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ALLOY CATALYSTS WITH MONOLITH SUPPORTS FOR METHANATION OF COAL-DERIVED GASES

Phase 2

Quarterly Technical Progress Report
For Period Oct. 23, 1976 to Jan. 22, 1977

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FOREWORD

This report summarizes technical progress during the seventh quarter period (October 23, 1976 to January 22, 1977) of a two-year study conducted for the Energy Research and Development Administration (ERDA) under Contract No. E(49-18)-1790. The principal investigator for this work is Dr. Calvin H. Bartholomew; Dr. Paul Scott is the technical representative for ERDA.

The following students contributed to the technical accomplishments and to this report: Graduates - George Jarvi, Gordon Weatherbee and Erek Erekson and Undergraduates - Kevin Mayo, Kenneth Atwood, and Glen Witt. Elaine Alger and Scott Folster provided typing and drafting services.

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ABSTRACT

This report details accomplishments during the seventh quarter of investigation of new pellet- and monolithic-supported alloy catalysts for methanation of coal synthesis gas. Monolithic-supported nickel and nickel-cobalt catalysts were prepared. Hydrogen adsorption uptakes were measured for several pelleted and monolithic nickel and nickel alloy catalysts. Differential activity tests were conducted at 225 and 250°C, 20.5 psia, and 30,000 hr^{-1} for nickel-cobalt and nickel-platinum catalysts before and after exposure to 10 ppm H_2S. Thermodynamic calculations were performed to determine conditions for formation of carbon, ammonia, and carbon dioxide in reactor tests. Effects of 1% water on methanation activity and selectivity were determined for nickel and nickel alloy catalysts. Conversion-temperature measurements were performed for pelleted and monolithic catalysts at high pressure (365 psia). The principal investigator attended the ASTM Catalyst Meeting, visited three other laboratories and presented three seminars related to methanation research. One paper was accepted and one submitted for publication.

I. OBJECTIVES AND SCOPE

A. Background

Natural gas is a highly desirable fuel because of its high heating value and nonpolluting combustion products. In view of the expanding demand for and depletion of domestic supplies of clean fuels, economical production of synthetic natural gas (SNG) from coal ranks high on the list of national priorities.

Presently there are several gasification processes under development directed toward the production of SNG. Although catalytic methanation of coal synthesis gas is an important cost item in the process, basic technological and design principles for this step are not well advanced. Extensive research and development are needed before the process can realize economical, reliable operation. Specifically, there appears to be important economical advantages in the development of more efficient, stable catalysts.

An extensive general review of the pertinent literature dealing with methanation catalysts was reported in the proposal, including reviews by Greyson (1) and Mills and Steffgen (2). From the literature, three major catalyst problems are apparent which relate to stability: (i) sulfur poisoning, (ii) carbon deposition with associated plugging, and (iii) sintering. These problems have received at best only modest attention. There has been very little research dealing with alloy catalysts for methanation, and there are no published investigations of the effects of catalyst support geometry on catalyst performance. This study deals specifically with sulfur poisoning, carbon deposition, and the effects of support (monolith and pellet) geometry on the performance of alloy methanation catalysts.

B. Objectives.

The general objectives of this research program are (i) to study nickel and ruthenium alloy catalysts in the search for catalysts resistant to poisoning and carbon deposition and (ii) to investigate the effects on catalytic efficiency of support (monolith and pellet) geometry. The work has been divided into five tasks to be completed over a period of two years:

Task 1. Prepare pellet- and monolithic-supported nickel and ruthenium alloy methanation catalysts by impregnation with metal salts of nickel, ruthenium, iron, platinum, etc. followed by reduction in hydrogen. Measure hydrogen and carbon monoxide chemisorption uptakes before and after exposure to hydrogen sulfide. Examine metallic phases of these catalysts by x-ray diffraction for chemical composition and particle size.

Task 2. Design and construct a continuous flow laboratory reactor system capable of 25-1000°C and 1-25 atm to be used for screening methanation catalysts and investigating effects of sulfur poisoning on methanation activity.

Task 3. Screen catalysts prepared in Task 1 using a reactor system constructed in Task 2 to determine methanation catalyst activity before and after exposure to 10 ppm H_2S.

Task 4. Compare the most promising catalysts based on the results of Tasks 1 and 3 for steady-state catalytic activity on different pellet and monolith supports of different hole sizes and geometries under various operating conditions, i.e., temperature, pressure, H_2/CO ratio and H_2S level.

Task 5. Maintain close liaison with organizations doing similar research such as the Bureau of Mines, Bituminous Coal Research, Institute of Gas Technology, and others.

C. Technical Approach

The technical approach which will be used to accomplish the tasks outlined above is presented in the revised proposal dated May 17, 1974. The main features of that approach are reviewed here along with more specific details and modifications which have evolved as a result of progress. It is expected that various other aspects of this approach will be modified and improved as the project develops and as new data are made available. Nevertheless, the objectives, tasks and principle features of the approach will remain the substantially the same.

Task 1: Catalyst preparation and characterization. Alumina pellets and extruded monolithic ceramic supports (provided by Corning Glass Works) coated with high surface area alumina will be impregnated with nickel nitrate and an alloying metal salt. Metals which will be alloyed with nickel include cobalt, iron, molybdenum, rhodium, ruthenium, platinum, and palladium. Ruthenium will be used in combination with nickel, cobalt and palladium. Approximately equimolar quantities of base metals will be used in combination with nickel or other base metals; relatively small amounts of noble metal will be used in combination with base metals. Catalyst samples will be dried in vacuum at 70-100°C, reduced at 500°C in flowing hydrogen, and carefully passivated with 1% air in preparation for further testing. A dedicated reduction apparatus will be used to reduce and passivate large batches of pellets and monolithic catalysts. Alloy catalysts will be initially prepared in pellet form for chemisorption, x-ray diffraction, and reactor screening measurements. Only the more promising catalysts will be prepared in monolithic form.

Hydrogen and carbon monoxide chemisorption uptakes will be measured using a conventional volumetric apparatus before and after exposure of each catalyst to hydrogen sulfide. Catalysts will be exposed to 10 ppm H_2S over a period of several hours in a dedicated poisoning apparatus. X-ray diffraction measurements will be carried out to determine the active metallic phases and metal crystallite size where possible. Selected "aged" samples from Task 4 will be analyzed (by x-ray and perhaps ESCA) to determine carbon content and possible changes in phase composition or particle size. More extensive study of catalyst sintering or thermal degradation will be undertaken as part of a separate study supported by NSF and perhaps as an extension of this work, but is not intended to be within the scope of this two-year study.

Task 2: Laboratory reactor construction. It was initially proposed to construct a combination pulse-continous flow reactor system for catalyst screening and testing. This apparatus was in fact constructed in 1974 as part of a previous methanation study supported by Corning Glass Works and Brigham Young University. The combination was found to be unworkable--unsatisfactory for pulse operation because of pulse broadening in the reactor and for continuous-flow operation due to high flow resistance in the small diameter tubing and sample valves. The reactor system was later modified for continuous-flow operation and collection of steady-state activity data, which were found to be more useful, realistic indicators of catalyst performance than the unsteady-state pulse measurements. Our continuous-flow reactor system was modified in 1976 for operation to 400 psig and significantly upgraded to enable convenient study of activity as a function of temperature, pressure, and feed composition.

Task 3: Reactor screening of alloy catalysts. Catalyst samples will be screened on the basis of steady-state methanation activity (reaction rate based upon catalyst surface area) measured in a differential flow reactor at atmospheric pressure and 225 or 250°C at a fixed H_2/CO ratio of 4.0. Samples to be screened will include freshly-reduced catalysts and catalyst samples exposed in a separate poisoning system to 10 ppm H_2S over a period of 6-18 hours.

Task 4: Catalyst geometry testing and design. The most promising catalysts based on the results of screening will be tested for activity and conversion as a function of pressure, temperature, H_2/CO ratio, and H_2S concentration. The conversion of carbon monoxide to methane as a function of temperature will be determined for various pellet and monolith geometries at both high and low pressures. The effects or water addition to the feed stream will also be investigated. Conversion of carbon monoxide to methane during in situ exposure to low levels of hydrogen sulfide and at low H_2/CO ratios will be used as a measure of stability toward sulfur poisoning and carbon deposition. A comparison of steady-state conversions at given temperature and pressure conditions for monolithic supports of different hole sizes and geometries will be used to optimize the geometry of the catalyst support. This task is not scheduled for completion until the end of 1977 (as outlined in the proposal).

Task 5: Technical visits and communication. Visits to other methanation laboratories such as the Pittsburgh Energy Research Center and the Institute of Gas Technology are planned. Close communication with other researchers working in methanation catlaysis both in industrial and academic locations is also planned. The principal investigator will attend coal and catalysis meetings regularly to communicate with other workers regarding methanation catalysis.

II. SUMMARY OF PROGRESS

A project progress summary is presented in Figure 1 and accomplishments during the past quarter are summarized below. Figure 1 shows that task accomplishments are either on or ahead of schedule. Particularly Task 4, Catalyst Testing and Design, is well ahead of schedule. Tasks 2 and 3 have been essentially completed.

Accomplishments during the last quarter are best summarized according to task:

Task 1. Several Ni/Al_2O_3/monolith catalysts and a Ni-Co/Al_2O_3/monolith catalyst were prepared. Hydrogen uptakes were measured for six pelleted nickel and nickel alloy catalysts and for five monolith supported Ni and Ni-Co catalysts.

Task 2. Mass flow meters were recalibrated and the system was pressure tested to 350 psig.

Task 3. Measurements of methanation activity at 225 and 250°C, 20.5 psia, and 30,000 hr^{-1} were carried out before and after exposure to 10 ppm H_2S (sufficient to cover 30-40% of the surface) for Ni-Co-A-100 and Ni-Pt-A-100.

Task 4. Thermodynamic calculations were performed to determine conditions for minimizing formation of carbon, ammonia, and carbon dioxide in kinetic reactor tests and for maximizing carbon formation in our long term steady state carbon deposition tests. Effects of 1% water on methanation activity and selectivity (at low pressures) were determined for seven pelleted nickel and nickel alloy catalysts. High pressure activity tests were also carried out for six pelleted nickel and nickel alloy catalysts. Conversion-temperature measurements were made for five monolithic-supported nickel and nickel-cobalt alloy catalysts at a space velocity of 30,000 GHSV. In addition, Ni-M-117 was run at 50,000 GHSV. Three of the monoliths were tested at high pressure (365 psia).

Task 5. The principal investigator attended the ASTM Catalyst Committee Meeting November 15-16 in Oakridge, Tenn. and made visits and presentations to Catalyst and Chemicals Research at Engelhard Industries in Edison, New Jersey, Engineering Research at Continential Oil Company in Ponca City, Oklahoma, and the University of Idaho Department of Chemical Engineering, Moscow, Idaho. One paper was accepted and one submitted for publication.

Miscellaneous. Mr. Erek Erekson joined the research group in January and began work towards his Ph.D.

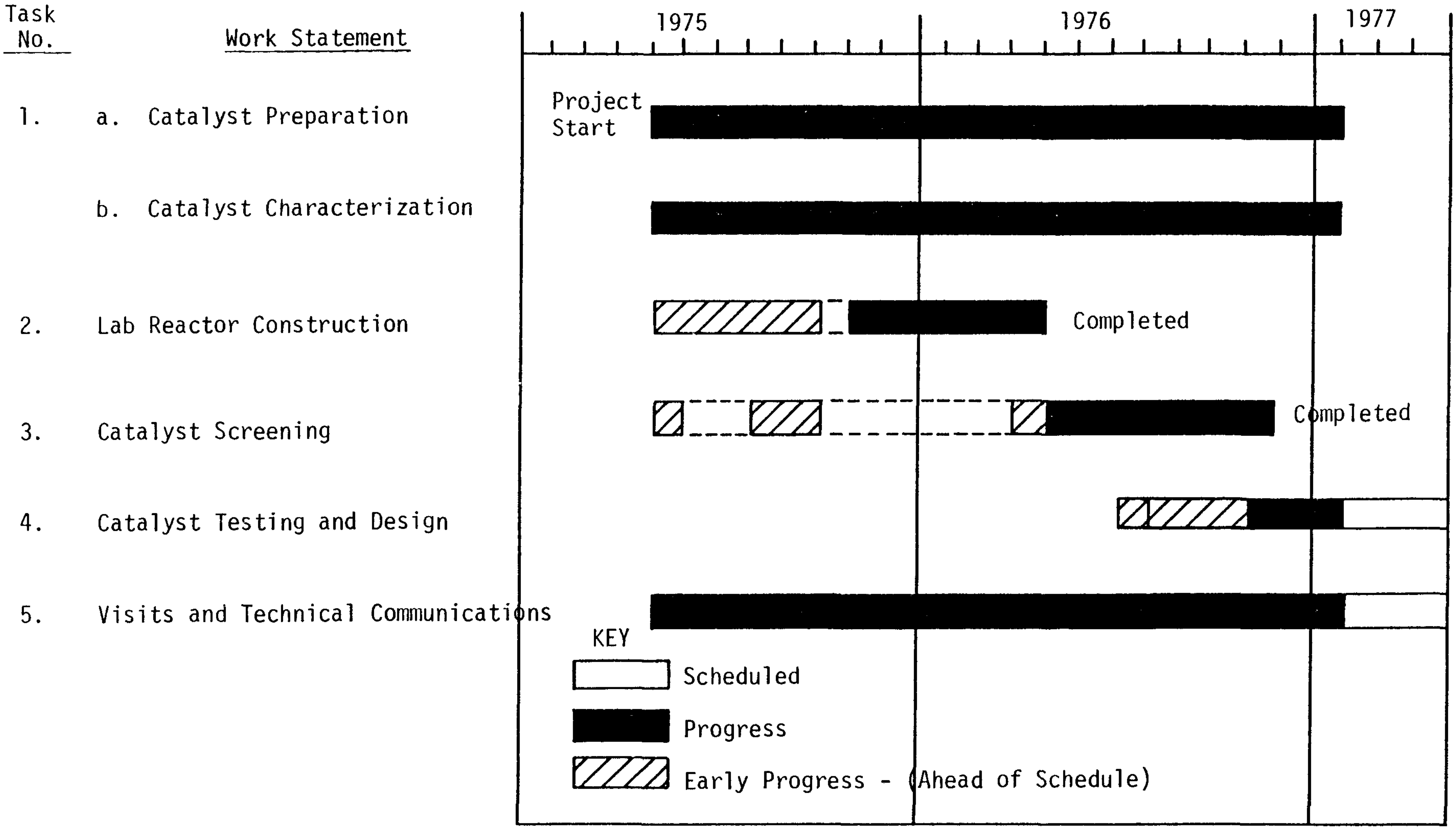

Figure 1. Project Progress Summary.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Task 1: Catalyst Preparation and Characterization

1. Catalyst Preparation: Three monolithic supported catalysts containing 11 to 12% nickel metal were prepared by the procedure outlined in previous reports (QPR-4, 5 and 6). Three other monoliths were prepared containing 5% nickel and 5% cobalt. Two problems in monolith preparation were recognized during the quarter. One, it is much easier on a lab scale to determine gravimetrically what the metal loading is after the fact, than to ensure a particular loading from the start. Two, a solution of nickel and cobalt nitrate behaves differently than either one alone. When combined with a small quantity of alumina from the monoliths being impregnated, the solution tended to solidify.

Integral performance tests were performed on these monolith catalysts at 20.5 psia and 360 psia. The results of these tests suggest that the 11% nickel loaded Ni-M-117, 118, 119 samples are better methanation catalysts than the 20% loaded Ni-M-113, 114, 115 monoliths. One difference in their preparation may account for this difference. As the 113-115 series catalysts were being reduced in hydrogen, the temperature did not stay at 230°C as programmed but rather shot up to 350°C for five minutes and then dropped to 250°C. The 117-119 series did not exhibit such a large excursion but was kept at 150 to 230°C for the first few hours of the reduction. Possibly the strongly exothermic reduction of the nitrate in hydrogen to ammonia partially sintered the 20% Ni catalysts (3). The 11% Ni monoliths did have larger surface areas. (See Table 1).

While a small temperature excursion was noted during the reduction of the nickel-cobalt alloy monoliths, the greatest difficulty was in impregnating the alumina/ceramic supports. After four dip-and-dry cycles, the alumina substrate began to slough off. Instead of the desired 20% metal loading, approximately half of that was obtained. Surface area measurement showed an unusually low area for these samples, but the CO conversions obtained are generally comparable to the others obtained so far.

It has become the standard practice in this laboratory to coat each finished monolith with a small exterior band of a mixture of alundum binder and Sauereisen No. 78 cement to prevent by-passing of the reactant gas around the monolith. While only about 7% of the surface area is lost, the weight of the monolith is increased significantly. The chemisorptive uptakes listed in Table 1 are based on the weight before coating with cement, but reflect the surface area available after coating.

2. Characterization: Hydrogen chemisorption uptakes, measured for six different pellet-type catalysts and three monolithic-types are reported in Table 1. Uptakes for four of the pellet-type catalysts were measured after reactor runs with 15 and 1 vol% steam in the reactants. The steam had a definite detrimental effect on the surface area of

Table 1

Hydrogen Chemisorptive Uptake Data for Alumina Pellet and Monolith Supported Catalysts

Catalyst	Nominal Composition	H_2 Uptake (μ mole/gram) Bulk Reduced	After reactor run with reactant steam	After reactor run
PELLETS:				
Ni-A-116	14% Ni	203.5[a]	152.2[d]	
		187.8[a]	152.4[e]	
Ni-A-112	3% Ni	40.1[a]	32.5[d]	
		40.1[a]	33.4[e]	
		35.5		27.8[f]
Ni-Co-A-100	10% Co, 10% Ni	116.3	108.5[d,e]	
		103.4[b]		
Ni-MoO_3-A-101	2.5% Ni, 3% MoO_3	18.6[a]	12.3[e]	
Ni-Ru-Ni-105	2.5% Ni, 0.5% Ru	52.4		
Ni-Rh-A-100	2.5% Ni, 0.5% Rh	30.0		
MONOLITHS:				
Ni-M-114	20% Ni	65.0[a]		
Ni-M-115	20% Ni	106.2		84.0
Ni-M-117	12% Ni	75.5[c]		
Ni-M-118	11% Ni	104.7		
Ni-M-119	12% Ni	108.5		
Ni-Co-M-100	5% Ni, 5% Co	33.0		

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[a] Data obtained in a previous quarter
[b] Bulk reduced at GHSV different than preceding sample
[c] Surface may have been damaged during tests
[d] 15 vol% water vapor in reactants
[e] 1 vol.% water vapor in reactants
[f] High pressure run

the catalysts tested.

Work was also completed that established that monolithic nickel catalysts are sufficiently rereduced in H_2 after two hours at 450°C at a GHSV of 2,000 hr^{-1}.

The work of Hardeveld and Hartog (4) indicates that evacuating a catalyst sample prior to chemisorption measurements at the same temperature at which it was reduced can liberate tightly bound water from the support which can oxidize some of the nickel metal surface sites to NiO. Therefore, all future evacuations will be performed at 400°C, rather than the previously used temperature of 450°C at which samples are reduced.

Work was begun during this past quarter to investigate the stoichiometry of hydrogen chemisorption on unsupported cobalt metal. A finely powdered cobalt metal sample was obtained, and BET and H_2 adsorption measurements were initiated. During the first run the sample cell developed a leak, and the experiment is now being repeated.

3. Forecast. During the next quarter several monolith supported nickel catalysts and monolithic supported Ni-Ru, Ni-Pt and Ni-MoO_3 catalysts will be prepared. Surface areas will be measured for these and for other pelleted and monolithic catalysts before and in selected cases after reactor testing. The investigation of hydrogen adsorption on cobalt will continue.

B. Task 2: Laboratory Reactor Construction.

Reactor system construction was completed during the fourth quarter and modifications were completed during the fifth and sixth quarters. During this past quarter those components of the system which could not tolerate 350 psig were replaced including tubing, valves, and the CO flow controller. The mass flow meters were recalibrated to ensure accuracy at high pressure. A multi-plexed digital temperature readout for the catalyst temperature was installed to facilitate the collection of data and to provide a closer control on temperature. The system was pressure-tested to 350 psig to check for leakage and to establish proper operating techniques including flow control, gas sampling time and pressure regulation.

C. Task 3: Reactor Screening of Alloy Catalyst.

During this past quarter two pellet-supported catalysts were screened in differential activity tests: Ni-Co-A-100 (10% Ni, 10% Co), and Ni-Pt-A-100 (15.7% Ni, 0.5% Pt). Both of these catalysts had been poisoned with 10 ppm H_2S until approximately 40% of the metal sites had been blocked for H_2 adsorption.

Measurements were made of CO conversion and CH_4 and CO_2 production. From these data the selectivities of each catalyst to methane and carbon dioxide, reaction rates per gram of catalyst, and turnover numbers based on both CO conversion and CH_4 production were calculated. These results are shown in Tables 2 and 3 for temperatures of 225 and 250°C respectively, a pressure of 20.5 psia and a space velocity of 30,000 hr^{-1}, using a reactant gas mixture containing 1% CO, 4% H_2, and 95% N_2. Rates (per gram of catalyst) and turnover numbers at 250°C are shown graphically in Figures 2 and 3.

