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CATALYST DEACTIVATION IN HOT-GAS-RECYCLE METHANATION REACTORS: ADUATHEMATICAL MODEL

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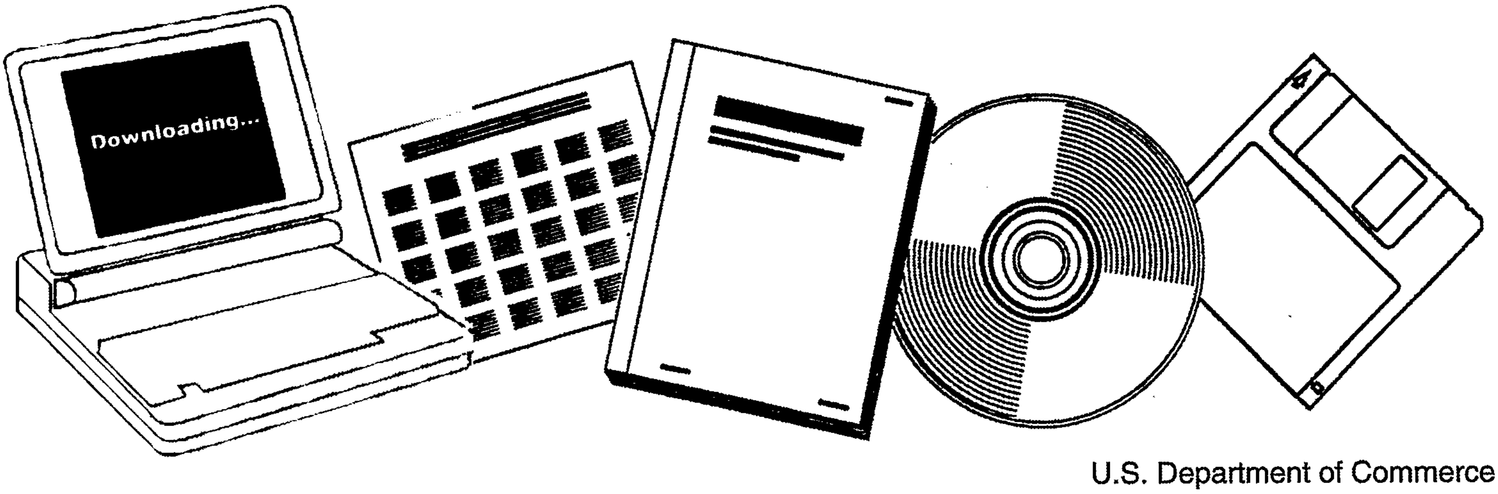

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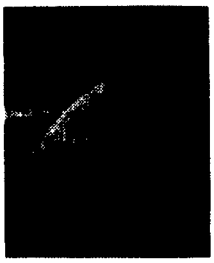

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CATALYST DEACTIVATION IN HOT-GAS-RECYCLE METHANATION REACTORS: A MATHEMATICAL MODEL

by

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

ABSTRACT

A mathematical model of the catalyst deactivation process occurring in the Energy Research and Development Administration methanation reactors is presented. The mechanism for the deactivation is postulated to obey an irreversible Langmuir-Hinshelwood type of rate expression for the formation of adsorbed poison on the catalyst surface. The model is utilized to simulate the performance of a typical hot-gas-recycle methanation run.

INTRODUCTION

The problem of catalyst deactivation is of great current interest in many industrial applications. Typically, in gas-solid catalytic reactions, the activity of the catalyst decreases with time on stream. Such poisoning can often be traced to deposition on the catalyst of a substance which reduces the active surface for the main reaction. Quantitative study of the activity-time relation is important in seeking the optimum design and operation of the reactor.

The poisoning of a catalyst may be induced by several different mechanisms. The poisoning may be caused by a side reaction involving the same reactants as the main reaction (a parallel fouling mechanism). Alternately, the deposited material may be the result of further reaction of the primary product (a series fouling mechanism). Still another possibility is deactivation induced by an independent reaction involving different reactants, for example, an impurity in the feed to the reactor (an independent poisoning mechanism). An additional phenomenon which leads to the deactivation of a catalyst, not associated with reactants, products, or impurities in the process stream, is that of sintering of the catalyst which leads to a decrease of active catalyst surface. In each case the extent of deposition, or deactivation, will depend upon time and position within the catalyst bed. Phenomena relating to catalyst deactivation have been considered extensively in the literature over the past few decades (2, 3, 7, 12, 13, 14, 15, 16, 19, 20, 22, 23, 24, 25, 28, 32, 33). This communication is not considered to be a survey of the field and only a few of the many significant publications are cited.

