CALCULATING CATALYST TEMPERATURE IN A HOT-GAS-RECYCLE METHANATION REACTOR

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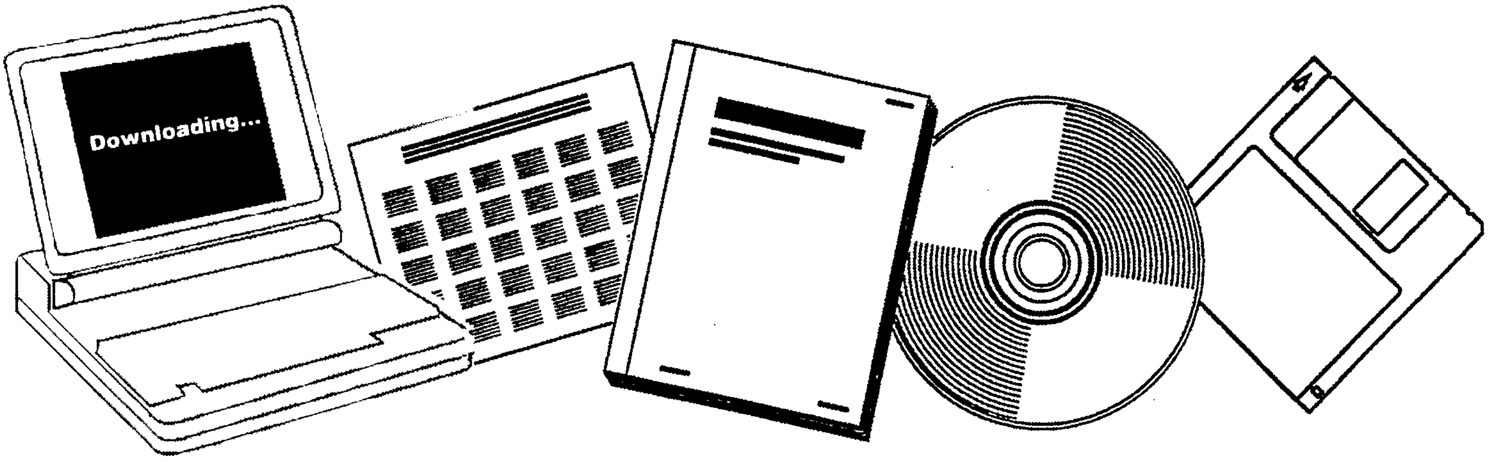

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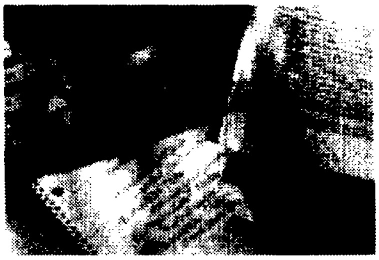

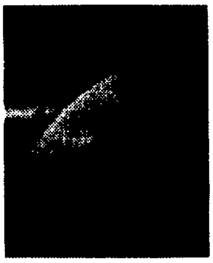

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CONTENTS

ILLUSTRATIONS

CALCULATING CATALYST TEMPERATURE IN A HOT-GAS-RECYCLE METHANATION REACTOR

by

R. R. Schehl,[1] W. P. Haynes,[2] and A. J. Forney[3]

ABSTRACT

A study of the heat-transfer characteristics of a hot-gas-recycle fixed-bed catalytic reactor is reported. Equations are developed, and a numerical method is described to solve the equations. Catalyst temperature and reaction rate profiles are calculated as functions of position in the reactor for different times on-stream. Rate profiles yield clear evidence in support of the claim that the catalyst is deactivated zonally.

INTRODUCTION

This paper deals with the problem of estimating catalyst surface temperature in a hot-gas-recycle methanation reactor (1-2, 4-5).[4] A methanation reactor of this type is to be utilized in the Synthane process (3, 6-7). The scope of the analysis is limited to that for a fixed bed of catalyst consisting of surface-catalyzed parallel plates. The treatment of the problem is sufficiently general, however, to be applicable to a variety of fixed-bed catalytic reactor geometries.

Quite frequently it is more convenient to monitor gas stream temperatures rather than the catalyst temperature within a reactor. A knowledge of the catalyst temperature is vital, nonetheless, in that reaction rates are generally temperature sensitive and catalysts are often adversely affected by extreme temperatures. To perform reactor modeling, it is essential that reaction rates be calculable as a function of position in the reactor. One must also be assured that portions of the catalyst bed are not being exposed to extreme temperatures.

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[2] Supervisory chemical engineer.

[3] Research supervisor.