Comparison of rates on a mass basis (Tables 2 and 3 and Figure 2) shows that Ni-Co-A-100 (20% Ni-Co/Al_2O_3) is more active than Ni-Pt-A-100 (16% Ni-Pt/Al_2O_3) and that the activity of Ni-Co-A-100 compares favorably with catalysts previously reported, with an activity intermediate between those of the nickel and cobalt catalysts.

Comparison of turnover numbers (Tables 2 and 3, and Figure 3) shows that the Ni-Co sites are more active than the Ni-Pt sites. Comparison of the Ni-Co catalyst with the nickel and cobalt catalysts (Figure 3) shows that the nickel-cobalt alloy has a turnover number close to that of the nickel catalyst but much lower than that of the cobalt catalyst. However, after exposure to H_2S, the nickel-cobalt has a higher turnover number than Co.

Selectivity data in Tables 2 and 3 show that in going from 225 to 250°C the Ni-Co catalyst showed a decrease in selectivity towards CH_4, whereas the Ni-Pt catalyst showed a significant increase in selectivity to CH_4, and is more selective at the higher temperature. The decrease in selectivity of the nickel-cobalt catalyst is similar to that previously reported for the cobalt catalyst (QPR-6). The selectivity of the Ni-Co catalyst at 250°C appears to be intermediate between that of the cobalt catalyst Co-A-100 (20% Co/Al_2O_3) and the previously reported 14% nickel catalyst Ni-A-116 (QPR-5), but is more similar to that of the nickel catalyst.

Table 4 shows the apparent activation energies calculated from the data in Tables 2 and 3. The value of 17.3 calculated for the nickel-cobalt alloy is much less than the value for the cobalt catalyst, but it is almost identical to the value for the nickel catalyst. The nickel-platinum alloy also has a value similar to that of the nickel catalyst. Because the conversion of CO was in the range of 10-30% for most of these high metal loading catalysts, the activation energies reported in Table 4 reflect diffusional influences and in each case the true activation energy should be higher. For example, the true activation energy for Ni/Al_2O_3 is about 25 kcal/mole (5-7).

Table 5 shows the fractional changes in hydrogen uptake and in turnover number with exposure of the catalysts to H_2S. The CH_4 turnover number of poisoned catalyst based on poisoned H_2 uptake divided by the CH_4 turnover number of fresh catalyst based on fresh H_2 uptake is called the poisoned site activity ratio (PSAR). The PSAR is a measure of the change in activity of the methanation sites as a result of partial poisoning. A value less than 1.0 indicates that either the most active sites are poisoned first or that H_2S interacts with the remaining sites to decrease their activity. Conversely, a PSAR value greater than 1.0 indicates that either the least active sites

Table 2

Reactor Screening Data
(225°C, GHSV = 30,000 hr^{-1}, 20.5 psia)

Catalyst	% Conversion	% Production		% Selectivity		Rate x 10^7 (gmoles/gcat-sec)		Turnover Number x 10^3 Based on Fresh H_2 Uptake		Turnover Number x 10^3 Based on Poisoned H_2 Uptake	
	CO	CH_4	CO_2	CH_4	CO_2	CO	CH_4	CO	CH_4	CO	CH_4
Ni-Co-A-100	14.8	12.3	3.6	84.0	2.4	8.4	7.0	3.6	3.0		
Ni-Co-A-100 Poisoned	14.8	12.25	0.29	82.8	2.0	8.5	7.0	3.7	3.0	6.5	5.4
Ni-Pt-A-100	12.3	9.6	0.1	79.0	0.0	7.4	5.8	2.9	2.3		
Ni-Pt-A-100 Poisoned	11.3	8.89	0.08	79.1	0.7	6.6	5.2	2.2	1.7	3.2	2.5

Table 3

Reactor Screening Data
(250°C, GHSV = 30,000 hr^{-1}, 20.5 psia)

Ni-Co-A-100	35.5	28.5	2.27	80.0	6.4	20.3	16.3	8.5	6.9		
Ni-Co-A-100 Poisoned	35.4	29.3	4.15	82.7	11.7	20.3	16.8	8.7	7.2	15.6	12.9
Ni-Pt-A-100	25.9	22.2	0.17	89.0	1.4	15.6	13.3	6.2	5.3		
Ni-Pt-A-100 Poisoned	21.2	18.4	0.21	86.7	1.0	12.3	10.7	4.1	3.5	6.0	5.2

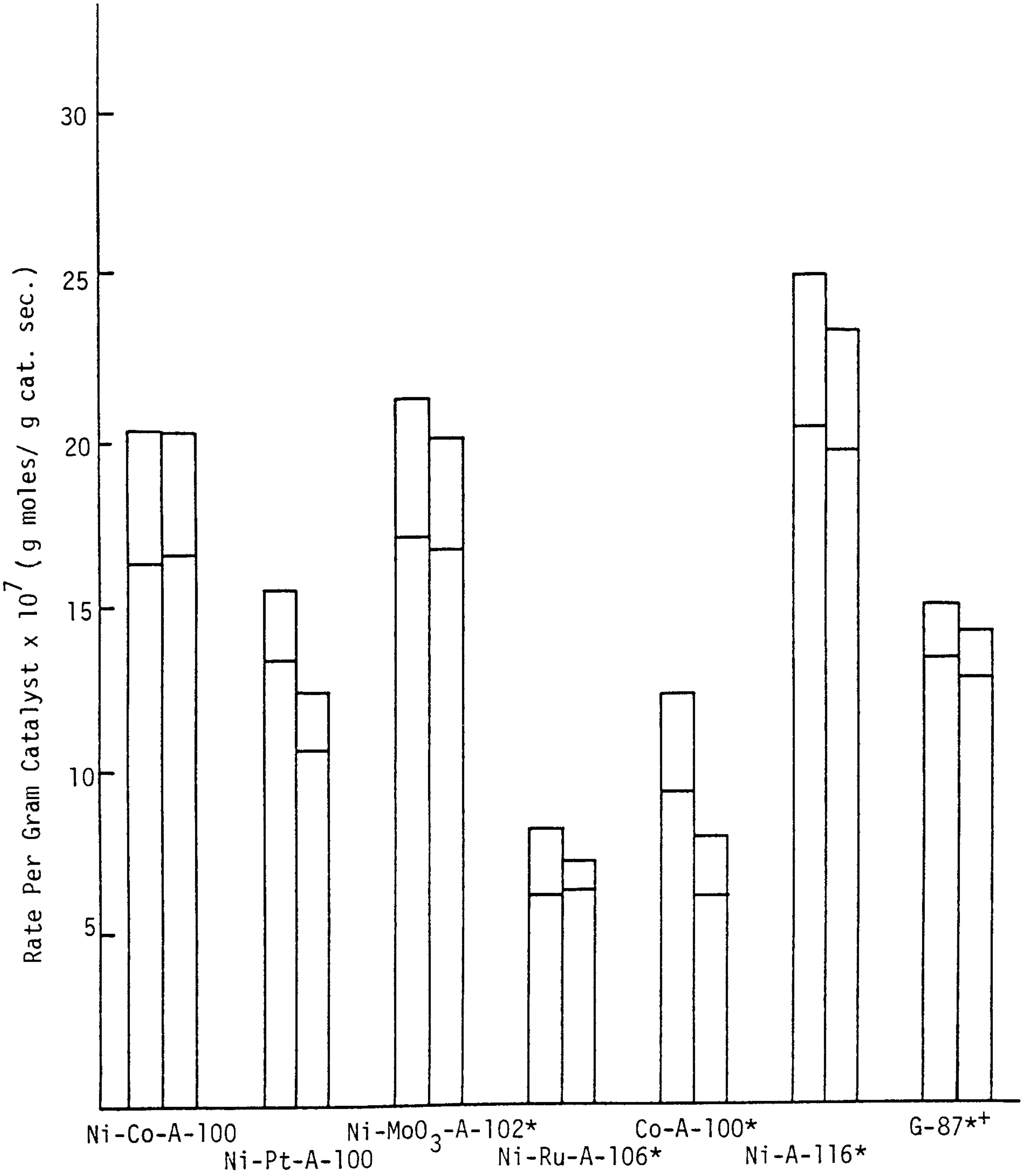

Figure 2. The effect of H_2S on Methanation Activity at 250°C (GHSV = 30,000 hr^{-1}). The first bar of each pair represents the activity of the fresh catalyst; the second indicates the activity after exposure to 10 ppm (molar basis) H_2S in H_2 until 30 to 40% of the metal sites were poisoned at a space velocity of 2,000 hr^{-1} and 450°C. The upper bar represents CO conversion while the lower bar represents methane production. The catalysts were reduced for 2 hours in flowing H_2 at 450°C.

*Previously reported catalysts.

+Exposed to 10 ppm H_2S in H_2 for 12 hours at a space velocity of 2,000 hr^{-1} and 450°C.

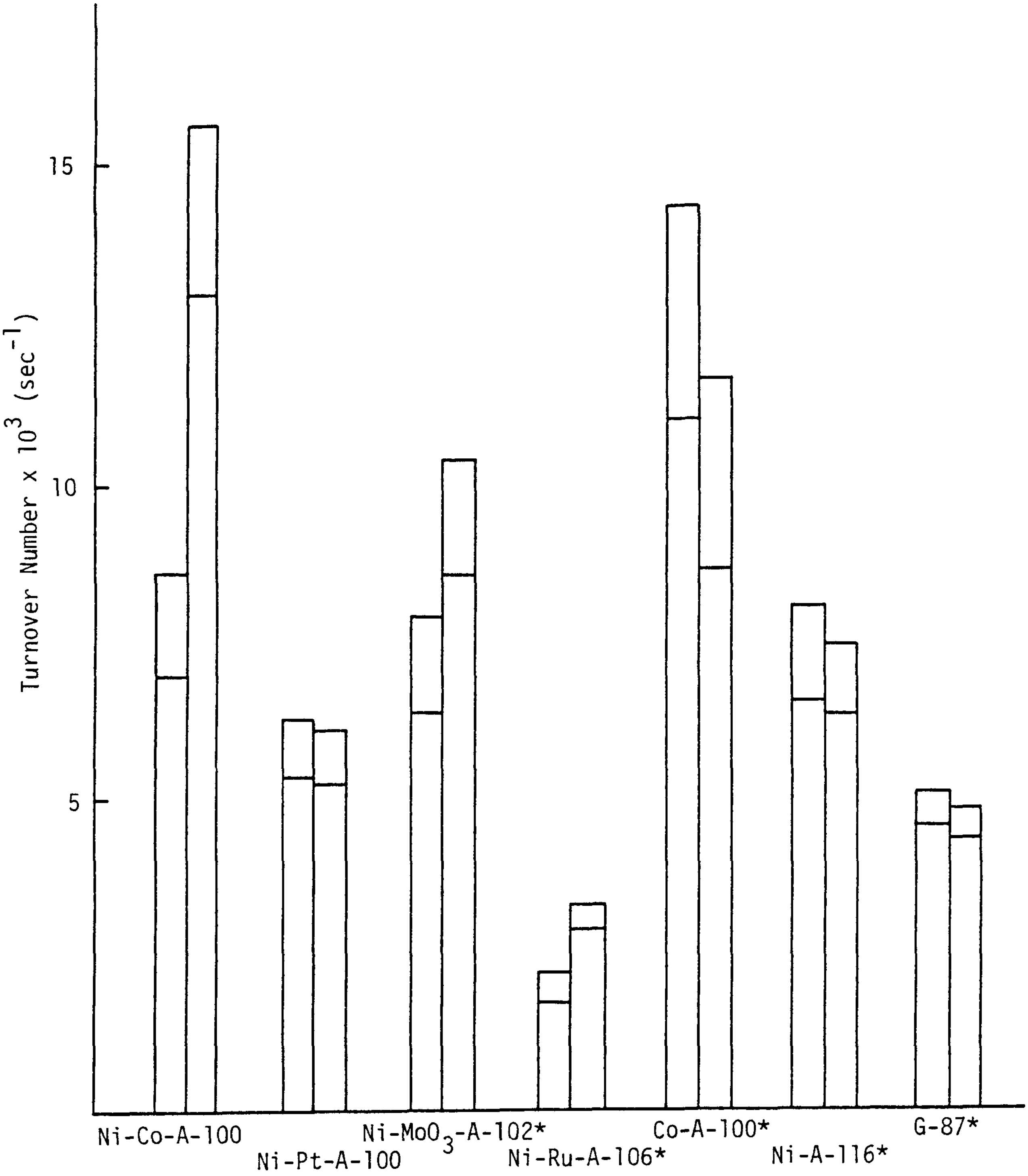

Figure 3. The effect of H_2S on Turnover Number at 250°C (GHSV = 30,000 hr^{-1}). For explanation of the bars see Figure 2. The catalysts were reduced for 2 hours in flowing H_2 at 450°C. Fresh catalyst turnover number based on fresh H_2 uptake; poisoned catalyst turnover number based on poisoned H_2 uptake.

*Previously reported catalysts.

Table 4

Apparent Activition Energies for Methanation Catalysts Based on Measurements at 225-250°C and a Space Velocity of 30,000 hr^{-1}

Catalyst	CO Conversion (K cal/mole)	CH_4 Production (K cal/mole)
Ni-Co-A-100	18.3	17.3
Ni-Co-A-100 Poisoned	18.0	18.0
Ni-Pt-A-100	20.5	17.2
Ni-Pt-A-100 Poisoned	13.0	15.0
Ni-MoO_3-A-102*	20.5	22.8
Ni-MoO_3-A-102 Poisoned*	19.4	22.1
Ni-Ru-A-106*	12.2	13.4
Ni-Ru-A-106 Poisoned*	13.2	15.0
Co-A-100*	28.0	26.0
CO-A-100 Poisoned*	22.5	22.5
Ni-A-116*	15.0	17.5
Ni-A-116 Poisoned*	14.9	16.7
G-87*	16.5	19.0
G-87 Poisoned*	14.9	16.8

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* Previously reported catalysts.

Table 5

Changes in H_2 Uptake and Turnover Number Due to Poisoning (250°C, GSHV = 30,000 hr-1)

Catalyst	H_2 Uptake^f/H_2 Uptake^i	Poisoned Site Activity Ratio **
Ni-Co-A-100	0.560	1.87
Ni-Pt-A-100	0.678	0.980
Ni-MoO_3-A-102*	0.719	1.35
Ni-Ru-A-106*	0.590	1.70
Co-A-100*	0.795	0.789
Ni-A-116*	0.347	0.944
G-87*	0.989	0.965

Superscripts: i = before poisoning
f = after poisoning

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* Previously reported catalysts

** PSAR value = $\dfrac{\text{CH}_4 \text{ turnover number of poisoned catalyst based on poisoned H}_2 \text{ Uptake}}{\text{CH}_4 \text{ turnover number of fresh catalyst based on fresh H}_2 \text{ Uptake}}$

are poisoned first or that H_2S interacts with the remaining sites to enhance their activity. Thus the Ni-Co catalyst appears to be much more resistant to low concentrations of H_2S than is the Ni-Pt catalyst. In fact the Ni-Co catalyst appears to be more resistant than any of the catalysts tested to date. On the basis of the PSAR values the three catalyst which show the greatest resistance to low concentrations of H_2S are Ni-Co, Ni-Ru, and Ni-MoO_3 catalysts (containing 16-20 wt.% metal).

These results possibly model the behavior of these catalysts in response to a plant upset where the catalyst bed is inadvertently exposed to 10 ppm H_2S over a 12-24 hour period. Accordingly it appears that high metal loading catalysts containing nickel alloyed with cobalt, molybdenum oxide, or ruthenium are more resistant than nickel to short term sulfur poisoning.

D. Task 4: Catalyst Life and Geometry: Testing and Design.

1. Thermodynamic Calculations. In planning our steady state reactor tests we have searched the literature and performed thermodynamic calculations to determine both conditions which might promote and those which might prevent carbon deposition. We have also been concerned about minimizing ammonia and carbon dioxide formation in our test reactor. Ammonia is a reaction poison, carbon deactivates the catalyst, and carbon dioxide is an undesirable by-product. Accordingly, we performed thermodynamic calculations of our reaction mixtures at various temperatures and pressures to determine the equilibrium formation of ammonia, carbon, and carbon dioxide. A detailed description of these calculations and results is found in Appendix 1.

Generally, we found that ammonia formation for our test mixtures would be less than 0.1 mole percent at equilibrium. Since NH_3 formation is very much kinetically limited at methanation reaction temperatures the ammonia concentration which the catalysts see can be estimated to be about 1 ppm or less.

For carbon formation we found that higher pressure, lower temperatures, higher H_2/CO ratios, addition of N_2 or He diluents, and the presence of small amounts of H_2O (1%) inhibit carbon formation. Conversely, lower pressures, higher temperatures, lower H_2/CO ratios, addition of CH_4 and the absence of H_2O promote carbon formation. Carbon dioxide formation is inhibited generally by lower temperatures, higher pressures, and the absence of H_2O.

2. Accomplishments - Pellet-Supported Catalysts. Water injection integral runs. During the past quarter activity vs. temperature tests with 1% water injected in the feed were completed with the exception of a 3% Ni-Co catalyst. The percent conversion of CO and the percent production of CH_4 and CO_2 are shown graphically in Figures 4 through 11. Each of the runs were conducted at a GHSV of 30,000 hr^{-1} with a reactant gas mixture containing 95% N_2, 4% H_2, and 1% CO on a dry mole basis with 1% (by vol) water vapor injected in the feed (except for the results shown in Figure 4 with no water). The presence of

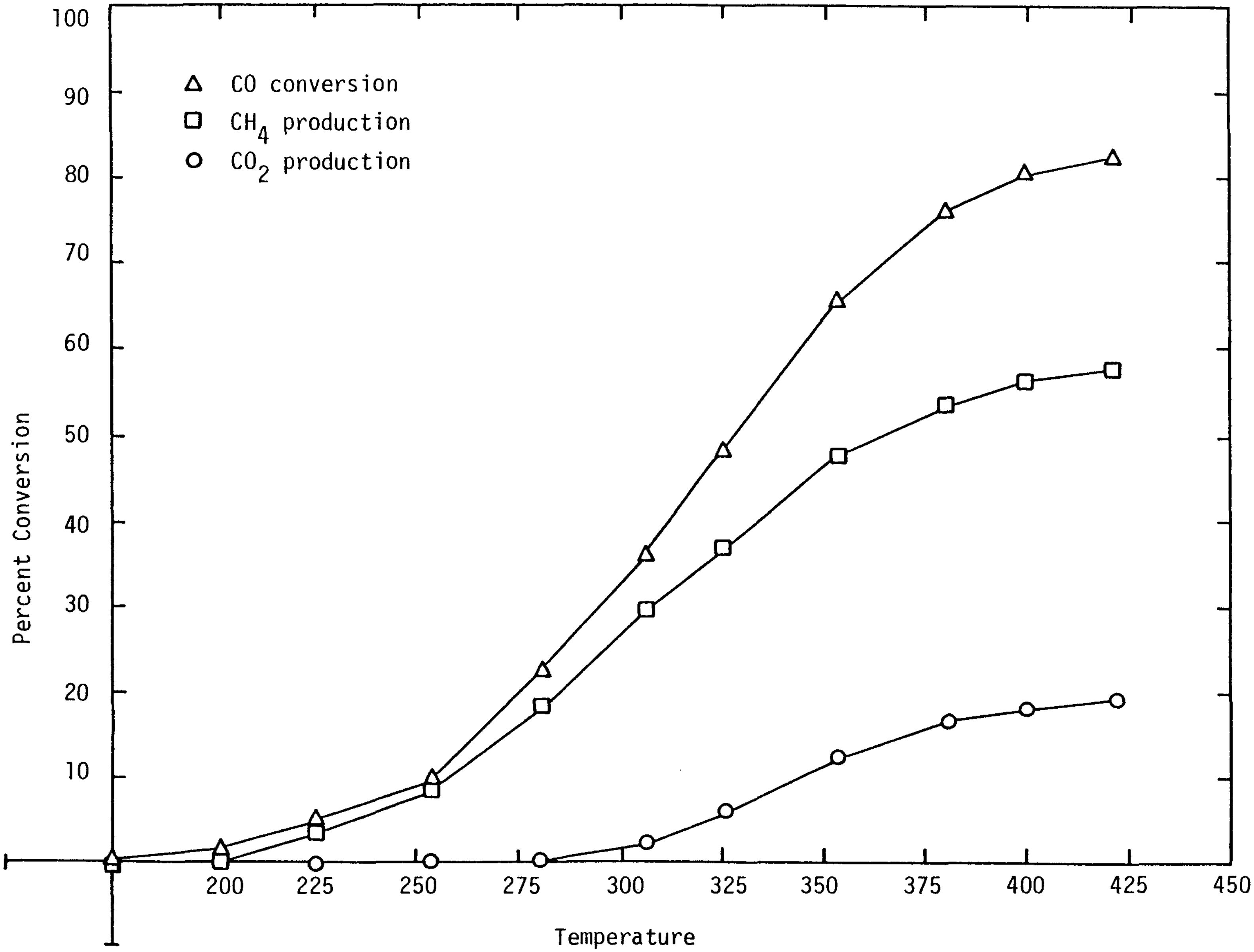


Figure 4. Conversion versus temperature Ni-A-112 (3% Ni/Al_2O_3), 20.5 psia, GHSV = 30,000 hr^{-1} 0% water vapor in feed.

