



DOEET10673T1

**NTIS**  
Information is our business.

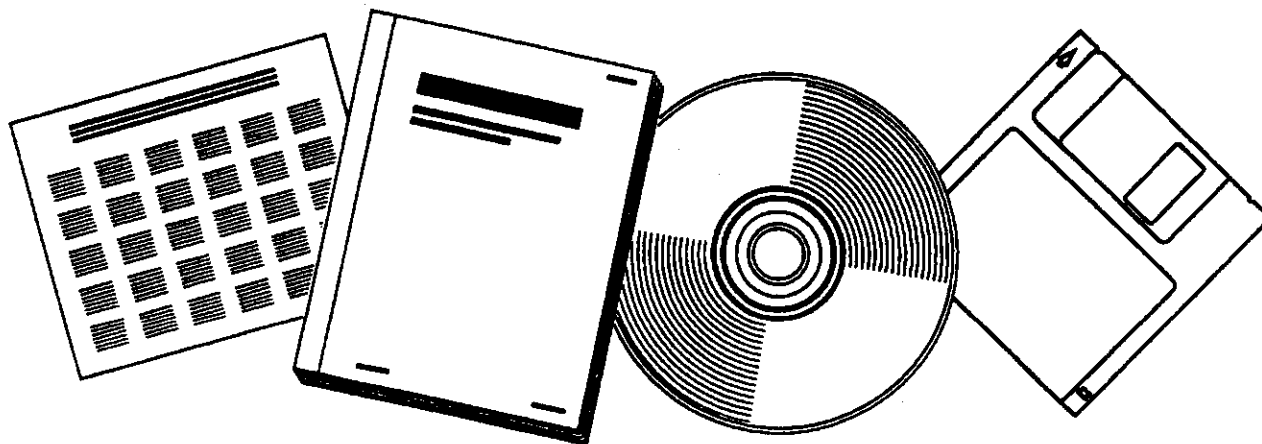
---

---

**TRANSITION METAL-GRAPHITE CATALYSTS FOR  
PRODUCTION OF LIGHT HYDROCARBONS FROM  
SYNTHESIS GAS. INTERIM REPORT, AUGUST 1,  
1976-APRIL 30, 1978**

TEXAS A AND M UNIV., COLLEGE STATION.  
DEPT. OF CHEMISTRY

MAY 1978



U.S. DEPARTMENT OF COMMERCE  
National Technical Information Service

---

---

# MASTER

## TRANSITION METAL-GRAPHITE CATALYSTS FOR PRODUCTION OF LIGHT HYDROCARBONS FROM SYNTHESIS GAS

Interim Report for the Contract Period

August 1, 1976 - April 30, 1978

Michael P. Rosynek

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors included herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Texas A & M University  
Department of Chemistry  
College Station, Texas 77843

Date Submitted - May 1978

PREPARED FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

Under Contract No. E(49-18)-2467

SDN 7/14/80 CUP

## I. INTRODUCTION

### A. Purpose

The purpose of this Interim Report is to summarize the most significant results that have been obtained during the first Phase of the contract project (comprising evaluations of the heterogeneous catalytic behaviors of transition metal-graphite intercalates for the atmospheric-pressure hydrogenation of carbon monoxide), and to present a justification for continuation of the research to Phase II (medium-pressure catalytic testing).

### B. Objective of Work and Scope of Report

The overall objective of the project during Phase I has been to identify and to qualitatively characterize those modifications in hydrocarbon selectivity behaviors for CO hydrogenation that occur when various transition metals, principally iron and cobalt, are intercalated between the layers of a graphite substrate, rather than being dispersed on conventional catalyst supports. The rationale for the study was that phenomena unique to the intercalated systems, such as diffusion effects caused by the required interlayer penetration of reactant/product molecules, or space limitations, imposed by restricted accessibility of intercalated metal sites, might result in significant and potentially useful alterations in the selectivity behaviors of these catalysts. For this reason, the major emphasis of the research thus far has been on collecting and evaluating comparative product distribution data for the various graphitic and conventional catalysts investigated, primarily as a function of reaction temperature in the range 200-325°C. Only secondary importance, on the other hand, was attached to making quantitative measurements of reaction rates and energetics and catalyst stabilities, except as they pertained to obtaining reproducibility of selectivity properties.

Although more than 100 separate and individual catalyst testing experiments, as well as the necessary catalyst preparations and pretreatments, were performed during the first Phase of this research, only the most important results will be considered in detail in this report. A considerable number of runs, particularly those involving alkali metal-containing intercalates, for example, were made using materials that eventually proved to be unacceptable as catalysts, due, in most cases, to irreversible deactivation during reaction. Hence, detailed discussion will center on graphite intercalates of iron and cobalt, whose unique selectivity behaviors during CO hydrogenation, in comparison to those of their conventionally-supported counterparts, definitely warrant, we feel, further characterization at elevated reaction pressures.

## II. SUMMARY OF WORK ACCOMPLISHED

Although the preparation and subsequent catalytic testing of graphite intercalates were treated as separate Tasks in the project's original "Statement of Work", the two functions were necessarily performed concurrently during the research, and the discussion below has been divided according to the method of preparation/acquisition of the catalysts.

### A. Alkali Metal Reduction

Our original intent was to prepare transition metal-graphite intercalates for catalytic testing using the method described previously by Tamaru and co-workers (U.S. Patent No. 3,842,121). The technique consists of heating an intimate mixture of crystalline graphite and the appropriate transition metal chloride in an evacuated vessel at 300-400°C for ~ 8 hrs, followed by *in situ* reduction of the resulting intercalated metal ions to the free metal by treatment with an excess of metallic potassium in vacuo at 300°C, and removal of unreacted alkali metal by distillation. Tamaru described the application of this method for preparing reduced graphite intercalates of several transition metals, including Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Ti, Zr, V, Mo, W, and Re, together with the corresponding activity/selectivity behaviors of these materials when used as catalysts for CO hydrogenation at 300°C and one atmosphere pressure. Despite the wide variety of intercalated metals investigated by Tamaru, overall activities for CO conversion and hydrocarbon product distributions unexpectedly varied only slightly, suggesting a fundamental similarity among the various catalysts.