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[4] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

The reactor system to be discussed is considered to be operating in steady state; that is, the time required for any significant change in temperature, catalyst activity, or other parameters is large with respect to the residence time of the gas. Heat loss to the reactor walls is neglected, and owing to the fact that the recycle stream is approximately a factor of 10 larger than the fresh-feed reactant stream, volumetric contraction due to reaction is ignored. The physical constants of the gas are considered to be temperature independent over the operating range of the reactor, and are evaluated at the mean reactor temperature and for average gas stream compositions. It was found that these simplifications introduced an error of no more than 1° to 2° C in the calculation of the catalyst temperature.

THEORETICAL DEVELOPMENT

Consider an element in the reactor at some position A, where A is the catalyst surface area measured from the inlet of the reactor, with an incremental catalyst surface area of δA (fig. 1). The reactor is assumed to be operating well into the turbulent range; therefore, heat transfer from the catalyst surface to the turbulent core may be viewed as conduction through the laminar film. We may then define the following quantities:

$\delta q = -H \frac{\partial G}{\partial A} \delta A$ = heat of reaction per hour within the element.

$\delta q' = h\ (T_c - T_b)\,\delta A$ = heat transferred per hour from the catalyst surface to the gas in the element.

$\delta q'' = C_pM \frac{\partial T_b}{\partial A} \delta A$ = heat per hour gained by the gas in the element.

In these definitions H is the heat of reaction (Btu/lb mole of CO converted to methane), G is the molar flow rate of CO (lb-mole/hr), h is the film heat transfer coefficient (Btu/hr-ft^2-° C), T_c and T_b are the temperatures of the catalyst and turbulent gas core, respectively (° C), C_p is the specific heat at constant pressure of the total gas stream (Btu/lb-mole-° C), and M is the molar flow rate of the total gas stream (lb-mole/hr). Since we assume that the reactor is operating in steady state, a heat balance on the gas in this element gives the following equations:

$$\delta q = \delta q' \qquad (1)$$

$$\text{or} \quad -H \frac{\partial G}{\partial A} \delta A = h\ (T_c - T_b)\,\delta A \qquad (2)$$

In the following analysis, the catalyst temperature will be of concern, hence, solving equation 2 for T_c we arrive at

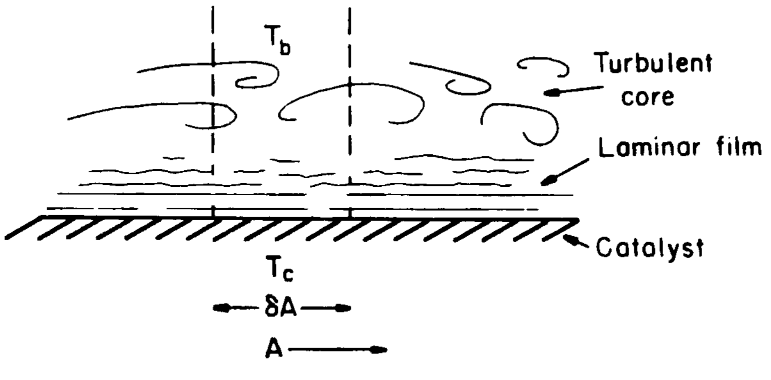

FIGURE 1. - Cross-section view of catalyst-gas interface.

$$T_c = T_b - \frac{H}{h}\frac{\partial G}{\partial A} . \tag{3}$$

Gas temperature profiles are measured experimentally; therefore, T_b and $\frac{\partial T_b}{\partial A}$ are known fractions of A. From the chain rule of calculus we have the following:

$$\frac{\partial G}{\partial A} = \frac{\partial G}{\partial T_b}\frac{\partial T_b}{\partial A} . \tag{4}$$

The rate of change of the CO molar flow rate with respect to the temperature of the gas stream $\left(\frac{\partial G}{\partial T_b}\right)$ will be constant provided the following assumptions are made: (1) The reactor is truly adiabatic and (2) the specific heat of the gas is considered to be constant over the operating temperatures of the reactor. Hence, we may express T_c in term of readily measured observables

$$T_c = T_b - \frac{H}{h}\frac{\partial G}{\partial T_b}\frac{\partial T_b}{\partial A} = T_b + \frac{H}{h}\frac{(G_I - G_E)}{(T_E - T_I)}\frac{\partial T_b}{\partial A} , \tag{5}$$

where T_I and G_I and T_E and G_E are the gas stream temperatures and CO molar flow rates at the inlet (I) and exit (E), respectively. All of the parameters in equation 5 are either observable or may be obtained from the literature.