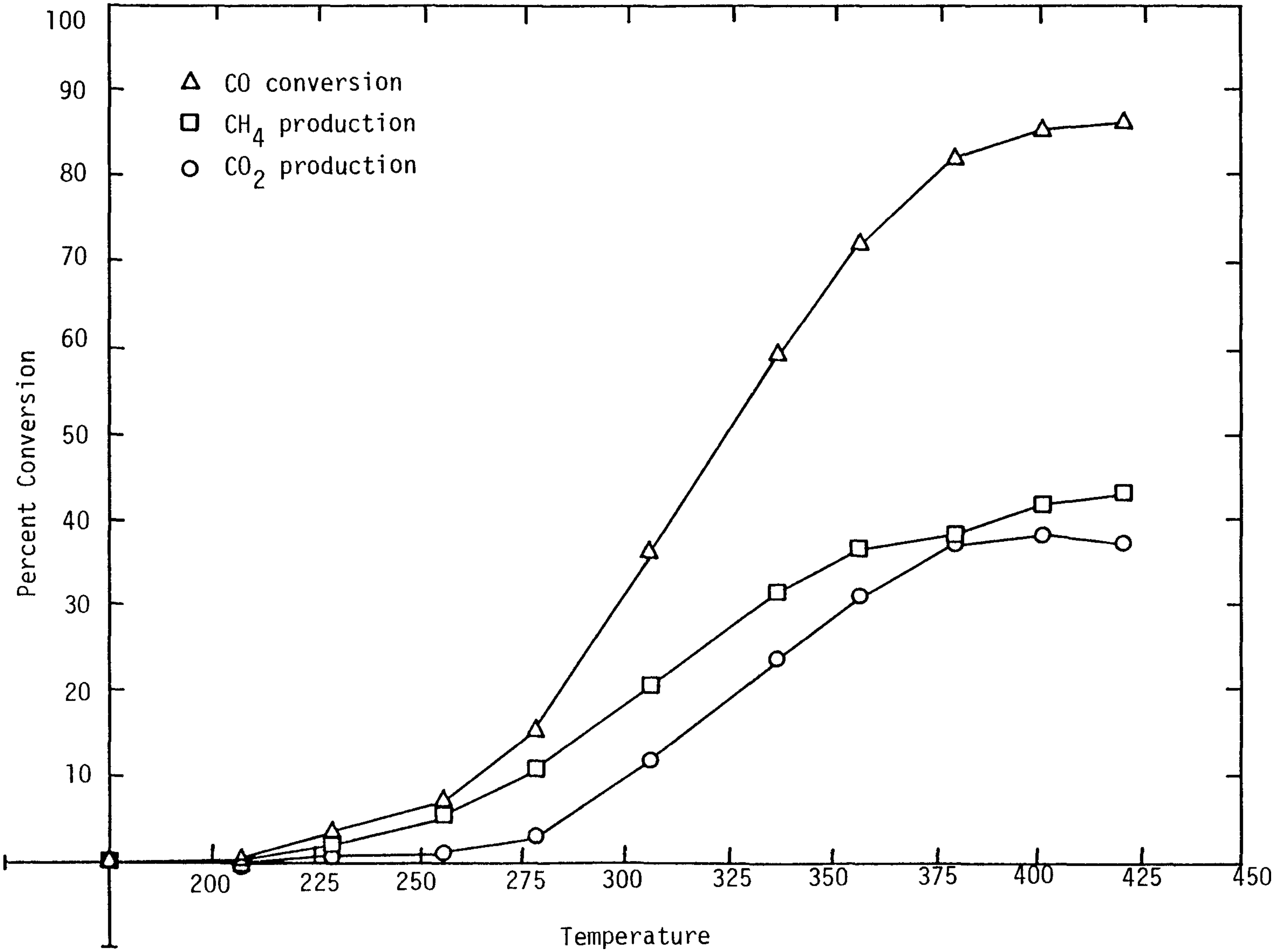
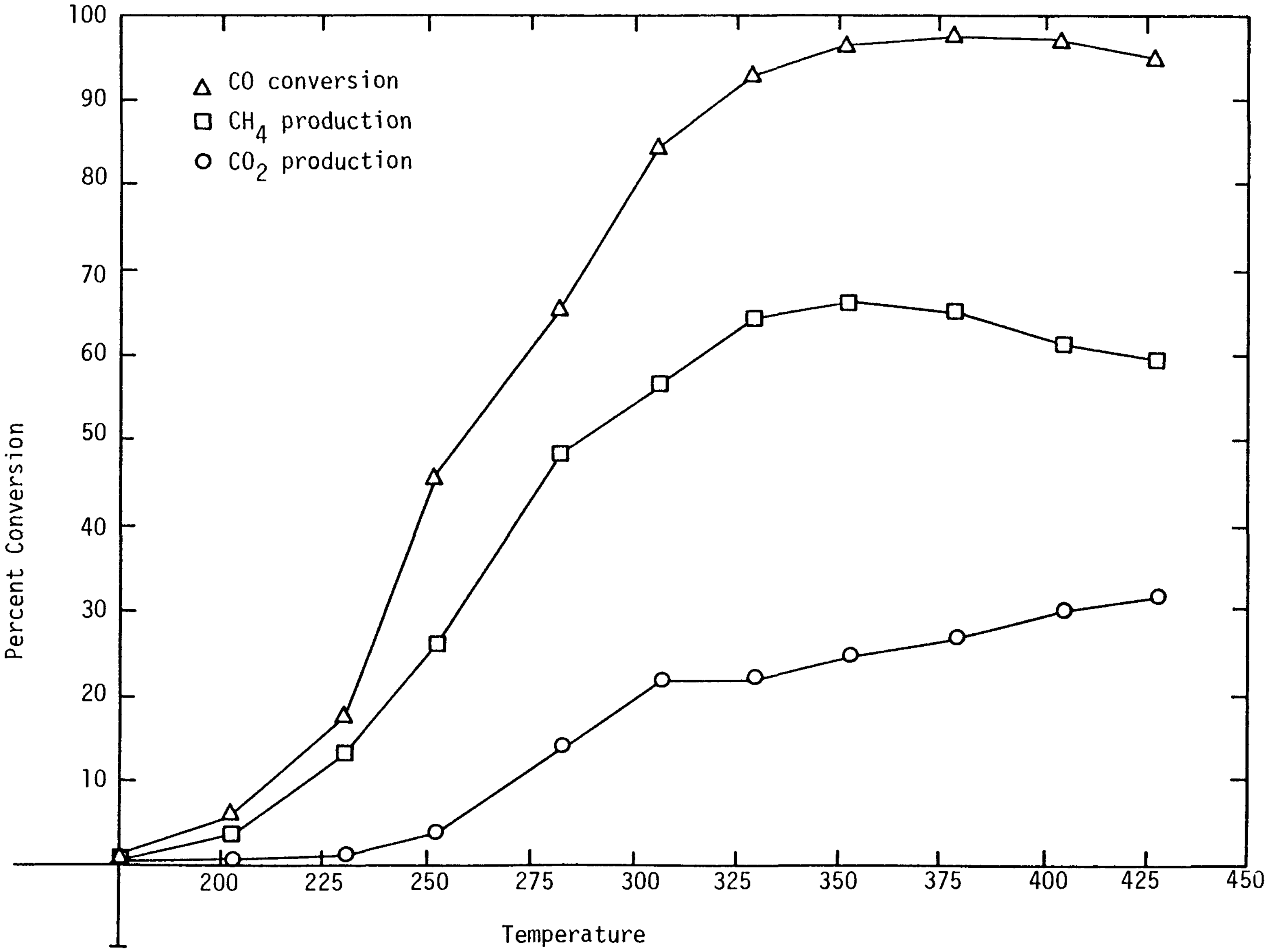


Figure 5. Conversion vs. temperature Ni-A-112 (3% Ni/Al_2O_3), 20.5 psia, GHSV = 30,000 hr^{-1}, 1% water vapor in feed.



Fibure 6. Conversion vs. temperature Ni-A-116 (14% Ni/Al_2O_3), 20.5 psia; GHSV = 30,000 hr^{-1}
1% water vapor in feed.

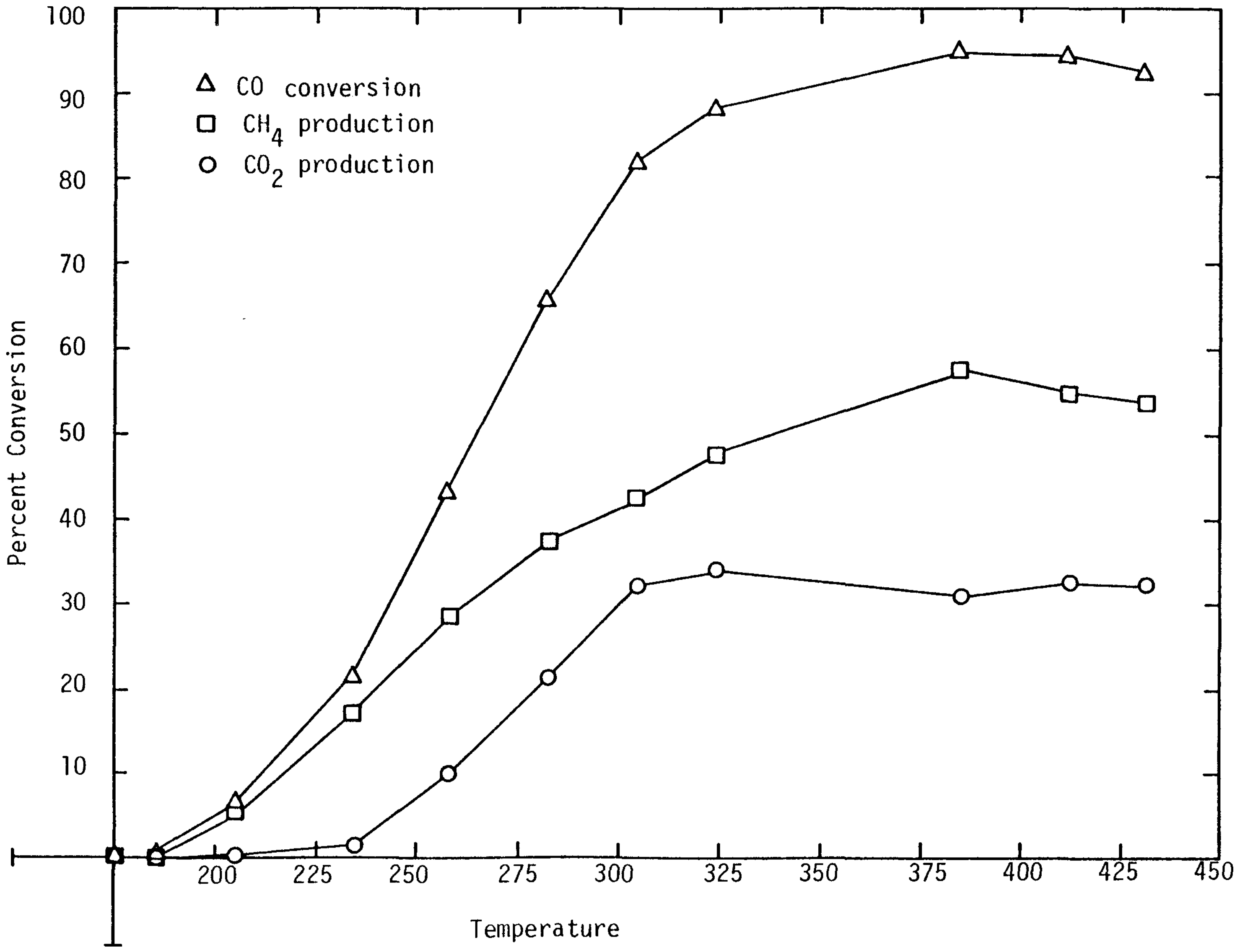


Figure 7. Conversion vs. temperature Ni-Co-A-100 (10% Ni, 10% Co/Al_2O_3), 20.5 psia, GHSV = 30,000 hr^{-1}, 1% water vapor in feed.

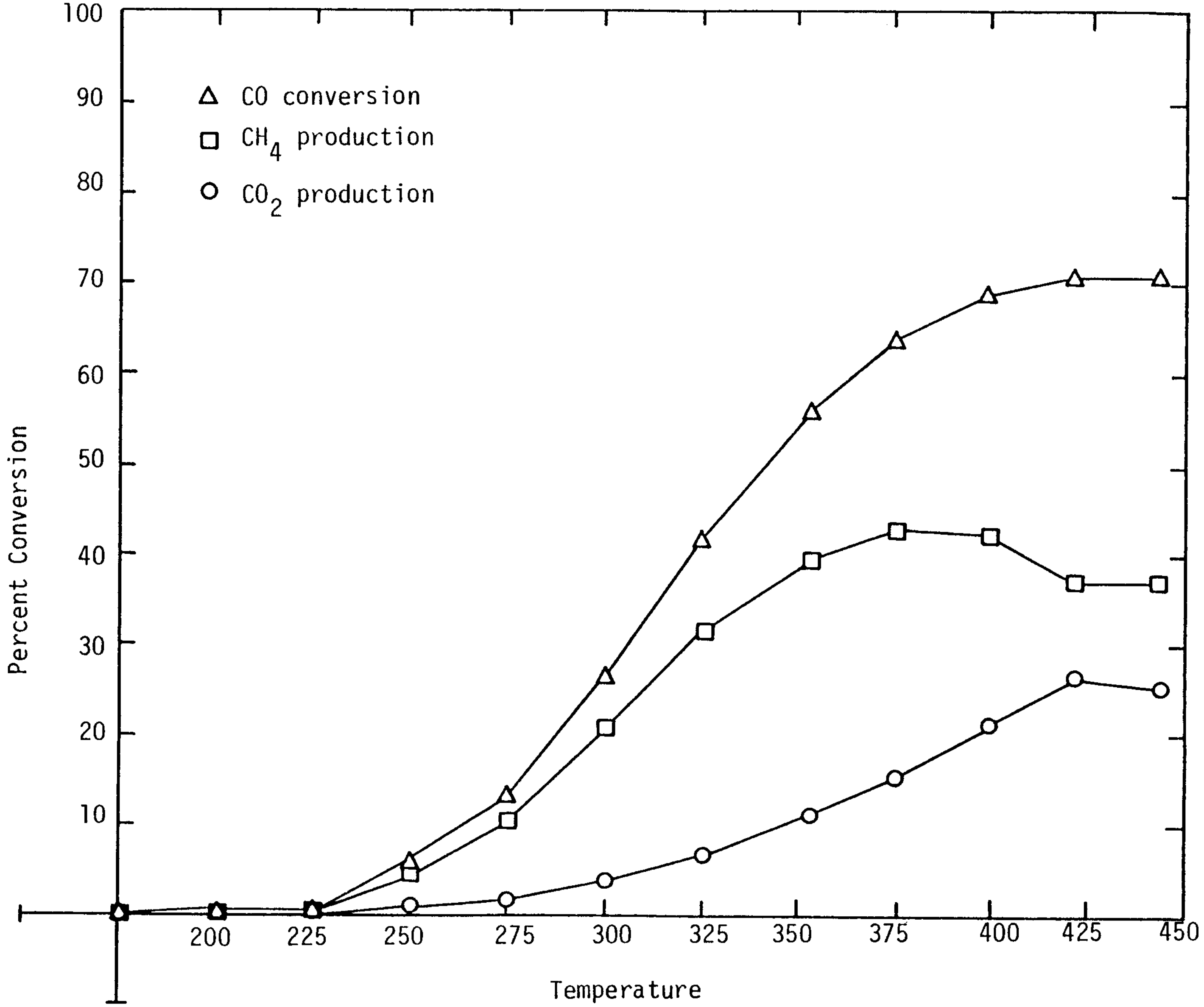


Figure 8. Conversion vs. temperature Ni-MoO_3-A-101 (2.5% Ni, 3% MoO_3/Al_2O_3) 20.5 psia, GHSV = 30,000 hr^{-1}, 1% water vapor in feed.

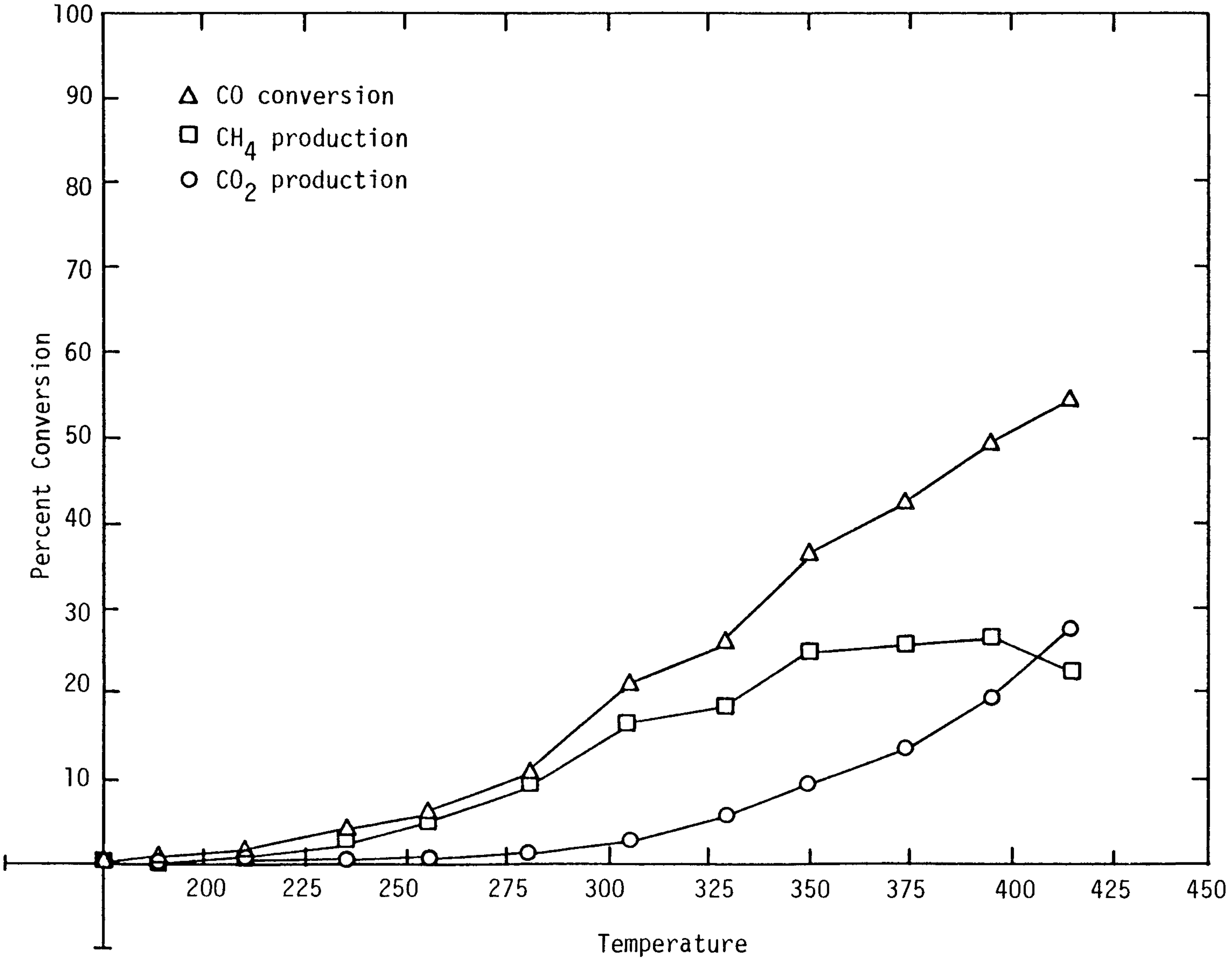


Figure 9. Conversion vs. temperature Ni-Ru-A-105 (2.5% Ni, 0.5% Ru/Al_2O_3), 20.5 psia; GHSV = 30,000 hr^{-1}, 1% water vapor in feed.

