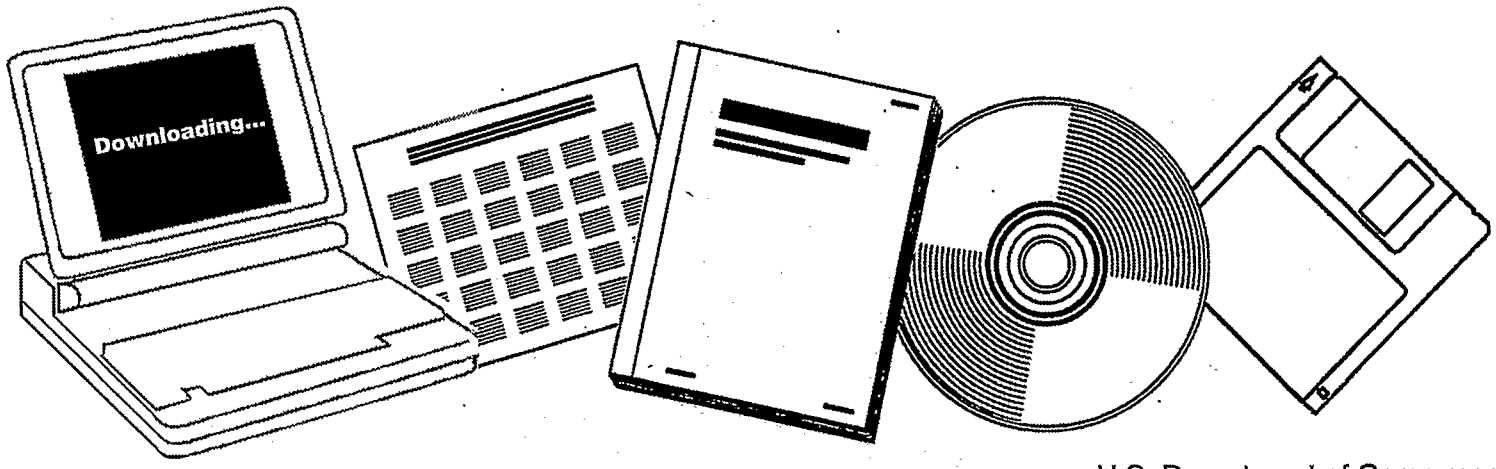
METHANE PRODUCTION FROM CARBON OXIDES OVER BOROHYDRIDE-REDUCED TRANSITION METALS

NEW MEXICO ENERGY INST., ALBUQUERQUE

JAN 1978



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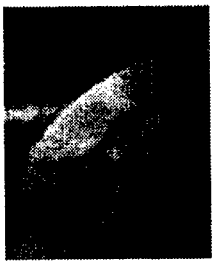

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Final Report

METHANE PRODUCTION FROM CARBON OXIDES OVER BOROHYDRIDE-REDUCED TRANSITION METALS

by

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This study was undertaken to continue the examination of the utility of borohydride-reduced transition metals as catalysts for the hydrogenation of carbon oxides to produce synthetic fuels.

While most related efforts deal only with carbon monoxide (the predominant oxide in coal gasification processes), we have included carbon dioxide as well in our work.

Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besides water). This is a definite improvement over many of the catalysts reported in the scientific literature, where a major problem is the production of numerous carbon-containing products.

Completion of construction of a second flow system has allowed several questions from earlier work (1) to be answered. Continuous methanation over nickel has shown no decrease in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during a two-week run.

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METHANE PRODUCTION FROM CARBON OXIDES OVER BOROHYDRIDE REDUCED TRANSITION METALS

Thomas W. Russell, Ph.D.
Principal Investigator

TECHNICAL COMPLETION REPORT
Project ERB No. 76-173

New Mexico Energy Resources Board
New Mexico Energy Institute at UNM
in cooperation with
Division of Natural Science
Eastern New Mexico University
Portales, New Mexico

January, 1978

SUMMARY

This study was undertaken to continue the examination of the utility of borohydride-reduced transition metals as catalysts for the hydrogenation of carbon oxides to produce synthetic fuels.

While most related efforts deal only with carbon monoxide (the predominant oxide in coal gasification processes), we have included carbon dioxide as well in our work. This has resulted in our being contacted by personnel at Jet Propulsion Laboratory to discuss possible incorporation of this work into a Viking Landing on Mars in the 1980's. This may develop into a NASA grant to develop a process to convert components in the Martian atmosphere into a combustible fuel.

Work with cobalt, copper, nickel and palladium has resulted in methane production from both carbon oxides, with carbon dioxide being only slightly less productive than carbon monoxide. From the last three metals, methane is the only product formed (besides water). This is a definite improvement over many of the catalysts reported in the scientific literature, where a major problem is the production of numerous carbon-containing products.

Our discovery that copper, prepared from sodium borohydride reduction of cupric salts, produces both methane and methyl alcohol is without comparison in the literature. Detailed studies on copper are just beginning.

Completion of construction of a second flow system has allowed several questions from earlier work (1) to be answered. Continuous methanation over nickel has shown no decrease in methane production during a two-week run. Continuous methanation over cobalt in the presence of 10ppm of sulfur dioxide has shown an increase in methane production during a two-week run.

This last result was instrumental in obtaining a 16-month grant from the Four Corners Regional Commission to study the effects of sulfur on borohydride-reduced metal methanation catalysts (2).

This work was presented at a Colloquium at New Mexico State University in June and will be presented at the National Conference on Technology for Energy Conservation in Albuquerque in January (3). Two manuscripts for submission to the "Journal of Catalysis" are nearing completion.

The Principal Investigator has received unsolicited offers of scientific assistance and collaboration from researchers at the University of New Mexico, Texas Tech University and the University of South Florida as well as Ventron Corporation and Catalysts and Chemicals International. He has recently been invited to present this work before the Second International Conference on Organic Synthesis sponsored by the International Union of Pure and Applied Chemistry (IUPAC) in Jerusalem in September. (Travel funds were, however, not offered.)

Three Masters Theses are resulting from this project. One student is now successfully enrolled in a Ph.D. program at Michigan State University; one ex-student now owns and runs a private chemical lab in Albuquerque; one ex-student has just started working for Diamond Shamrock in Dumas, Texas (4). No undergraduate students working on the projects have as yet graduated.

Travel funds permitted the Principal Investigator to attend the Rocky Mountain Fuel Symposium in Salt Lake City in February. (A paper submitted for the program was never received.) Personnel contacted during other grant-sponsored travel included chemical engineers working on energy research, ERDA contract holders for synthetic fuels research and an ERDA proposal reviewer. Also, a chemist from the University of Oklahoma was brought in as a consultant concerning possible high pressure studies.

Work is continuing on all aspects of the project. A flow system designed to operate at pressures up to 1500 psi should enhance results when finished. Publications, increased publicity, and information obtained during travels and meetings should result in federal funding with the new fiscal year in October.

RESULTS AND DISCUSSIONS

I. Palladium Catalyst

1. Preparation

Palladium chloride was used exclusively as it was the most accessible source of palladium for this research. It was easily dissolved in small amounts of water, so a 95% ethanol solution was easy to prepare. Further, it has been found that borohydride can chemically reduce certain other common anions, i.e. nitrate, acetate, etc.

In the preparation of an aqueous solution of palladium, a metallic mirror was formed along the beaker walls after a minute amount of borohydride was added. This was witnessed also of nickel by Sterlyadkina (5) and Hofer, et.al., (6). When prepared in an ethanol solution (95%) no metallic mirror was oberved, instead a fine gray material settled to the bottom of the beaker. Sodium borohydride was added until the evolution of gas was complete. When the first catalyst was allowed to drip dry and then placed immediately in the catalyst bed and flushed with hydrogen at 200°C, the glass catalyst bed shattered, sending glass shrapnel through the heating tape and asbestos tape. It was found that the catalyst must air dry for at least 48 hours before it is sufficiently "deactivated" to not cause an explosion of the catalyst bed. It is possible that if the catalyst is indeed deactivated by the 48-hour air dry process, then a stainless steel reactor may be able to contain a catalyst not allowed to set for 48 hours with better methane yield than the catalyst which has been allowed to set. No x-ray studies (which would show % palladium, palladium boride or palladium chloride) were made to determine exact catalyst composition. This combination may be a relevant factor in the methane production.

Production of methane was expressed as percentage with respect to a standard peak, or as percentage composition. Only two carbon-containing compounds (carbon monoxide and methane) were observed.

2. Continuous Flow Studies

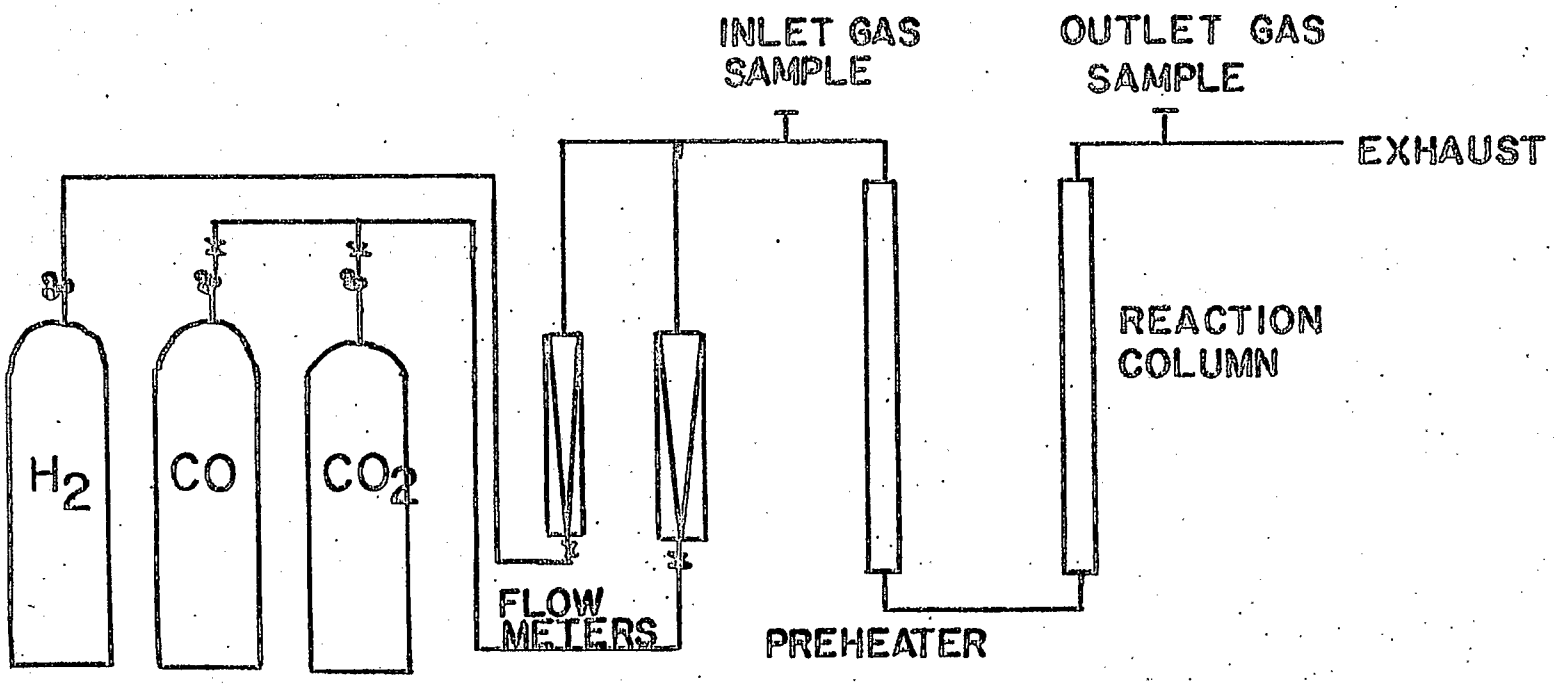
All work was done in the continuous flow systems designed and constructed from Energy Institute funds (Figures 1 and 2). Temperatures were allowed to stabilize before an analysis was made. Effect of temperature on methane production is shown in Figure 3, where the conversion is 48% methane with a 0.36% supported catalyst at 420°C.