Potassium itself forms a series of well-defined graphite intercalation compounds, all of which possess a high initial activity for CO hydrogenation. In addition to generating KCl reduction byproduct, the preparation method employed by Tamaru, although leading to the formation of reduced intercalated transition metals, cannot avoid the formation of these potassium-graphite complexes, whose catalytic behaviors almost completely mask those of the transition metal components and lead to the observed similarity in catalytic properties among the wide range of intercalated metals investigated. More importantly, our initial investigations with potassium-reduced iron-graphites showed that these materials suffer the same gradual and irreversible loss of catalytic activity as that exhibited by pure potassium-graphite, due to permanent destruction of intercalated potassium atoms/ions by the water molecules that are inevitably generated during CO hydrogenation. Furthermore, following total destruction of accessible potassium species, no residual catalytic activity remained that could be ascribed to the transition metal component, apparently due to blockage of potentially active iron sites by the KOH formed during the K/H<sub>2</sub>O reaction.

Based on these initial results with potassium-reduced iron-graphite, we began a lengthy series of experiments involving pure sodium- and potassium-graphites, in an effort to establish their individual catalytic behaviors and to enable their contributions to the overall properties of the three-component catalysts to be recognized. Apart from slight differences

in total CO conversion activity and hydrocarbon selectivity, the catalytic behaviors of pure potassium-graphite (C<sub>8</sub>K) and its iron-containing homolog (containing 4.5 wt% Fe) for CO hydrogenation at 300°C and 700 torr were virtually identical. Additionally, the rates of activity loss and cumulative extents of CO conversion at the point of total deactivation were parallel for the two types of intercalate. These observations, together with the non-trivial complexities associated with the preparation and handling of these substances, caused us to abandon alkali metal reduction as a suitable method for synthesizing transition metal-graphite catalysts, and to explore alternative sources and methods of reduction.

#### B. Borohydride Reduction

We investigated briefly the potential applicability of aqueous sodium borohydride as a reducing agent for preparing transition metal-graphite intercalates of both iron and cobalt from the corresponding metal chloride-graphites. However, the method proved to be difficult to properly control, and yielded materials having relatively low overall activities and poorly reproducible hydrocarbon selectivities, and its examination was discontinued in favor of the catalysts described in the next section.

#### C. Anion-Radical Reduction

Alfa Chemicals Div. of Ventron Corp. markets an extensive series of reduced transition metal-graphite intercalates, under the generic trade name of "Graphimets". They are prepared by first intercalating the appropriate high-valent metal chloride in the usual manner, followed by treatment with a tetrahydrofuran solution of an aromatic anion-radical to effect intralayer reduction of the metal ions to free metal, and final removal of excess solvent. Although the reduction technique is a proprietary process whose details the Company would not divulge, the reducing agent employed is known to be sodium naphthalide, or one of its derivatives, and the general nature of the method has been described previously in the open literature. The ready availability of these materials prompted us to explore their potential applicability as CO hydrogenation catalysts for our research, in an attempt to circumvent the time-consuming catalyst synthesis procedures with which we had previously been occupied, and thus to provide additional time for catalyst testing studies. Their suitability has proven to be excellent, and experiments during the past 12 months have been devoted exclusively to evaluating the catalytic behaviors of these materials.

The intercalates chosen for detailed study were an iron-graphite (Alfa No. 89654, containing 2.2 wt% Fe) and a cobalt-graphite (Alfa No. 89650, containing 3.4 wt% Co). The corresponding conventionally-supported metals selected for comparative investigation were commercially-available catalysts obtained from Harshaw Chemical Co., viz., iron/alumina (Harshaw No. FE-0301, 14.9 wt% Fe) and cobalt/kieselguhr (Harshaw No. CO-0127, 59 wt% Co). The graphite intercalates were received and used as finely-powdered materials, while pellets of the supported catalysts were crushed and sized to 20/40 mesh granules. Pretreatment of all catalysts prior to initial use involved exposure to excess circulating H<sub>2</sub> for 3 to 4 hrs at 400°C, followed by overnight evacuation at 300°C to a residual pressure of < 10<sup>-4</sup> torr.

All experiments described below were performed with reactants and products in the gas phase, using a closed-loop recirculation reaction system of the stirred-batch type. Total reactor volume was 340 ml, and appropriate provisions existed for both admitting known pressures of H<sub>2</sub> and CO reactants and for periodically removing 0.5 vol% gas samples for gas chromatographic analyses. Quantitative analyses were based on peak areas of all carbon-containing components, as reported by a computing digital integrator, following the usual corrections for differing thermal responses of the various compounds. Each run employed a 0.5 g (total weight) charge of catalyst, an initial H<sub>2</sub>/CO reactant ratio of 2/1, and a total initial pressure of 700 torr. Both metal-graphite catalysts exhibited important differences in hydrocarbon selectivity behavior, compared to their supported counterparts, and the most significant results obtained with each material will be discussed separately.

### 1. Iron-Graphite vs. Iron/Alumina

Although numerous ancillary experiments, aimed at establishing the general features of the CO hydrogenation process, were performed with both iron-containing catalysts, only those results pertaining to reaction selectivity comparisons will be discussed in detail. Product distribution characteristics of the two catalysts were determined as a function of reaction temperature by performing separate experiments, each employing a freshly-pretreated catalyst sample, at 25° increments over the temperature range 225-325°C. Figs. 1 and 2 summarize the composite product distributions obtained for several series of runs over the alumina-supported and graphitic catalysts, respectively, at an arbitrarily-selected CO conversion level of 5%. (Apart from expected increases in olefin + paraffin transformations, little significant change in product distribution occurred with increasing CO conversion over either catalyst at any given temperature.) In these figures, the mole fraction of each gaseous, carbon-containing product has been corrected to account for the number of carbon atoms per molecule, and the summed results normalized to 100 moles of CO converted. Thus, the numerical difference, along the ordinate axis, between any adjacent pair of plotted curves corresponds to the percentage of all reacted CO that was involved in forming the product indicated between the curves.