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[1] Research physicist
[2] Supervisory chemical engineer
[3] Research supervisor

A recent publication (26) presented a mathematical model, along with its application, of a tube-wall methanation reactor to be utilized in the Energy Research and Development Administration Synthane Process (10, 11). This model made no provisions for deactivation of the catalyst. The object of this paper is to improve the mathematical model by taking into account catalyst deactivation with increasing time on stream,and to extend the model to applications in hot-gas-recycle methanation (4, 5, 8, 9).

The catalyst used in methanation reactors associated with the Synthane Process is Raney nickel powder, flame-sprayed onto a stainless steel substrate. The aluminum is leached from the coating leaving a highly porous nickel catalyst approximately 0.025 inches thick. The mechanism responsible for deactivation of this catalyst is not well understood at the present time. It is possible that deactivation is caused by several processes acting simultaneously, such as sintering, poisoning by trace amounts of sulfur in the feed stream, and trace amounts of iron carbonyl depositing iron at an active site which subsequently acts as a center for carbon deposition.

The model presented in the forthcoming sections presupposes the following. First, the catalyst is poisoned via some mechanism independent of that of the main reaction, that is, the feed contains a trace amount of some unspecified poison. The reactions may be written

$$CO + 3H_2 \overset{k}{\rightleftharpoons} CH_4 + H_2O \qquad \text{(main reaction, fast)}$$

$$P \xrightarrow{k_P} W \qquad \text{(poisoning reaction, slow)}$$

It is assumed that the poison reaction is much slower than the main reaction. Consequently, the main reaction may be assumed to approach a steady state behavior over short periods of time. This assumption has the effect of decoupling the equations associated with the main reaction model, from those associated with the poisoning model. Second, since there is little experimental evidence with regard to the poisoning mechanism an irreversible Langmuir-Hinshelwood type of expression for the rate of formation of adsorbed poison is assumed.

METHANATION REACTION MODEL

A mathematical model for tubewall methanation reactors has been previously described (26) along with several applications of the model. The model to be described in this communication is similar in many respects to the tube-wall model in that it accounts for both bulk diffusion and kinetic resistence and is applicable only to reactors operating in turbulent flow. The significant differences between the models are as follows:

(1) The Energy Research and Development Administration's tube-wall methanation reactors operate under near isothermal conditions (~390°C), whereas, the hot-gas-recycle methanators operate adiabatically, using cooled recycle gas to remove the heat of reaction. The gas temperature rise across the catalyst bed in a typical hot-gas-recycle methanator is from 300°C to 400°C. As a result of this nonisothermal condition, the effect of temperature upon the physical properties of the gas must be taken into account.

(2) The previous model utilized the rate expression given by Wen (31) for the consumption of CO, namely

$$-r_w = k_w \tilde{C}_{co}^{\,0.7} \, \tilde{C}_{H2}^{\,0.3} \, , \tag{1}$$

where k_w is the rate constant, ft/hr, (in this communication, rate constant and catalyst activity constant will be used synonymously) and $\tilde{C}_{co}$ and $\tilde{C}_{H2}$ are the CO and H_2 concentrations at the catalyst surface, respectively, lb mole/ft^3. More recently, A. L. Lee at IGT developed a rate expression (17, 18) which fits all the data from the literature and data reported by IGT. Lee's rate expression is of the form

$$r_L = \frac{A_1 \, e^{-E/RT'} \, P_{co} \, P_{H_2}^{\,0.5}}{1 + K_2 \, P_{H_2} + K_3 \, P_{CH_4}} \, , \tag{2}$$

where A_1 is the frequency factor, K_2 and K_3 are equilibrium constants, P_i are partial pressures, psig, r_L is the rate of methane formation, lb mole./hr - g catalyst, E is the activation energy, Btu/lb mole, R is the universal gas constant, Btu/°R-lb mole, and T' is the gas temperature, °R. This rate expression was developed using data from commercial supported nickel catalysts. A modified form of equation 2 is used in this study, along with the assumption that a rate model of this form may be extended to surface catalyzed methanation reactors.