APPLICATION

The catalytic reactor operation (experiment HGR-15) to be discussed herein consists of an 8-foot bed of stainless steel grids flame-sprayed with Raney nickel. Each grid assembly contains 15 plates 0.05 inch thick and 6 inches long. The plates are separated from one another by spacers 0.135 inch thick. As indicated in figure 2, adjacent grid assemblies are rotated 90° with respect to each other. The catalyst bed is contained in a 3-inch schedule 40 stainless steel pipe. The system is designed for a recycle-to-fresh-feed ratio of approximately 10:1, to allow a 100° C temperature rise in the catalyst bed with inlet gas being 300° C and exit gas being 400° C.

Using equation 5, the catalyst temperature may be calculated from experimental data. The heat of reaction for

$$CO + 3\,H_2 \rightleftarrows CH_4 + H_2O$$

is 94,252 Btu/lb mole of CO at 700° F (11). The film heat transfer coefficient is calculated using the Dittus-Boelter (8) correlation for flow through circular conduits:

$$\frac{hD}{k} = 0.023\,\frac{(DG_F)^{0.8}}{\mu}\left(\frac{C_p\mu}{k}\right)^{0.4} \tag{6}$$

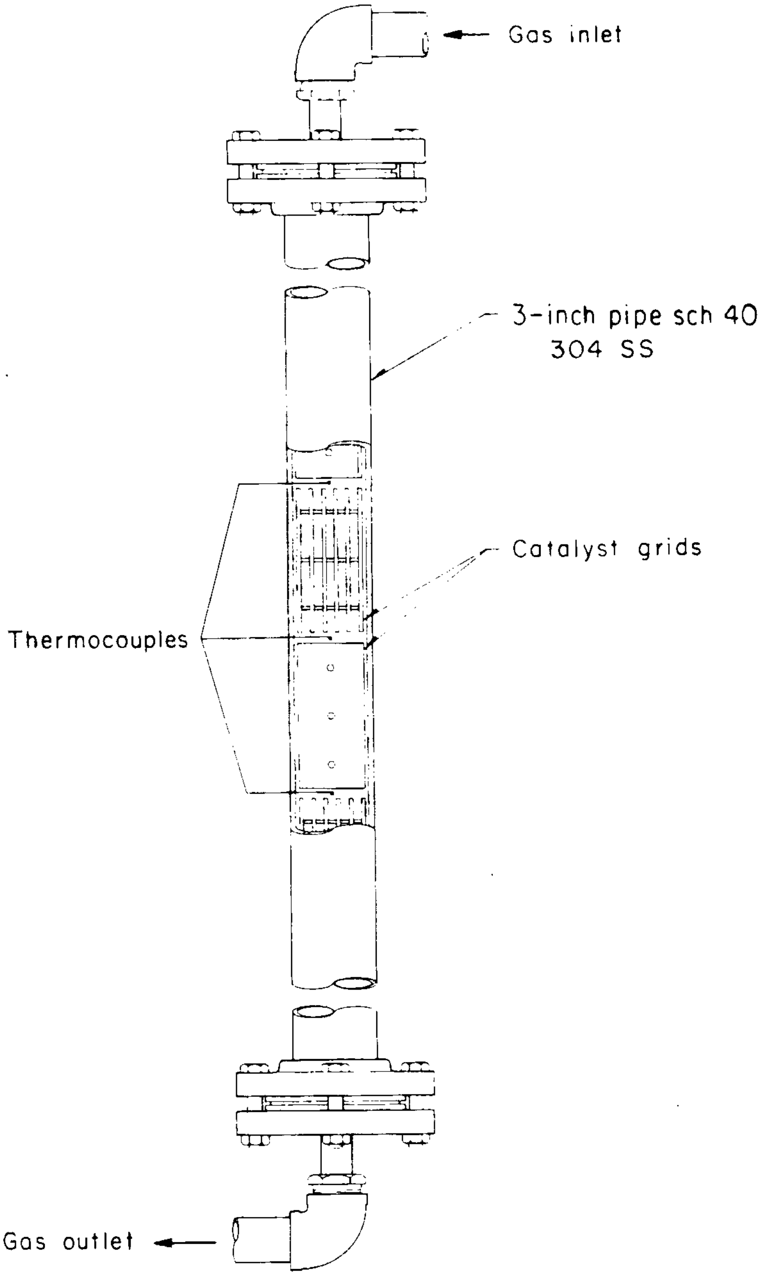

FIGURE 2. - Hot-gas-recycle methanation reactor.

where k is the thermal conductivity of the gas (Btu/hr-ft^2-° F/ft), μ is the gas viscosity (lb/ft-hr), D is the characteristic diameter (ft), and G_F is the mass velocity (lb/ft^2-hr). The parameters, k, μ, and C_p, were calculated for average stream compositions and at 350° C. The characteristic diameter, D, is four times the hydraulic radius. For flow between parallel plates of high aspect ratio, the hydraulic radius is approximately d/2. The distance between the plates is d.