Upon comparison of the selectivity behaviors of the two catalysts, it is immediately evident that iron-graphite produces considerably less carbon dioxide (accounting for < 5% of all CO converted over the entire temperature range studied) than does the alumina-supported iron catalyst (15-30% of all CO reacted), and correspondingly more hydrocarbon products than the latter. Since the principal source of CO<sub>2</sub> during H<sub>2</sub>/CO conversions is via a water-gas shift reaction, these results suggest that the intercalated iron catalyst possesses a markedly lower tendency to promote this process than does its supported homolog. More importantly, if the contribution made by CO<sub>2</sub> to each product distribution is ignored, it becomes apparent that the hydrocarbon selectivities of the two catalysts are also quite different, as shown in Fig. 3 where these data are compared at each of the five reaction temperatures investigated. (In each case, the open bars represent the hydrocarbon selectivities of the iron/alumina, while the solid bars correspond to that of the iron-graphite.) The observed differences

in selectivity behaviors of the two catalysts conform to the same general pattern over the entire temperature range studied. Although the percentage of CO converted to  $C_1$  hydrocarbons was approximately the same in both cases, particularly at  $\leq 275^\circ\text{C}$ , the iron-graphite consistently produced a larger  $C_4+C_5^+$  fraction and correspondingly smaller  $C_1+C_2$  fraction than did the iron/alumina at all temperatures. The disparity in relative hydrocarbon yields for the two catalysts increased, moreover, with increasing reaction temperature. The greater tendency of the iron-graphite to generate longer-chain hydrocarbons may be due to certain important structural features of intercalation system, and will be discussed in greater detail after the selectivity behavior of cobalt-graphite has been considered.

## 2. Cobalt-Graphite vs. Cobalt/Kieselguhr

Experiments comparable to those discussed above for the two iron-containing catalysts were also performed to compare the selectivity behaviors of a cobalt-graphite intercalate and a commercial cobalt/kieselguhr catalyst in the temperature range  $200-300^\circ\text{C}$ . The composite distributions of all carbon-containing products observed for several such series of runs are presented, at 5% CO conversion, in Figs. 4 and 5, while Fig. 6 summarizes the hydrocarbon yields for the two catalysts. (Note the difference in ordinate scales in Figs. 3 and 6). Although the amount of  $\text{CO}_2$  produced, primarily via a water-gas shift process, is similar and relatively constant over both catalysts (accounting for  $\sim 5\%$  of all converted CO), the temperature dependence of hydrocarbon selectivity is dramatically different for the two materials. Over the supported cobalt catalyst, the percentage of all reacted CO involved in methane formation increased from 27% at  $200^\circ$  to 87% at  $300^\circ\text{C}$ , while the percentage yielding  $C_2^+$  hydrocarbons decreased correspondingly from 69% to only 7%. In particular, the  $C_4^+$  hydrocarbon fraction accounted for 35% of all converted CO at  $200^\circ$ , but had decreased to  $< 10\%$  at  $250^\circ$ , and was entirely absent at  $300^\circ\text{C}$ . It should be noted that this overall behavior is typical of that normally observed over supported, unpromoted cobalt catalysts in this temperature range.

The outstanding and atypical selectivity feature exhibited by the cobalt-graphite intercalate, on the other hand, is the relative insensitivity of product distribution to variations in reaction temperature. Methane accounted for a virtually constant 35% of all converted CO over the entire temperature range investigated, while the  $C_2+C_3$  olefin/paraffin fraction increased slightly from 31% at  $200^\circ$  to 41% at  $300^\circ\text{C}$ , and  $C_4^+$  hydrocarbons only decreased from 30% to 20% of all converted CO over the same temperature range.

The unusual selectivity behaviors displayed by both iron- and cobalt-graphites, particularly the latter, may be due to the unique structural natures of the metal-graphite systems. Active iron or cobalt sites are located between graphitic planes that are spaced approximately 3.5 to 4.0 Å apart. Thus, unlike the situation encountered with conventional supported catalysts, CO and  $\text{H}_2$  reactant molecules must not only diffuse through the gas phase to the catalyst surface, but must then penetrate between the narrowly-spaced layers of the graphite lattice in order to reach the metallic sites and allow adsorption and subsequent reaction to occur. If the

average depth of intercalation of the reduced iron or cobalt atoms is sufficiently large, it is conceivable that the overall rate-limiting step of the process may be the interlayer diffusion of reactants. Such a restriction of molecular movement at or near the catalytically active sites could result in carbon chain growth that is larger than would otherwise be the case, and cause the observed tendency of both intercalated catalysts to produce larger average product molecules than their supported counterparts. Indeed, semi-quantitative rate data for the cobalt-graphite catalyst yielded an apparent activation energy of only 10-12 kcal/mole, a value considerably lower than that (24 kcal/mole) observed with the cobalt/kieselguhr and consistent with the postulate of a diffusion-controlled process. It should be noted, however, that the interlayer diffusion rates of CO and H<sub>2</sub> reactant molecules should also increase with increasing temperature. Thus, the virtual constancy of product distribution observed over a 100° range of reaction temperature for the cobalt intercalate is still unclear and may result from the combined effects of several factors.



### III. CONCLUSIONS

We feel that the unusual and potentially significant selectivity behaviors exhibited by iron- and, particularly, cobalt-graphite intercalates during CO hydrogenation definitely warrant continued investigation, using a differential/integral flow-type reactor capable of operating at elevated reaction pressures, i.e., 0-300 psig. Such a system will enable further characterization of these catalysts to be made in at least three important, but heretofore unexamined, areas:

#### A. Reaction Rates and Energetics

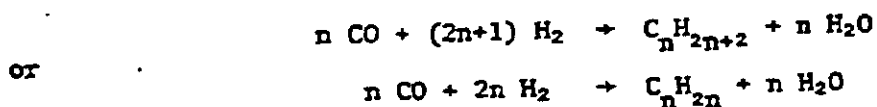
As noted previously, our studies thus far have been aimed primarily at determining selectivity properties of the graphite intercalates, in comparison to their conventionally-supported counterparts, and relatively little emphasis has been placed on quantifying reaction rates and energetics. Use of a flow reactor, coupled with H<sub>2</sub> and CO adsorption measurements to determine percentages of metal exposure, will permit the rapid acquisition of such important data as comparative turnover frequencies and apparent activation energies for CO conversion over the two pairs of catalysts. Although semi-quantitative information in both of these areas can be obtained with the closed reaction system now being employed, the accuracy, convenience, and flexibility of the measurements will be greatly improved with a flow-type reaction system.