Since 0.36% supported catalyst seemed to be a very small percent load, it was decided to see what, if any, effect increasing and decreasing the loading would have on methane yield. Figure 4 shows 33% methane yield on the 9.36% supported catalyst, while a catalyst of 1% loading could not produce 10% methane at what was thought to be an optimum temperature of 420°C. A catalyst of 1.02% palladium produced zero percent methane which indicates that of the three, the 0.36% loading is indeed optimum. The actual percentage CO_2 converted to methane on the 1.02% support is shown in Figure 5.

Reactant ratio was a question of concern in previous work and was investigated in this research. Figure 6 indicates that the stoichiometric ratio of four hydrogen to one carbon dioxide produces the best yield of methane. Again, optimum temperature is 420°C. Lower ratios (3:1,2:1) were run which showed no methane production.

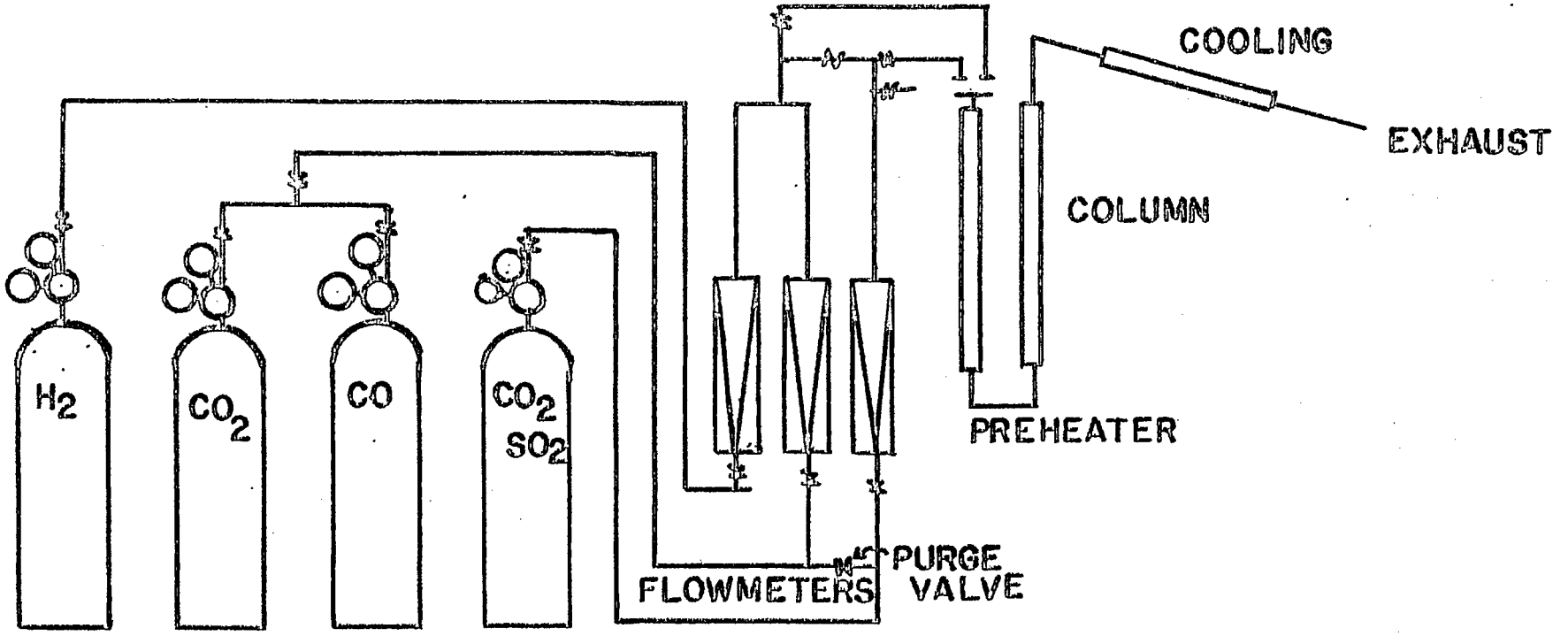
Two other parameters were studied. These were solvent and support. Water was used as a solvent for catalyst preparation, but the catalyst so generated afforded less than 1% methane under identical conditions to which the ethanol catalysts were subjected. Two supports were tried also, silica gel and alpha alumina. Figures 3,4,5 and 6 and all silica gel supports. Alpha alumina yielded less than 1% methane under conditions identical to those reported for silica gel.

Another variable studied was flow rate. Original work was done at 7-10 liters per hour. Later, it was decided to reduce the flow to 0.8 liters per hour



FLOW SYSTEM I SCHEMATIC

Figure 1



FLOW SYSTEM II SCHEMATIC

Figure 2

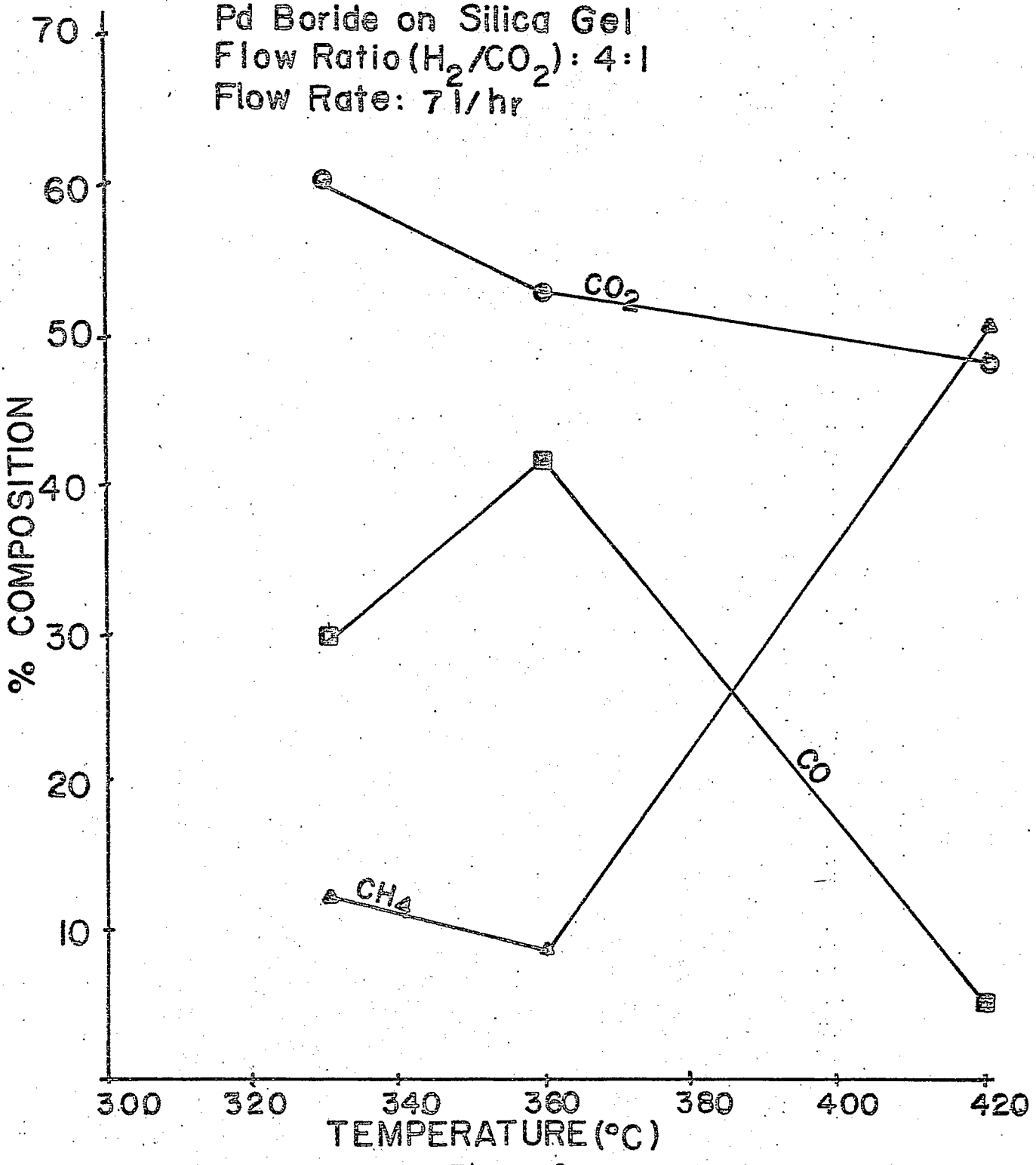

Pd Boride on Silica Gel
Flow Ratio (H_2/CO_2) : 4:1
Flow Rate: 7 l/hr
70
60
50
40
30
20
10
% COMPOSITION
CO_2
CO
CH_4
300
320
340
360
380
400
420
TEMPERATURE (°C)