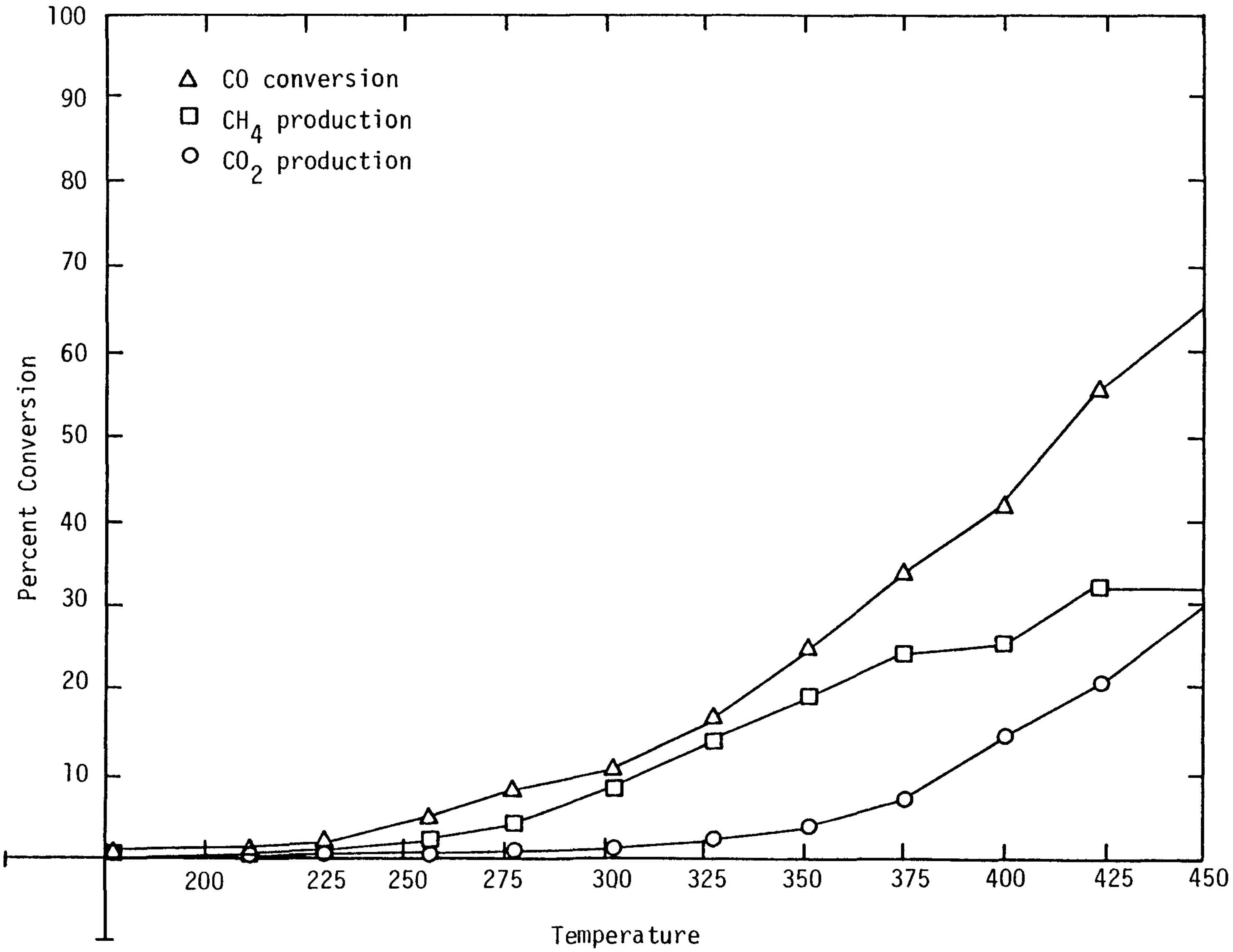


Figure 10. Conversion vs. temperature Ni-Rh-A-100 (2.5% Ni, 0.5% Rh/Al_2O_3), 20.5 psia, GHSV = 30,000 hr^{-1}, 1% water vapor in feed.

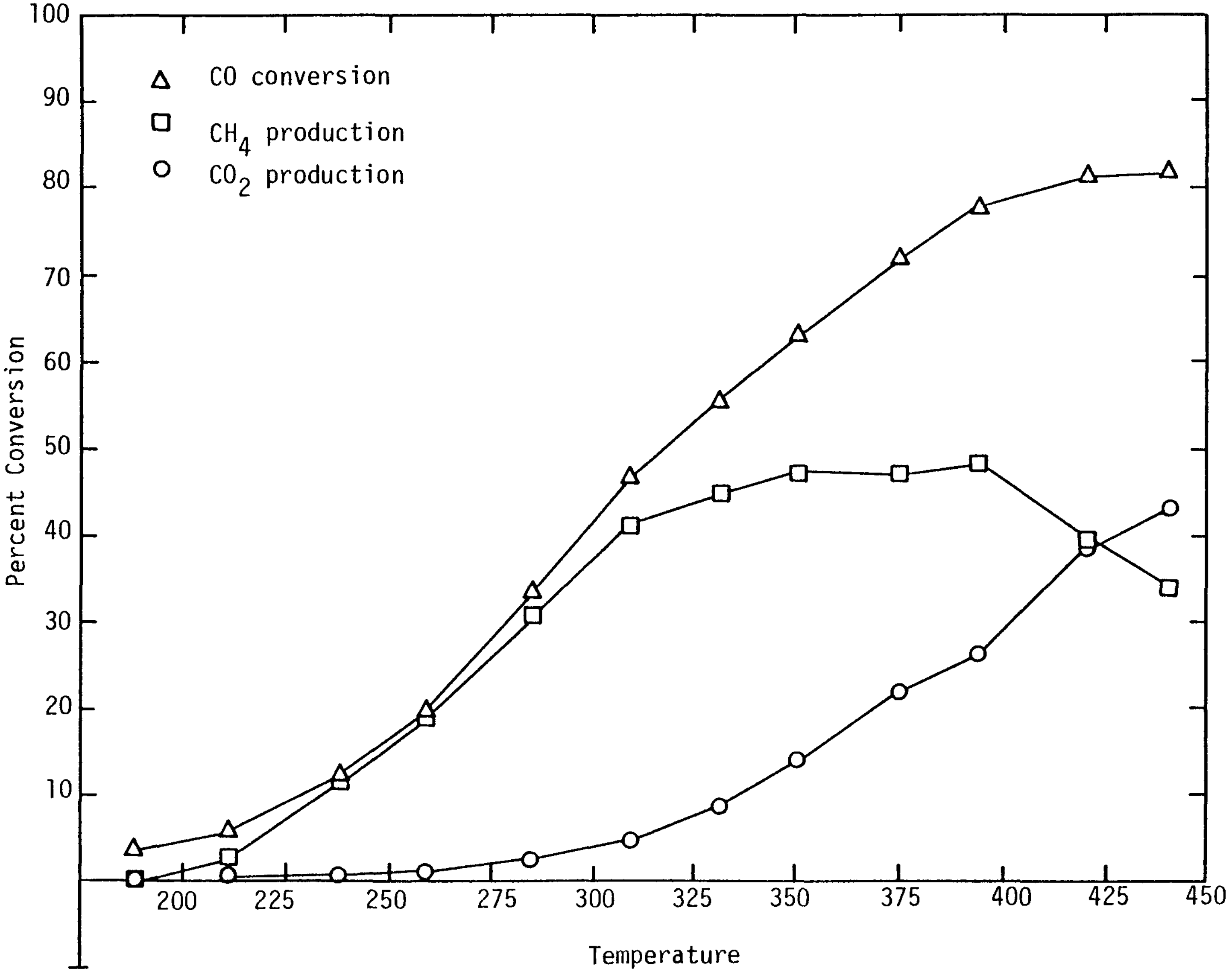


Figure 11. Conversion vs. temperature Ni-Pt-A-100(15.7% Ni, 0.5% Pt/Al_2O_3), 20.5 psia, GHSV = 30,000 hr^{-1}, 1% water vapor in feed.

water in the feed causes the total conversion of CO to be increased at any given temperature. The CH_4 production is significantly decreased and the CO_2 production correspondingly increased. This can be seen by comparing Figures 4 and 5 for Ni-A-112 (3% Ni). The effect of 1% water is not nearly as great as the effect of 15% water which was detailed in our last report (QPR-6).

The presence of water vapor changes the general trend of the conversion vs. temperature graph as well as increasing the total conversion of CO. With no water present the conversion of CO usually reaches a maximum between 325 and 400°C and then declines. With water present, however, the maximum does not occur but the CO conversion continues to increase with temperature. The conversion to CH_4 does reach a maximum at about 350 to 400°C and then declines. The maximum CH_4 production for each catalyst as well as its corresponding CO_2 production and selectivity to CH_4 (defined as the percent of converted CO which is converted to CH_4) are listed in Table 6. The behavior for conversion to CO_2 as a function of temperature generally falls into two categories: (i) CO_2 production rises quickly with increasing temperature and then levels off (Ni and Ni-Co catalysts) and (ii) CO_2 production increases steadily (Ni-MoO_3, Ni-Ru, Ni-Rh, and Ni-Pt).

From Table 6 it can be seen that the Ni-A-116 (14% Ni) has the highest CH_4 production and the highest selectivity and also reaches its maximum at the lowest temperature. The Ni-Co catalyst also has a high CH_4 production and high selectivity. The Ni-Pt catalyst has the second highest selectivity but has a much lower CH_4 production than the Ni or Ni-Co catalysts. In contrast to the 14% Ni, the 3% Ni catalyst has the worst selectivtiy and reached its maximum at the highest temperature of the catalysts tested.

Since thermodynamics favors the water gas shift reaction and CO_2 production at high temperatures, it is interesting that the catalysts which have the highest CH_4 production and selectivity in the presence of water vapor are the ones that achieve high conversions at low temperature. In contrast the catalysts which achieve low conversions at low temperatures have very poor CH_4 production and selectivity in the presence of water vapor.

The maximum selectivity for each of the catalysts is listed in Table 6c; the maximum occurs at a low temperature where the CH_4 production is low (5-20%). Ni-Pt has the highest selectivity on this basis, and the Ni catalysts have the worst. When a comparison is made at 350°C (Table 6b) Ni-Pt and Ni-Rh are found to have the highest CH_4 selectivities. However the Ni-Rh has a low conversion to CH_4. The Ni and Ni-Co catalysts have the highest CH_4 productions but their selectivity is not quite as good as the Ni-Pt.

Activity vs. temperature tests were conducted before and after the water injection tests to see what effect the water vapor had on the catalyst surface area and degree of reduction. Generally there was no significant decrease in the activity or in the levels of CH_4 and CO_2 production as observed in the tests with 15% water vapor. There was, however, a loss of catalyst surface area as seen from Table

Table 6

Summary of Water Injection Integral Runs
(GHSV = 30,000 hr^{-1}, 20.5 psia, 1% water vapor in feed)

a. At Maximum CH_4 Production

Catalyst	% CH_4 Prod.	Temp.°C	%CO_2 Prod.	% Sel. CH_4
Ni-A-112	43	421	37	50
Ni-A-116	66	353	25	69
Ni-Co-A-100	57	386	31	60
Ni-MoO_3-A-101	42	399	21	61
Ni-Ru-A-105	26	395	19	53
Ni-Rh-A-100	32	451	30	50
Ni-Pt-A-100	48	394	26	62

b. At Approximately 350°C

Catalyst	% CH_4 Prod.	Temp.°C	%CO_2 Prod.	% Sel. CH_4
Ni-A-112	37	357	31	51
Ni-A-116	66	353	25	69
Ni-Co-A-100	57	386	31	60
Ni-MoO_3-A-101	40	353	11	71
Ni-Ru-A-105	25	350	9.4	68
Ni-Rh-A-100	19	351	3.6	78
Ni-Pt-A-100	47	350	14	75

c. Maximum Selectivity for CH_4

Catalyst	% CH_4 Prod.	Temp.°C	%CO_2 Prod.	% Sel. CH_4
Ni-A-112	5.3	256	2.9	75
Ni-A-116	13.2	230	1.2	74
Ni-Co-A-100	16.9	234	1.5	79
Ni-MoO_3-A-101	10.5	275	1.7	80
Ni-Ru-A-105	9.0	280	1.3	84
Ni-Rh-A-100	10.5	302	1.0	82
Ni-Pt-A-100	19.0	259	1.2	95

1. We are presently investigating the sintering of Ni/Al_2O_3 and nickel alloy catalysts in H_2 and H_2/H_2O atmospheres as part of our NSF study.

High pressure integral runs. High pressure conversion vs. temperature tests for pellet supported catalysts were completed except for the Ni-Pt, Co, 20% $NiMoO_3$, 20% Ni-Ru and 20% Ni-Rh catalysts. The maximum conversion for the catalysts tested is 98% or greater for all except the 3% Ni-Ru and the Ni-Co (GHSV = 50,000 hr^{-1}) which have maximums of 94 and 96 percent respectively. Conversion vs. temperature plots are shown in Figures 12 to 18. Since maximum CO conversions are all about the same (98%) over a wide range of temperature, comparisons of temperature for maximum conversion are not meaningful. Thus, the temperatures for 50 and 95 percent conversion of CO are listed in Table 7 along with the CH_4 production and selectivity. The Ni and Ni-Co catalysts reach the 95% conversion level at the lowest temperature (280°C). The other catalysts have more gradual increases in conversion as temperature is increased.

Selectivities to CH_4 production are much greater at high pressure than at low pressure. All the catalysts tested have selectivities which approach 100% except Ni-Ru and Ni-Rh which have maximum selectivities of 94 and 92% respectively. Figures 19 and 20 show the selectivity to CH_4 production under various reactor conditions for the two Ni catalysts tested. In the high pressure test both 3 and 14% Ni evidence significantly higher selectivities than in the low pressure tests (except at 225-250°C). At high pressure the selectivity increases with increasing temperature, whereas at low pressure it decreases with increasing temperature.

CH_4 and CO turnover numbers at 225°C and 365 psia for four low loading catalysts are listed in Table 8 along with the corresponding turnover numbers for low pressure. The turnover numbers at 365 psia are generally much higher than those reported previously for 20.5 psia, except for Ni-Ru for which the CO turnover number is about the same as before and the methane turnover number a factor of 3-4 less suggesting that selectivity to higher molecular weight hydrocarbons is increased at the higher pressure, while maintaining low temperatures. Hence, the conditions for using Ni-Ru in Fischer-Tropsch synthesis are defined. The turnover numbers at 50 and 95% CO conversion are listed in Table 7. They are generally much larger than those found for low pressures (see QPR-6). For example, the methane turnover number for Ni-Co-A-100 at 325°C and 20.5 psia is 11.1 compared to 38.6 at 325°C and 365 psia.

In using an activated charcoal trap to purify our reactant gases of iron carbonyl, H_2S and organics, we discovered that it produced small amounts of CO_2 (0.1%). During attempts to eliminate this CO_2 contamination it was noticed that at approximately 400°C and 20 psia that the CO_2 was converted almost completely to CH_4 by the Ni and Ni-Co catalysts. The N_2 concentration was 96% and the H_2 concentration was 4% (no CO was present). The space velocity was varied from about 3,000 hr^{-1} to 15,000 hr^{-1} with the same results. No further quantitative measurements were attempted. At present we have removed the carbon trap and are using only Molecular Sieve 5A for purification.

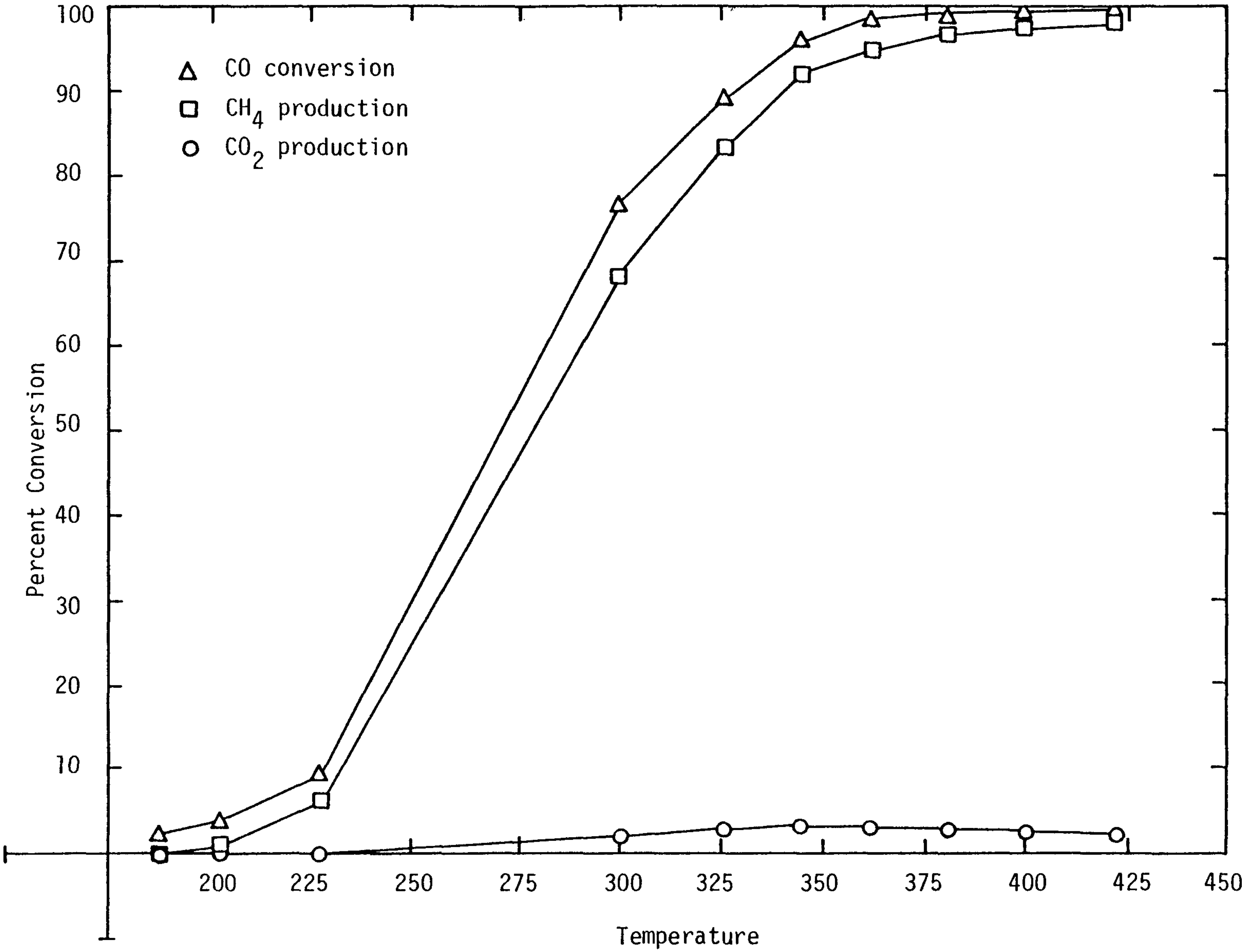


Figure 12. Conversion vs. temperature Ni-A-112 (3% Ni/Al_2O_3), 365 psia, GHSV = 30,000 hr^{-1}.

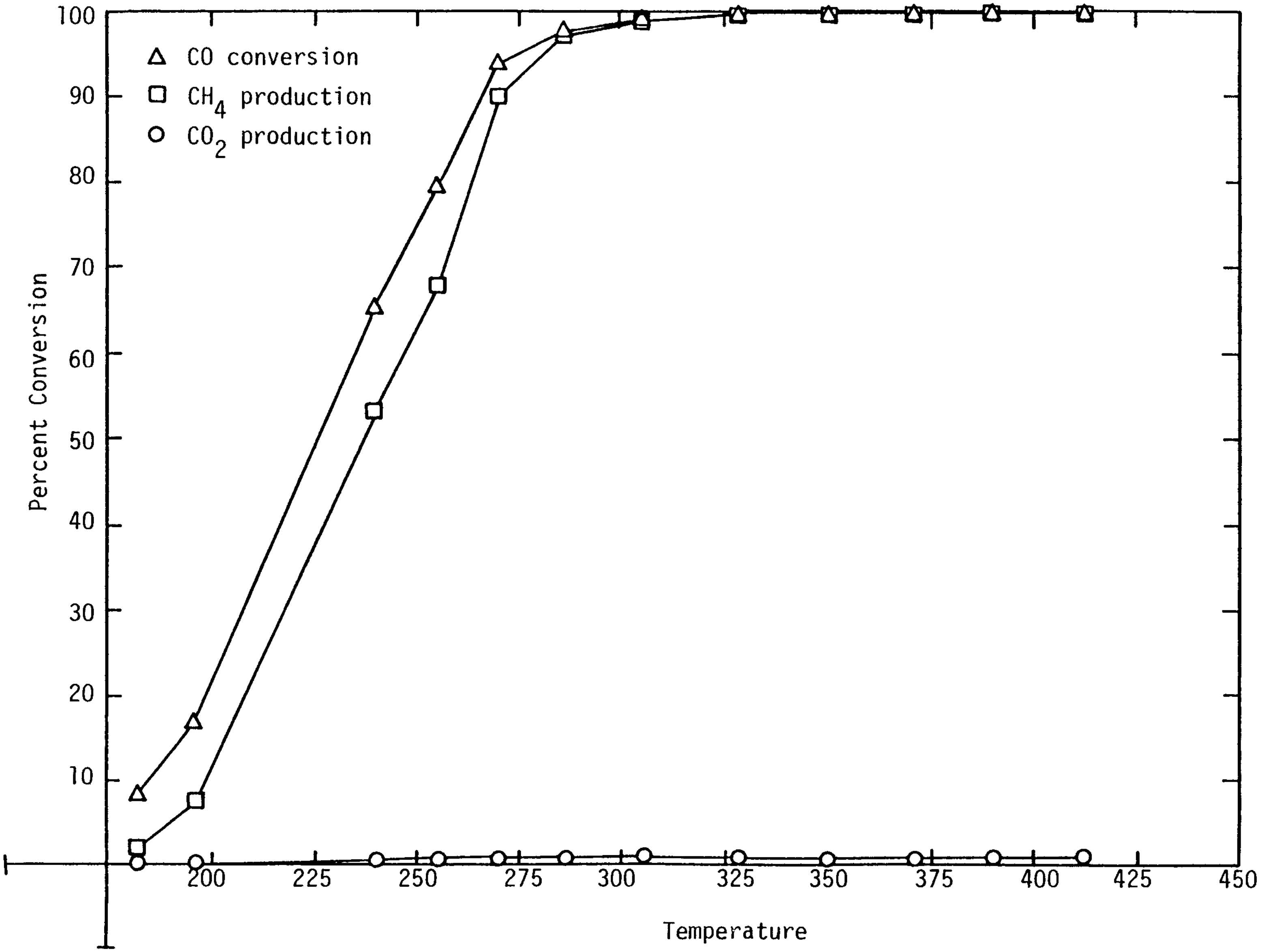


Figure 13. Conversion vs. temperature Ni-A-116 (14% Ni/Al_2O_3), 365 psia, GHSV = 30,000 hr^{-1}.