#### B. Catalyst Stability and Ageing

In addition to the lack of quantitative comparative rate data, relatively little information has thus far been obtained regarding the long-term stability and equilibration behaviors of the metal-graphite intercalates. Such measurements of deactivation properties perforce require the use of a flow reactor and cannot be meaningfully made using a closed reaction system. Particular emphasis will be placed on establishing the effects of varying pretreatment conditions on activity/selectivity responses of the graphitic materials compared to their supported homologs. Additional information about catalyst coking properties and consequent mass balances will also be obtainable from such experiments.

#### C. Pressure Dependence of Selectivities

The most important information that will be made accessible by an elevated-pressure flow reactor are the comparative dependences of product selectivities on reaction pressure for both pairs of catalysts. Because the generation of hydrocarbons via CO hydrogenation is accompanied by a decrease in the total number of moles in the reaction zone,



increases in total system pressure favor the formation of longer-chain hydrocarbon products. In view of the already greater tendency of iron- and cobalt-graphite catalysts to produce longer average product molecules than their supported counterparts, even at one atmosphere pressure, it is of obvious importance to determine whether this behavior persists at higher reaction pressures. The situation for cobalt-graphite will be of particular interest because of its unusually constant selectivity properties over a 100°C range of reaction temperatures.

FIGURE CAPTIONS

Figure 1 Temperature dependence of carbon-containing product distribution over iron/alumina (14.9 wt% Fe) at 5% total CO conversion.

Figure 2 Temperature dependence of carbon-containing product distribution over iron-graphite (2.2 wt% Fe) at 5% total CO conversion.

Figure 3 Comparative hydrocarbon selectivities at 5% total CO conversion for five reaction temperatures in the range 225-325°C. (Open bars = iron/alumina; solid bars = iron-graphite).

Figure 4 Temperature dependence of carbon-containing product distribution over cobalt/kieselguhr (39 wt% Co) at 5% total CO conversion.

Figure 5 Temperature dependence of carbon-containing product distribution over cobalt-graphite (3.4 wt% Co) at 5% total CO conversion.

Figure 6 Comparative hydrocarbon selectivities at 5% total CO conversion for five reaction temperatures in the range 200-300°C. (open bars = cobalt/kieselguhr; solid bars = cobalt-graphite).