(3) Perhaps the most significant change in the reactor model that was previously reported is the encorporation of a catalyst deactivation process. A mechanism for catalyst deactivation is postulated and equations governing the activity of the catalyst bed as a function of time on stream and position in the bed are derived and solved.

Since the catalyst is deposited in a very thin layer, the catalyst thickness is neglected in this model, and the catalyst is considered to be only an active superficial surface. The form of equation 2 used to describe the kinitics in the present model is

$$-r = A \, e^{-E/RT} \, \tilde{C}_{co} \, \tilde{C}_{H_2}^{\,0.5} \, , \tag{3}$$

where A is the frequency factor, r is the rate of CO conversion, lb mole/hr-ft^2 superficial catalyst surface, and T is the catalyst temperature, °R. The denominator in equation 2 has been neglected in writing equation 3. The volume of recycled product gas in a hot-gas-recycle methanator is on the order of ten times that of the fresh feed. As a result, hydrogen and methane concentrations do not change appreciably with distance through the catalyst bed. The denominator term involving the concentration or partial pressure of H_2 decreases while the one involving CH_4 increases, thus, tending to diminish any net change in the denominator. Typically, the denominator of equation 2 will change approximately 1 percent while the numerator changes two orders of magnitude. Hence, little error is introduced by simplifying to equation 2.

Carbon monoxide is the limiting reactant in the hot-gas-recycle methanator. Inlet H_2/CO ratios are typically on the order of four to five while the stoichiometric ratio for the methanation reaction is three. This, coupled with the higher diffusivity of hydrogen (approximately three times that of CO), leads to to the further simplification of equation 3:

$$\tilde{C}_{H_2} = C_{H_2}$$

and therefore

$$-r = A\ e^{-E/RT}\ \tilde{C}_{co}\ C_{H_2}^{\frac{1}{2}}. \qquad (4)$$

The assumption that the hydrogen concentration at the catalyst surface is the same as the bulk hydrogen concentration is equivalent to neglecting the diffusion resistance of hydrogen to the catalyst surface.

At steady state conditions there is no net change in the reactant concentrations at the catalyst surface. Thus, the rate of reaction must be equal to the rate at which CO diffuses through the laminar film to the catalyst surface. The mass transfer rate is given by

$$-r = k_c\ (C_{co} - \tilde{C}_{co})\ , \qquad (5)$$

where k_c is the film mass transfer coefficient, lb mole/hr-ft^2-concentration difference. The mass transfer coefficient is determined from the standard j-factor correlation (29, 30). For a given Reynold's number, the value of j may be read from figure 1, curve 1.

Equations 4 and 5 may easily be solved for $\tilde{C}_{co}$ giving

$$\tilde{C}_{co} = C_{co} k_c\ /\ (k_c + A\ e^{-E/RT}\ C_{H_2}^{\ 0.5})\ .$$

Substitution of the expression for $\tilde{C}_{co}$ into either equation 4 or 5 yields the global reaction rate expression in terms of the bulk concentrations;

$$-r = k_c\ C_{co}\left[1 - 1/\ \ (1 + \frac{A}{k_c} e^{-E/RT}\ C_{H_2}^{\ 0.5})\right]. \qquad (6)$$

Since the reactor is operating adiabatically, there is an appreciable temperature dependence in the global rate expression which is accounted for through an Arrhenius type expression. Knowledge of the catalyst temperature is required to evaluate this expression, hence, we write

$$-r\,\mathcal{H} = h\ (T - T_B) \qquad (7)$$

and

$$-r\,\mathcal{H} = C_p M\ \frac{\partial T_B}{\partial\ a} \qquad (8)$$

where $\mathcal{H}$ is the heat of reaction (Btu/lb mole of CO converted to CH_4), h is the film heat transfer coefficient (Btu/hr-ft^2-°C), C_p is the specific heat of the gas (Btu/lb mole-°C), M is the gas molar flow rate (lb mol/hr), T_B is the bulk gas temperature, and a is superficial catalyst surface area (ft^2). The film heat transfer coefficient is calculated in a manner similar to that of the mass transfer coefficient (Figure 1, curve 2). Equation (8) is used to calculate the gas temperature as a function of distance through the reactor, and given T_B, the catalyst temperature may be estimated from equation 7.

