Power Systems Division

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INVESTIGATION OF CARBON-FORMATION MECHANISMS AND FUEL-CONVERSION RATES IN THE ADIABATIC REFORMER

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DISCLAIMER

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The work of this program was under the technical direction of Dr. John A. S. Bett. Messrs. Herbert J. Setzer, Peter F. Foley, Richard A. Sederquist, and Saul J. Rothstein of United and Dr. Michael B. Cutlip of the University of Connecticut conducted the experimental and analytical efforts of the program. Alfred P. Meyer served as United Technologies' program manager.

INTRODUCTION

Fuel cell power plants may be required to use coal derived liquid fuels or heavy petroleum distillates as fuels. The fuel processor in present power plants is a catalytic steam reformer which is limited to the use of fuels such as naphtha or natural gas. There has been extensive work by United Technologies and other investigators to develop alternative reactors to process sulfur-containing fuels. Among these candidates, the adiabatic reformer is at the most advanced state of development.[1] In the adiabatic reformer air is added to the process fuel and steam to provide by combustion the endothermic heat for reforming in the catalyst bed. To obtain optimum power plant efficiency the amount of air added must be kept to a low value. Early tests showed, however, that air in excess of desired values was required both to prevent accumulation of carbon in the catalyst bed and to raise the catalyst to a temperature sufficient to achieve suitable activity for reforming. The development of efficient mixing nozzles for fuel, steam, and air, and of advanced catalysts with properties for limiting carbon accumulation and promoting reforming has resulted in the demonstration of considerably improved performance in a bench scale adiabatic reformer.[1] Further improvements may be achieved with mechanistic understanding of the fuel conversion and carbon forming processes in the reactor.

The objective of the present program is to establish a reactor model for the adiabatic reformer which will predict process stream compositions and include carbon formation processes. Four subordinate tasks were proposed to achieve the objective. These were:

(1) To determine on selected catalysts rate expressions for catalytic reactions occurring in the entrance section of the adiabatic reformer.

(2) To determine with microbalance experiments critical conditions for carbon formation on selected catalysts.

(3) To establish a reactor model to predict process stream compositions in the adiabatic reformer using data from Task 1 for catalytic reactions and data from the literature for homogeneous gas phase reactions.

(4) To establish a model to predict carbon formation by combination of the model for process stream composition from Task 3 and data for carbon formation from Task 2.

RESULTS

Task 1

The reaction rate measurements of Task 1 are close to completion. Catalytic reactions of methane and ethane in the presence of hydrogen sulfide were investigated on three catalysts; a commercial nickel steam reforming catalyst, a supported noble metal catalyst and a metal oxide catalyst. A flow reactor was used to determine differential rates for steam reforming, catalytic combustion and the carbon monoxide shift reaction on 0.5 gm catalyst samples at temperatures up to 1800°F.

Rates for steam reforming in every case were strictly first order in hydrocarbon partial pressure with unusually high activation energy (e.g., 69 and 88 k cal/mole, respectively for the reforming of methane and ethane on the nickel catalyst). In the steam reforming experiments cracking reactions and the shift reaction also occurred. Material balances were used on particular reacting species to obtain desired rates for the individual catalytic reactions for each experiment. The conversions due to homogeneous reactions were obtained by calculation, using the results from experiments with an empty reactor, and this contribution was removed from the reactor material balance so that only the catalytic rates remained. These catalytic rates were then input to a non-linear regression analysis to evaluate individual reaction rate expressions. Table 1, for example, lists the reactions used to describe the experiments with ethane and Table 2 summarizes the rate expressions so obtained including those for the shift reaction (2, 3).

To evaluate the catalytic contribution to the combustion reactions of methane and ethane, the same flow reactor was used. Blank experiments were initially run with the empty reactor to establish the extent of homogeneous combustion. For both methane and ethane, the homogeneous reactions were similar to those reported by Dryer (4) in his turbulent flow reactor. For ethane, dehydrogenation to ethylene was the primary reaction. For methane, both ethylene and ethane appeared as intermediates. Typical data are shown in Figures 1 and 2. The effect of various catalysts on the combustion of methane is summarized in Figure 3 which shows the conversion of methane to oxides of carbon at comparable space velocity and inlet

process steam composition in the empty reactor and in the reactor with nickel, noble metal and metal oxide catalyst. The nickel catalyst, although active for steam reforming, gave no significant acceleration of the combustion reaction, when oxygen was added, over the reactor blank. By contrast the metal oxide catalyst, though less active for steam reforming than the nickel catalyst, had significant activity for combustion. The noble metal catalyst was active for steam reforming and extremely active for combustion (5, 7).

