₈	-	0.10
C ₃ H ₆	-	0.02
C ₄ ⁺	-	-
N ₂ **	0.30	0.59

*This correction factor includes the correction for water vapor present, as well as the temperature and pressure corrections to 60°F and 30 in. Hg.

**Nitrogen was present as an impurity in the carbon monoxide feed.

Carbon Deposition Date: (for entire run 50-A)

Carbon deposited	7.7 grams
Avg temp of run	1088°F
Minutes at temp	150
Avg % CO + CO ₂ in feed	50.4

Calculated Data

Flow Rates.—The feed and product flow rates, in standard cubic feet per hour at 30 in. Hg and 60°F, were calculated from the times for 0.10 cu ft of gas to flow through the wet-test meter.

$$\text{Feed rate: } \frac{(0.912)(3600)(0.10)}{65.2} = 5.04 \text{ SCFH}$$

$$\text{Product rate: } \frac{(0.912)(3600)(0.10)}{127.8} = 2.57 \text{ SCFH}$$

Space Velocity.—The space velocity was calculated by dividing the feed rate by 379 cu ft/mol and by the number of square feet of catalyst surface.

$$\text{Space velocity: } \frac{5.04}{(379)(0.132)} = 0.1005 \text{ mole/hr-sq ft}$$

Feed Ratio, H₂/CO.—The H₂/CO ratio was calculated directly from the feed gas analysis.

$$\text{H}_2/\text{CO ratio: } \frac{49.24}{50.25} = 0.980$$

Total Product Composition.—The analysis of the product determined by mass spectrometer was on a water-free basis, since water produced by the synthesis reaction was condensed out before the product samples were collected. The quantity of water formed was determined by material balance, as shown in the following calculation, since no provision was made to collect and measure the amount of water condensed.

A basis of 100 moles of total feed has been used in the following calculations. $N = \text{mols}/100 \text{ mols of total feed}$. The subscript "i" refers to inlet moles, and the subscript "e" refers to exit moles.

The number of moles of each component of the feed entering the reactor, N_i , was determined directly from the feed analysis.

$$N_i(\text{CO}) = 50.25$$

$$N_i(\text{CO}_2) = 0.20$$

$$N_i(\text{H}_2) = 49.24$$

$$N_i(\text{N}_2) = 0.30$$

The number of moles of product gas (on a water-free basis) leaving the reactor per 100 moles of inlet gas, $N_{e(\text{W.F.})}$, was determined by dividing the product rate by the feed rate and multiplying by 100.

$$N_{e(\text{W.F.})} = \frac{2.57}{5.04} \times 100 = 51.02$$

The number of moles of each constituent of the water-free product gas leaving the reactor was found by multiplying $N_{e(\text{W.F.})}$ by the mol fraction of each component as given by the product analysis.

$$N_e(\text{CO}) = (51.02)(0.1427) = 7.28$$

$$N_e(\text{CO}_2) = (51.02)(0.3737) = 19.07$$

$$N_e(\text{H}_2) = (51.02)(0.0996) = 5.08$$

$$N_e(\text{CH}_4) = (51.02)(0.3659) = 18.67$$

$$N_e(\text{C}_2\text{H}_6) = (51.02)(0.0108) = 0.55$$

$$N_e(\text{C}_2\text{H}_4) = (51.02)(0.0002) = 0.01$$

$$N_e(\text{C}_3\text{H}_8) = (51.02)(0.0010) = 0.05$$

$$N_e(\text{C}_3\text{H}_6) = (51.02)(0.0002) = 0.01$$

$$N_e(\text{N}_2) = (51.02)(0.0059) = 0.30$$

The number of mols of water produced per 100 mols of total feed was calculated by making an oxygen and a hydrogen balance and averaging the two results.