FIGURE 1

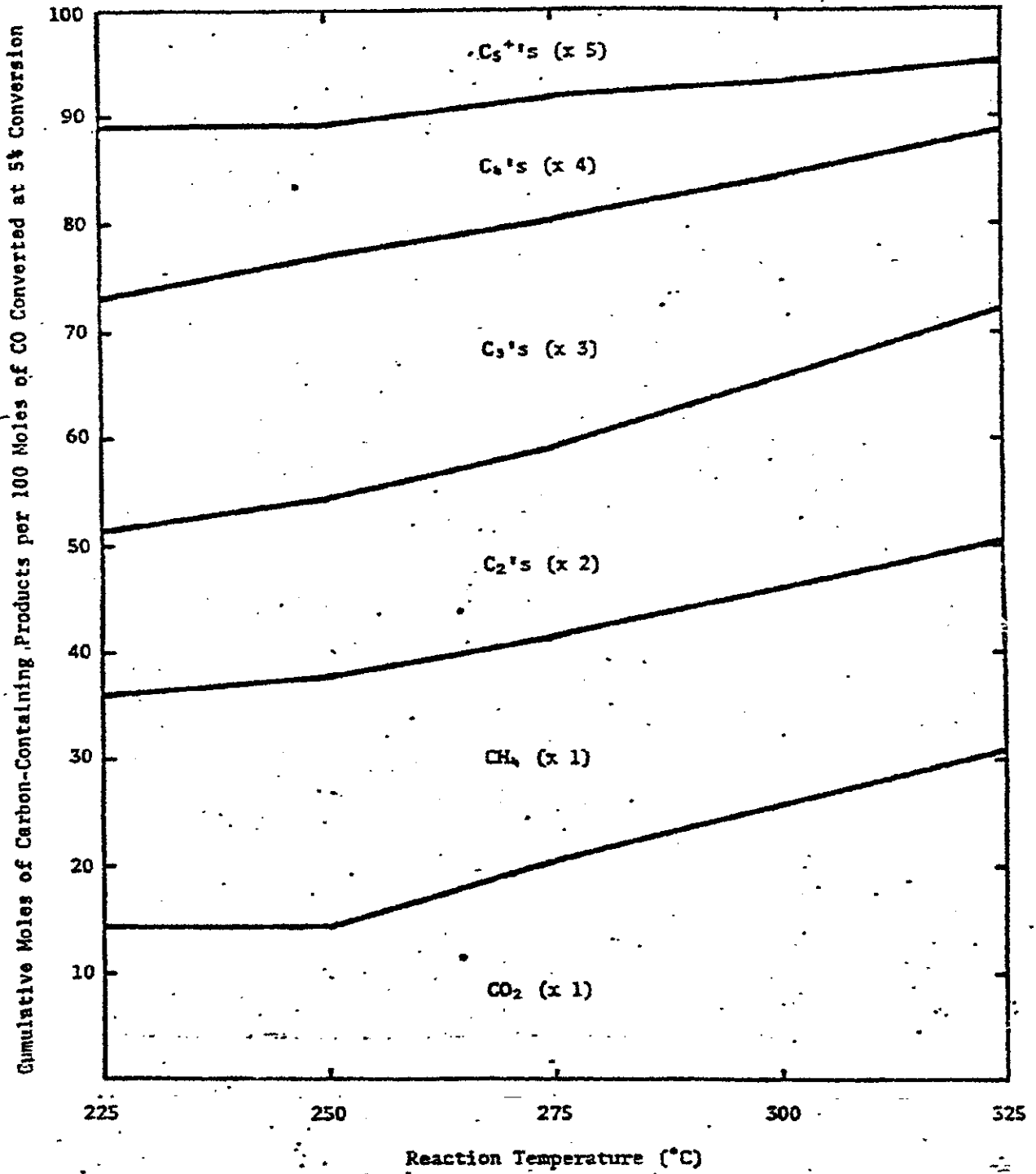


FIGURE 2

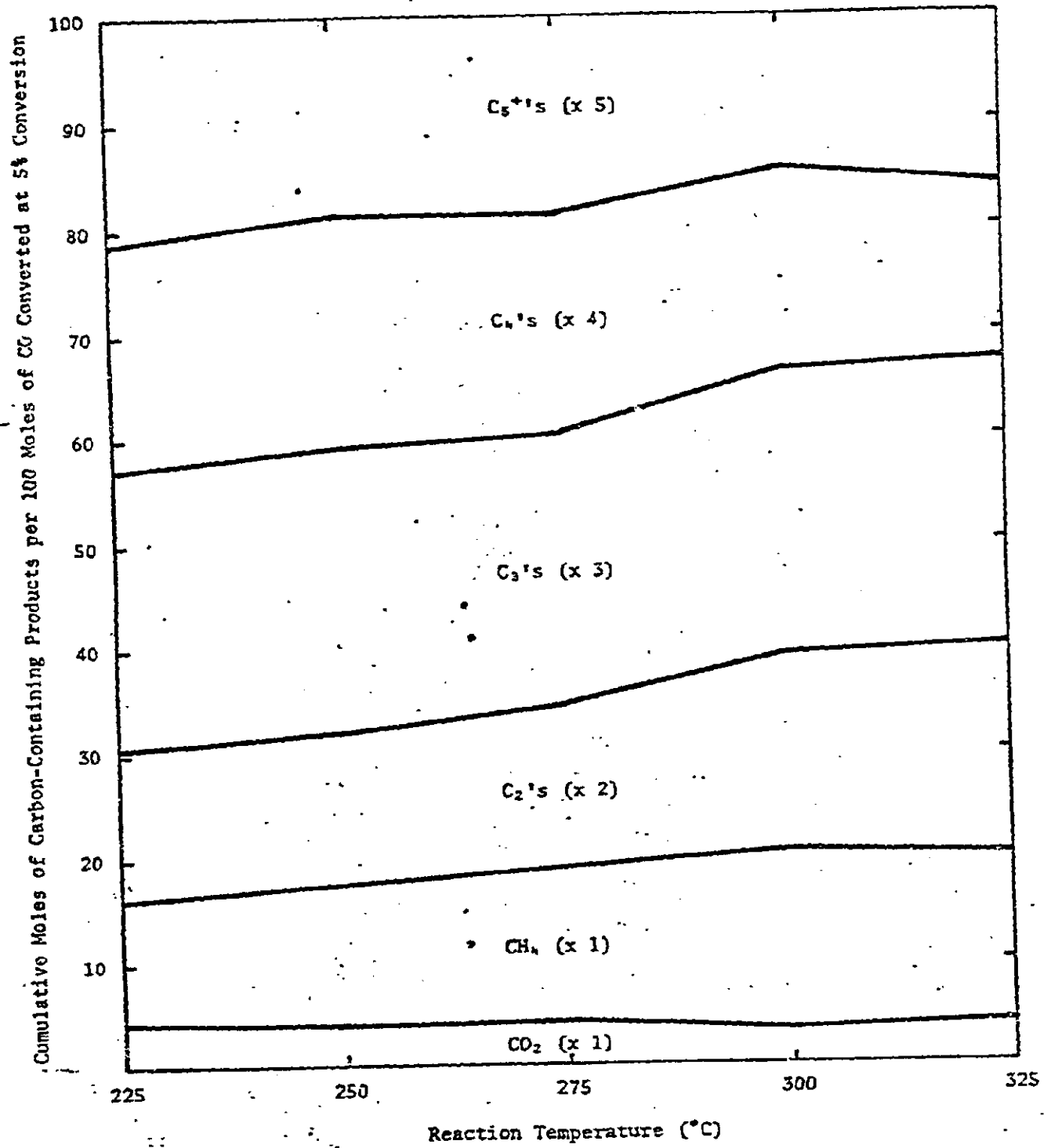