Task 2

Characteristic carbon formation behavior in the adiabatic reformer has been discussed in a number of reports (1), (6), (7). At the boundary between carbon-free and carbon forming conditions in the reactor the rates for formation and removal must be in steady state equilibrium. Experiments are in progress with a microbalance to determine conditions critical for carbon accumulation on the catalysts used in the adiabatic reformer. The effect of the catalysts on the rates of carbon accumulation and gasification will be determined in atmospheres of ethylene, steam, and hydrogen sulfide.

The balance, gas delivery, and gas analysis systems have been calibrated and initial tests are in progress.

Task 3

In Task 3, kinetic data obtained in Task 1 are to be used to establish a model to predict process stream composition in the adiabatic reformer. Data to be fitted were obtained in a previous test program at United Technologies funded by the Electric Power Research Institute (1). Typical experimental temperatures and conversion profiles in a reactor filled with nickel catalyst operating on No. 2 fuel oil are shown in Figures 4 and 5. A minimum reaction set necessary to represent this data is given in Tables 3 and 4. Rates for the catalytic reforming of methane and ethylene and of the shift reaction were discussed in an earlier report. The rate for steam reforming No. 2 fuel oil was represented as a composite of the rates for methane and ethylene. Experiments had shown its rate to fall in a range between those for the two lighter reactants (2).

The rates for the homogeneous reactions were obtained from various literature sources. The rates for combustion of methane and ethylene are those of Dryer (4). By analogy with steam reforming of No. 2 fuel oil, the rate for combustion of the unreacted fuel is represented as a composite of the rates for the lighter gases. Rates and product distributions in the cracking reaction were evaluated from the literature for steam cracking. The product C_6H_6 represents, not benzene, but merely the residue of the cracking reaction with lower hydrogen content. Its reactivity in subsequent reactions was assumed to be that of methane.

The reaction set can be reduced to 7 differential equations, and 3 material balances describing the variation of the reactants and products distributions with bed position and temperature. A routine has been developed which solves the equations for a known temperature profile. This routine is the core of the complete solution algorithm, and is being correlated with test data, prior to adding the temperature and energy balance calculations. Solution of the equation set is accomplished by the Continuous System Modeling Program III (CSMP III), a program product of IBM. The program numerically integrates the equation set using, for this application, a time step technique which varies the increment size until the variance is within user specified tolerances.

Figures 6 and 7 present the results of an initial simulation of the test conditions represented in Figures 4 and 5. Rate constants were taken from Tables 3 and 4. Comparison with test data shows qualitative and fair quantitative agreement. Thus, the disappearance of oxygen and fuel occur at close to the correct rate. Concentrations of both methane and ethylene reach a maximum at the correct reactor position and with approximately correct values. Unlike the test data, no maximum in carbon monoxide concentration occurred. Apparently the rate for oxidation of carbon monoxide, in Table 4, was too large. This would be consistent with reported moderation of the rate of this reaction under fuel rich conditions (8). Initially a large error also existed in the exit methane concentration which the model calculated to be at equilibrium. When an upper limit was set on this rate to bring the exit methane concentration into agreement with that of Figure 4 the upper value was coincident with values predicted for methane flux by diffusion at the catalyst pellet boundary layer. Apparently the intrinsic methane reform rate was too great and was limited by mass transfer effects.

Current efforts are directed at introduction of the mass transfer effects and refinement of the individual component rates to obtain a fit to test results of the reactor with the nickel catalyst. Temperature and energy balance calculations will then be added. Application of the model to other reactor conditions and tests with different catalyst loadings will then be possible.

Task 4

Combination of the reactor model for the process stream composition and the experimental data for carbon formation will proceed as Task 2 and 3 approach completion.

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(1) "Development of the Adiabatic Reformer to Process No. 2 Fuel Oil and Coal-Derived Liquid Fuels," Electric Power Research Institute Report EM1701, Research Project PO41-4, February 1981.

(2) "Investigation of Carbon-Formation Mechanisms and Fuel Conversion Rates in the Adiabatic Reformer," Quarterly Progress Report No. 1, June 1980, DOE Contract DE-AC-21-80-MC14395.

(3) Quarterly Progress Report No. 2, Sept. 1980, DOE Contract DE-AC-21-80-MC14395.

(4) Dryer, F. S. and Glassman, I., Prog. in Astronautics and Aeronautics, 62, 255, (1977).

(5) Quarterly Progress Report No. 3, Dec. 1980, DOE Contract DE-AC-80-MC14395.

(6) Bett, J. A. S., Lesieur, R. R., McVay, D., and Setzer, H. J., "Adiabatic Reforming of Distillate Fuels," Proc. of Workshop on Hydrocarbon Processing Mixing and Scale-up Problems," Washington, D.C., Dec. 1978.

(7) Bett, J. A. S., Foley, P. F., Lesieur, R. R., Rothstein, S. J., Sederquist, R. A., and Setzer, H. J. Report to Steam Reforming Working Group, at DOE, Germantown, MD, February 24, 1981.