Figure 3

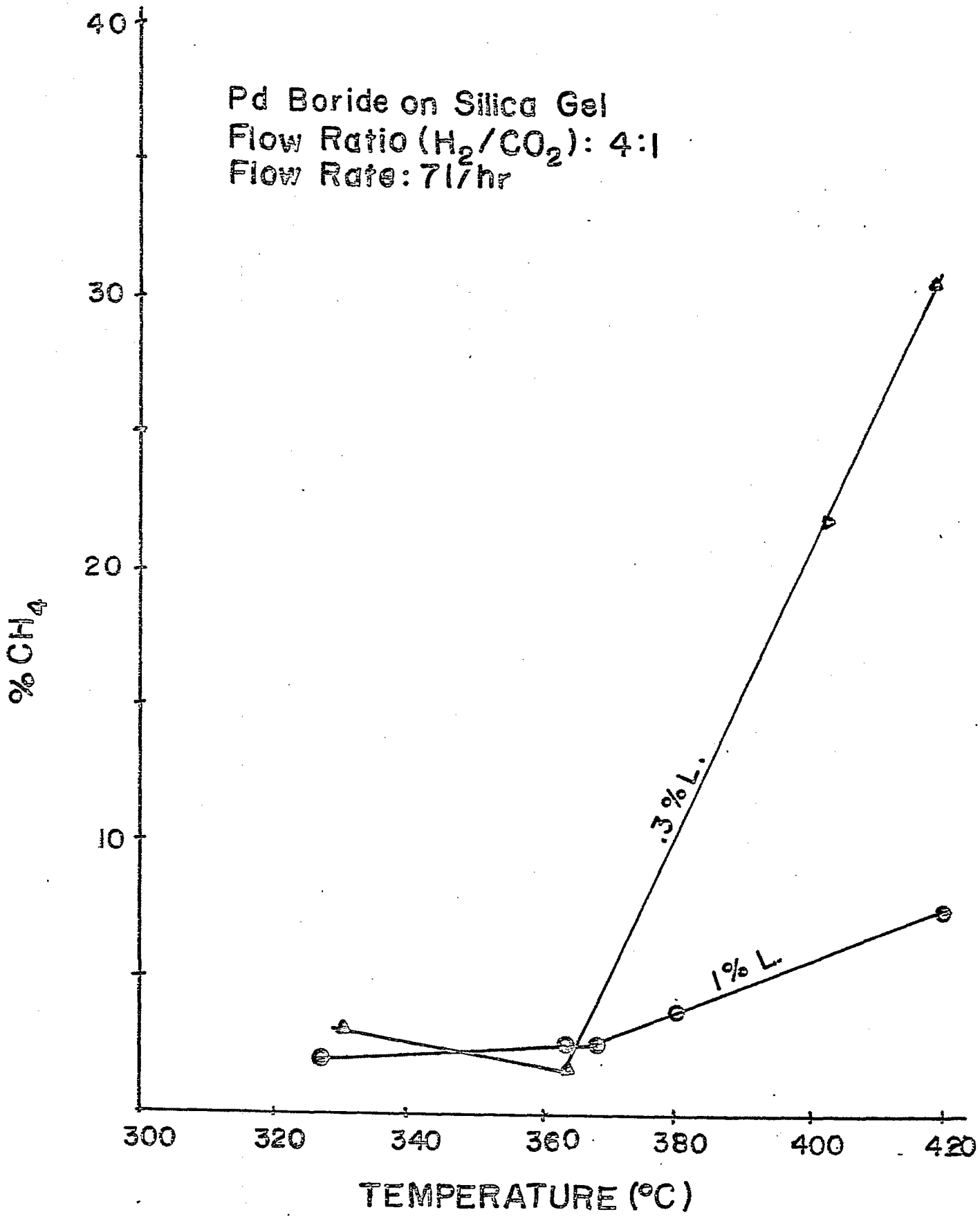

Pd Boride on Silica Gel
Flow Ratio (H_2/CO_2): 4:1
Flow Rate: 7l/hr
40
30
20
10
% CH_4
.3% L.
1% L.
300
320
340
360
380
400
420
TEMPERATURE (°C)

Figure 4

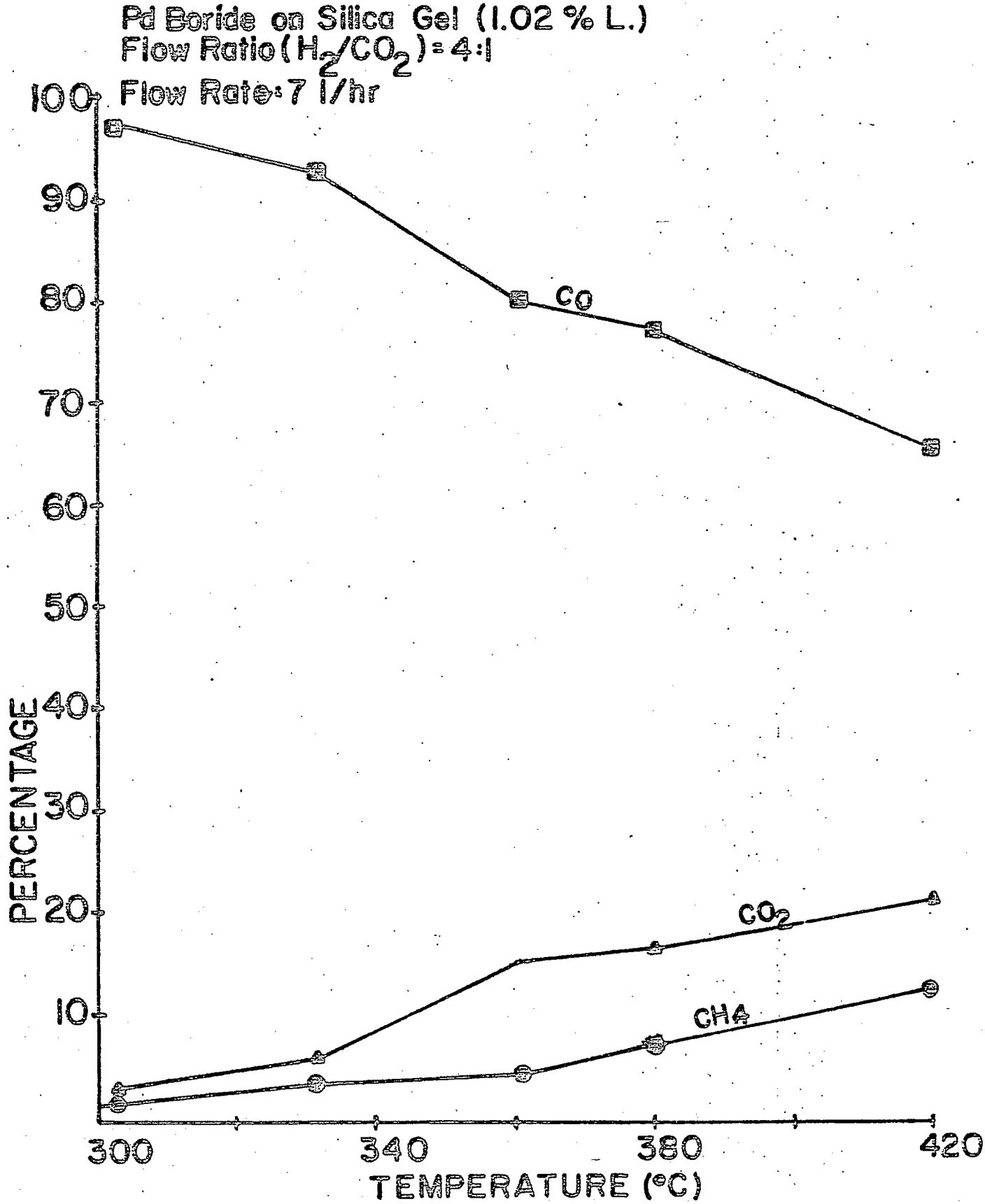

Pd Boride on Silica Gel (1.02 % L.)
Flow Ratio (H_2/CO_2) = 4:1
Flow Rate: 7 l/hr
100
90
80
70
60
50
40
30
20
10
PERCENTAGE
CO
CO_2
CH_4
300
340
380
420
TEMPERATURE (°C)

Figure 5

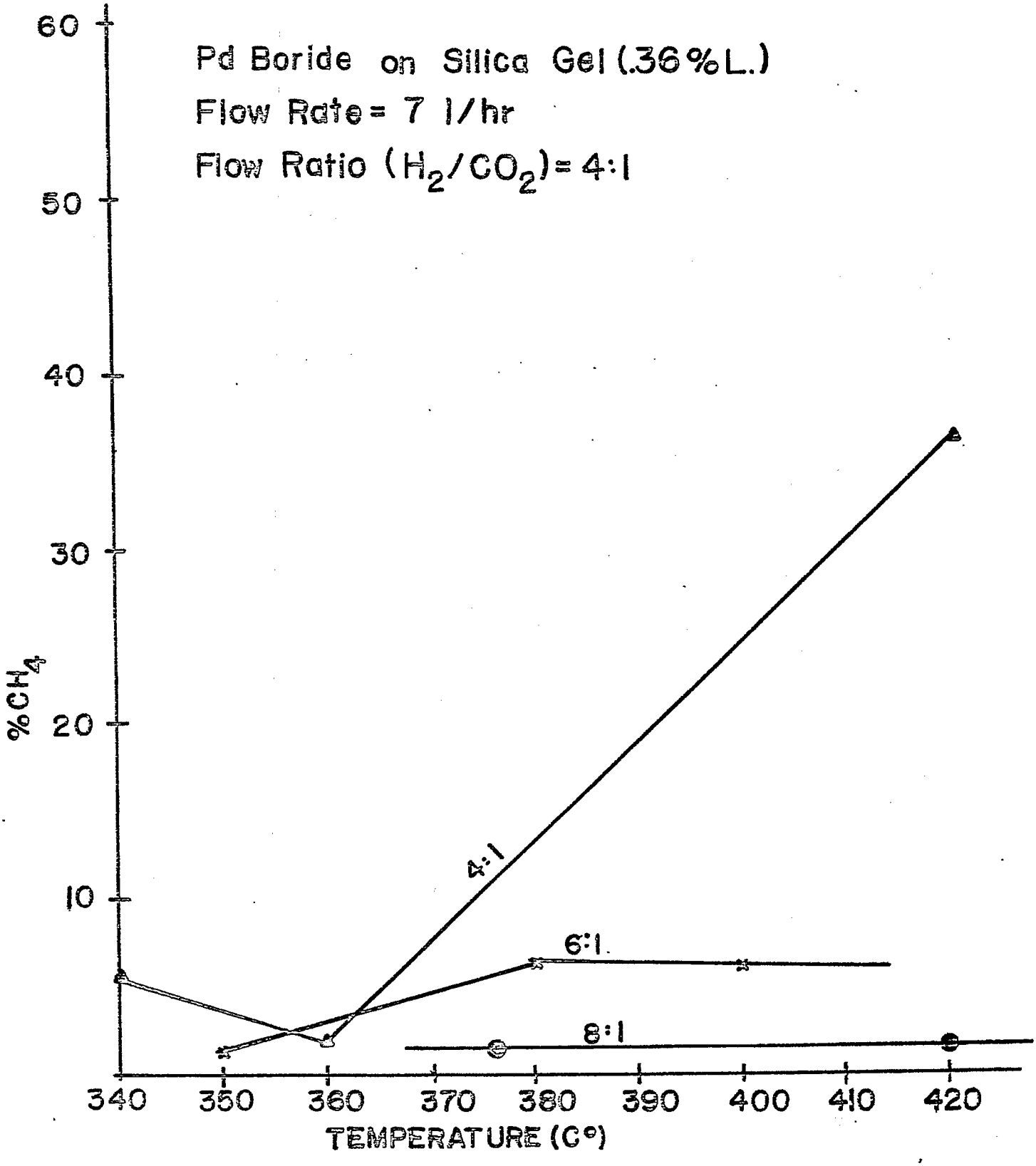

Pd Boride on Silica Gel (.36% L.)
Flow Rate = 7 l/hr
Flow Ratio (H_2/CO_2) = 4:1
60
50
40
30
20
10
%CH_4
4:1
6:1
8:1
340
350
360
370
380
390
400
410
420
TEMPERATURE (C°)

Figure 6

with a resultant yield of no methane. However, there was total conversion of carbon dioxide to carbon monoxide at 410°C with reactant ratio 4:1. The catalyst used for this study was 0.36% support.

Work with palladium has ceased pending efforts to ascertain the explosive nature of "new" catalyst.

II. Cobalt Catalyst

1. Preparation

Cobaltous chloride was used exclusively for the same reasons as elaborated for palladium. The preparation of supported cobalt boride in water did not have the metallic sheen as reported with nickel or palladium.

The preparation of the 95% ethanolic catalyst did not show this metallic sheen but produced a fine black catalyst in the beaker and on the support.

The formula for cobalt boride is not known; but for purposes of calculations, the formula $(CO_2B)_5.H_3$ (proposed by Maybury, et. al. (7)) was used in calculation of the hydrogen to the weight of catalyst.

2. Static Reactions for Carbon Dioxide

Silica supported cobalt boride made from ethanolic solution was gray at the start of the reactions. The static reactions were carried out in the Parr reactors with appropriate reactant gas ratios of 4 moles hydrogen per mole of carbon dioxide. Temperatures were varied from 100°C to 350°C at an initial pressure at room temperature of 150 psig. All runs were carried out for 12 hours.

Production of methane is expressed as percent composition. The only other products noted were carbon monoxide and water. Percentage compositions of methane are shown in Figure 7. The maximum production noted was 6.8% at 350°C, with production of mathane starting with the 100°C run. Also shown on Figure 7 are the results reported previously from nickel. These comparative results are the basis for the supplemental request for funds to construct a flow system to operate at pressures up to 1500 psi.