Gas stream temperatures were measured at 6-inch intervals throughout the catalyst bed. To attain an accurate measure of the derivative of gas temperature with respect to catalyst area, a "sliding" quadratic function was fitted to the experimental temperature data. A brief description of this technique is given in the appendix.

Figures 3 through 9 illustrate the observed gas stream temperature (●), the least-squares fit to the gas stream temperature (——), and the calculated catalyst temperature (-----) as functions of distance through the reactor. The gas stream temperature profiles show that the reaction is distributed over a relatively wide zone. As the catalyst within the reaction zone becomes deactivated, the zone moves down the reactor. This type of zonal reactor "burnout" has been observed in other investigations (9). Once the reaction reaches the end of the reactor, the conversion drops off rapidly and the reactor is considered dead.

A profile plot of heat liberated, $\frac{\delta q}{\delta A}$, versus distance through the reactor for different times on-stream yields a more lucid description of the reaction zone. The heat liberated by the reaction per hour, per unit catalyst area $\left(\frac{\delta q}{\delta A}\right)$, is directly proportional to the reaction rate. From equation 1 it follows that

$$\frac{\delta q}{\delta A} = - H \frac{\partial G}{\partial A} = C_p M \frac{\partial T_b}{\partial A} = \frac{H\,(G_I - G_E)}{(T_E - T_I)} \frac{\partial T_b}{\partial A} .$$

Figure 10 shows the heat liberation profiles for several times on-stream. At the time of the last observation (955 hours on-stream), the maximum heat liberated in the reaction zone occurs approximately three-fourths of the way through the reactor.

The arithmetic mean positions of the reaction zone, $\bar{x}$, were calculated, and figure 11 illustrates the time dependence of the movement of the reaction zone through the reactor. The reactor was shut down several times during the run for unscheduled equipment repairs. The duration of the shutdowns ranged from several hours to as long as 6 days. Figure 9 shows that $\bar{x}$ decreased slightly after each indicated shutdown. This is indicative of a partial recovery in catalyst activity. During a shutdown the reactor is purged and maintained in a 50-psig hydrogen environment, which accounts for the partial reactivation. The time dependence of $\bar{x}$ is linear during the interim periods between shutdown, and it is likely that the lifetime of a catalyst bed may be predicted by extrapolating data of this type.

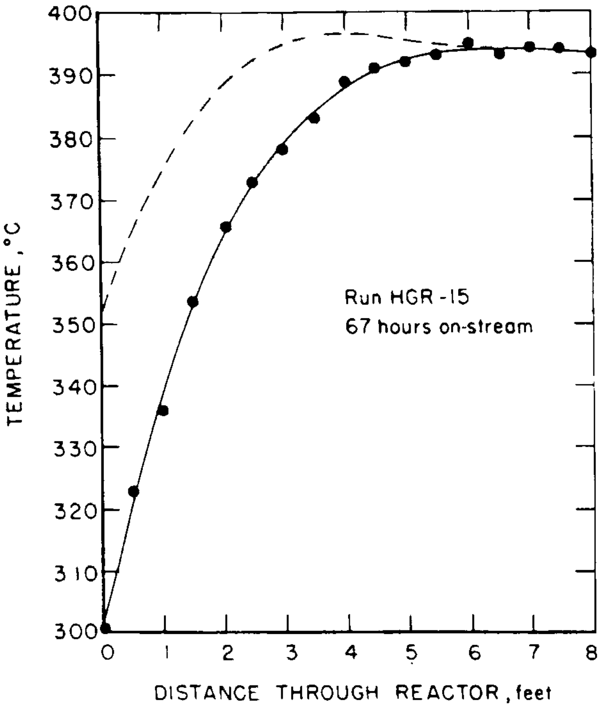

FIGURE 3. - Catalyst and gas temperature profiles at 67 hours on-stream.

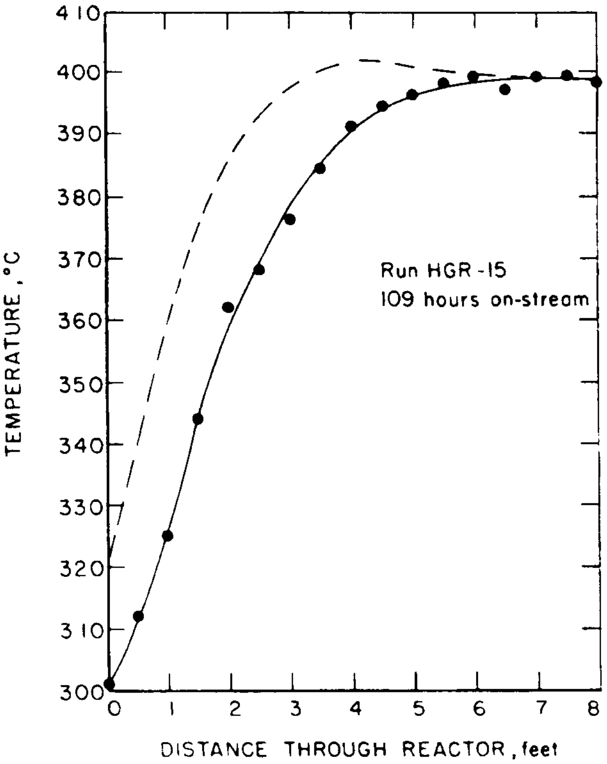

FIGURE 4. - Catalyst and gas temperature profiles at 109 hours on-stream.