(8) R. Farmer, private communication.

TABLE 1

ANALYSIS OF STEAM REFORMING DATA TO DERIVE ELEMENTARY REACTION RATES

$$C_2H_6 + 2H_2O \xrightarrow{k_1} 2CO + 5H_2$$

$$CO + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO_2 + H_2$$

$$C_2H_6 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_2H_4 + H_2$$

$$C_2H_6 + H_2 \xrightarrow{k_4} 2CH_4$$

$$C_2H_4 + 2H_2O \xrightarrow{k_5} 2CO + 4H_2$$

TABLE 2

RATE CONSTANTS FOR REACTIONS OF ETHANE ON NICKEL AND NOBLE METAL CATALYSTS

	NICKEL	NOBLE METAL
k_1	$2.52 \times 10^{15} \exp\left(\frac{-86,900}{RT}\right)$	$3.71 \times 10^{9} \exp\left(\frac{-51,500}{RT}\right) \frac{m^3}{kg\ sec}$
k_2	$2.58 \times 10^{11} \exp\left(\frac{-54,792}{RT}\right)$	$2.105 \times 10^{5} \exp\left(\frac{-17,674}{RT}\right) \frac{m^6}{k\ mole\ kg\ sec}$
k_3	-	$3.36 \times 10^{4} \exp\left(\frac{-31,644}{RT}\right) \frac{m^3}{kg\ sec}$
k_4	-	$1.65 \times 10^{6} \exp\left(\frac{-30,189}{RT}\right) \frac{m^3}{kg\ sec}$
k_5	$3.98 \times 10^{15} \exp\left(\frac{-84,700}{RT}\right)$	- $\frac{m^3}{kg\ sec}$

TABLE 3

REACTION SET - NICKEL CATALYST

CATALYTIC

$O_2 + FUEL \rightarrow CO + H_2$	$r_1 = 0$
$H_2O + FUEL \rightarrow CO_2 + H_2$	$r_2 = [k_4 (1 - \alpha)^2 + k_3\alpha^2] C_F$ *
$H_2O + CH_4 \rightarrow CO_2 + H_2$	$r_3 = 1.8 \times 10^8 \exp(-70{,}000/RT) C_{CH_4}$
$H_2O + C_2H_4 \rightarrow CO_2 + H_2$	$r_4 = 9.4 \times 10^{13} \exp(-88{,}000/RT) C_{CH_4}$
$CO + H_2O \rightarrow CO_2 + H_2$	$r_5 = 2.6 \times 10^{17} \exp(54{,}800/RT) [C_{CO} C_{H_2O} - C_{CO_2} C_{H_2}/K]$

* All rates in units - moles/g. cat. sec.

Concentrations - moles/cm^3.

TABLE 4

REACTION SET

HOMOGENEOUS

$O_2 + FUEL \rightarrow CO + H_2$	$r_1 = k_3 (1 - \alpha)^2 C_F^m C_{O_2}^n + k_2 \alpha^2 C_F^m C_{O_2}^n$ *
$O_2 + CH_4 \rightarrow CO + H_2$	$r_2 = 10^{13.2} \exp(-48{,}400/RT) C_{CH_4}^m C_{O_2}^n$
$O_2 + C_2H_4 \rightarrow CO + H_2$	$r_3 = 10^{11.9} \exp(-50{,}970/RT) C_{C_2H_4}^m C_{O_2}^n$
$O_2 + H_2 \rightarrow H_2O$	$r_4 = 2 \times 10^{13} \exp(-24{,}700/RT) C_{H_2}^m C_{O_2}^n$
$FUEL \rightarrow S_1CH_4 + S_2C_2H_4 + S_3C_3H_6 + S_4C_6H_6$	$r_5 = 8.85 \times 10^{12} \exp(-55{,}372/RT) C_F^m C_{O_2}^n$
$CO + O_2 \rightarrow CO_2$	$r_6 = 4.2 \times 10^{13} \exp(-24{,}000/RT) C_{CO} C_{O_2}$

* All rates in units - moles/g cat sec, concentrations - moles/cm^3

m and n = variable as per references

TABLE 4 (Continued)

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r_4 R. H. Edelman and P. T. Harsha, Prog. Energy and Combust. Sci, 4, 1, 1978

($H_2 + O_2 \rightarrow 2OH$)

r_5 S. B. Zdonik, E. J. Green, L. P. Hallee, Oil and Gas Journal June 26, 96, (1967)

r_6 Williams, G. C., Hottel, H. L. and Morgan, A. C., Proc. 12th Symp. (Intl.) on Combustion 1969, p. 913