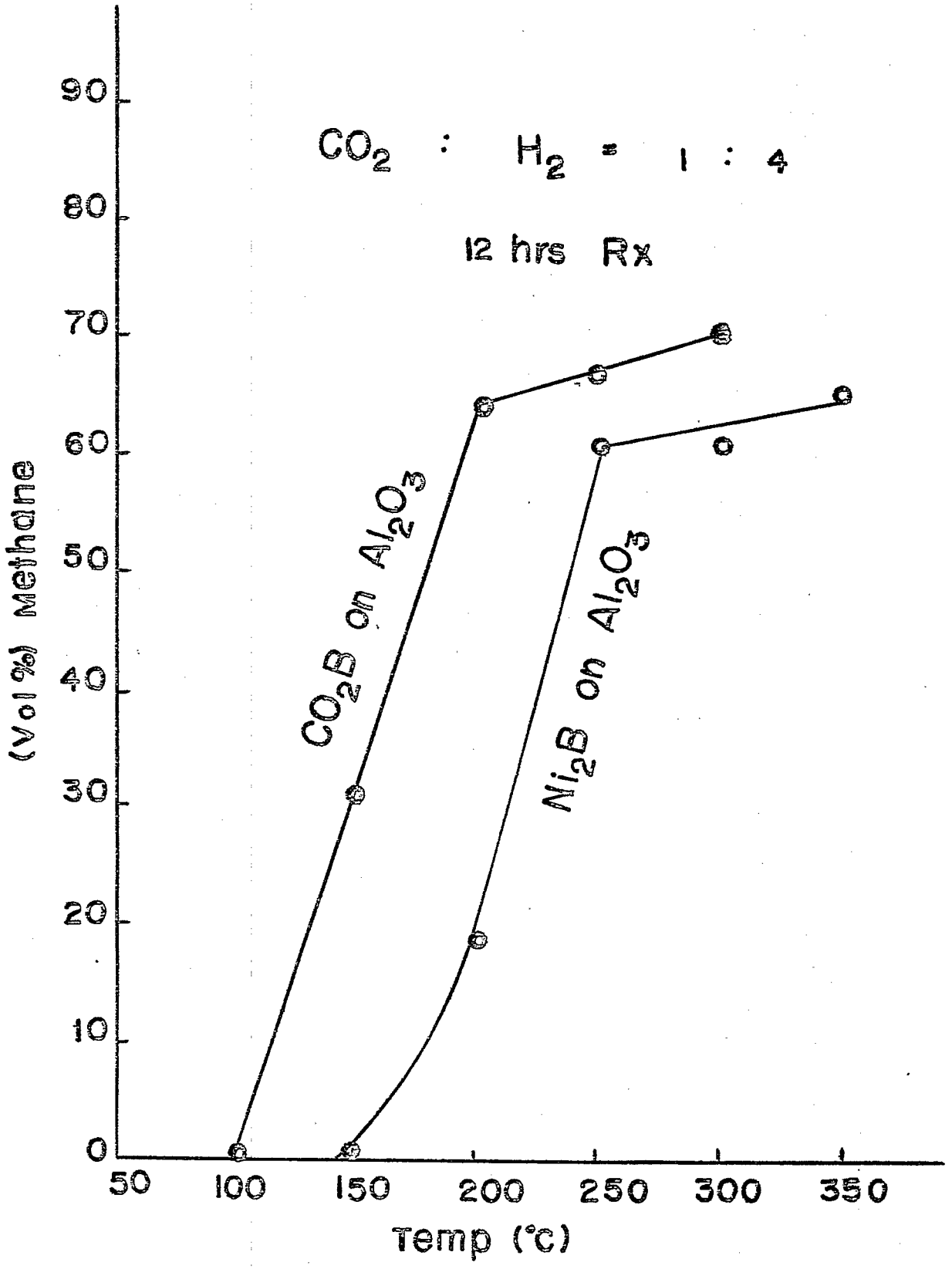

CO_2 : H_2 = 1 : 4
12 hrs Rx
CO_2B on Al_2O_3
Ni_2B on Al_2O_3
(Vol %) Methane
Temp (°C)
0
10
20
30
40
50
60
70
80
90
50
100
150
200
250
300
350

Figure 7

3. Continuous Reaction for Carbon Dioxide

Because of the results from the hydrogenation of carbon dioxide over cobalt boride in the static reactor, cobalt boride was expected to exhibit significant methane production in a practical continuous reaction at atmosphere pressure. The flow systems shown in Figures 1 and 2 were used for cobalt studies, also.

All attempts to produce active aqueous solution catalysts proved unsuccessful. All cobalt catalysts used in the continuous flow system were made in 95% ethanol.

The catalyst was also made by an immersion process. The process of flash evaporation process proved to be of little importance in comparison. This was probably due to the drawing of the hydrogen blanket by the vacuum placed on the evaporation apparatus and the inevitable replacement of it with air.

A. Reactions at Various Temperatures

A 44% cobalt boride catalyst on silica gel ($400 m^2/g$) was used with the stoichiometric reactant ratio of 4 moles of hydrogen to one mole of carbon dioxide with a flow rate of 5 l/hr. The conversion of carbon dioxide to methane and carbon monoxide are plotted versus temperatures in Figure 8. The maximum conversion of carbon dioxide to methane in the temperature range covered was about 47%. Infrared spectra of the gas products showed methane production beginning around 170°C. The conversion of carbon dioxide to carbon monoxide seemed noncompetitive. It started at about 230°C and increased until about 400°C, about which it started to decrease with increasing temperature.

Another catalyst was made having 4% of cobalt boride on micron silica gel. The methane and carbon monoxide production of this catalyst is shown in Figure 9. This shows that there is tendency of the carbon dioxide to carbon monoxide conversion to follow the methane production. The maximum conversion that was seen was 18% for the low-loaded catalyst. The maximum efficient temperature was not indicated by this study.

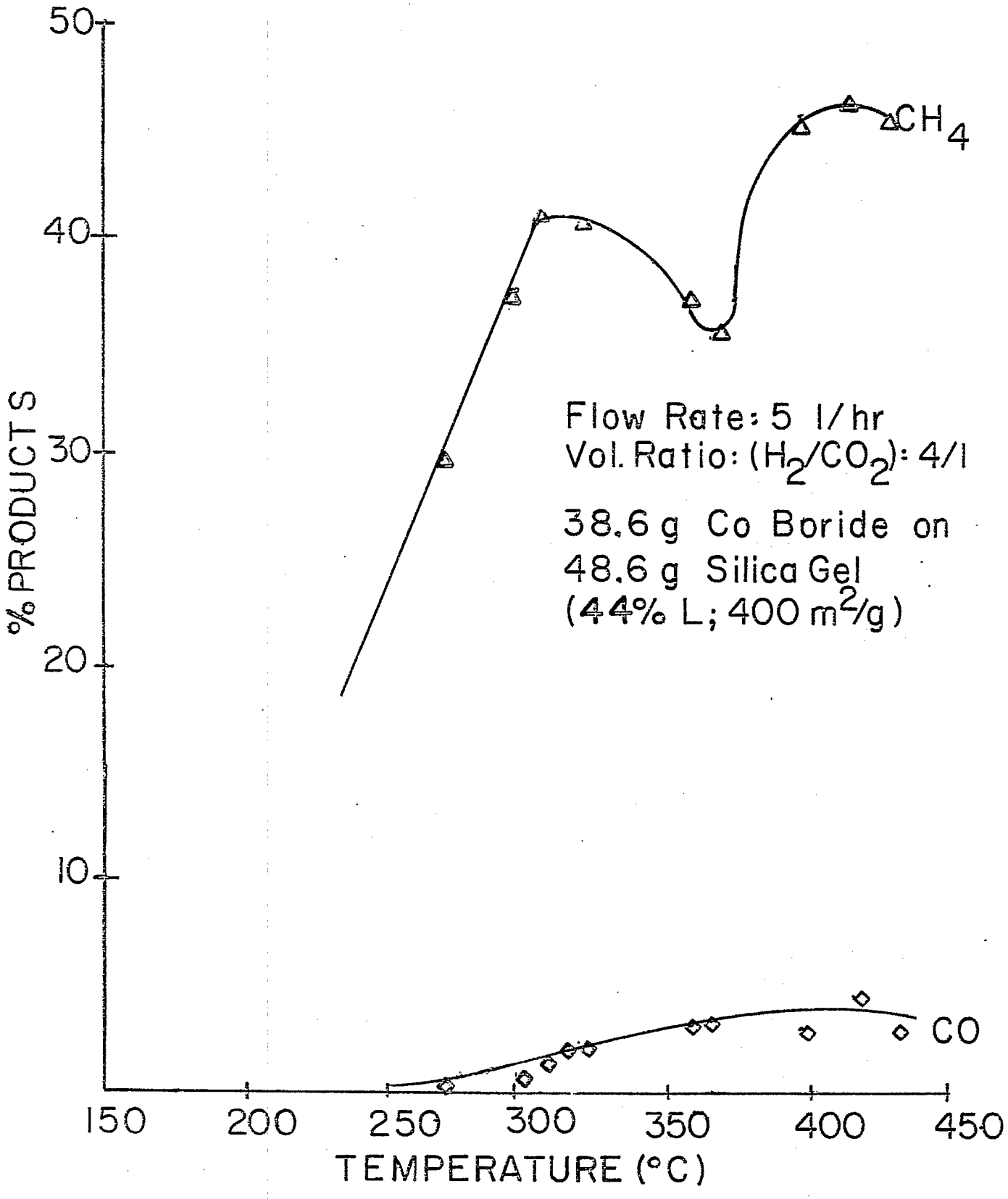

50
40
30
20
10
% PRODUCTS
CH4
Flow Rate: 5 l/hr
Vol. Ratio: (H2/CO2): 4/1
38.6 g Co Boride on
48.6 g Silica Gel
(44% L; 400 m2/g)
CO
150
200
250
300
350
400
450
TEMPERATURE (°C)

Figure 8

B. Reactions at Various Flow Rates

With the 4% loaded catalyst and a volume ratio of 4 moles of hydrogen to each liter of carbon dioxide. The comparison of the reaction at 5 liters/hour (with various temperatures as shown in Figure 9) to the 10 liters/hour runs with various temperatures as shown in Figure 10, show what was expected that increased flow rate would decrease reaction conversion, (Figure 11).

C. Reactions at Various Reactant Ratios

With the 4% loaded catalyst and 10 liters per hour flow rate, the number of moles of hydrogen per mole of carbon dioxide was varied from 1 to 10 by units. The conversion increased rapidly to a ratio of about 8 and tended to level off above that. The amount of conversion to carbon monoxide also increases with increased amount of hydrogen, (Figure 12).

D. Reactions in Relationship to Sulfur Dioxide Poisoning

Dalla Betta, et. al. (8) reported that sulfur compounds had a marked decrease in the activity of many methanation catalysts. A study of the effect of sulfur dioxide was initiated with silica gel supported cobalt catalyst (8%). It was found with a reactant ratio of 4 liters of hydrogen to each liter of carbon dioxide with 10 ppm sulfur dioxide as sulfur poison that no decrease in methane production and no conversion of the sulfur dioxide to sulfur or hydrogen sulfide was found, Table 1.

This run is the basis for the contract from the Four Corners Regional Commission to continue study in this area.