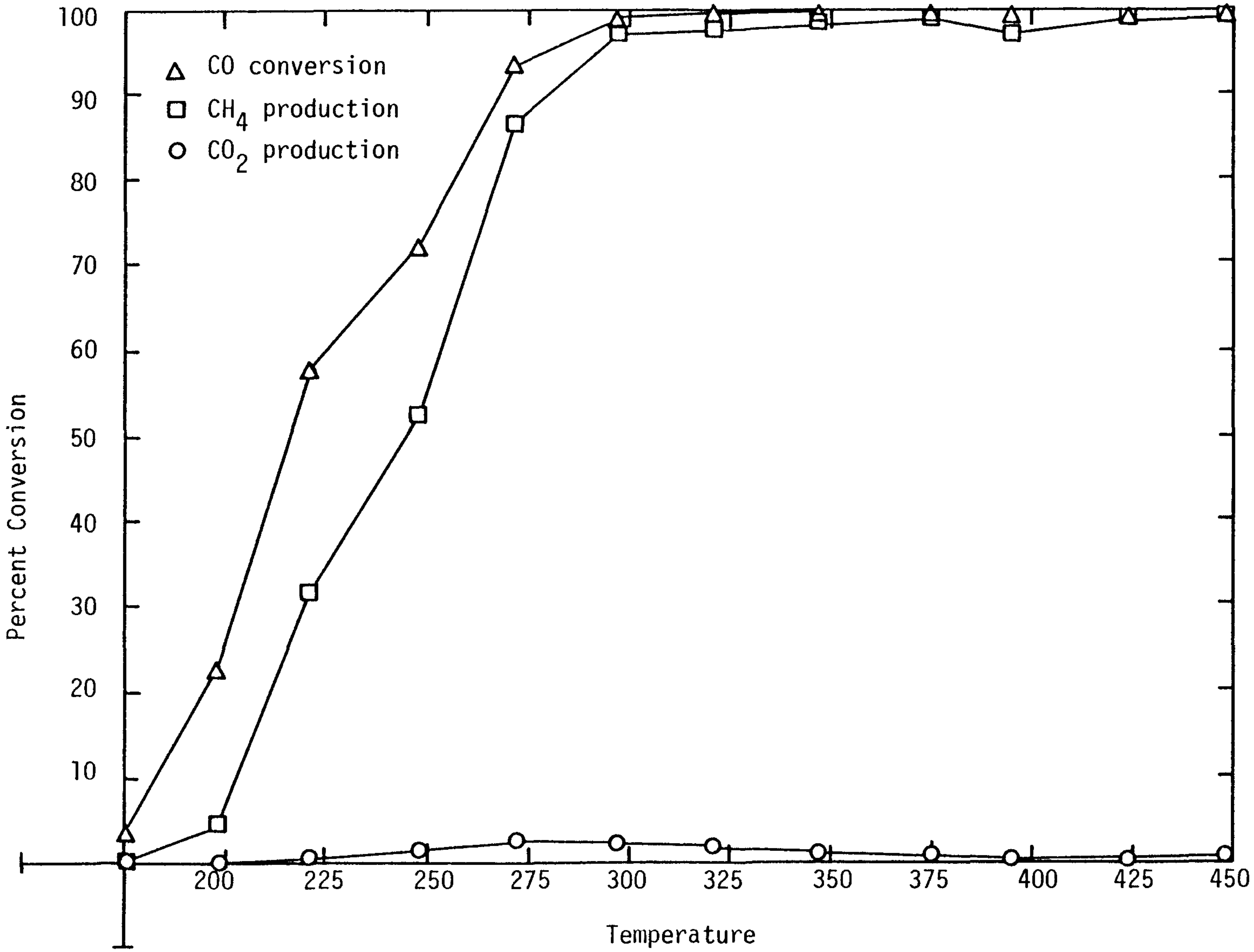


Figure 14. Conversion vs. temperature Ni-Co-A-100 (10% Ni, 10% Co/Al_2O_3), 365 psia, GHSV = 30,000 hr^{-1}.

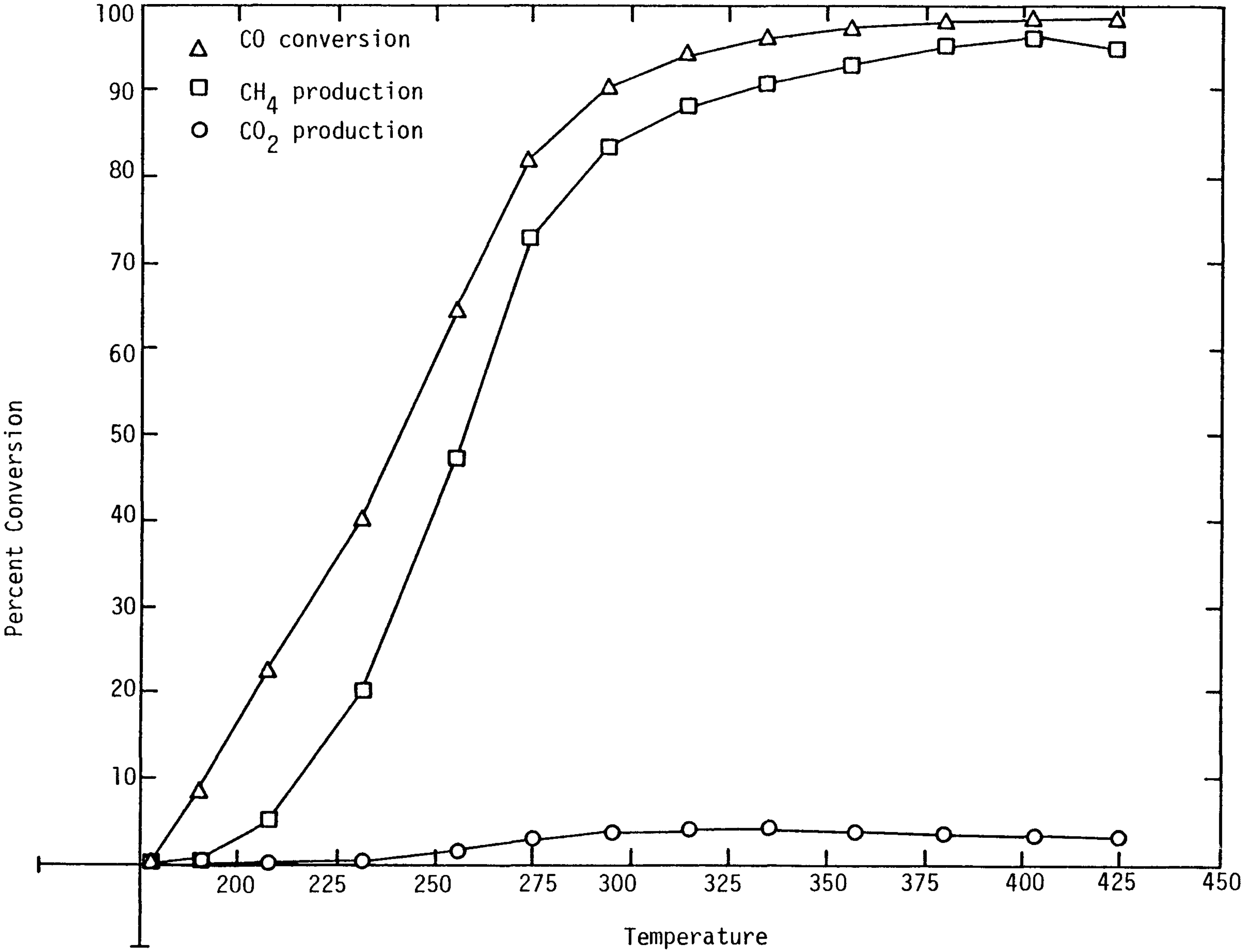


Figure 15. Conversion vs. temperature Ni-Co-A-100 (10% Ni, 10% Co/Al_2O_3), 365 psia, GHSV = 50,000 hr^{-1}.

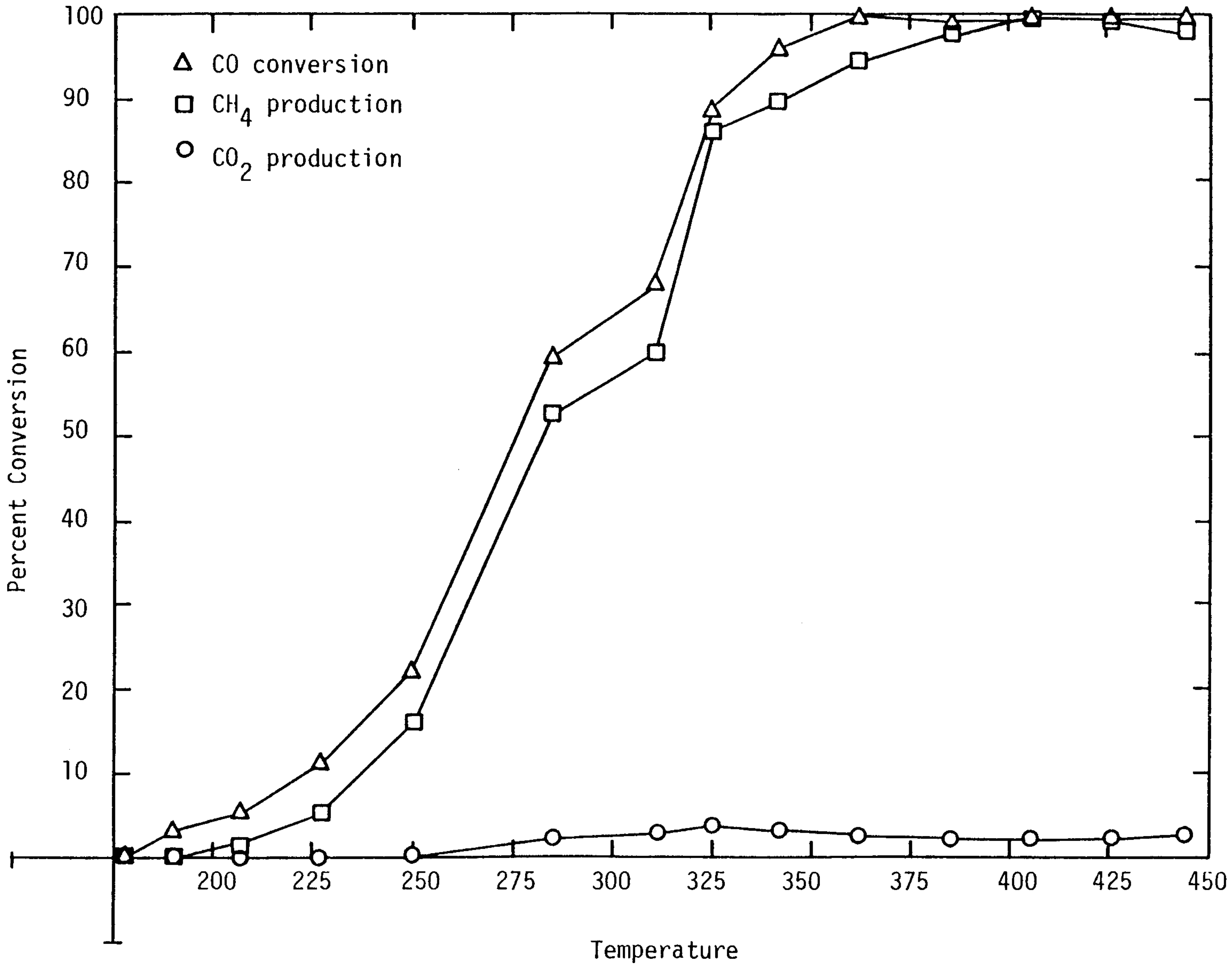


Figure 16. Conversion vs. temperature Ni-MoO$_3$-A-101 (2.5% Ni, 3 % MoO$_3$/Al$_2$O$_3$), 365 psia GHSV = 30,000 hr^{-1}.

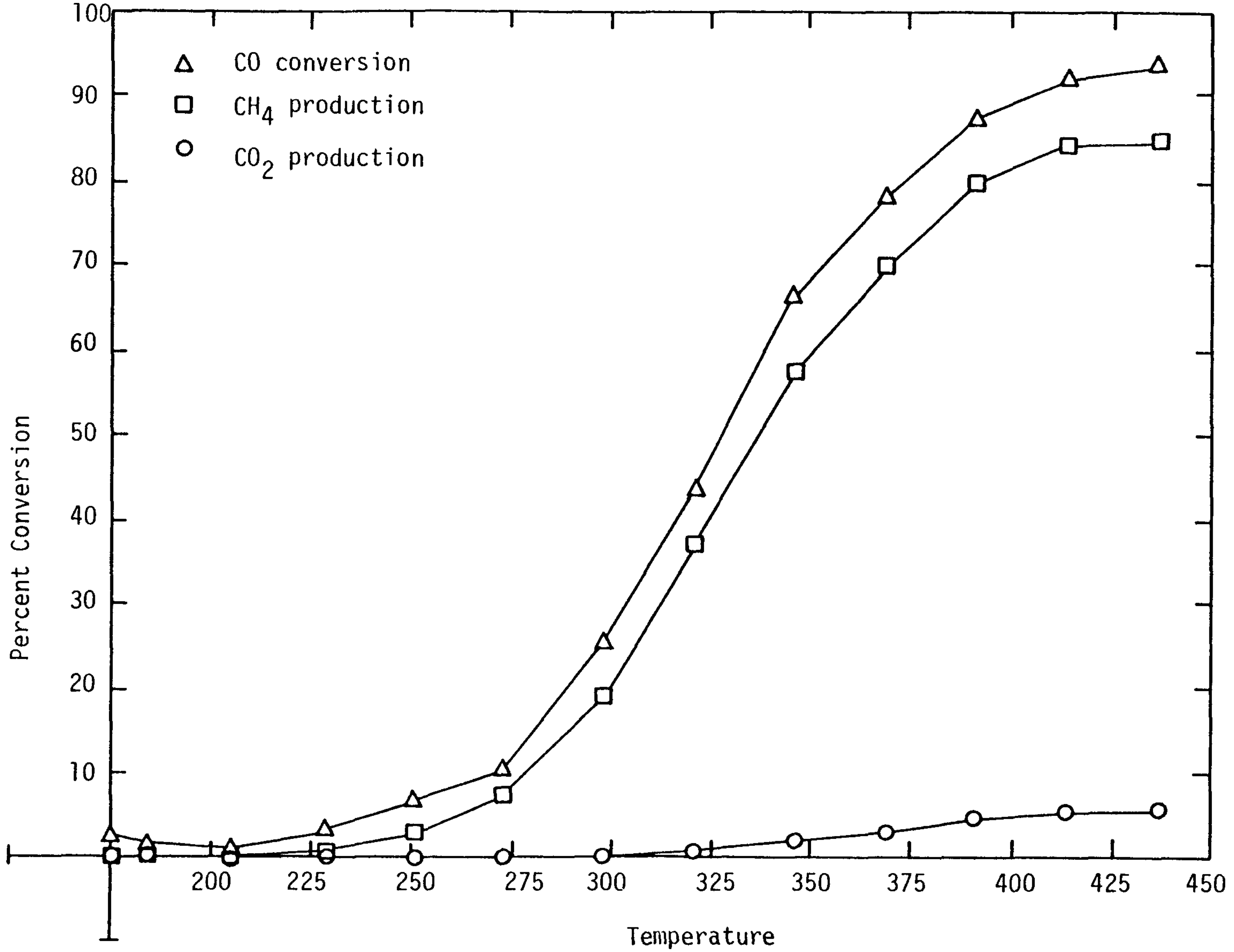


Figure 17. Conversion vs. temperature Ni-Ru-A-105 (2.5% Ni, .5 % Ru/Al_2O_3), 365 psia, GHSV = 30,000 hr^{-1}.

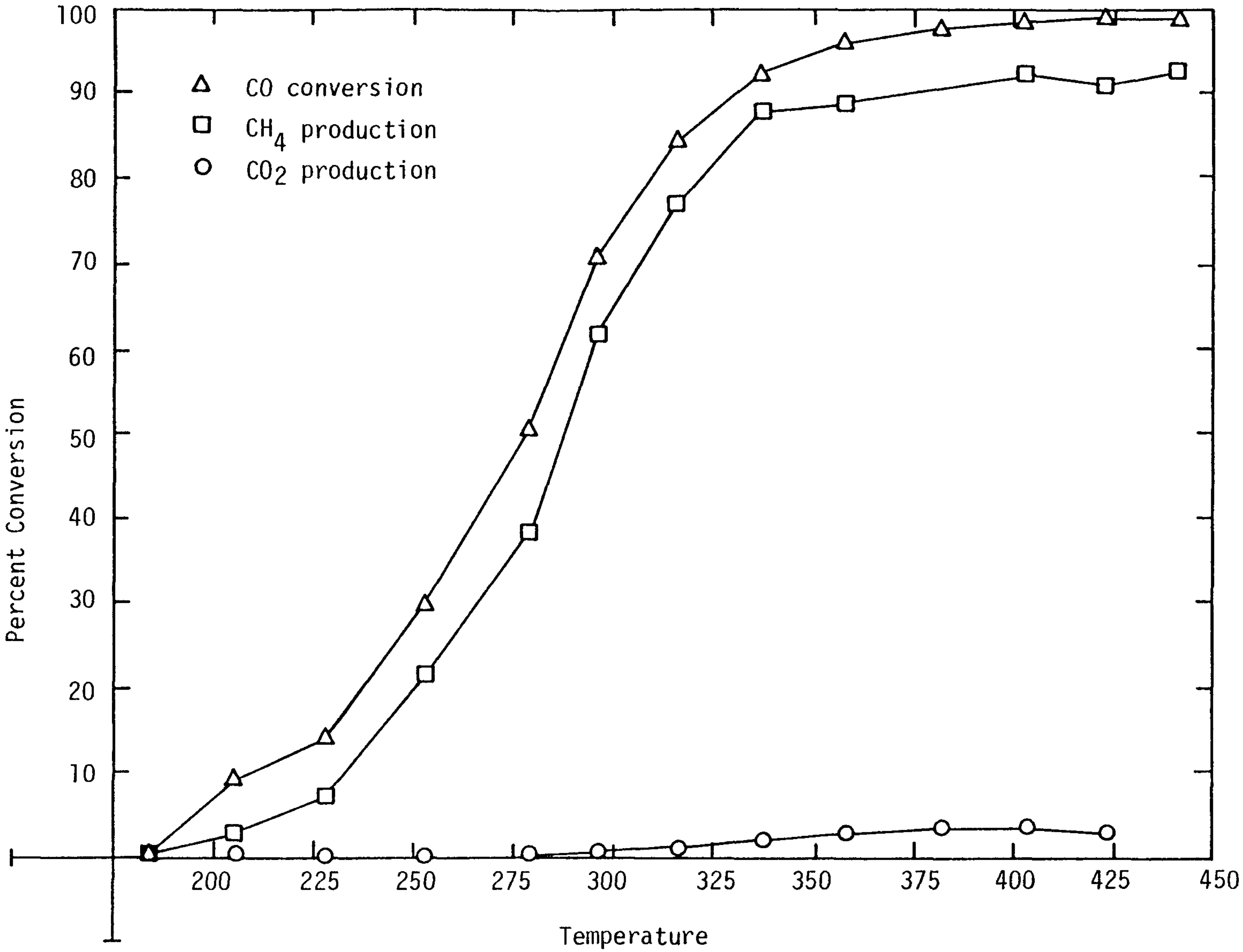


Figure 18. Conversion vs. temperature Ni-Rh-A-100 (2.5% Ni, .5% Rh/Al_2O_3), 365 psia, GHSV = 30,000 hr^{-1}.