FIGURE 1

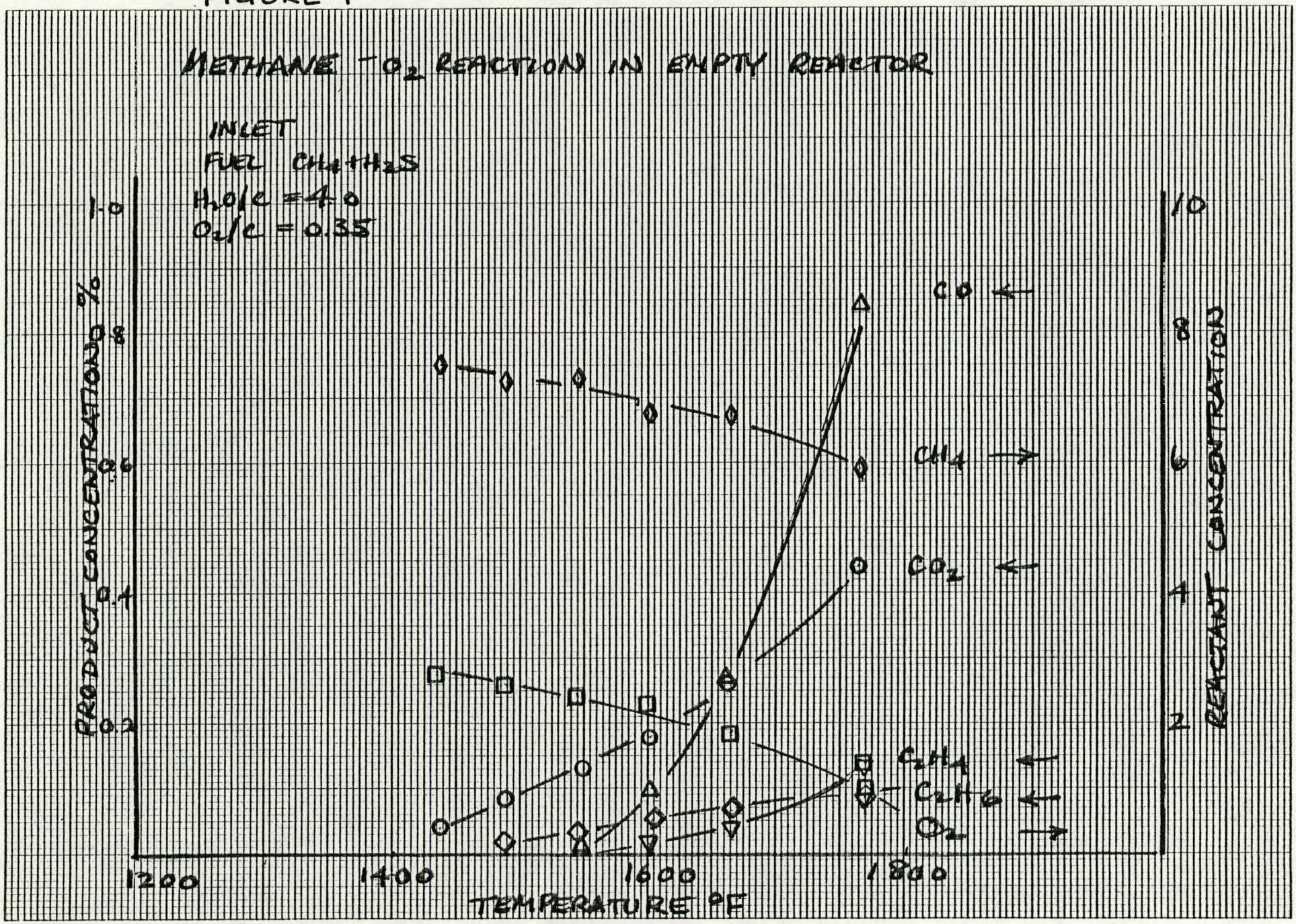

FIGURE 2

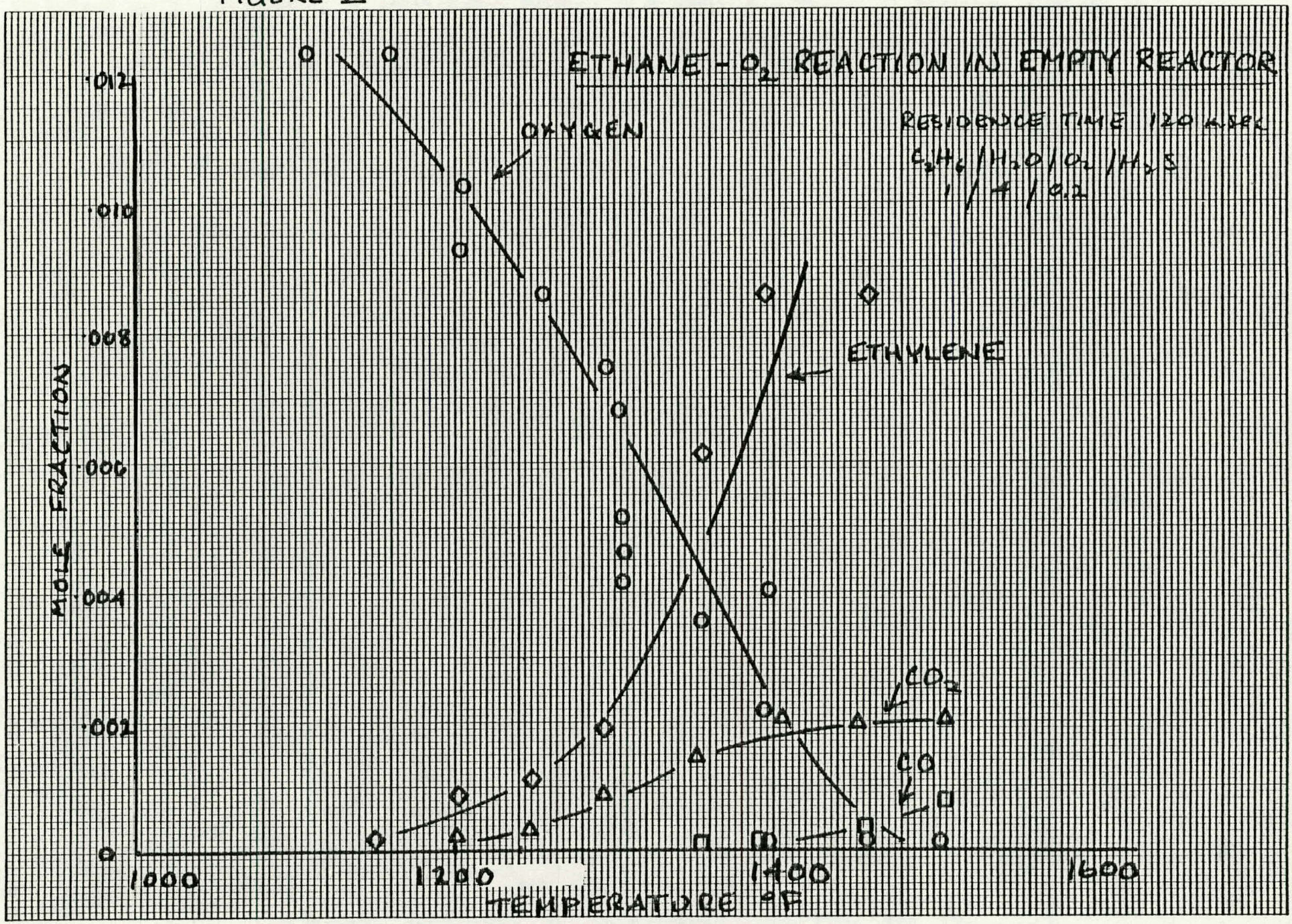

FIGURE 3

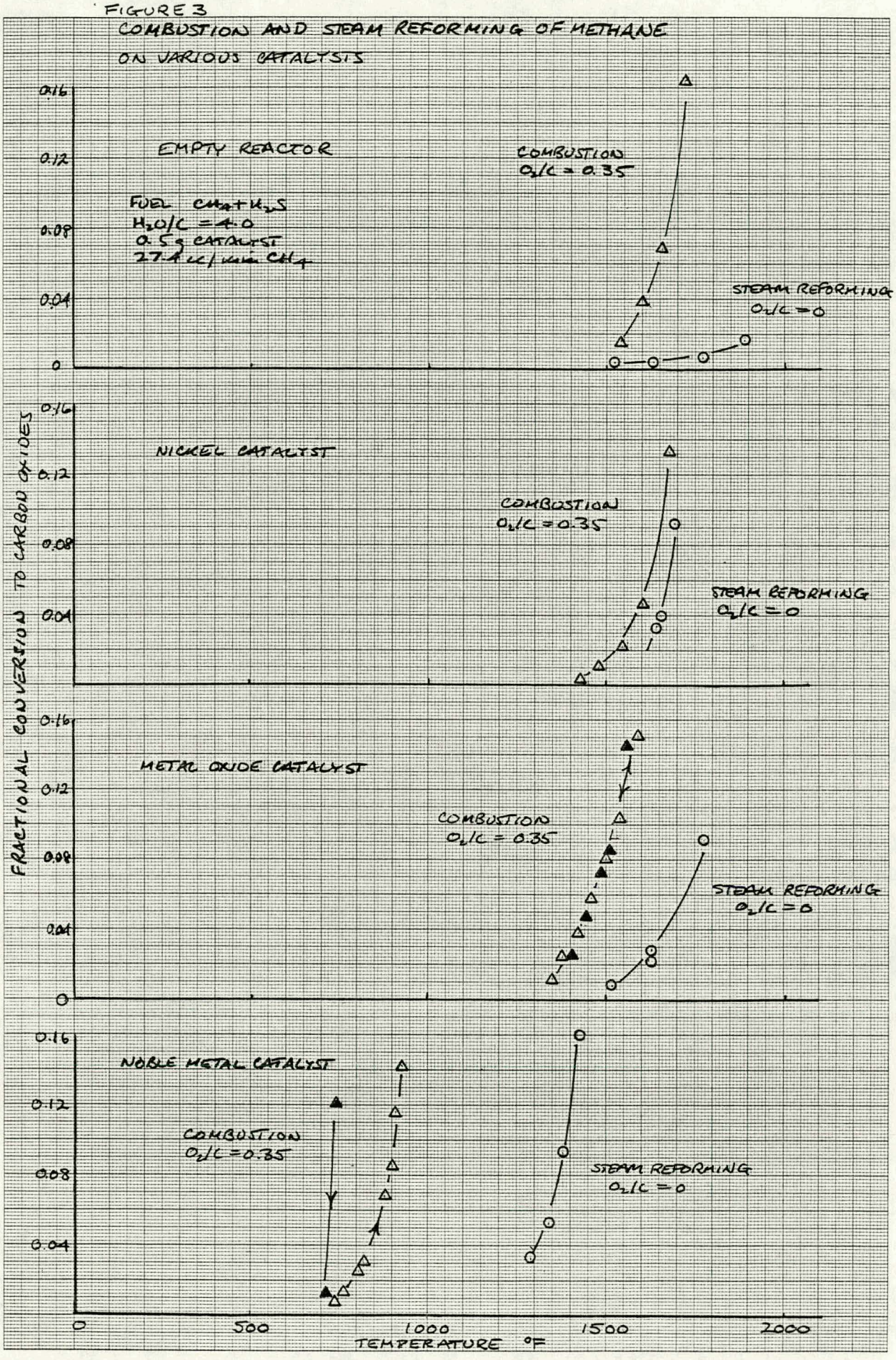