$$\text{Oxygen balance: } 50.25 + 2(0.20) - 7.28 - 2(19.07) = 5.23$$

$$\begin{aligned} \text{Hydrogen balance: } 49.24 - 5.08 - 2(18.67) - 3(0.55) - 2(0.01) \\ - 4(0.05) - 3(0.01) = 4.92 \end{aligned}$$

$$N_{e(\text{H}_2\text{O})} = \frac{5.23 + 4.92}{2} = 5.08$$

The number of exit mols on a water-free basis was then added to the mols of exit water to give the total mols of product per 100 mols of feed.

$$N_{e(\text{total})} = N_{e(\text{W.F.})} + N_{e(\text{H}_2\text{O})} = 51.02 + 5.08 = 56.10$$

The total product composition was calculated from $N_{e(\text{total})}$ and the N_e for each product component.

CO	$\frac{7.28}{56.10}$	x 100 = 12.98%
CO ₂	$\frac{19.07}{56.10}$	x 100 = 33.99%
H ₂	$\frac{5.08}{56.10}$	x 100 = 9.06%
CH ₄	$\frac{18.67}{56.10}$	x 100 = 33.28%
C ₂ H ₆	$\frac{0.55}{56.10}$	x 100 = 0.98%
C ₂ H ₄	$\frac{0.01}{56.10}$	x 100 = 0.02%
C ₃ H ₈	$\frac{0.05}{56.10}$	x 100 = 0.09%
C ₃ H ₆	$\frac{0.01}{56.10}$	x 100 = 0.02%
N ₂	$\frac{0.30}{56.10}$	x 100 = 0.53%
H ₂ O	$\frac{5.08}{56.10}$	x 100 = 9.06%

Conversion of Carbon Monoxide to Products.---The percent conversion of the feed carbon monoxide to methane and to carbon dioxide was calculated as follows:

$$\text{Conv. to CH}_4 = \frac{N_e(\text{CH}_4) - N_i(\text{CH}_4)}{N_i(\text{CO})} \times 100$$

$$\text{Conv. to CH}_4 = \frac{18.67 - 0}{50.25} \times 100 = 37.2\%$$

$$\text{Conv. to CO}_2 = \frac{N_e(\text{CO}_2) - N_i(\text{CO}_2)}{N_i(\text{CO})} \times 100$$

$$\text{Conv. to CO}_2 = \frac{19.07 - 0.20}{50.25} \times 100 = 37.6\%$$

The total conversion of carbon monoxide to products was calculated by dividing the difference between the mols of carbon monoxide entering and leaving the reactor by the number of mols of inlet carbon monoxide.

$$\text{Total conv.} = \frac{50.25 - 7.28}{50.25} \times 100 = 85.5\%$$

Carbon Balance.---The carbon balance was determined by calculating the difference between the mols of carbon which entered in the feed gas and the mols of carbon which left the reactor in the product gas, and by dividing the result by the mols of inlet carbon.

$$\text{Inlet carbon: } 50.25 + 0.20 = 50.45$$

$$\begin{aligned} \text{Exit carbon: } & 7.28 + 19.07 + 18.67 + 2(0.55) + 2(0.01) + 3(0.05) \\ & + 3(0.01) = 46.32 \end{aligned}$$

$$\text{Carbon balance: } \frac{50.45 - 46.32}{50.45} \times 100 = 8.19\%$$

This value represents the weight percent of the carbon that entered the reactor in the form of carbon dioxide and carbon monoxide that was deposited

as free carbon during synthesis.

The amount of carbon deposition was also determined by weighing the free carbon removed from the catalyst bed at the end of an experimental run. From the length of time at the synthesis temperature and the average CO + CO₂ content of the feed gas, the grams of carbon which entered the reactor during the run were calculated. Dividing the grams of deposited carbon by the grams of carbon fed during the run yielded the weight percent of the carbon fed as CO + CO₂ which was deposited as free carbon.

$$\frac{7.7 \text{ grams deposited}}{90.7 \text{ grams fed}} \times 100 = 8.5\%$$

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