Table 7

Summary High Pressure Tests
(365 psia, GHSV = 30,000 hr^{-1})

a. At 50% CO Conversion

				(x 10^3 sec^{-1})	
Catalyst	Temp.	$\%CH_4$ Prod.	% Sel. CH_4	N_{CH_4}	N_{CO}
Ni-A-112	270	43	98	46.6	53.4
Ni-A-116	225	38	69	6.1	8.0
Ni-Co-A-100	215	26	47	7.6	14.7
Ni-Co-A-100*	240	30	59	13.2	21.4
Ni-MoO_3-A-101	275	43	84	77.8	*****
Ni-Ru-A-105	330	43	86	25.5	29.7
Ni-Rh-A-100	280	38	76	35.8	47.0
b. At 95% CO Conversion					
Ni-A-112	342	91	96	97.6	*****
Ni-A-116	275	92	97	15.0	15.5
Ni-Co-A-100	280	90	94	26.0	27.5
Ni-Co-A-100*	325	89	94	38.6	41.0
Ni-MoO_3-A-101	340	89	94	****	*****
Ni-Ru-A-105	437#	85	90	51.5	57.2
Ni-Rh-A-100	350	89	93	82.9	88.7

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* Run at a GHSV = 50,000 hr^{-1}

\# Max conversion was 94% at 437°C

***** Turnover number greater than 100

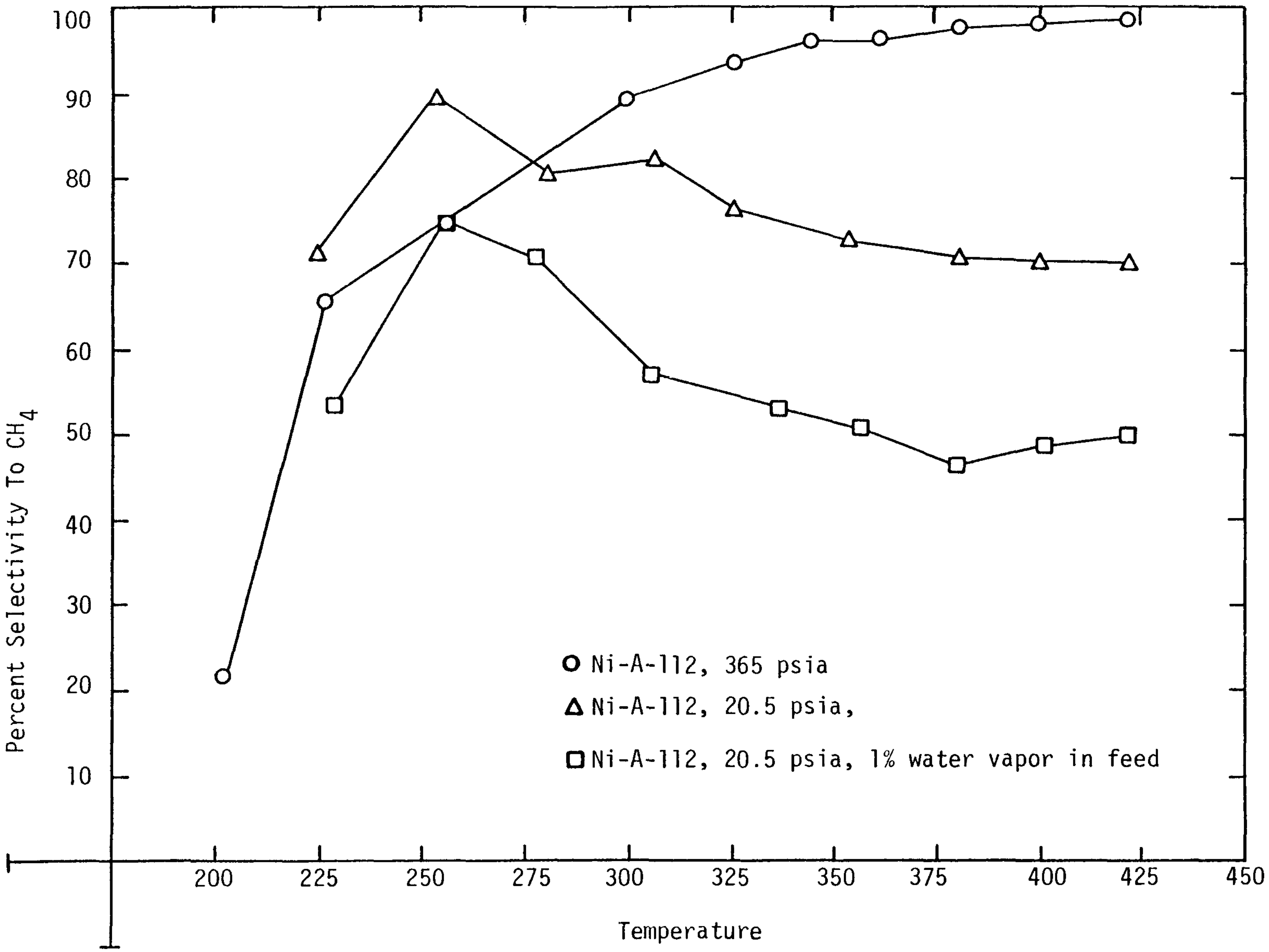

Figure 19. Selectivity vs. temperature Ni-A-112 (3%.Ni/Al_2O_3) GHSV = 30,000 hr^{-1}.

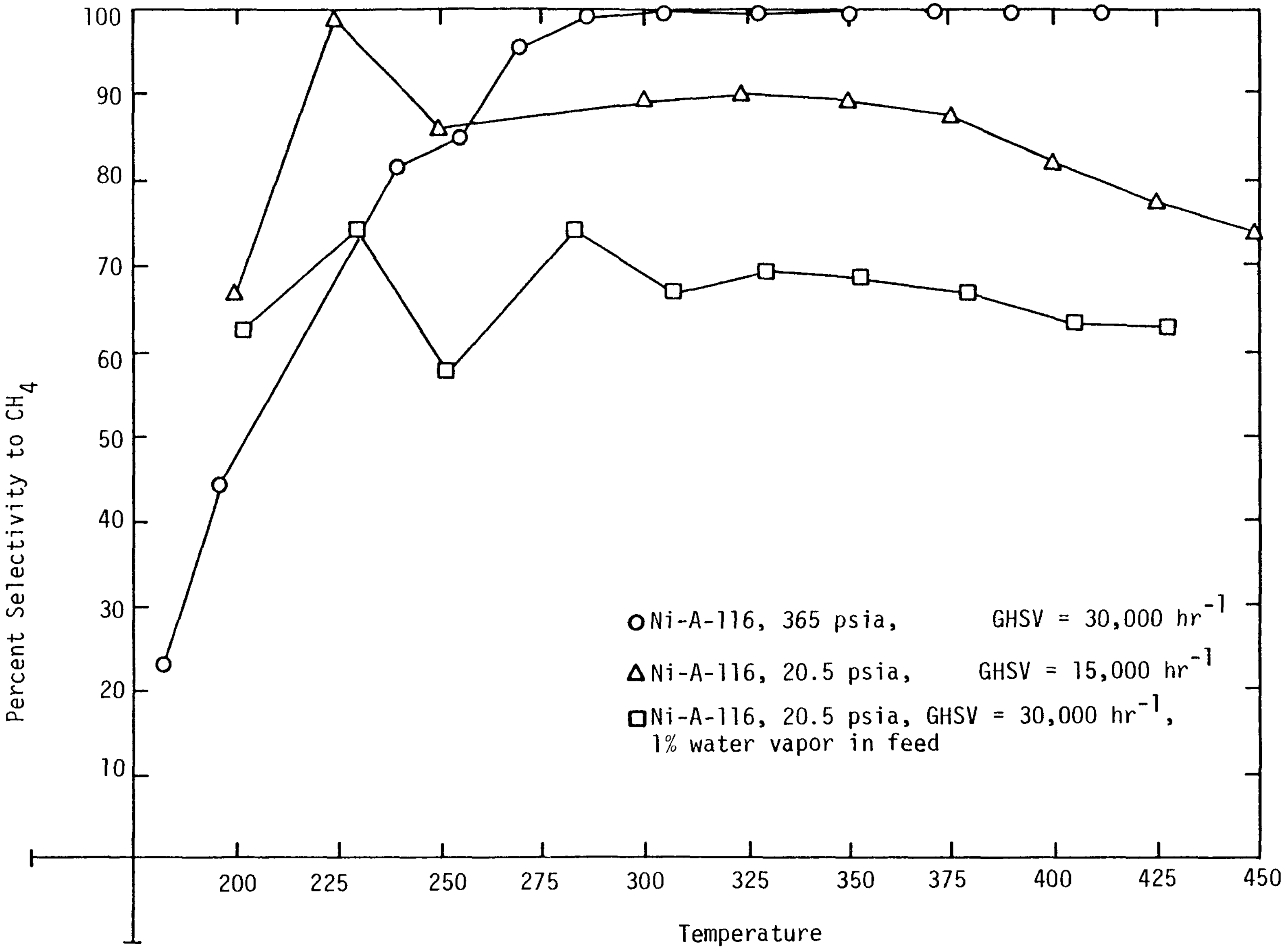

Figure 20. Selectivity vs. temperature Ni-A-116 (14% Ni/Al_2O_3).

Table 8

Turnover Numbers for Nickel and Nickel Alloys at High and Low Pressures

Catalyst	$N_{CH_4} \times 10^3$ sec^{-1}	$N_{CO} \times 10^3$ sec^{-1}	% Selectivity CH_4
	225°C, GHSV = 30,000 hr^{-1}, 365 psia		
Ni-A-112	6.3	9.6	66
Ni-MoO_3-A-101	9.1	18.8	48
Ni-Ru-A-105	0.44	1.9	23
Ni-Rh-A-100	5.9	11.7	51
	225°C, GHSV = 30,000 hr^{-1}, 20.5 psia		
Ni-A-112	1.2	1.8	67
Ni-MoO_3-A-101	1.6	2.8	57
Ni-Ru-A-105	1.5	2.2	68
Ni-Rh-A-100	1.6	2.4	67

3. Accomplishments - Monolithic-Supported Catalysts. Experiments planned in the preceding quarter were performed for two monolith compositions (Ni and Ni-Co). The results are summarized in Table 9 and discussed below for each catalyst.

Ni-M-114 (20% Ni). The system was tested at high pressure using Ni-M-114. However, the CO flow indication was false as we adjusted the mass flow meter well beyond its calibrated linear operating range. Over 40% CO was allowed to flow across the monolith at 350 psig and 250°C. A heavy layer of carbon formed over the monolith and the reactor cell.

Ni-M-115 (20% Ni). One low pressure integral run was performed on Ni-M-115. The results of that run, shown as Figure 21, are similar to those of Ni-M-114, given in QPR-6 in Figure 13 (also see Table 9).

Ni-M-117, 118, and 119 (11 to 12% Ni). The data in Table 9 shows that Ni-M-117 and 118 achieve 95% conversion at the lowest temperatures whereas 117 and 118 are the most selective to methane. Both Ni-M-117 and -118 achieved almost complete conversion over a wide temperature range (see Figures 22 and 23). A plateau of nearly complete conversion was also observed for Ni-M-117 at high pressure, 350 psig and a space velocity of 50,000 hr^{-1}, as shown in Figure 25. These results are explained in part by the higher surface areas measured for -117 and -118.

Ni-Co-M-100, and -101 (5% Ni and 5% CO). Table 9 and Figure 24 show the result of the low pressure integral test performed on Ni-Co-M-101 and Figure 26 shows the result of the high pressure run on Ni-Co-M-100. Note that these monoliths have relatively low surface areas compared to the nickel monolithic catalysts. The low pressure integral data show that the maximum conversion of CO over the alloy is less and occurs at at a much higher temperature than for nickel metal.

At high pressure, Ni-Co-M-100 performed in a manner similar to the nickel monoliths in that there exists a range of nearly complete conversion. However, the temperature of 95% conversion was 360 compared to 317°C for nickel.

For both Ni and Ni-Co catalysts, CO_2 formation is much less at high pressure than at the low pressure. High pressure apparently favors the production of methane due to the Le Chatelier principle.

Comparison of the 95% conversion and selectivity data in Tables 7 and 9 for monoliths and pellets suggests very little difference in conversion and selectivity at high pressure (and high conversions) for Ni-M-117 (11% Ni) and Ni-A-116 (14%) nickel.

Reaction rates expressed as turnover numbers (at maximum conversion) are given in Table 10. Comparing the turnover numbers for pellets given in Table 7 with the turnover numbers for the monoliths in Table 10 shows that much higher turnover numbers are observed for

Table 9

Summary of Integral Test Results for Monolithic Catalysts (GHSV = 30,000 hr^{-1})

	Temp. at CO conv. of		At 95% CO conversion	
Catalyst	50%	95%	CH_4 Prod.	CO_2 Prod.
Low Pressure (20.5 psia)				
Ni-M-114	265		85%	13%
Ni-M-115	275	325	76%	12%
Ni-M-117	275	315	82%	11%
Ni-M-118	270	305	84%	10%
Ni-Co-M-101	320	✦	63%✦	18%✦
High Pressure (360 psia)				
Ni-M-114	no data			
Ni-M-117*	240	317	93%	2%
Ni-Co-M-100	250	360	89%	4%

✦ Maximum conversion was 84%

* Ni-M-117 high pressure run was at 50,000 hr^{-1}.

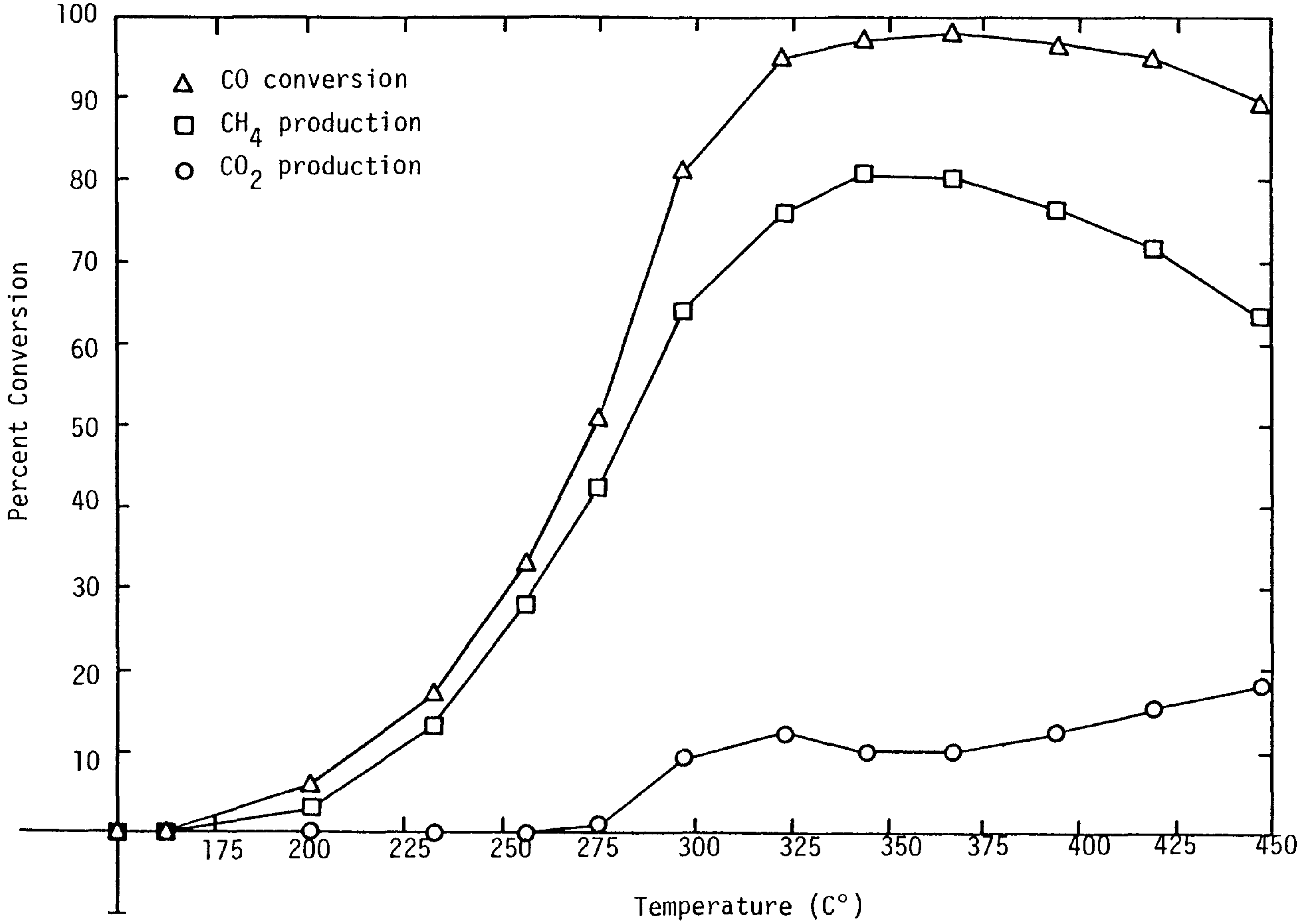

Figure 21. Conversion vs. temperature for Ni-M-115 (20% Ni/Al_2O_3/Monolith), 20.5 psia, GHSV = 30,000 hr^{-1}

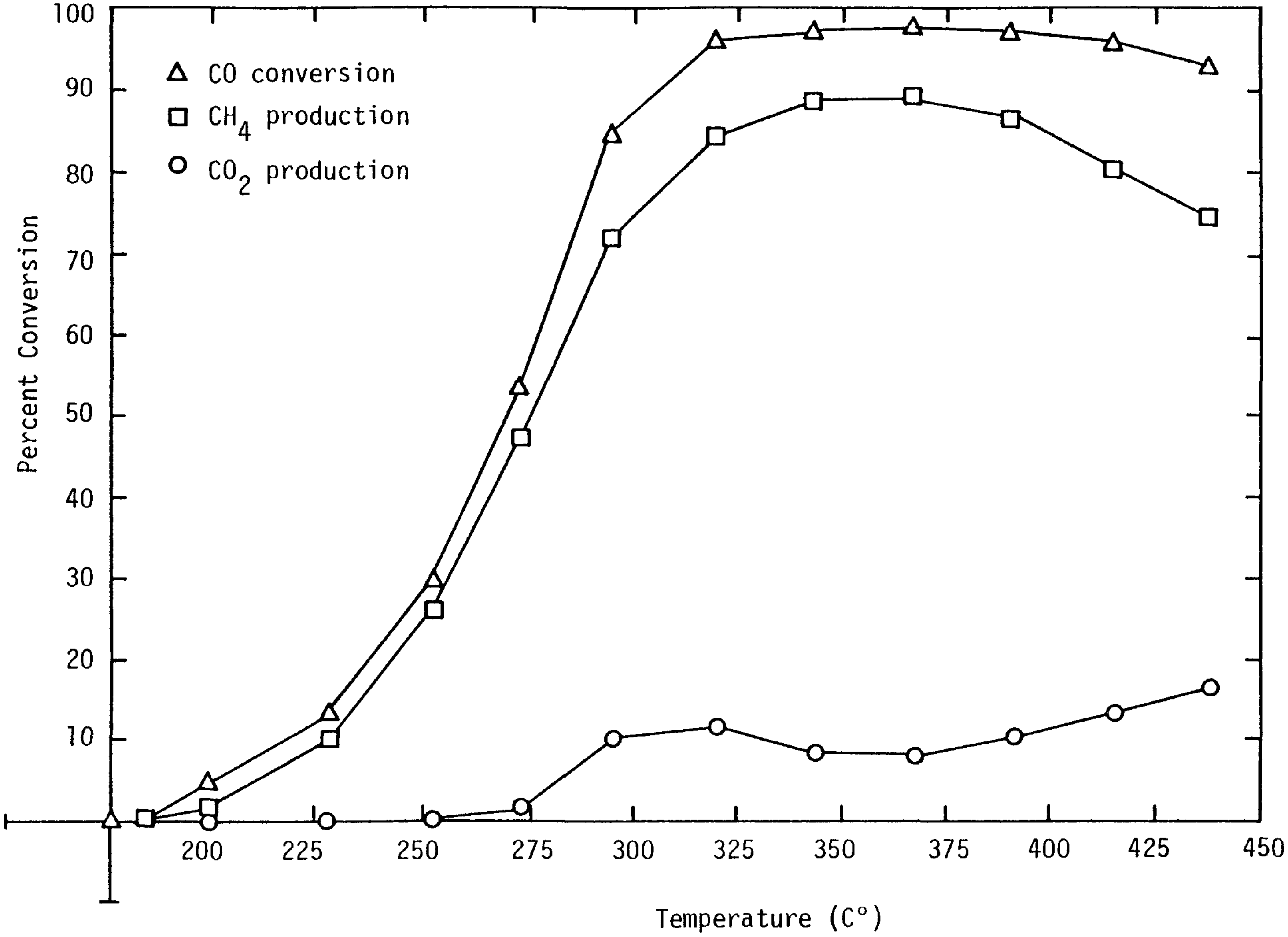

Figure 22. Conversion vs. temperature for Ni-M-117 (12% Ni/Al_2O_3/Monolith), 20.5 psia, GHSV = 30,000 hr^{-1}.