FIGURE 1

PRODUCT DISTRIBUTION IN THE ADIABATIC REFORMER COMMERCIAL NICKEL CATALYST CONFIGURATION 10 NOZZLE

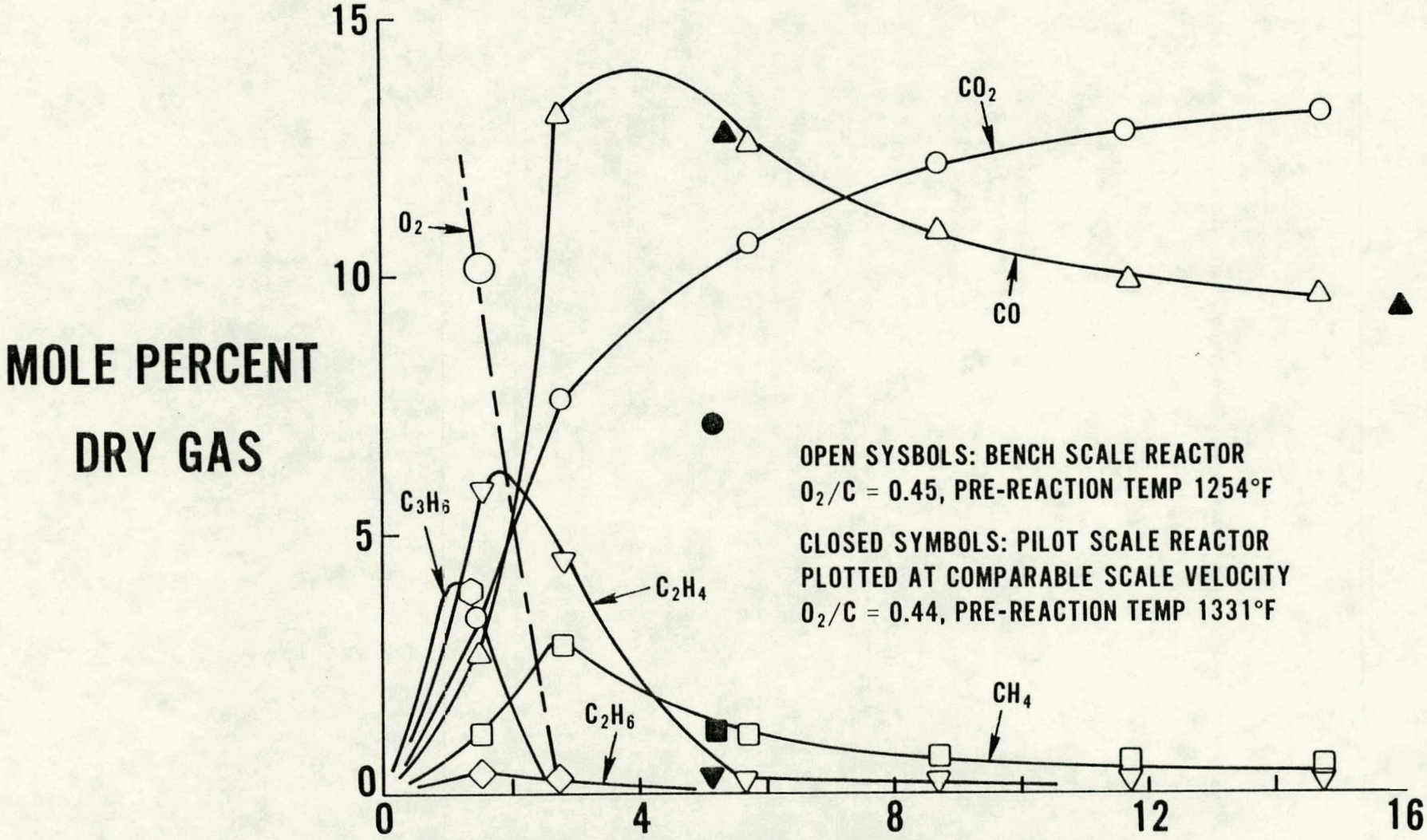