FIGURE 3

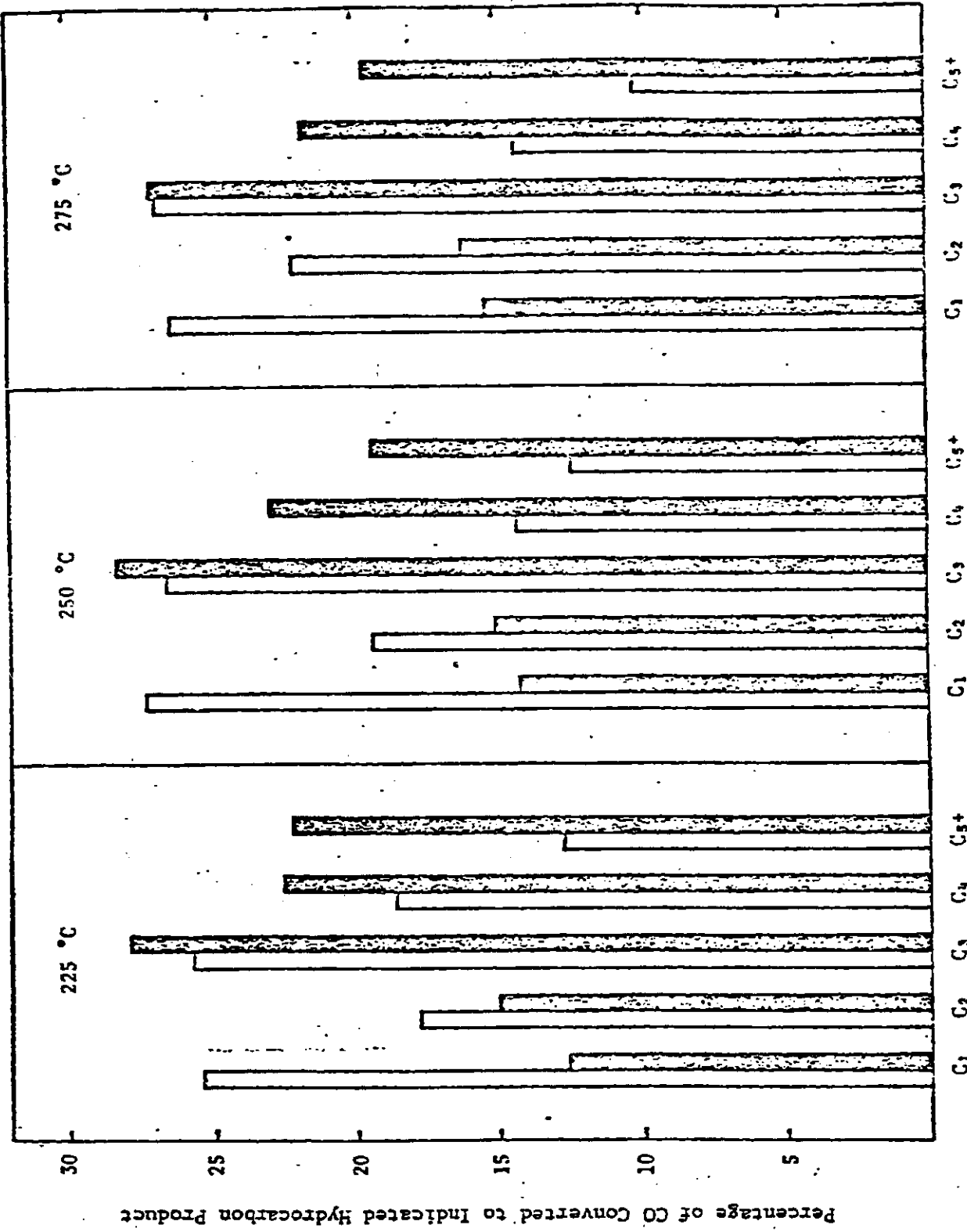


FIGURE 3 (cont.)