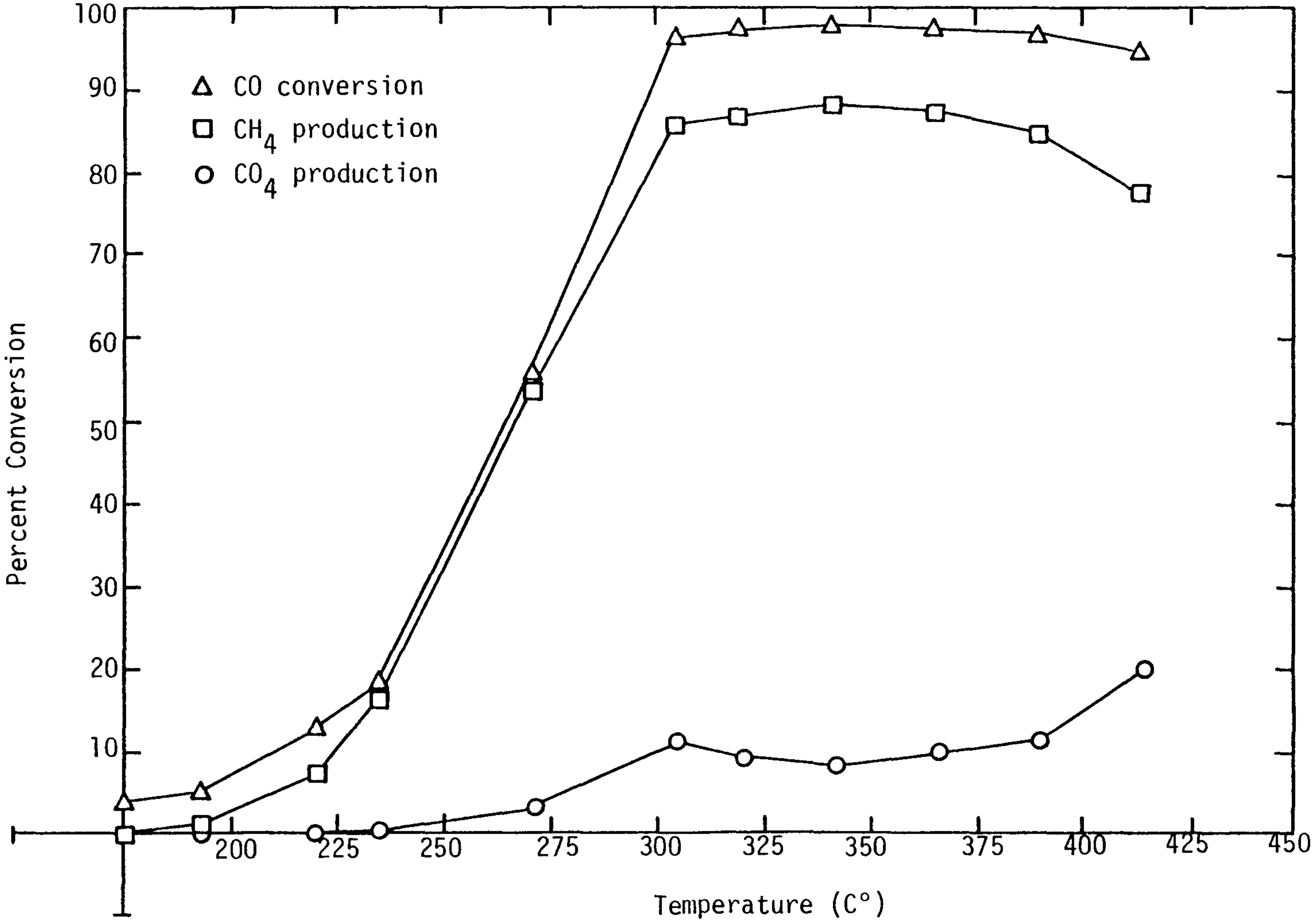

Figure 23. Conversion vs. temperature for Ni-M-118 (11% Ni/Al_2O_3/Monolith), 20.5 psia, GHSV = 30,000 hr^{-1}

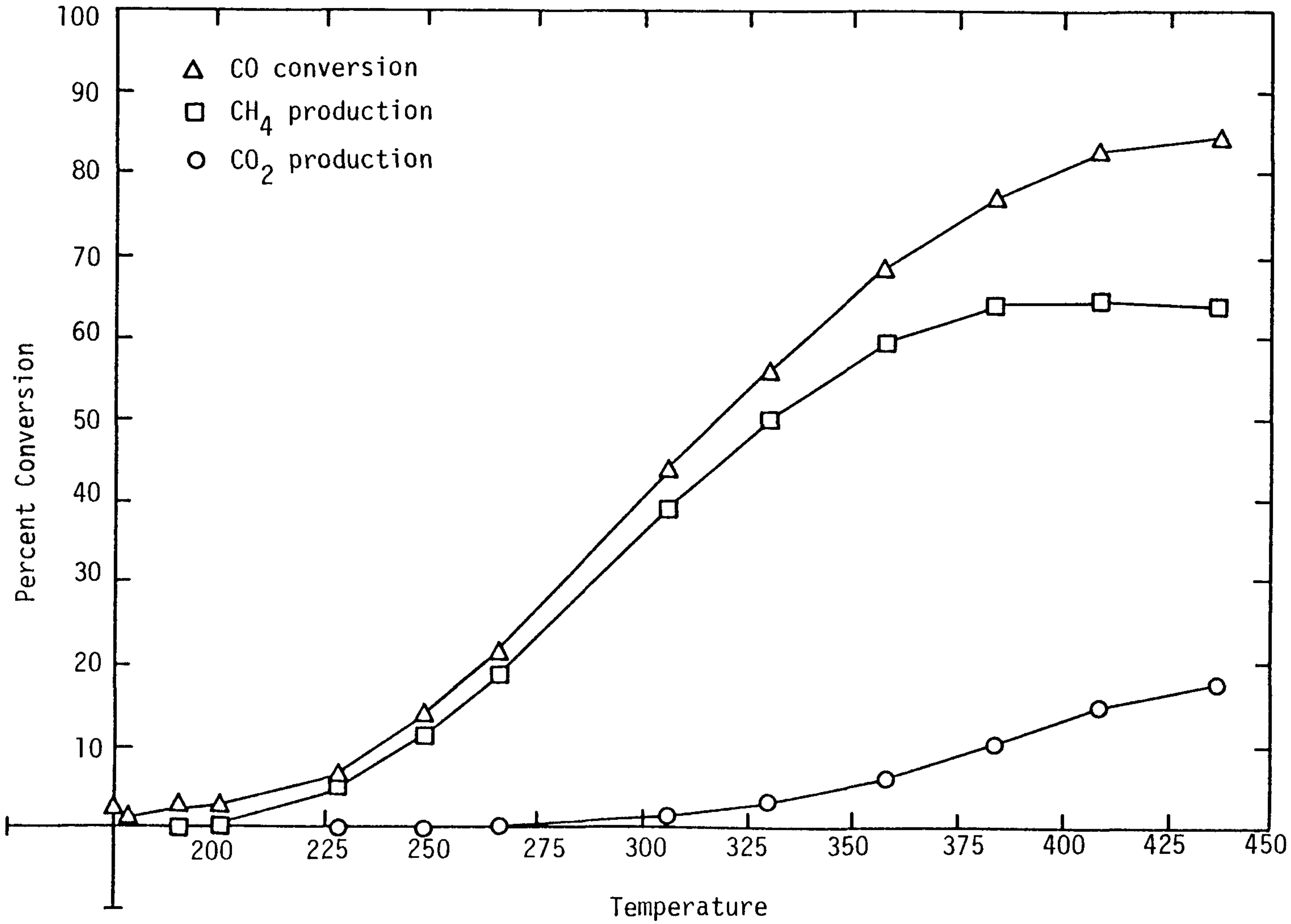

Figure 24. Conversion vs. temperature for Ni-Co-M-101 (5% Ni/5% Co/Al_2O_3/Monolith), 20.5 psia, GHSV = 30,000 hr^{-1}.

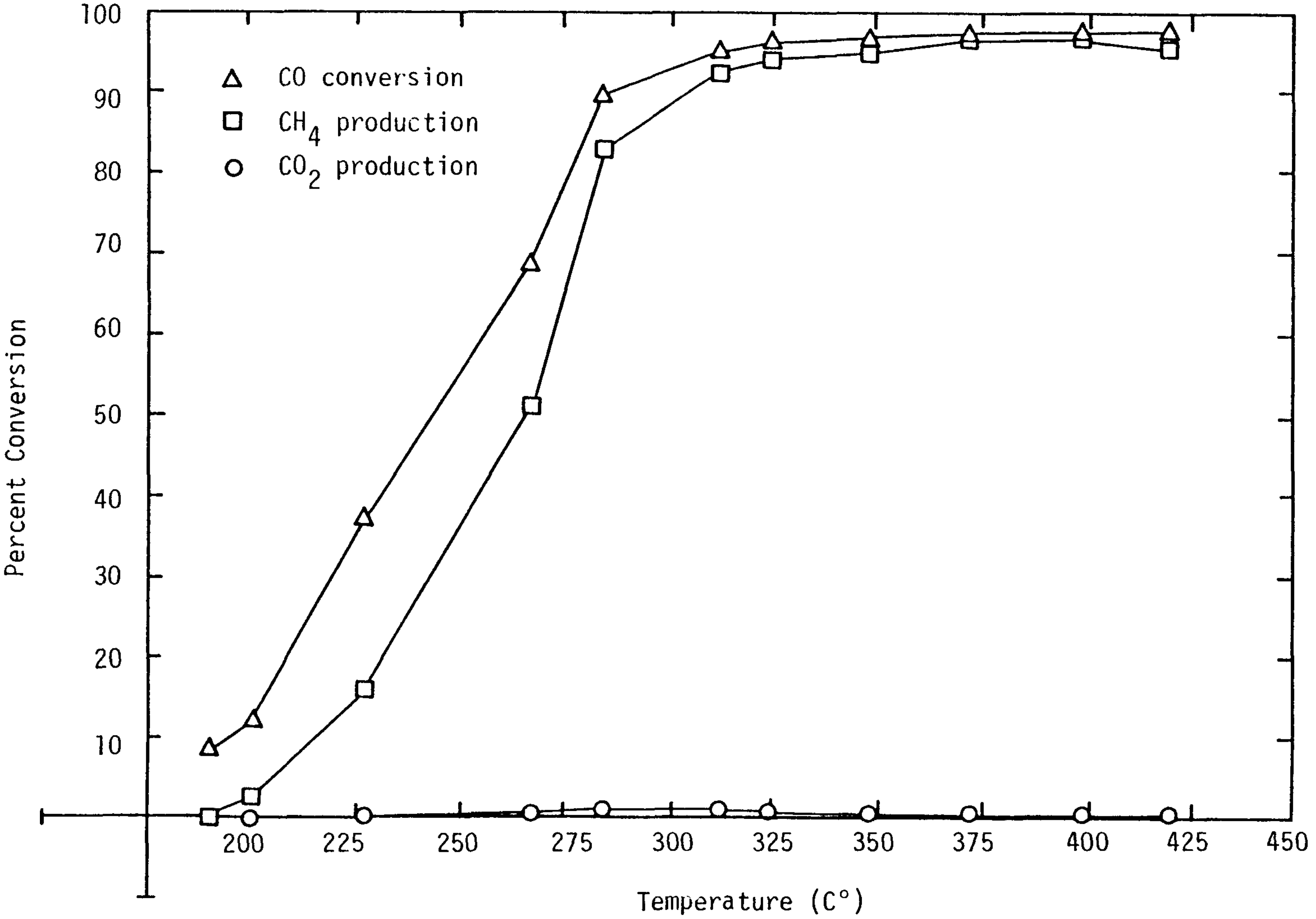

Figure 25. Conversion vs. temperature for Ni-M-117 (12% Ni/Al_2O_3/Monolith), 365 psia, GHSV = 50,000 hr^{-1}

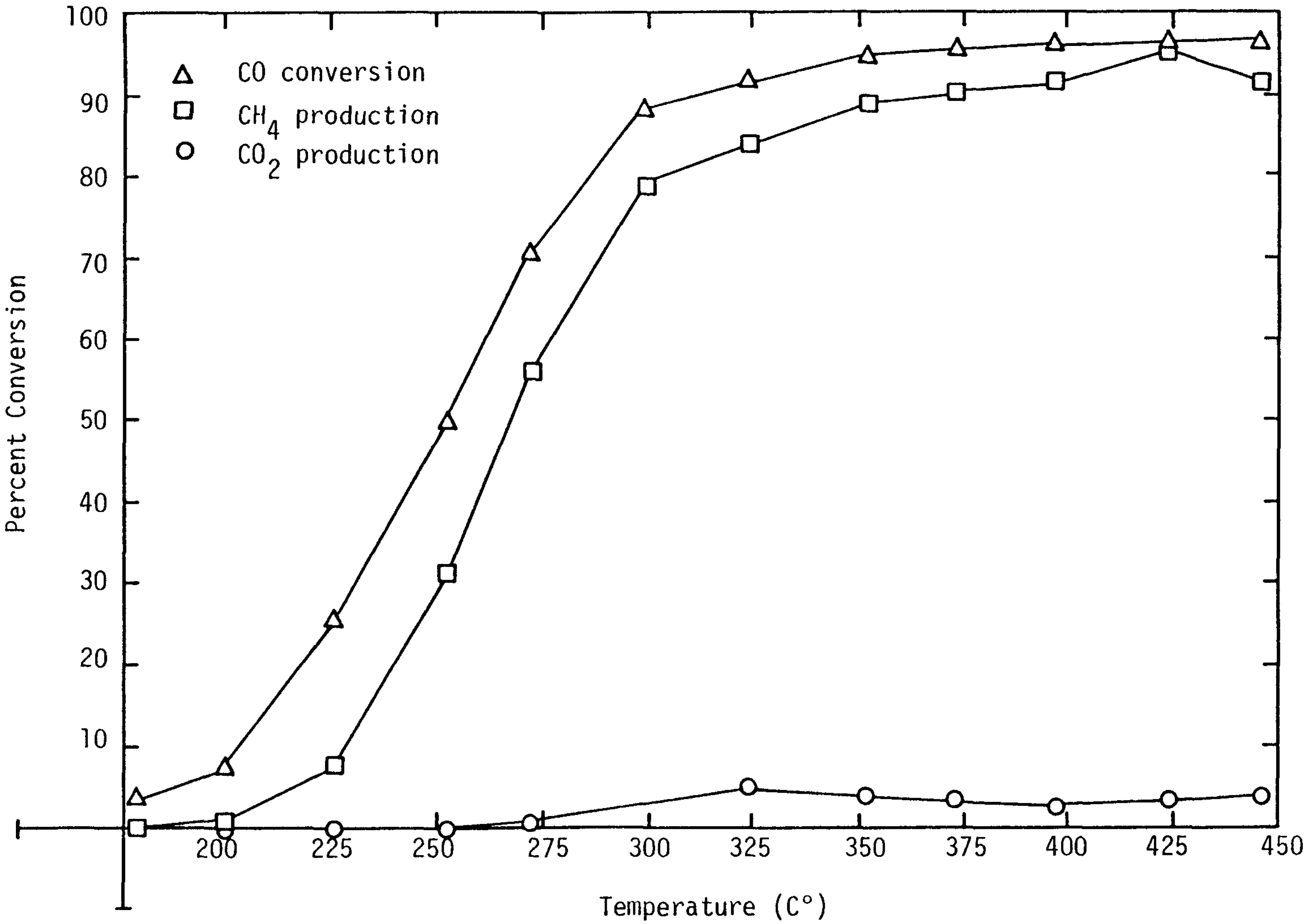

Figure 26. Conversion vs. temperature for Ni-Co-M-100 (5% Ni/5% Co/Al_2O_3/Monolith), 365 psia, GHSV = 30,000 hr^{-1}.

the monoliths (Ni-Co-M-100, high pressure and maximum conversion) than for the pellets (Ni-Co-A-100 at high pressure and 95% conversion), e.g. 67 vs. 26 for methane. Comparison of Ni-M-117 with Ni-A-116 having approximately the same nickel loading (12% monolith vs. 14% pellet) shows a methane turnover number of 34 compared to 15. This result bears out the hypothesis presented earlier that the diffusional resistance of monoliths with thin substates may be less than for 1/8 inch alumina beads.

4. Forecast. During the next quarter steady state runs to determine resistance to carbon deposition will be carried out for several pelleted samples. High pressure tests will be completed for the remaining pelleted samples. High pressure tests will be made for other monolithic catalysts and geometry tests will begin.

E. Task 5: Technical Visits and Communications.

Accomplishments. The principal investigator, Drs. Bartholomew, attended the ASTM D-32 Catalyst Committee Meeting held November 15 and 16 in Oakridge, Tennessee where he presented a summary of nickel surface area measurements obtained at Brigham Young University and other laboratories. Dr. Bartholomew is task force leader for standardization of metal surface area measurements. On November 17, Dr. Bartholomew visited with Drs. Larry Campbell and Robert Farrauto of Catalyst and Chemicals Research, Engelhard Industries, Edison, New Jersey where he presented a seminar on "Methanation - Alloys and Sulfur Poisoning." The seminar was followed by a tour of the catalyst research laboratories and discussions regarding characterization of catalysts. Activity measurements obtained at Brigham Young University for ruthenium catalysts were presented and the preparation of chloride-free ruthenium catalysts was discussed (chloride salts are poisons for methanation). Dr. Campbell agreed to send us additional samples of Ru/Al_2O_3 for testing.

On November 18, Dr. Bartholomew was the guest of Mr. Ralph Beaty, Director of Engineering Research, Continential Oil Company, Ponca City, Oklahoma where he also toured research facilities, visited with Paul Poynor, Research Group Leader, Joseph Kleinpeter, Manager of Liquifcation Research, and John Dew, Director of Fuels Technology Development, and presented a seminar entitled "Methanation Catalyst Activities of Alumina-Supported Nickel and Alloys," Discussions with Dr. Poynor focused on hydrodesulfurization and reforming catalyst process testing. Dr. Dew, who formerly managed the successful Conoco Methanation plant testing in Westfield, Scotland offered constructive criticisms, feedback and suggestions for our methanation catalyst testing program. He was also kind enough to provide us with a copy of an important British Gas Research Board report. Both Drs. Dew and Kleinpeter offered useful suggestions in regard to tests for carbon deposition.

Dr. Bartholomew was also invited by the Department of Chemical Engineering, University of Idaho (Moscow) to visit and present a research seminar on December 9, 1976. In addition to the seminar on "Kinetic

Table 10

Turnover Numbers from Monolith Integral Tests (GHSV = 30,000 hr^{-1})

Catalyst	225°C N_{CO} ($\times 10^3$ sec^{-1})	225°C N_{CH_4} ($\times 10^3$ sec^{-1})	325°C N_{CO} ($\times 10^3$ sec^{-1})	325°C N_{CH_4} ($\times 10^3$ sec^{-1})	At Maximum CO Conversion N_{CO} ($\times 10^3$ sec^{-1})	At Maximum CO Conversion N_{CH_4} ($\times 10^3$ sec^{-1})
Low Pressure (20.5 psia)						
Ni-M-115	7.5	5.5	42	34	43	36
Ni-M-117	5.0	3.4	36	32	37	34
Ni-M-118	8.0	4.5	56	50	58	52
Ni-Co-M-101	7.0	5.0	58	52	88	67
High Pressure (360 psia)						
Ni-M-114	no data					
Ni-M-117*	23	10	61	59	62	60
Ni-Co-M-100	26	8	95	87	100	95

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* Ni-M-117 high pressure run was at 50,000 hr^{-1}.

Studies of Alloy Methanation Catalysts," he held discussions with faculty members including Professor Bill Thomson, who is actively pursuing methanation research. Professor Thomson offered some useful suggestions and information regarding the use of Berty reactors.

Altogether the visits, meetings, presentations, and interactions with other workers have stimulated many useful interchanges of up-to-date, pertinent information regarding the project. We have recently received quite a number of requests for copies of our quarterly reports and are presently in close communication with more then 20 other methanation laboratories in the United States and Europe.

During the past quarter, a paper entitled, "The Stoichiometry and Poisoning by Sulfur of Hydrogen, Oxygen, and Carbon Monoxide Chemisorption on Unsupported Nickel," was accepted by the Journal of Catalysis. A note entitled "Crystallite Size, Support, and Alloying Effects in Methanation on Nickel," was also submitted to the same journal. Both papers are based on research supported by NSF and this contract. Two large publications dealing with effects of H_2S on CO and H_2 adsorption and with methantion activities of alloy catalysts are still in preparation.

Forecast. During the next quarter, the principal investigator and students will attend and present papers at the 2nd Rocky Mt. Fuel Symposium and the Spring Meeting of the California Catalysis Society. Dr. Bartholomew has also been invited by the Department of Chemical Engineering at Madison, Wisconsin to present a seminar on our research.

Miscellaneous. In January, Mr. Erek Erekson joined our research group and began work towards his Ph.D. in Chemical Engineering. Mr. Erekson has experience working in industry plus a Masters from Purdue where he worked in catalysis research.

IV. CONCLUSIONS

1. Surface areas of nickel and nickel alloy catalysts are decreased after testing in the presence of water vapor (1 and 15%).

2. The order of specific activity for fresh nickel and cobalt catalysts is $Co/Al_2O_3 > Ni\text{-}Co/Al_2O_3 = Ni/Al_2O_3$. For catalysts exposed to 10 ppm H_2S (12 - 24 hours) the order is $Ni\text{-}Co/Al_2O_3 > Co/Al_2O_3 = Ni/Al_2O_3$.

3. Based upon specific rates before and after exposure to H_2S, the order of decreasing resistance to sulfur poisoning is Ni-Co > Ni-Ru > Ni-MoO_3 > Ni-Pt = Ni > Co. These data possibly model the response to a plant upset resulting in 24 hour exposure of the catalyst to 10 ppm H_2S.

4. Thermodynamic calculations show that higher pressure, lower temperatures, higher H_2/CO ratios, and the presence of water inhibit carbon formation. Addition of CH_4 promotes carbon deposition. The extent of NH_3 formation in our reactor tests is estimated at less than 1 ppm.

5. The presence of 1% water vapor in the reactant mixture results in a significant decrease in selectivity to methane and a large increase in selectivity to CO_2. The overall conversion of CO is increased. These effects are undoubtedly a result of an increase in the rate of the water gas shift reaction as well as oxidation of surface sites (which affects selectivity). Nickel has a higher selectivity and activity than nickel alloys in the presence of water.

6. Specific methanation rates and selectivities to methane are generally increased at high pressure (365 psia) relative to near ambient pressure (20.5 psia) for nickel and nickel alloys. Selectivities to methane increase with increasing temperature at 365 psia and decrease with increasing temperature at 20.5 psia. The specific rate of methane production decreases as the pressure is increased for Ni-Ru at 225°C probably because of increased hydrocarbon production.

8. Pelletized and monolithic nickel catalysts (1/8 inch pellets versus 200 squares/in^2) show approximately the same conversions and selectivities to methane at high pressure. However, the turnover numbers at high conversions for the monolithic nickel are larger than for the pelletized nickel catalyst suggesting that diffusional influences are less important in the monolithic catalyst.