4. Continuous Reactions of Carbon Monoxide

A. Reactions at Various Temperatures

The 4% loaded catalyst was run with a volume ratio of 3 moles of hydrogen to each mole of carbon monoxide. The conversion of carbon monoxide to methane and carbon dioxide is shown in Figure 13.

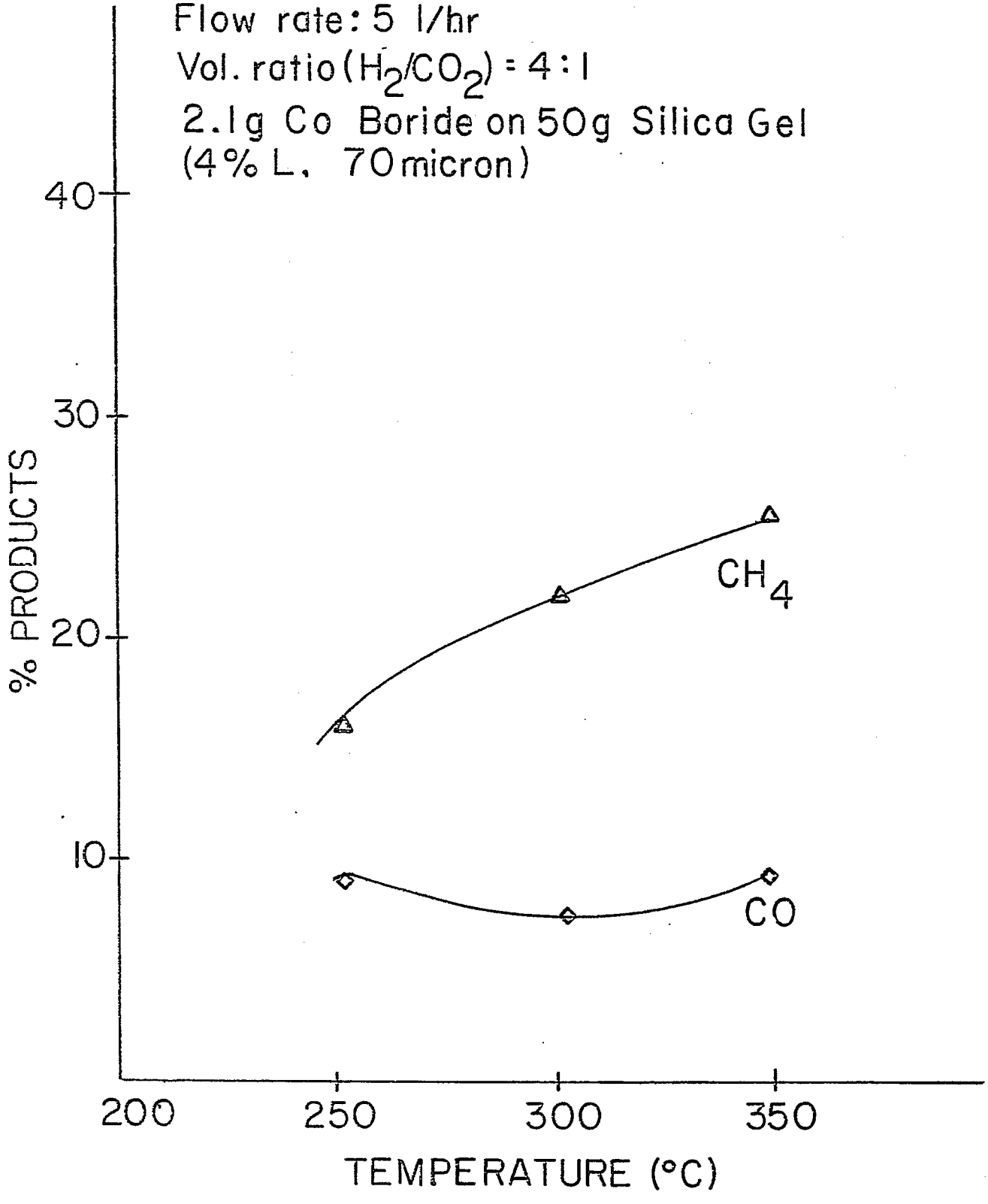

Flow rate: 5 l/hr
Vol. ratio (H_2/CO_2) = 4 : 1
2.1g Co Boride on 50g Silica Gel
(4% L. 70 micron)
40
30
20
10
% PRODUCTS
CH_4
CO
200
250
300
350
TEMPERATURE (°C)

Figure 9

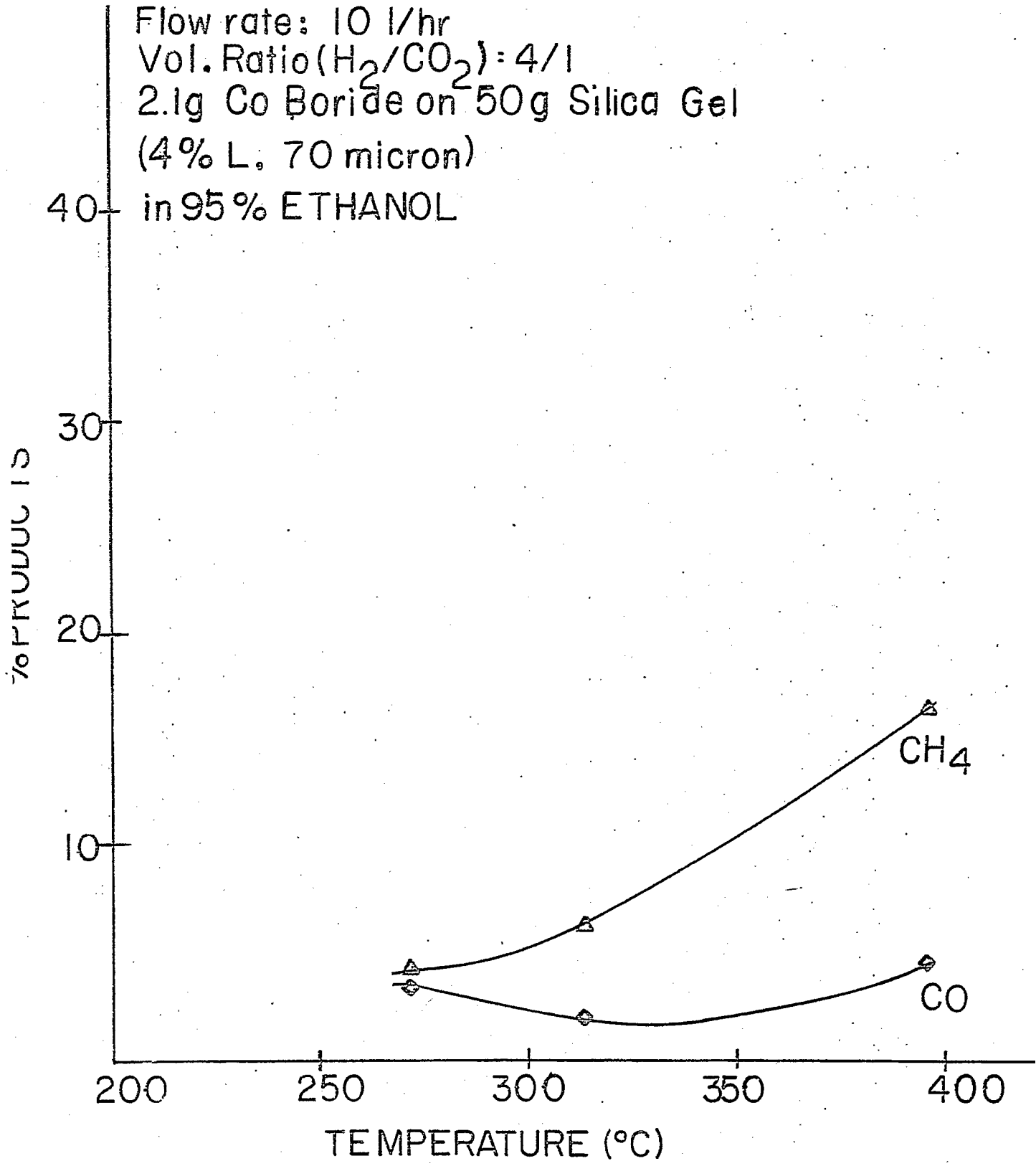

Flow rate: 10 l/hr
Vol. Ratio (H_2/CO_2): 4/1
2.1g Co Boride on 50g Silica Gel
(4% L. 70 micron)
in 95% ETHANOL
40
30
20
10
% PRODUCTS
CH_4
CO
200
250
300
350
400
TEMPERATURE (°C)

Figure 10

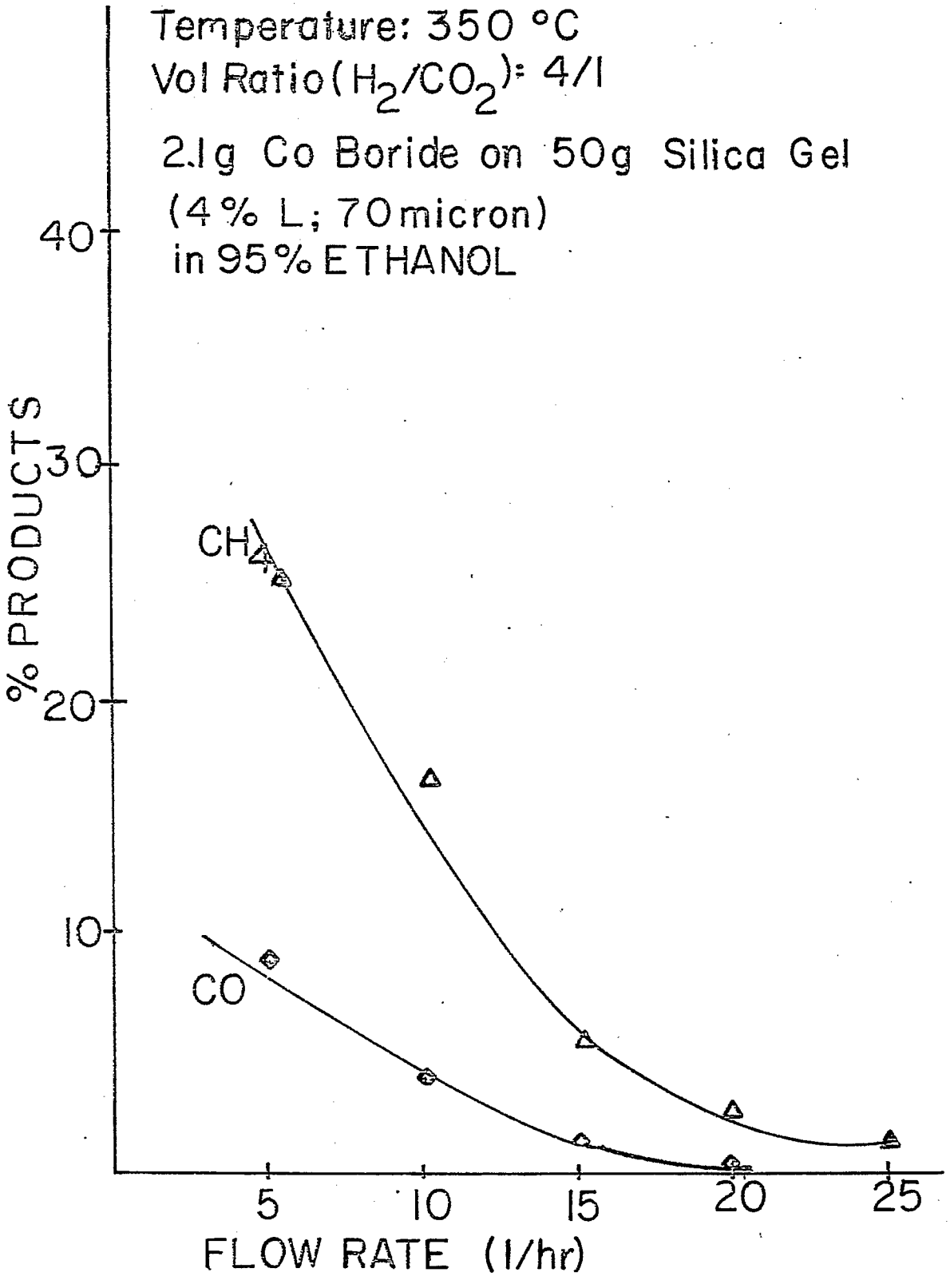

Temperature: 350 °C
Vol Ratio (H_2/CO_2): 4/1
2.1g Co Boride on 50g Silica Gel
(4% L; 70 micron)
in 95% ETHANOL
% PRODUCTS
40
30
20
10
CH_4
CO
5
10
15
20
25
FLOW RATE (l/hr)