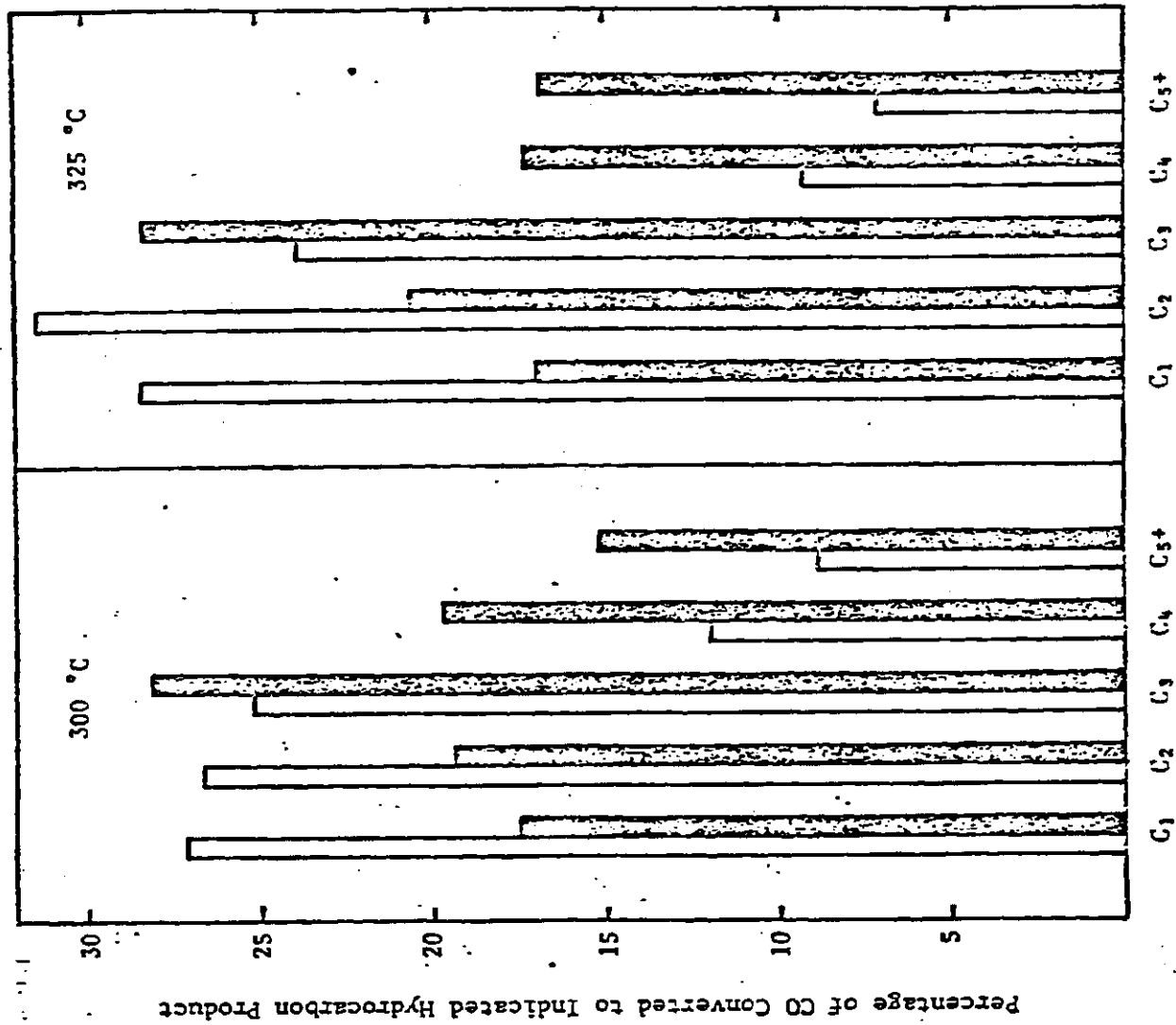


FIGURE 4

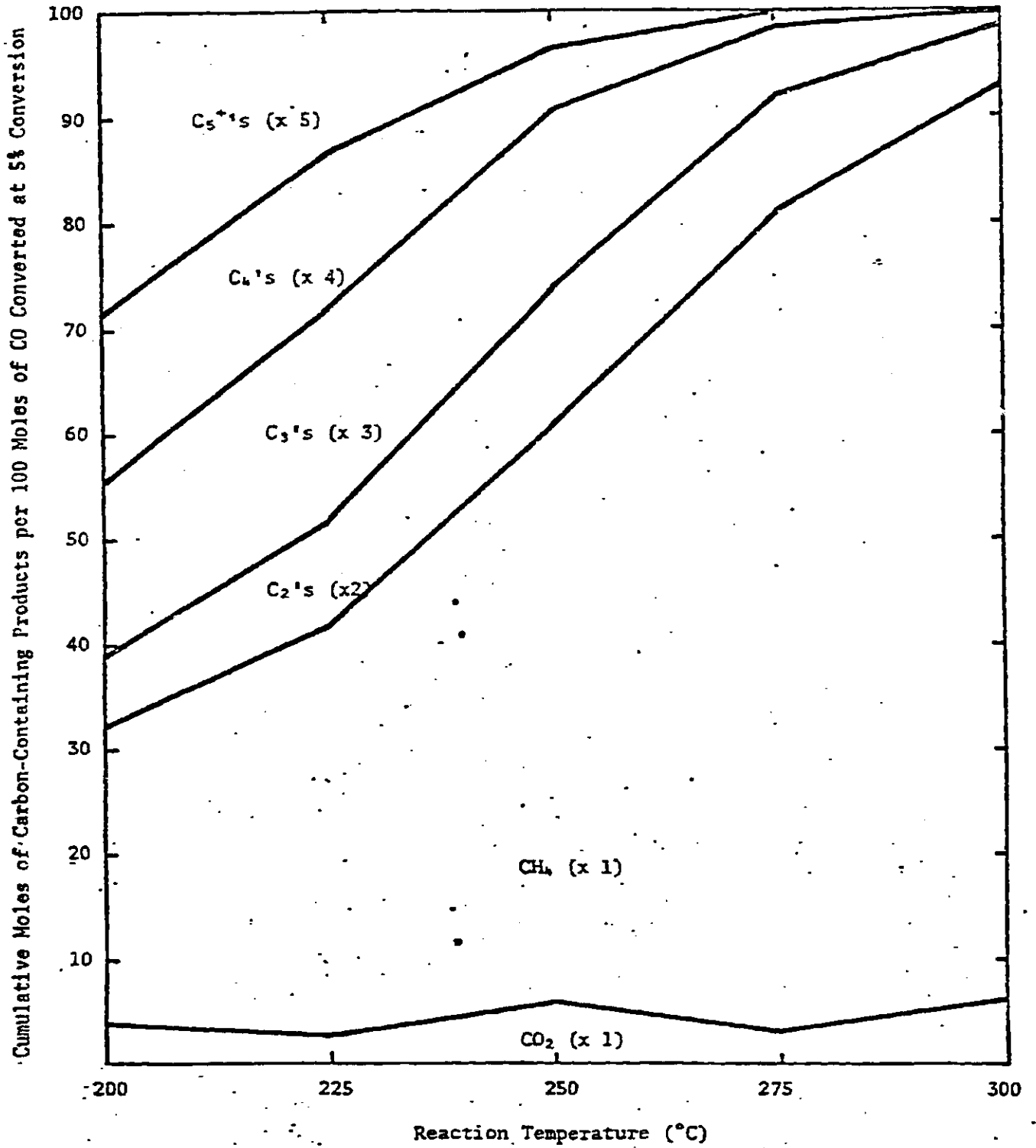




FIGURE 5