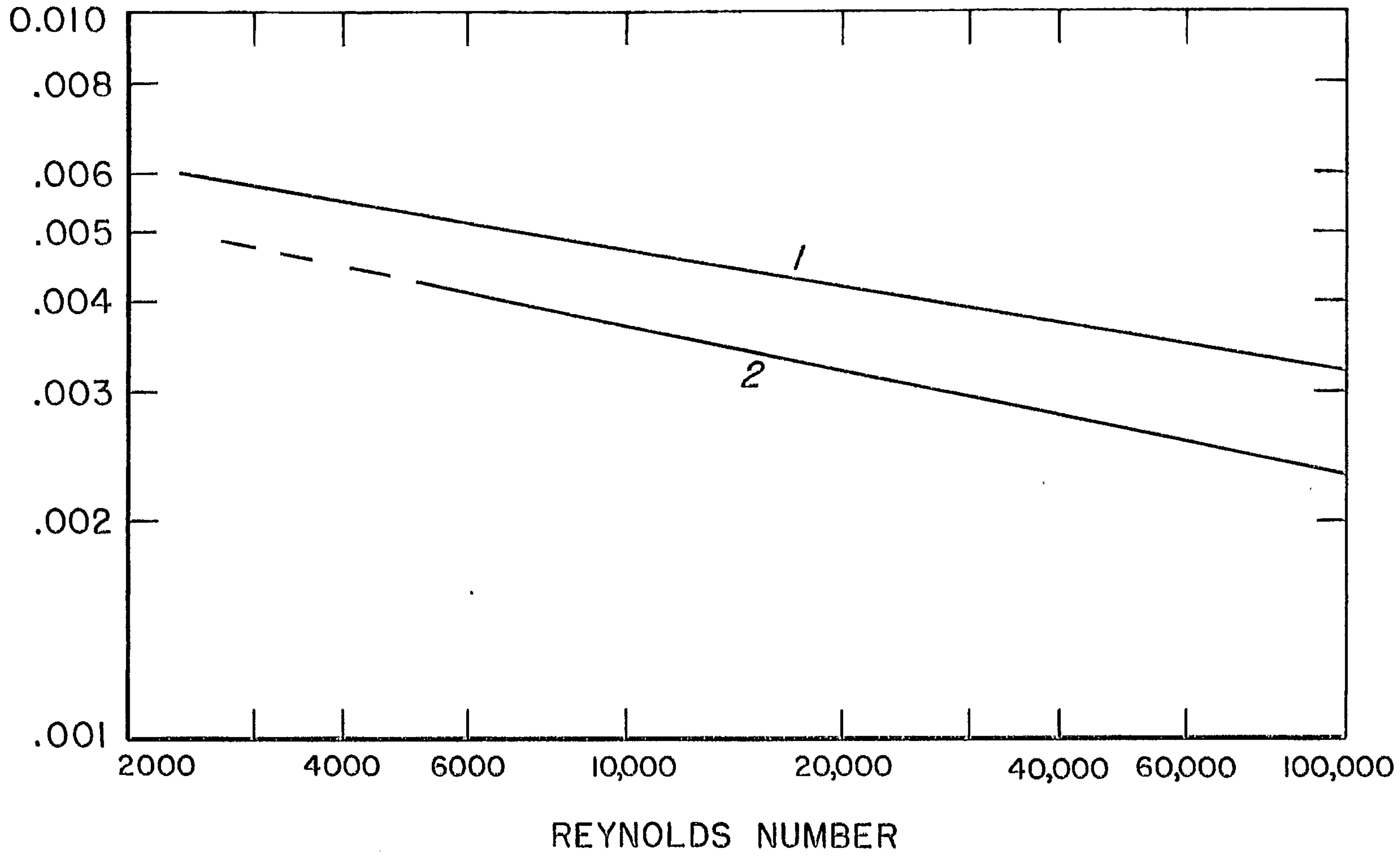

Figure 1. - Mass and heat transfer correlations for flow inside pipes

POISONING REACTION MODEL

The poisoning mechanism assumed in this paper is that of the irreversible adsorption of compounds other than the principle reactants and products on the catalytically active sites. This is commonly referred to as type I, or independent poisoning. In the absence of any experimental evidence to the contrary, it is reasonable to assume an irreversible Langmuir-Hinshelwood type of expression for the rate of formation of adsorbed poison:

$$r_P = k_P C_P (1 - W/W_s) \quad , \tag{9}$$

where k_P is the first order rate constant for poisoning, ft/hr, C_P is the concentration of poison in the stream, lb mol/ft^3, W is the concentration of adsorbed poison on the catalyst surface, lb mol/ft^2, W_s is the value of W corresponding to complete deactivation of the catalyst, and r_P is the rate of formation of adsorbed poison, lb mol/ft^2-hr.