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FIGURE 6T

TEMPERATURE PROFILE IN THE ADIABATIC REACTOR COMMERCIAL NICKEL CATALYST – CONFIGURATION 10 NOZZLE

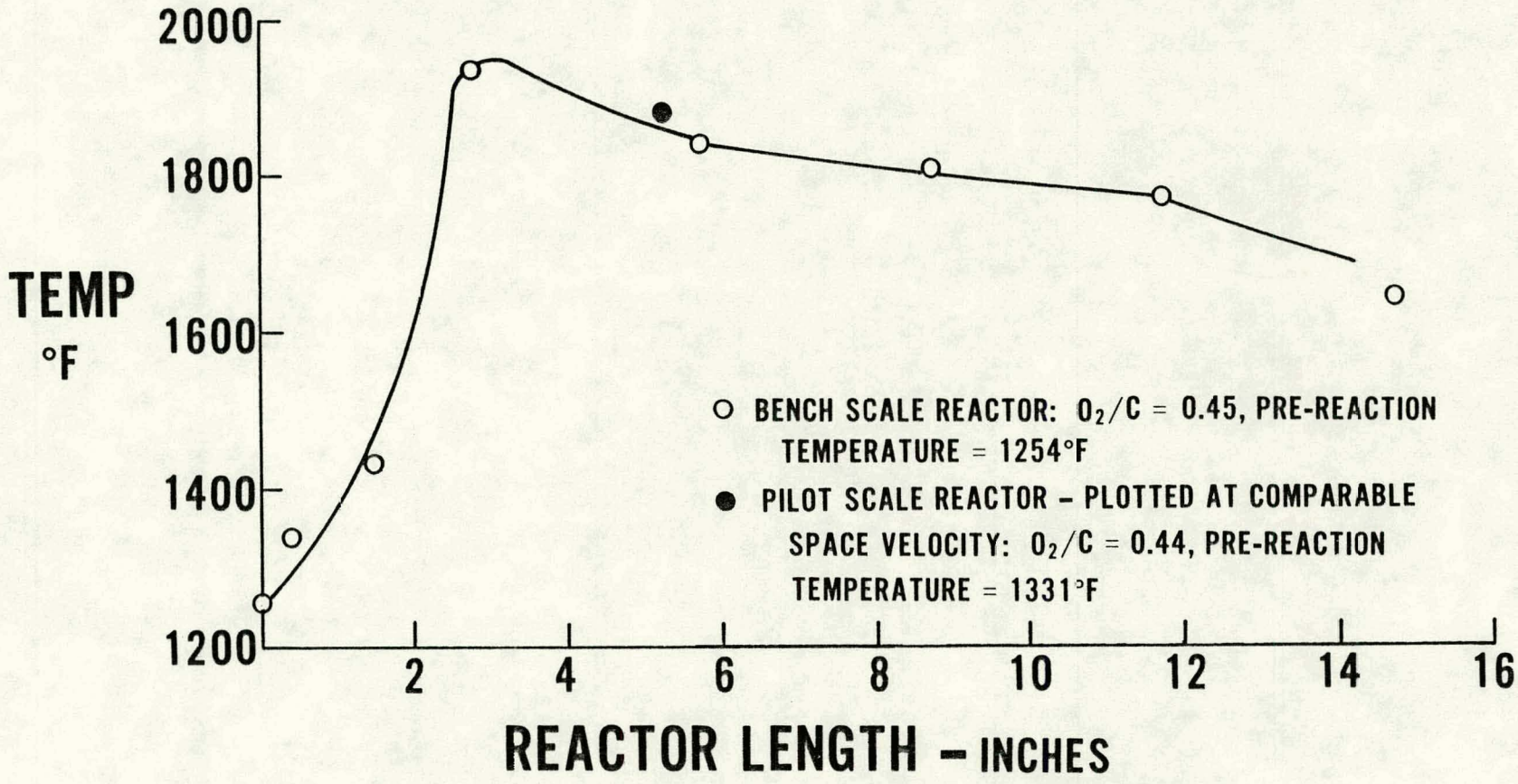

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FIGURE 6
CALCULATED PROCESS STREAM COMPOSITION FOR TEST CONDITIONS