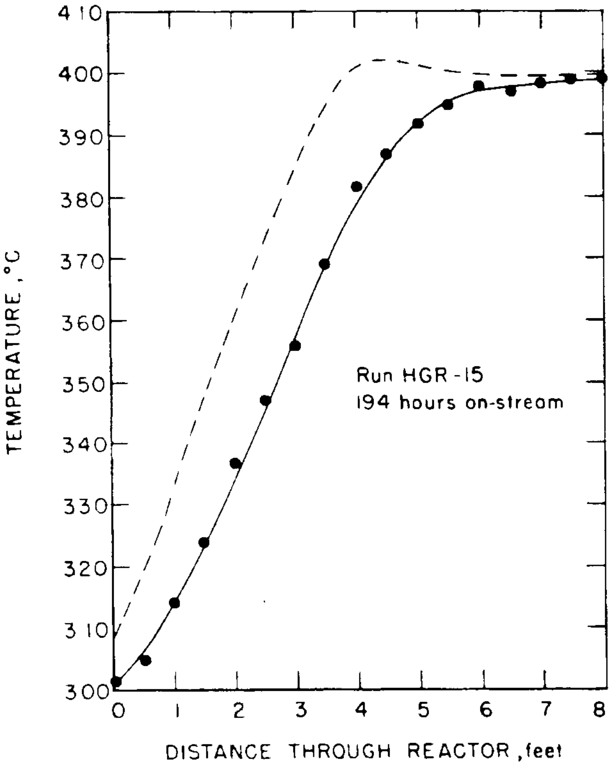

FIGURE 5. - Catalyst and gas temperature profiles at 194 hours on-stream.

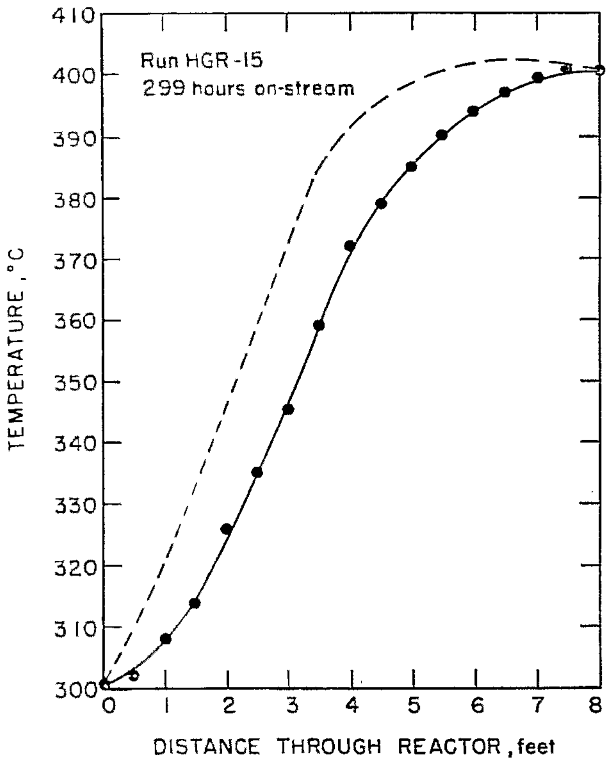

FIGURE 6. - Catalyst and gas temperature profiles at 299 hours on-stream.