Figure 11

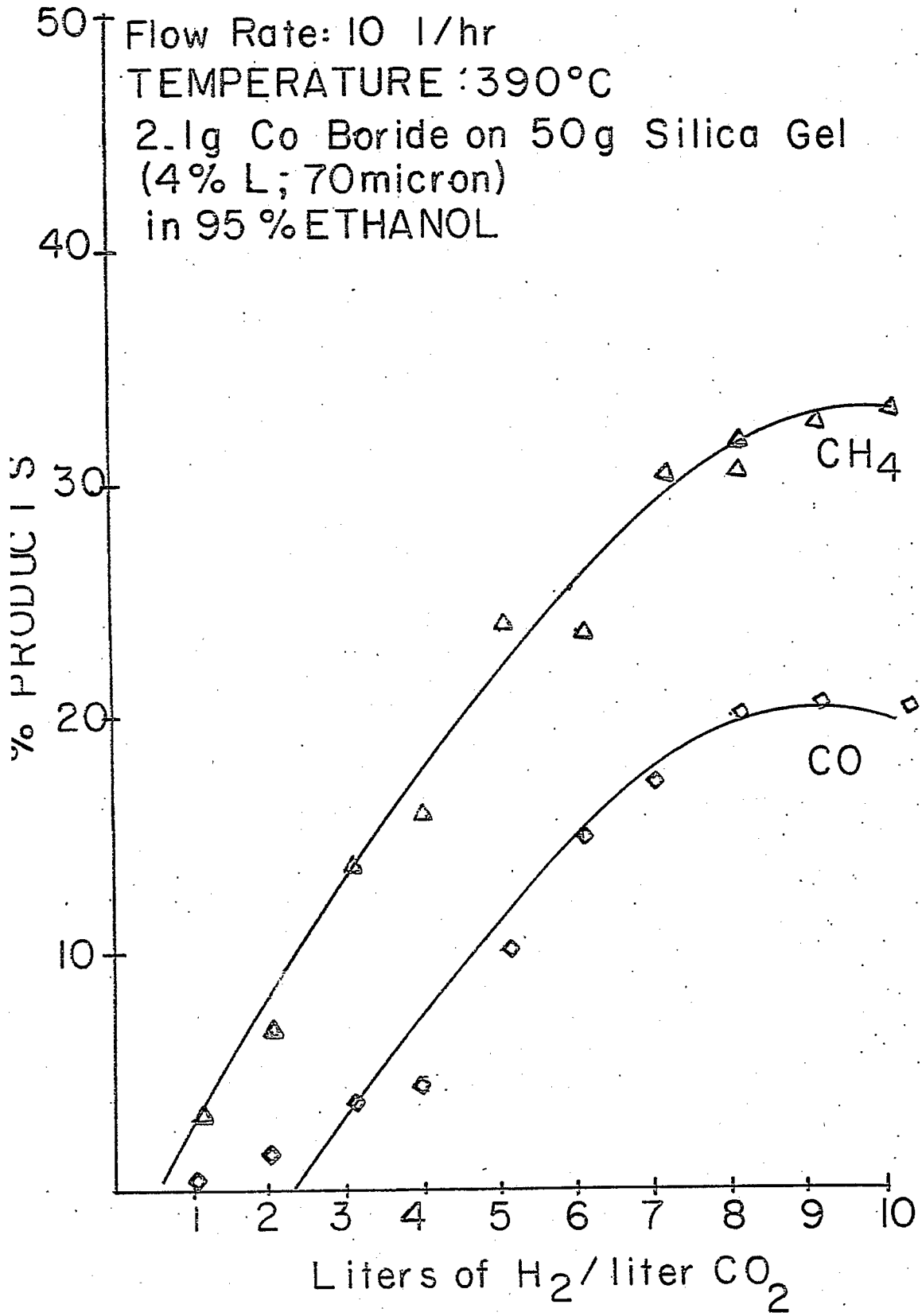

Flow Rate: 10 l/hr
TEMPERATURE: 390°C
2.1g Co Boride on 50g Silica Gel
(4% L; 70micron)
in 95 % ETHANOL
50
40
30
20
10
% PRODUCTS
CH4
CO
1
2
3
4
5
6
7
8
9
10
Liters of H2 / liter CO2

Figure 12

Table I

Effects of Sulfur Poisoning of Methanation of Carbon Dioxide

Time in Hrs.	Temp. ^{o}C	%CO	$\%CH_4$	$\%CO_2$
0	385	7.18	1.64	92.17
10	418	15.11	1.27	83.62
25	397	13.69	1.17	85.13
29	401	13.11	1.00	85.88
58	400	16.21	1.24	79.39
60	415	24.11	2.04	73.83
70	390	14.47	1.46	84.06
76	412	19.50	1.87	78.75
97	388	31.71	3.74	65.54
101	358	30.78	3.29	65.92
106	364	31.54	3.51	65.3

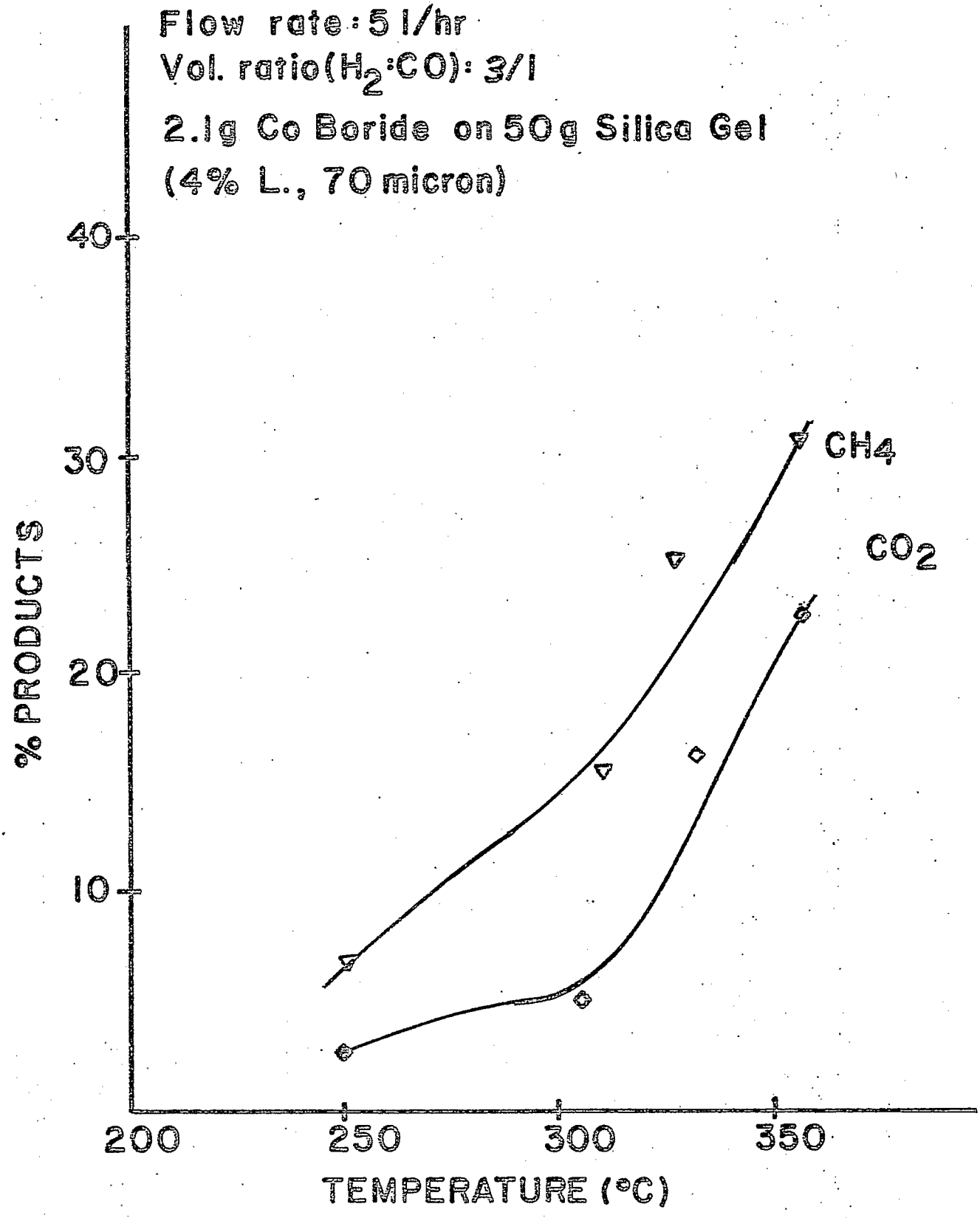

Flow rate: 5 l/hr
Vol. ratio(H_2:CO): 3/1
2.1g Co Boride on 50g Silica Gel
(4% L., 70 micron)
40
30
20
10
% PRODUCTS
CH_4
CO_2
200
250
300
350
TEMPERATURE (°C)

Figure 13

The 44% catalyst was run with a volume ratio of 3 moles hydrogen to 1 mole of carbon monoxide having a maximum conversion to methane of 40% at 346°C and with another smaller peak at 397°C and 35% methane conversion (Figure 14). This curve is similar to one reported by Kurita in 1961 (9).

B. Reactions at Various Flow Rates

Using a 30% cobalt boride catalyst supported on #70-micron silica gel, reactant gas flow rate was varied from 1 to 10 liters per hour. The gases again produced a decrease in methane production with an increase in flow rate (Figure 15).

C. Reactions at Various Reactant Ratios

With the 30% cobalt catalyst supported on 70-micron silica gel, reactant ratios were varied from 1 to 10 liters of hydrogen for each liter of carbon monoxide. The increase of hydrogen resulted in a steady increase in methane production (Figure 16).