OF FIGURES 4 AND 5

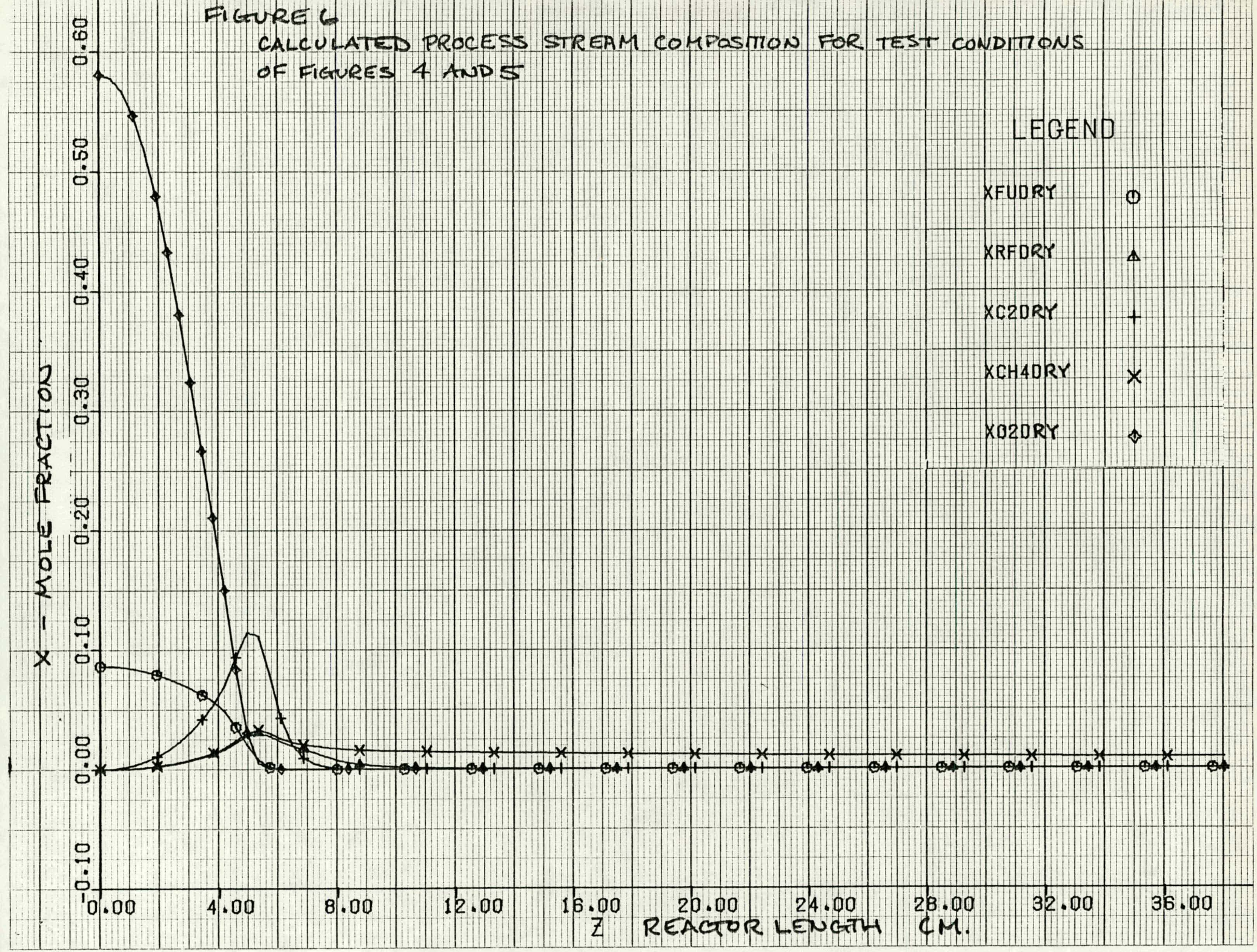

FIGURE 7
CALCULATED PROCESS STREAM COMPOSITION FOR TEST CONDITIONS OF FIGURES 4 AND 5