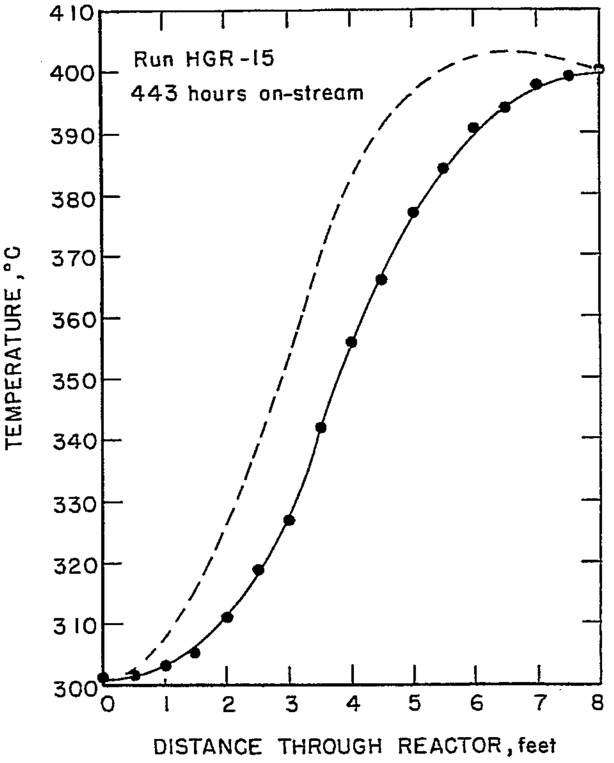

FIGURE 7. - Catalyst and gas temperature profiles at 443 hours on-stream.

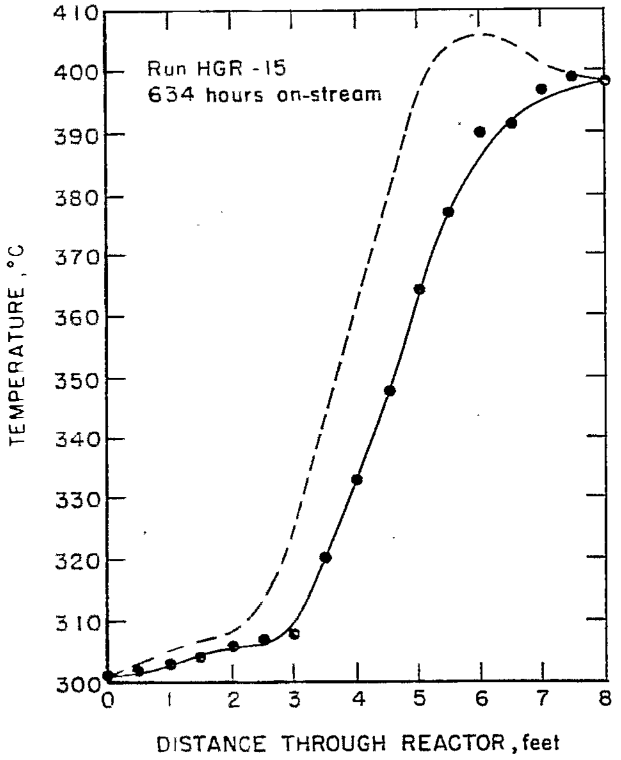

FIGURE 8. - Catalyst and gas temperature profiles at 634 hours on-stream.

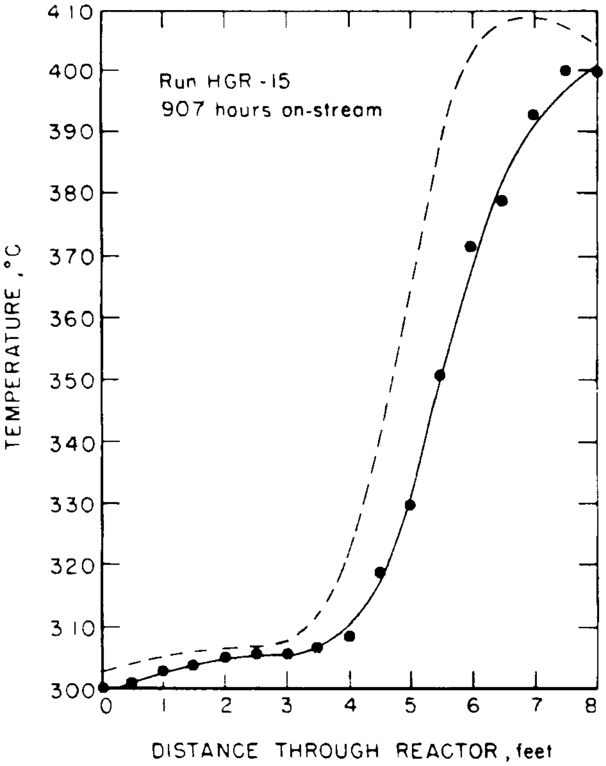

FIGURE 9. - Catalyst and gas temperature profiles at 907 hours on-stream.