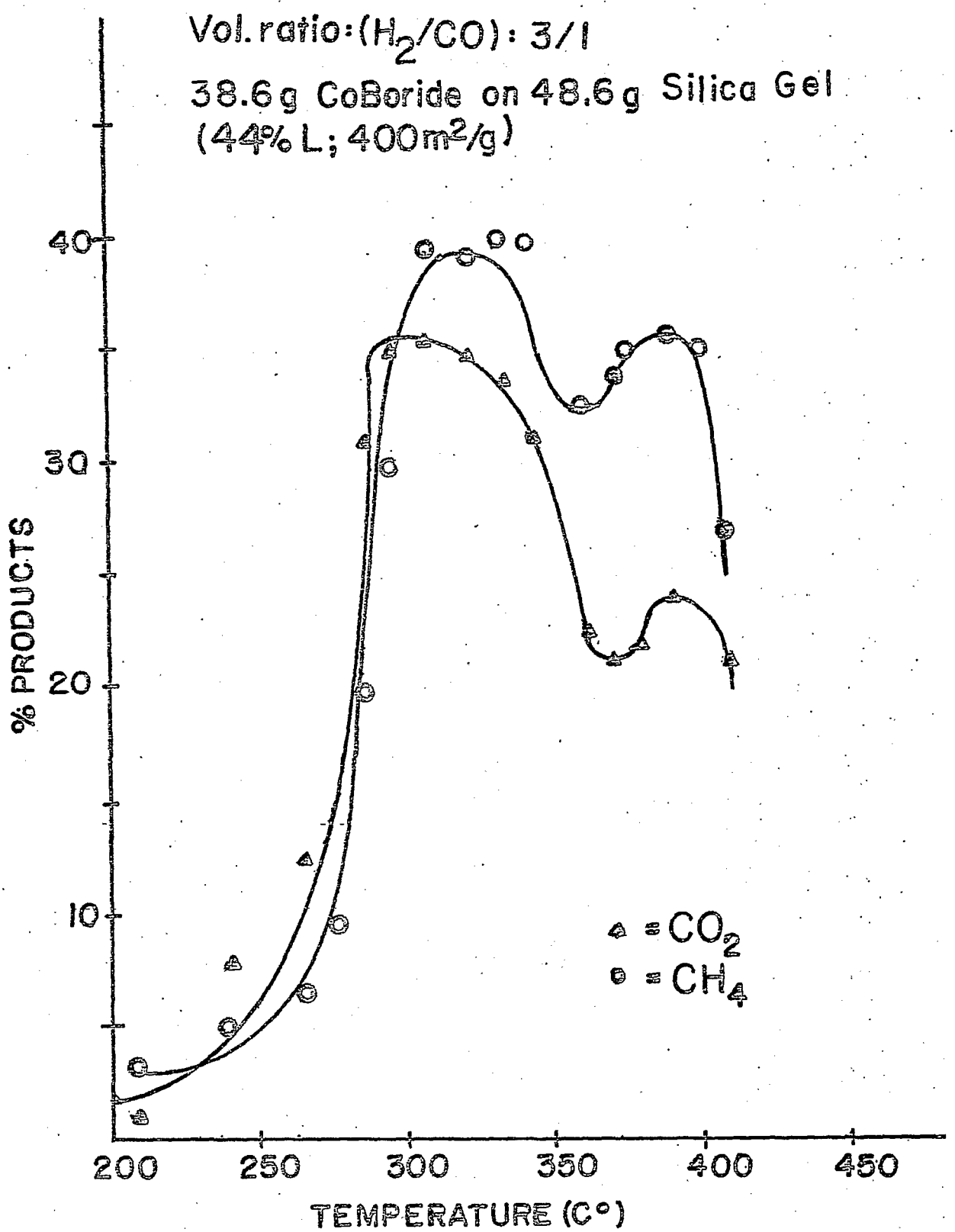

Flow rate : 5 l/hr
Vol. ratio: (H_2/CO) : 3/1
38.6 g CoBoride on 48.6 g Silica Gel
(44% L; 400 m^2/g)
40
30
20
10
% PRODUCTS
200
250
300
350
400
450
TEMPERATURE (C°)
Δ = CO_2
o = CH_4

Figure 14

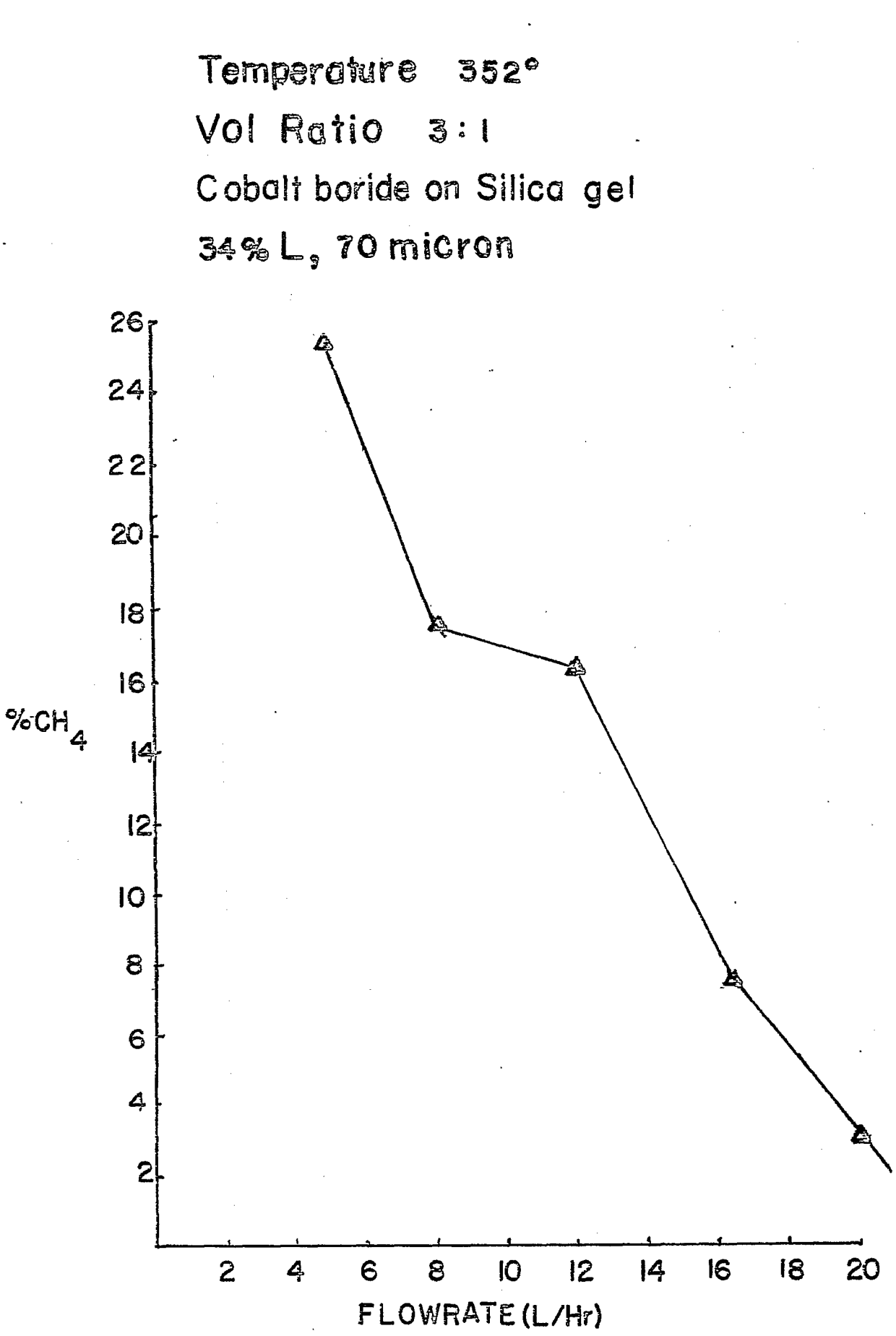

Temperature 352°
Vol Ratio 3:1
Cobalt boride on Silica gel
34% L, 70 micron
26
24
22
20
18
16
14
12
10
8
6
4
2
%CH4
2
4
6
8
10
12
14
16
18
20
FLOWRATE (L/Hr)

Figure 15

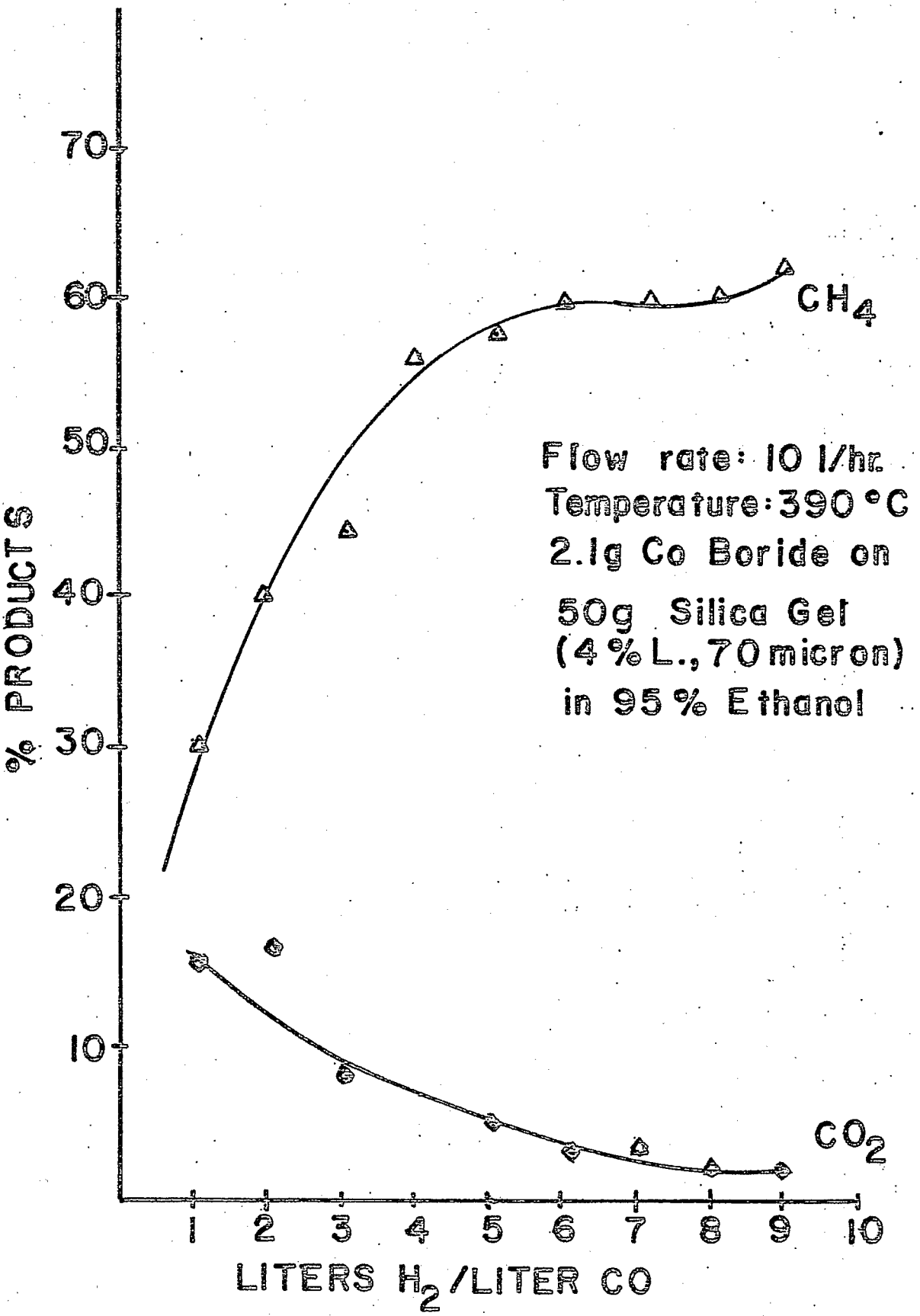

% PRODUCTS
70
60
50
40
30
20
10
CH_4
CO_2
Flow rate: 10 l/hr.
Temperature: 390 °C
2.1g Co Boride on
50g Silica Gel
(4% L., 70 micron)
in 95% Ethanol
1 2 3 4 5 6 7 8 9 10
LITERS H_2 / LITER CO

Figure 16

Esperimental

I. Equipment

Parr Model 4563 minireactors with automatic temperature controls (purchased on a previous ERB contract) were used for all static reactions. Two flow systems were designed and built for the continuous flow work. One flow system is used for flow gas studies only (Figure 1). Both are equipped with semi-automatic temperature control. At present, 2.5 x 25cm columns are being used for catalyst bed containers. Catalyst column, preheater column and cooling condensors are all Pyrex glass. Some rubber and copper tubing are used in the first system. The second system was designed to allow for study on the effects of sulfur compounds, and is constructed of stainless steel, (Figure 2). Rotometers are used to determine flow rates.