V. REFERENCES

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APPENDIX A
THERMODYNAMIC CALCULATIONS

In our reactor testing program we have been concerned about the undesirable products that may form in our reactor under test conditions. These products are carbon (C), ammonia (NH_3), and carbon dioxide (CO_2). Carbon and ammonia are methanation catalyst poisons. Nevertheless, in some of our reactor tests we actually wish to operate under conditions where carbon is formed in order to measure resistance to carbon deposition. Carbon dioxide is an undesireable product because its formation means that some of the reactant carbon has been oxidized to a nonfuel rather than reduced to methane. In order to determine the maximum extent of C, CO_2, and NH_3 formation under various conditions we performed thermodynamic calculations of the equilibrium concentrations of these products at the same temperatures and pressures as our reactor tests using the Edwards Thermochemical Program developed at Edwards Air Force Base based on the thermodynamic data from the JANAF tables. This program performs a search of a minimum free energy for all possible combinations of the elements in the reaction mixture. At the minimum free energy, the equilibrium compositions of the of the product stream is the output of the program.

Carbon Formation

Our first concern was carbon (C) formation under various reactor test conditions. We wanted to know how to cause C formation as well as prevent it. Figure 1A shows a graph of the mole fraction of C formed at equilibrium vs. reaction temperature (°C). The graph shows the temperatures where C is formed for various reaction conditions. Generally, C formation occurs only at high temperatures and low pressures. Low H_2/CO ratios promote the formation of C. At a H_2/CO ratio of 3 a higher mole fraction of carbon is obtained for the undiluted stream relative to N_2 or He diluted streams. However, carbon does not form at temperatures below 400°C for the case of the undiluted stream but does in the presence of inerts. For the low pressure runs with a H_2/CO ratio of 3 using a N_2 diluent, C forms at or above 300°C. This is in contrast to work by Greyson (1) which showns that in actual reactor systems for H_2/CO ratios of 3, carbon does not form until higher temperatures. However, his general curves did not specify diluents. Also, equilibrium cannot be achieved in actual reactors.

Interestingly, the mechanism of carbon deposition is far from certain. For example, Dalla Betta, et al. (5) reported that carbon deposition in methanation does not necessarily occur by the reaction:

$$2\ CO = C + CO_2$$

The other possible carbon deposition reaction would be:

$$H_2 + CO = H_2O + C$$

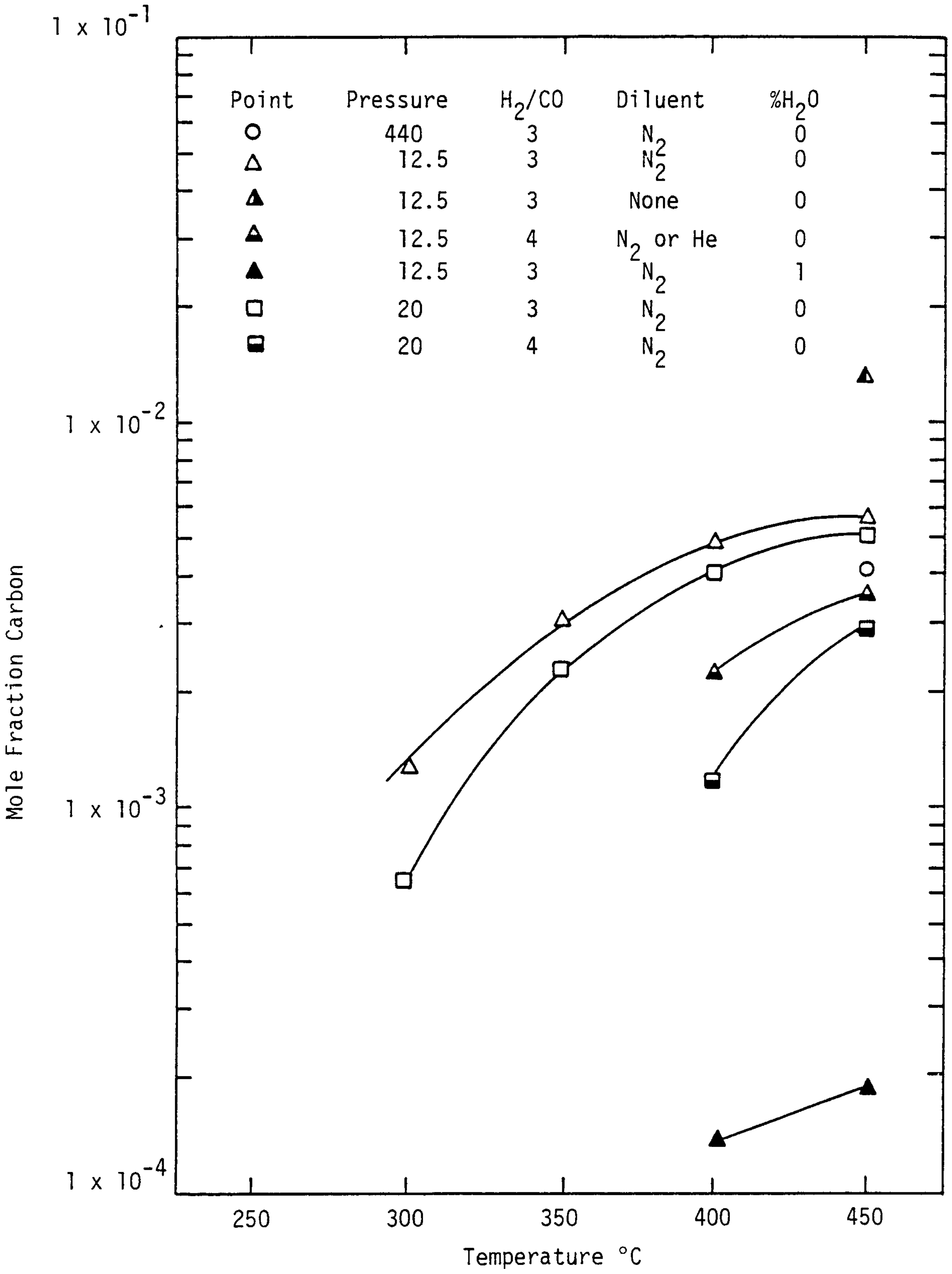

Figure 1A. Formation of Carbon at Equilibrium for Various Test Conditions.

the reverse of the steam-carbon reaction. Adding H_2O to the reaction mixture should shift the equilibrium to the left hand side. We made Edwards program runs for two mixtures containing H_2O. First, we considered a mixture with 1% H_2O, $H_2/CO = 4$ with N_2 diluent. No C was formed for the temperature range 225 to 450°C. Thus, this run does not appear on Figure 1. Secondly, we considered a mixture with 1% H_2O, $H_2/Co = 3$ with N_2 diluent. For this run C was formed only above 400°C at 12.5 psia. The value of mole fraction of C was about two orders of magnitude less than a similar run without H_2O. This shows that addition of small amounts of H_2O to our reaction mixtures will inhibit C formation.

We also wanted to find conditions that would promote carbon formation. So, we made Edwards program runs using methane (CH_4) as the diluent. Figure 2A shows the mole fraction C formed at equilibrium vs. reaction temperature (°C) for three different pressures. Generally as the pressure is increased the mole fraction C decreases. However, for the 12.5 psia run the mole fraction C becomes as high as 0.18 at 450°C. These high values of mole fraction C are undesireable except for purposely carbonizing the catalyst surface. The C formation mechanism in this case is possibly the reverse of the hydrogenation of carbon:

$$CH_4 = C + 2\,H_2$$

Ammonia Formation

While ammonia formation may not be important in commercial methanation units, it is important to consider in our studies since we are using nitrogen as a diluent gas and since ammonia (NH_3) is a poison for the reaction. Figure 3A shows a graph of mole fraction NH_3 formed at equilibrium vs. temperature for various pressures an compositions. All of the mole fractions of NH_3 formed are less than 1% and most are less than 0.1% of the product gas. As shown, in higher pressure runs significantly more NH_3 is formed. In runs with excess H_2 ($H_2/CO = 4$) higher amounts of NH_3 are formed at equilibrium for all temperatures. The addition of small amounts of H_2O to the feed only slightly affects ammonia formation as shown by the runs with 1% H_2O, $H_2/CO = 4$ with N_2 diluent.

While most of our nickel catalysts have some activity for the ammonia synthesis reaction, it is very unlikely that equilibrium is achieved in our test reactor.

Perhaps the most active catalyst[1] for the ammonia synthesis is iron with turnover numbers of 1-10 ks^{-1} at 400°C and 1 atm. Our nickel[2] alloy catlaysts probably have an ammonia synthesis activity of 10^{-2} to 10^{-3} that of iron catalysts. Also, the reaction is normally run at 400°C. At 225°C to 300°C where the highest amounts of NH_3 are formed[3] in the equilibrium case, we have an estimated activity of 10^{-2} to 10^{-3} that of the higher temperature. This means that NH_3 mole fraction in our reactor is at most about 1/10,000 the equilibrium formation or about 1 ppm for the worst case ($H_2/CO = 4$, with N_2 diluent,

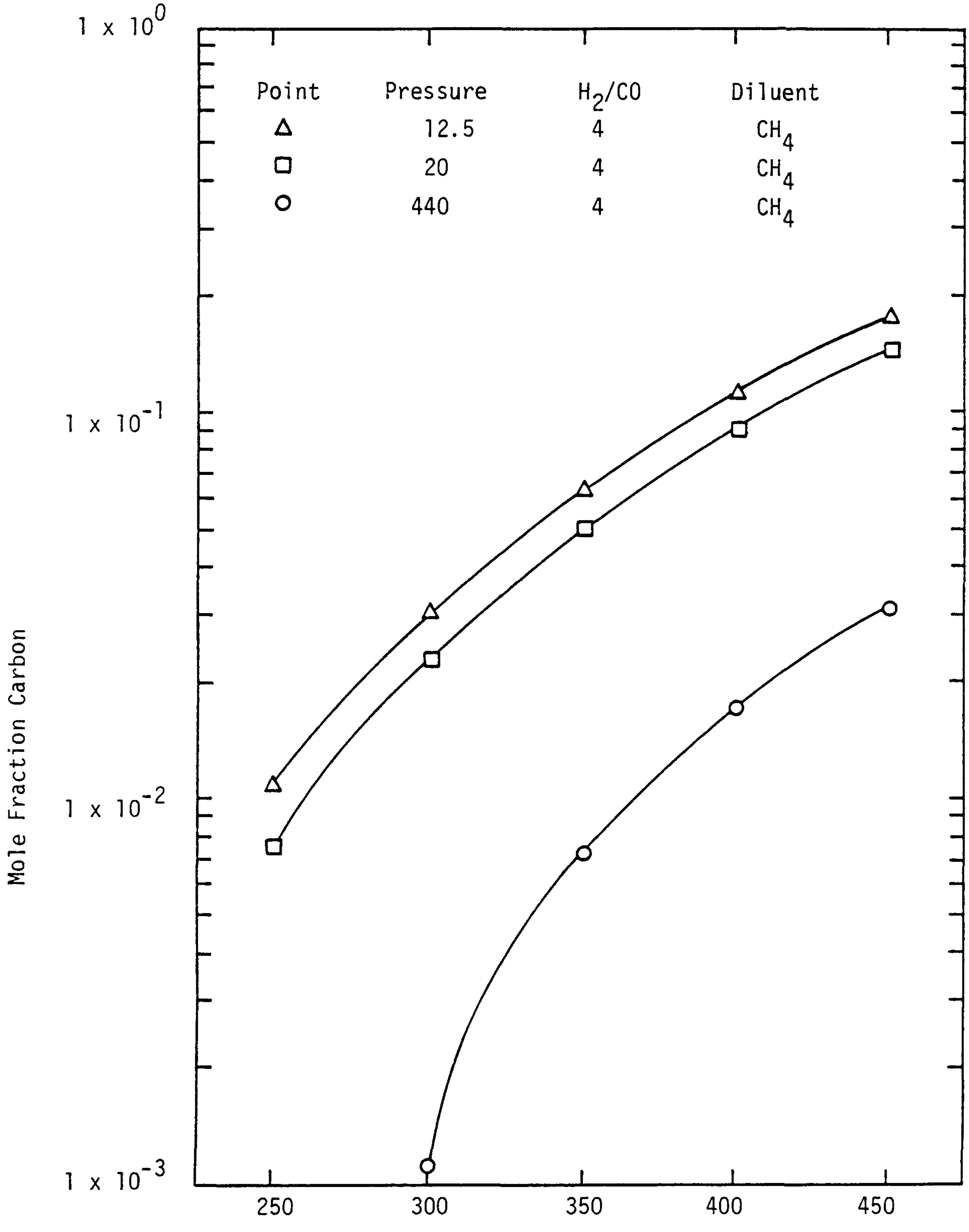

Figure 2A. Formation of Carbon at Equilibrium with Methane Diluent.

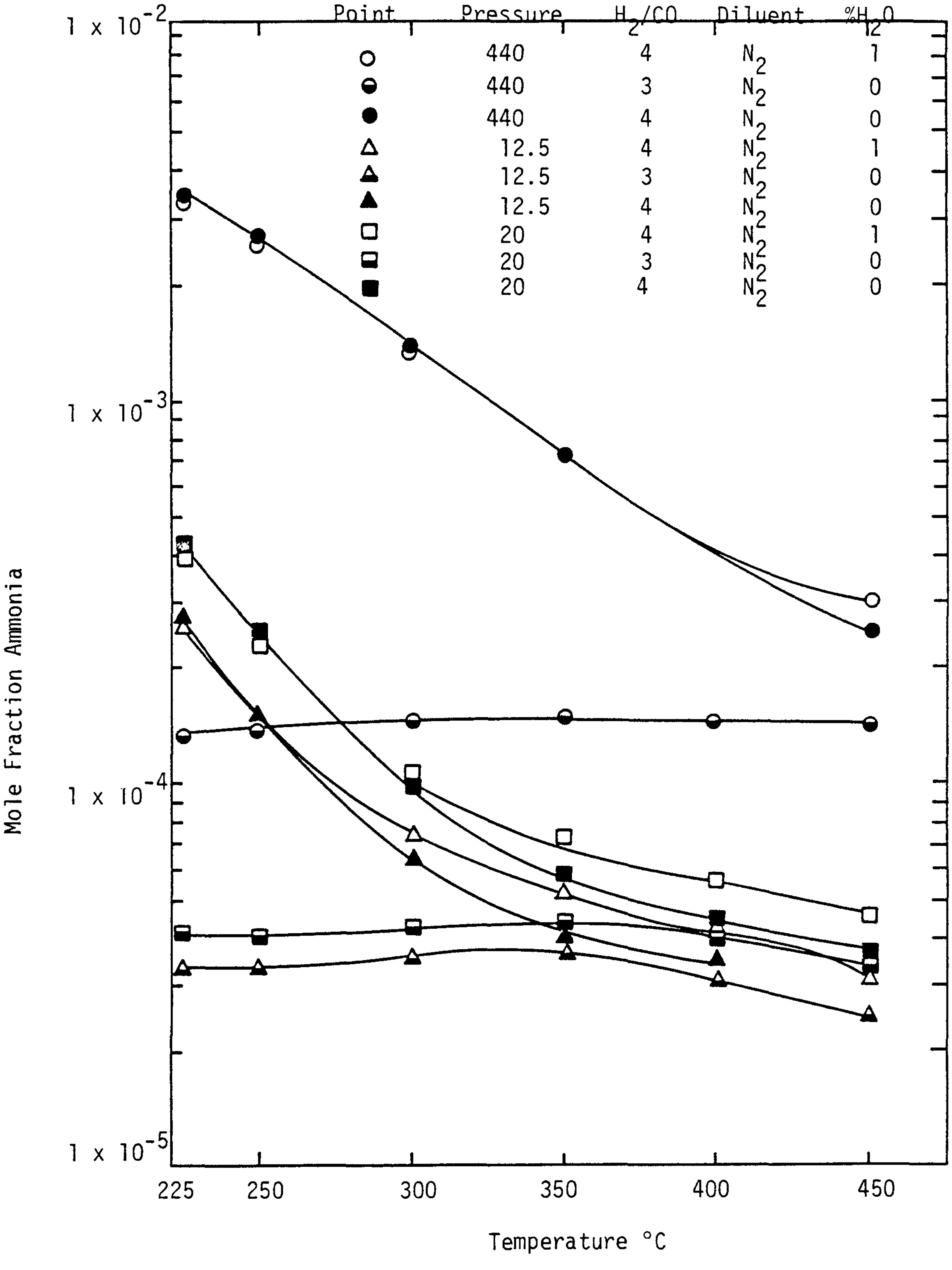

Figure 3A. Formation of Ammonia at Equilibrium for Various Test Conditions.

440 psia) at 225°C.

Carbon Dioxide Formation

Carbon dioxide (CO_2) is an undesireable byproduct of the methanation reaction. Its presence in the product stream means that some of the carbon monoxide in the feed was oxidized to carbon dioxide rather than reduced to methane, the desired product.

As shown in Figure 4A as temperature is increased the mole fraction CO_2 increases. Also, for runs with similar composition the higher pressure runs produce less CO_2 at equilibrium. However, runs which had 1% H_2O added to the mixture had higher CO_2 mole fractions than similar run with H_2O. The addition of H_2O promotes the water gas shift reaction

$$H_2O + CO = CO_2 + H_2$$

Generally lower temperatures, higher pressures and the absence of H_2O inhibit the formation of CO_2. Comparison of our experimental results with the calculations also shows that we generally produce substantially larger amounts of CO_2 in our reactor tests than predicted for the equilibrium case.

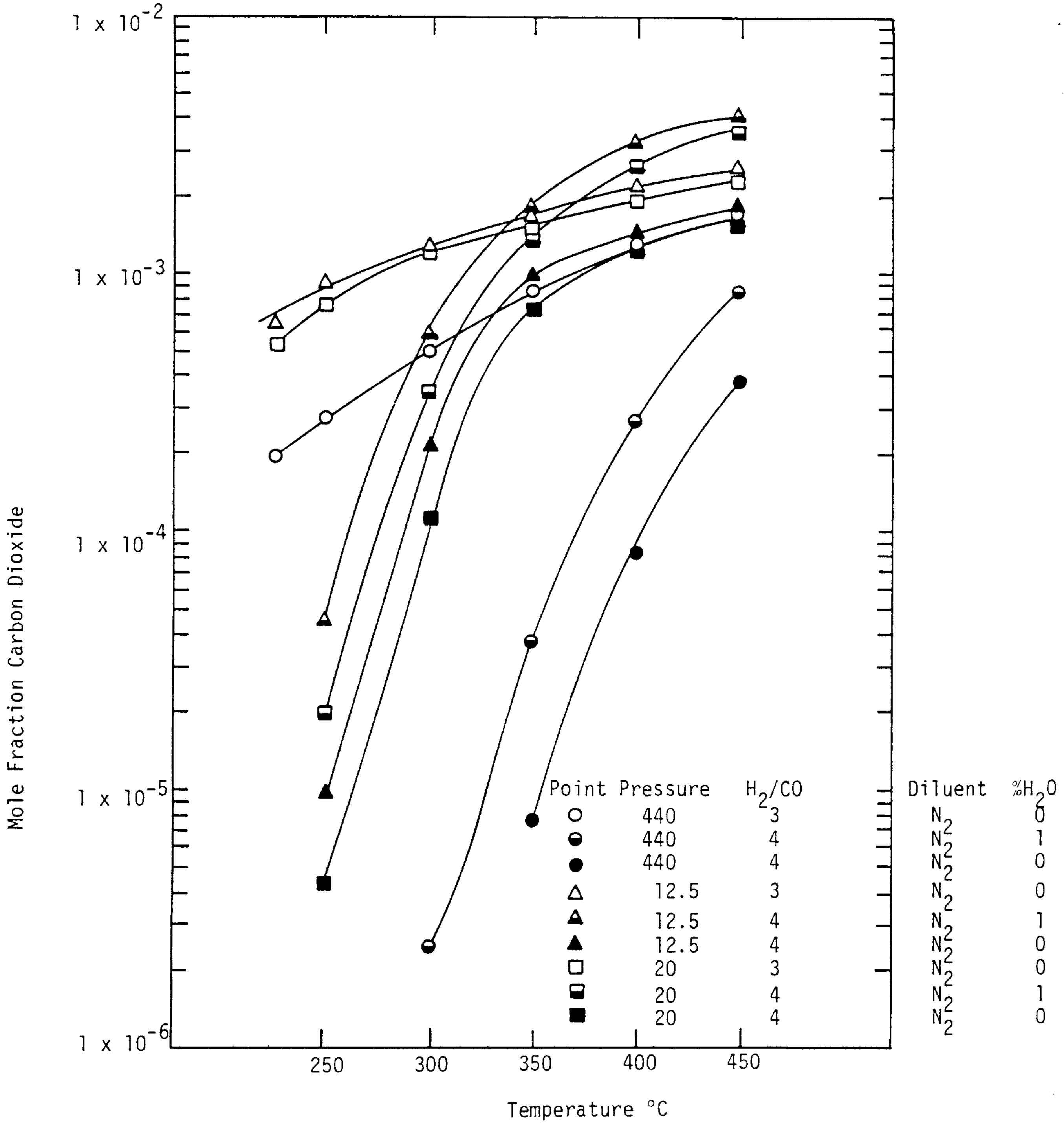

Figure 4A. Formation of Carbon Dioxide at Equilibrium for Various Test Conditions.