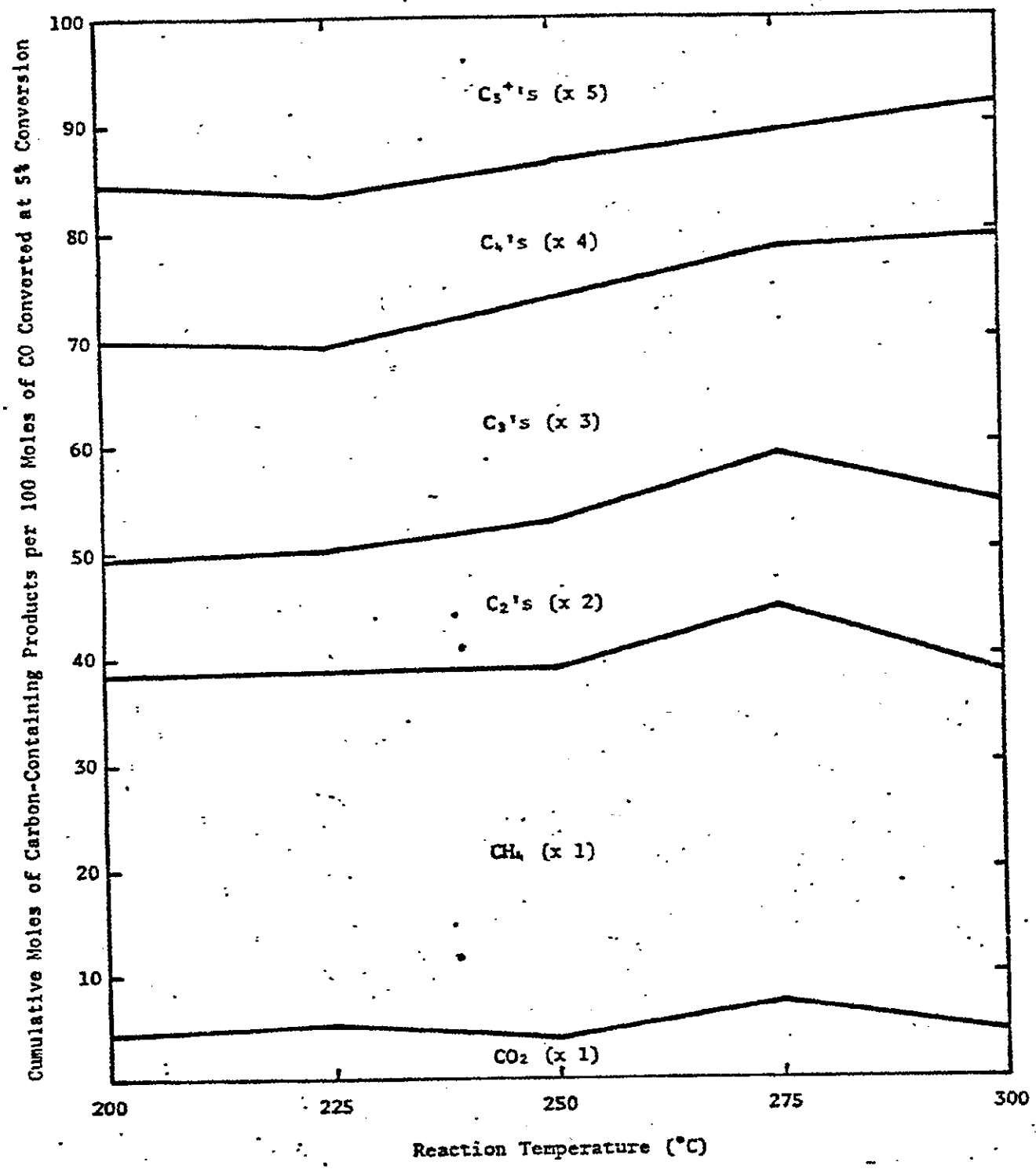


FIGURE 6

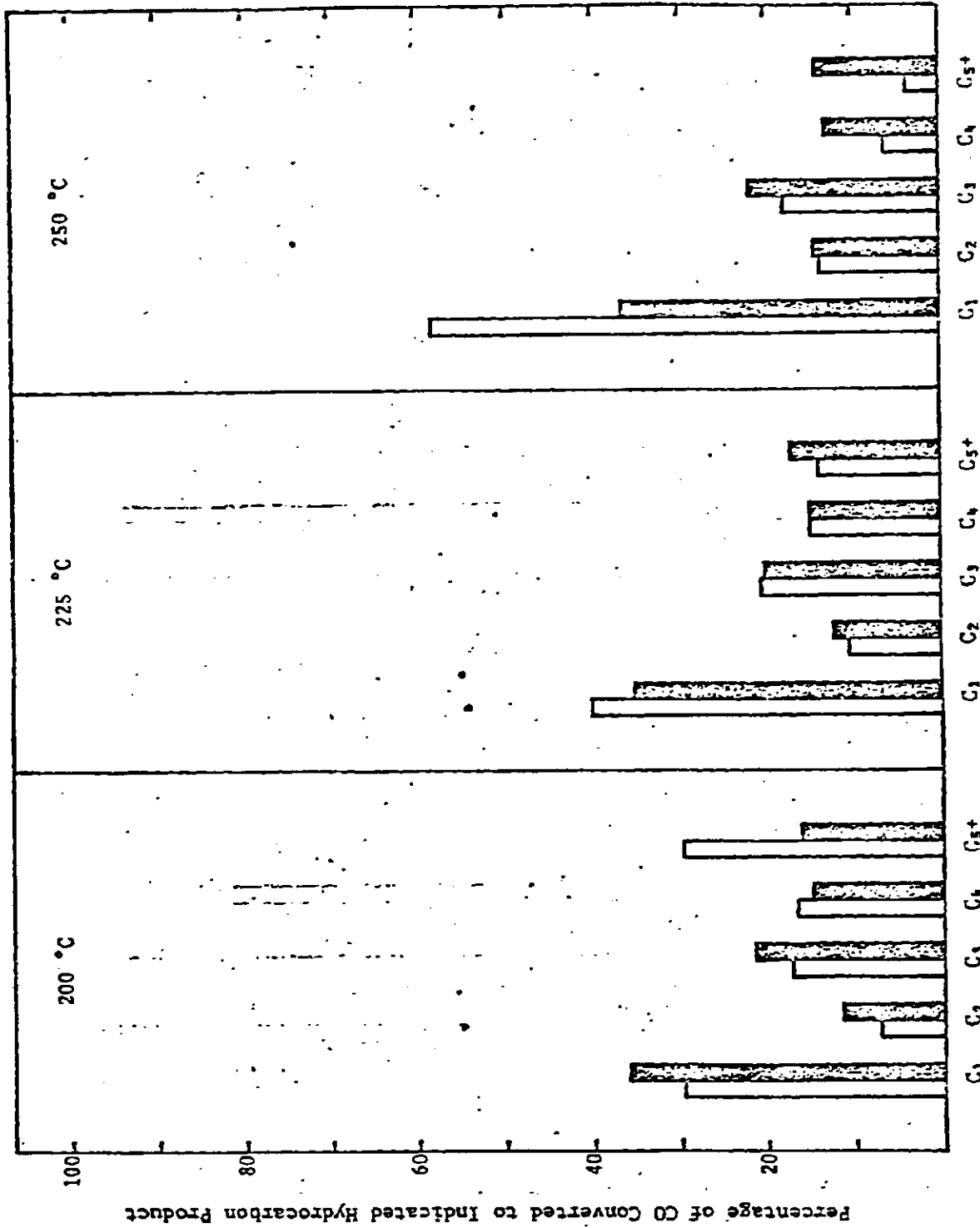


FIGURE 6 (cont.)