Fisher 2400 and Aerograph Model A-90-P gas chromographs were used for most qualitative and quantitative analyses using thermal conductivity detectors. Perkin-Elmer Model 281 infrared spectrophotometer (purchased with this grant) was used to confirm qualitative analyses.

Gas-tight 5ml syringes were used to obtain gas samples directly from the static and flow reactors for gas chromatographic analysis. Liquid phase sampling was done using Hamilton 701-N microliter syringes. The gas chromographic columns used for gas analyses were Molecular Sieve 13 x (¼" x 8'), Porapak Q 100/200 (¼" x 8') and Spherocarb 100/120 (1/8" x 4'). Ethofat 1% on Fluoropak (¼" x 5m) was for formaldehyde, water, and methanol analysis. Carbowax 20M 20% on Chromosorb W and XF-1150 15% on Chromosorb W were prepared for analysis of possible higher molecular-weight hydrocarbons.

II. Materials

All chemicals used were reagent grade, except the raw systhesis gases. Cobaltous chloride, methanol and formaldehyde were from Fisher Scientific. Ethanol was from U.S. Industrial Chemicals. Sodium borohydride, silica gel aluminum oxide and palladium chloride were products of Ventron Corporation. Molecular Sieve 13X was from Linde. Ethofat 80, Chromosorb W-AW 45/60, Carbowax 20M, and XF-1150 were from Supelco Company. Spherocarb 100/120 was from Analabs.

The raw systhesis gases were commercial grade gases from Linde Division of Union Carbide Corporation. Hydrogen had almost no impurities, as determined by gas chromotography and infrared spectroscopy. Carbon dioxide contained only trace amounts of nitrogen and oxygen. Carbon monoxide contained only trace amounts of methane and carbon dioxide. Helium was used as carrier gas for gas chromotography. Methane and dimethyl ether were high purity gases obtained from Linde for standards. All stainless steel used was type 316 or 304. Temperature monitoring was by iron-constantan thermocouples.

III. Preparation of Catalysts

1. Palladium

Fifty grams of support were immersed in 100 ml of solvent and palladium chloride was added to yield a chosen percentage of supported catalyst i.e., 0.5g $PdCl_2$ added would yield 0.60% supported catalyst. The resultant mixture was stirred frequently and kept in a dessicator until all solvent had evaporated. Absorption/adsorption was complete. A solution of sodium borohydride, dissolved in a small quantity of water with absolute ethanol added to yield a 95% solution, was added to the supported palladium (II) until the reduction was complete. The reaction was believed to be complete when the evolution of gas did not occur when more borohydride solution was added. The catalyst was allowed to air dry and was then placed in the flow system.

2. A cobalt catalyst prepared from aqueous solutions (similar to one prepared for nickel in previous work) proved ineffective in the methanation process, so this method was abandoned. All cobalt catalysts were prepared in 95% ethanol solutions.

3. Cobalt Catalyst by Immersion Process

A selected support of known weight was immersed in a solution of 5ml of 1M cobaltous chloride in 95% ethanol solution per gram of support for 4-5 hours. The supported metal salt was then drip-dried of excess cobalt chloride solution. It was then cooled and 25ml of freshly prepared 0.1M 95% ethanolic sodium borohydride solution was allowed to react for 2-4 hours in a refrigerator. The liquid phase was then decanted and discarded.

Another 125ml of freshly prepared sodium borohydride solution per 100 of support was then added and again allowed to react for 2-4 hours. This was repeated until there was no more reaction, as evidenced by evolution of hydrogen gas. The catalyst was washed twice with water, then three times with 95% ethanol. It was predried to a powder at 70° to 80°C. It was then packed into the catalyst column of the flow system and dried under hydrogen flow at temperatures between 150° - 200°C for 4 hours.

4. Cobalt Catalyst by Flash Evaporation

A selected support of known weight was placed in a flask of sufficient size to hold the support and liquid cobalt chloride solution without loss of part of contents when placed on the flash evaporator. A solution of 5ml of cobaltous chloride in 95% ethanol solution per gram of support was then placed in the flask. The flask was placed on the flash evaporator for stirring to insure sufficient mixing of support. After about 4 hours, a vacuum was placed on the solution and the water under the flask heated to 70°C to remove excess solvent.

When solvent evaporated, the flask was removed and 125ml of .1M sodium borohydride in 95% ethanol solution per 100g of support was added to the flask for reaction. The flask was returned to the evaporator for reaction under constant stirring and a slight vacuum. Cool water was run over the flask until completion of the reaction.

The flask was again removed and the solution decanted. Fresh sodium borohydride solution was introduced and the above method repeated until fresh borohydride solution no longer gave a reaction with cobalt salt.

The flask was again removed and the solution filtered. The catalyst was washed twice with water and three times with 95% ethanol. The wet catalyst was returned to the evaporator and dried under a vacuum at 70°C until powder dry.

The catalyst was then placed in a flow system column and dried at 150° - 200°C under hydrogen flow for 4-5 hours.

5. Preparation of Unsupported Cobalt Catalyst

Previous work indicated that unsupported nickel catalyst was colloidial in nature and unusable as a flow system catalyst. A cobalt catalyst with a large particulate size was produced by the following procedure: A 300ml aloquot of a 1M solution of cobaltous chloride in 95% ethanol was placed in a beaker. Sodium borohydride (.15 mole) was added in small amounts to the beaker allowing time for the reaction to slow. The beaker was cooled in an ice water bath. The solution was allowed to react to completion with the settling of the cobalt catalyst. The catalyst was then filtered and washed as before. The catalyst was dried in an oven at 70° - 80° until powder dry and then under hydrogen flow at 150° - 200°C for 4-5 hours.

6. Determination of Catalyst Loading on Support

The support was weighed before preparing the catalyst. The catalyst was made, dried and weighed; and the catalyst loading was calculated by the formula:

$$\% \text{ loading} = \frac{(\text{wt of supported catalyst}) - (\text{weight of support})}{(\text{wt of supported catalyst})} \times 100$$

IV. Static Reactions with Cobalt

1. Hydrogenation of Carbon Dioxide

A Parr reaction bomb was charged with wet supported catalyst made in 95% ethanol. The catalyst was dried at 150° under 100 psig of hydrogen by releasing and charging every half hour and repeating this three to four times. Finally, it was cooled to room temperature in a hydrogen atmosphere.

The hydrogen was vented. Carbon dioxide was introduced and vented several times, finally charged to 30 psig. Then, hydrogen was introduced to 150 psig. This set a reactant ratio that was close to the stoichiometric relationship of 4 moles hydrogen to 1 mole carbon dioxide. The reactor was turned on and the reaction temperature selected. The reaction was considered started at the time the desired temperature was reached. At this time, time and pressure were recorded and at regular intervals until reaction time was completed.

2. Hydrogenation of Carbon Monoxide

The catalyst was introduced and dried as described above. Carbon monoxide was introduced and vented several times, finally being charged to 40 psig. Hydrogen was then added to 150 psig to bring the reactant reaction to approximately 3 moles hydrogen to 1 mole carbon monoxide. The reactor was turned on and the reactor temperature selected. Time and pressure were recorded at regular intervals.

V. Continuous Reactions

The flow systems shown in Figure 1 and 2 were used for the continuous reactions. The flow rate, reactant ratio, preheater temperature and column temperature were selected. After the temperature had been reached and system parameters had stabilized the outlet gases were sampled.

Experiments were performed varying the parameters of reaction temperature reactant, flow rate, reactant ratios and the carbon oxide.

VI. Analysis

1. Qualitative

Porapak Q had a good performance in the separation of methane and carbon dioxide. Hydrogen, air, and carbon monoxide peaks were not separable in this column. Molecular sieve 13X separated carbon monoxide and air. The separation order was hydrogen, oxygen, nitrogen, carbon monoxide and methane, with carbon dioxide coming out as an insignificant peak.

Spherocarb was selected later because it would separate all the gases. Using temperature programming from 60-200°C, the order of separation was hydrogen, oxygen, nitrogen, carbon monoxide, methane, carbon dioxide and water.

The operating condition of the columns were: Poropak Q (¼" x 8') and Molecular Sieve 13X (¼" x 8') temperatures of 200° for the injector, 50° for the column and 250° for the detector. The filament current to the thermoconductivity detector was 150 mA with helium as the carrier gas at a flow rate of 40-45ml/min.

Spherocarb 100/120 (1/8" x 4') had operating temperatures held at 60°C for 3 minutes programmed at a rate of 20°C per minute to 200°C; then held for 4 minutes at a temperature of 250° and an injector temperature of 200°C. The thermal conductivity detector filament current was 150 mA with helium as carrier gas at a flow rate of 25-30ml/min.

The qualitative analyses were confirmed by infrared. The individual spectrums were compared with the spectrum of an authentic sample for each suspected component of the gas sample mixture. The infrared sample was in a 10cm gas cell.

2. Quantitative Analysis

Composition of gas sample was computed as a corrected area:

$$\frac{\text{gas A}}{\text{gas A}_{\text{std}}} \left(\frac{\text{peak area of system gas}}{\text{peak area of authentic gas sample}}\right) = \text{gas-corrected area}$$

The gas-corrected areas were added to get a gas total area and used to obtain percentage compositions. One ml was used as sample size for the reaction gas

mixtures and standards of methane air, carbon monoxide, and carbon dioxide. Since there were difficulties in setting up internal standards, response factors were used for each of the gases. These response factors were checked frequently and one of the standards was run each time. Percentage conversion of carbon dioxide or carbon monoxide to methane was calculated from the following equation:

$$\%\text{conversion to methane} = \frac{\%\text{methane}}{\text{sum of \% all gas products}} \times 100$$

The percent conversion of carbon monoxide or carbon dioxide to other carbon-containing products could be calculated with similar equations by substitutions in the numerator the appropriate percent composition.

All reactions were repeated and reproducable data were obtained.

VII. Palladium Recovery Procedures

When the catalyst was found to yield less than 10% methane, when compared to previous runs, it was removed from the flow system. More sodium borohydride solution was added until the evolution of gas was complete. All "dead" palladium catalysts reacted with the borohydride. After the catalyst was again air dried, it was placed in the catalyst column once and another run was made. The results were the same as when the catalyst was initially run. The catalyst is active at flow ratios of 4:1 (H_2:CO_2) for about 15 days, but for peak performance it should be regenerated every 6-7 days.

Such degeneration has not been noted with cobalt or nickel.

The palladium can be recovered by adding aqua regia and dissolving the palladium. The palladium-containing solution is decanted from the support and is then reduced with borohydride to produce what is believed to be palladium boride.

VIII. Blank Runs

To determine the effect of the catalyst (proof that the metal and borohydride are necessary), a catalyst support with sodium borohydride and one of support and metal chloride were run as blanks. The blanks yielded less than 1% methane at the optimum conditions and less yield at other temperatures and ratio of reactants. No other products were observed during these runs.

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