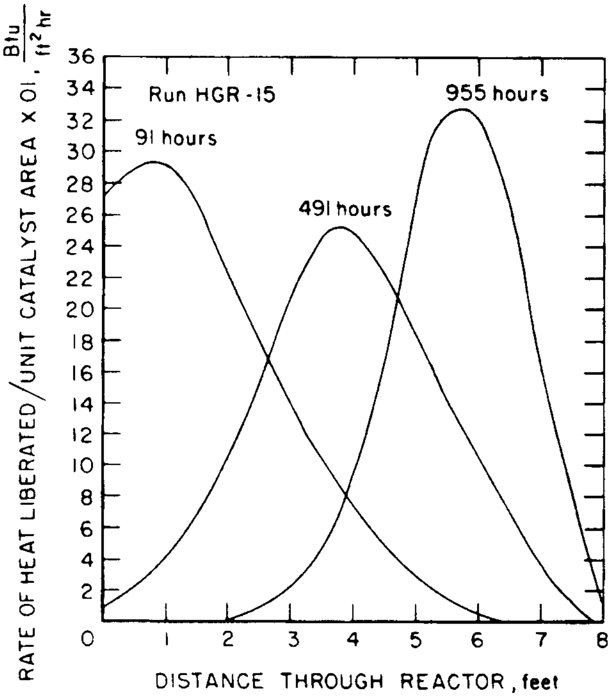

FIGURE 10. - Heat liberation profiles for different times on-stream.

SUMMARY

Catalyst temperature profiles were calculated for a hot-gas-recycle methanation reactor. These temperature data indicate that no portion of the Raney nickel catalyst reached excessive temperatures. It has been shown (10) that in the extreme case where the global reaction rate is mass transfer controlled, the catalyst-gas temperature difference cannot exceed 0.7 of the adiabatic temperature rise. For the hot-gas-recycle methanator described in this paper, the maximum temperature difference attainable would be approximately 70° C. The greatest temperature difference calculated for run HGR-15 was 52° C. The catalyst temperature profiles will be utilized to estimate the intrinsic reaction rate in subsequent reactor modeling that incorporates catalyst deactivation.

The catalyst temperature profiles, when viewed with respect to time on-stream, indicate that the reactor is deactivating zonally. Laboratories are in a continuing search of techniques for performing accelerated lifetime tests on catalysts or means with which to project the lifetime of a catalyst. The method leading to the plot shown in figure 11 may prove to be quite useful

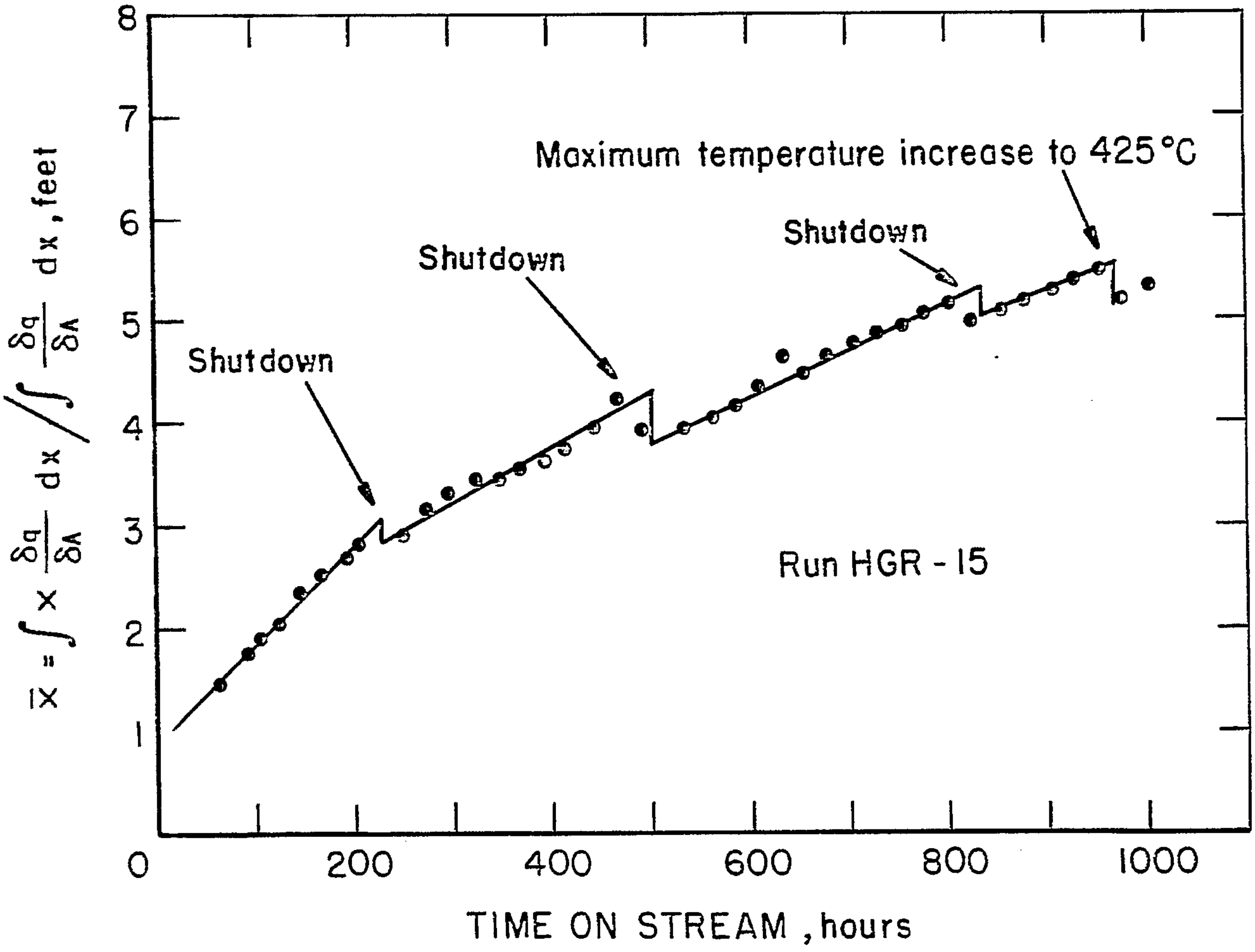

FIGURE 11. - Time dependence of the mean position of the reaction zone.

for predicting the lifetime of the particular type of catalytic reactor described previously, although additional runs with a minimal number of shutdowns will be required to support this idea.

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APPENDIX

A useful technique for fitting or "smoothing" a set of experimental data points, $\{x_i, y_i\}, 1 \leq i \leq N$, is the sliding polynomial. This method is of value when the entire set of data points may not be well fitted to a simple analytic function. (A Fourier series is, of course, a combination of simple analytic functions which may be used to represent such a data set.)

Consider a hypothetical set of data, such as illustrated in figure A-1, and suppose that one requires the m th derivative of y with respect to x at $x = x_k$, $1 \leq k \leq N$. This derivative may be calculated from the least-squares fit of an n th order polynomial, $y = \sum_{i=0}^{n} \xi_i x^i$, $n \geq m$, to a subset of the experimental data numbering $\ell = \ell_2 - \ell_1 + 1 \geq n + 1$, with the central point being x_k, y_k. The vector, $\{\xi'_i\}$, is the solution of the matrix equation

$$a_{ef} \; \xi_f = b_e ,$$

where

$$a_{ef} = \sum_{i=\ell_1}^{\ell_2} x_i^e x_i^f \qquad o \leq e \leq n \; ; \; o \leq f \leq n$$

$$b_e = \sum_{i=\ell_1}^{\ell_2} y_i x_i^e \qquad o \leq e \leq n .$$

The m th derivative of y with respect to x at $x = x_k$ is then

$$D^m y = \sum_{i=m}^{n} \frac{\xi_i \; (i!)}{(i-m)\,!} \; x^{i-m} .$$

The phraseology "sliding polynomial fit" is derived from the fact that the preceding algorithm may easily be used in a computer program to generate the least-squares fit of a function and its derivatives to the entire set of data points by simply "sliding" the required subset of points along the curve. The beginning and end of the experimental curve are exceptional in that the first or last $\frac{\ell}{2} + 1$ points must be calculated with the same polynomial.

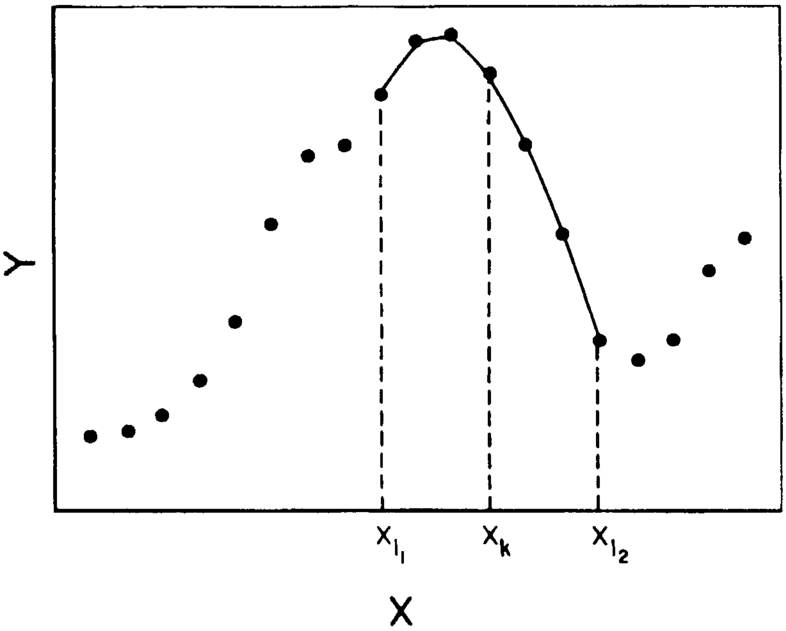

FIGURE A-1. - Plot of a hypothetical set of data.

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