In terms of the dimensionless groupings

$$\psi = W/W_s$$

$$\phi = C_P/C_P^\circ$$

$$\theta = k_P C_P^\circ t/W_s \quad , \tag{10}$$

where C_P° is the concentration of poison at the reactor inlet, lb mole/ft^3, the equation for the poisoning rate may be expressed as

$$\frac{\partial\psi}{\partial\theta} = \phi(1-\psi). \tag{11}$$

Equation 11 can be solved simultaneously with a differential mass balance of the poison species across an element of catalyst surface,

$$\frac{\partial C_P}{\partial a} + \frac{1}{V} r_P = 0 \quad , \tag{12}$$

where V is the volumetric flow rate at operating temperature and pressure.

The following assumptions must be made if equations 11 and 12 are to describe the temporal and spatial dependence of C_P in the catalyst bed. (1) External mass transfer resistance is neglected. In other words, the poisoning is reaction controlled with the reaction rate given in equation 11. (2) The catalyst is considered to be only an active superficial surface. (3) Volumetric contraction of the gas due to the methanation reaction is neglected.

Substituting equation 11 into equation 12, along with definitions $\lambda = a/a_o$ and $N_P = a_o k_P/V$, where a_o is the total superficial catalyst area, we arrive at

$$\frac{\partial\phi}{\partial\lambda} + N_P \phi (1-\psi) = 0. \tag{13}$$

Equations 11 and 13 must be solved simultaneously for ψ and ϕ as functions of λ and θ. If the catalyst bed is initially free of adsorbed poison and the concentration of poison precursor in the feed remains constant with time, then the following boundary conditions are applicable:

$$\psi(0,\lambda) = 0$$
$$\phi(\theta,0) = 1 \qquad (14)$$

The analytical solution of this system is rather tedious. It has, however, been solved in closed form by Bohart and Adams (6) and in more general terms by Amundson (1). The solution is,

$$\psi(\theta,\lambda) = (1-e^{-\theta})/(1+e^{-\theta}(e^{Np\lambda}-1)). \qquad (15)$$

The function $\psi(\theta,\lambda)$ may be directly related to the catalyst activity at any point (t,A) as follows:

$$A = A_{initial} \ (1 - \psi) \qquad (16)$$

provided that the initial catalyst activity is uniform over the entire catalyst bed.

$\psi(\theta,\lambda)$ has, essentially, two parameters which must be determined from experiment as there is insufficient independent data to predict them a priori. Let these parameters be called p_1 and p_2, and be defined by

$$\theta = p_1 t$$
$$Np\lambda = P_2 a \qquad (17)$$

From previous definitions, it may be recognized that $p_1 = k_p C_p°/W_s$ and that $p_2 = Np/a_o = k_p/V$. At a given time on stream, t, and for particular values of P_1 and P_2, the general shape of the function $(1 - \psi)$ is shown in figure 2-A. The ratio P_1/P_2 is a measure of the "velocity" of the deactivation front as it traverses the catalyst bed while P_2 has the effect of making the deactivation front more or less sharply defined (see figure 2-B). A more detailed analysis of the dependence of the deactivation profile "velocity" and shape upon P_1 and P_2 is given in appendix A.

Combining equations 6 and 16 results in

$$-r = -\frac{dM_{co}}{da} = k_c C_{co}\left\{1 - 1/\left[1+\frac{A_{initial}}{k_c}\ e^{-E/RT}\ C_{H_2}^{\ 0.5}\ \left(1-(1-e^{-\theta})/(1+e^{-\theta}.(e^{N_{P}\lambda}-1))\right)\right]\right\}$$

which, along with equations 7 and 8, constitute the quasi steady state design equations for the reactor. M_{co} is the CO molar flow rate at some point in the catalyst bed.

APPLICATION

The mathematical model was applied to the reactor experiment HGR-15. The reactor consisted of an 8 foot bed of stainless steel grids flame-sprayed with Raney-nickel. Each grid assembly contained 15 plates 0.05 inches thick and 6 inches long. Individual plates were separated from one another by spacers 0.135 inches thick. As indicated in figure 3, adjacent grid assemblies were rotated

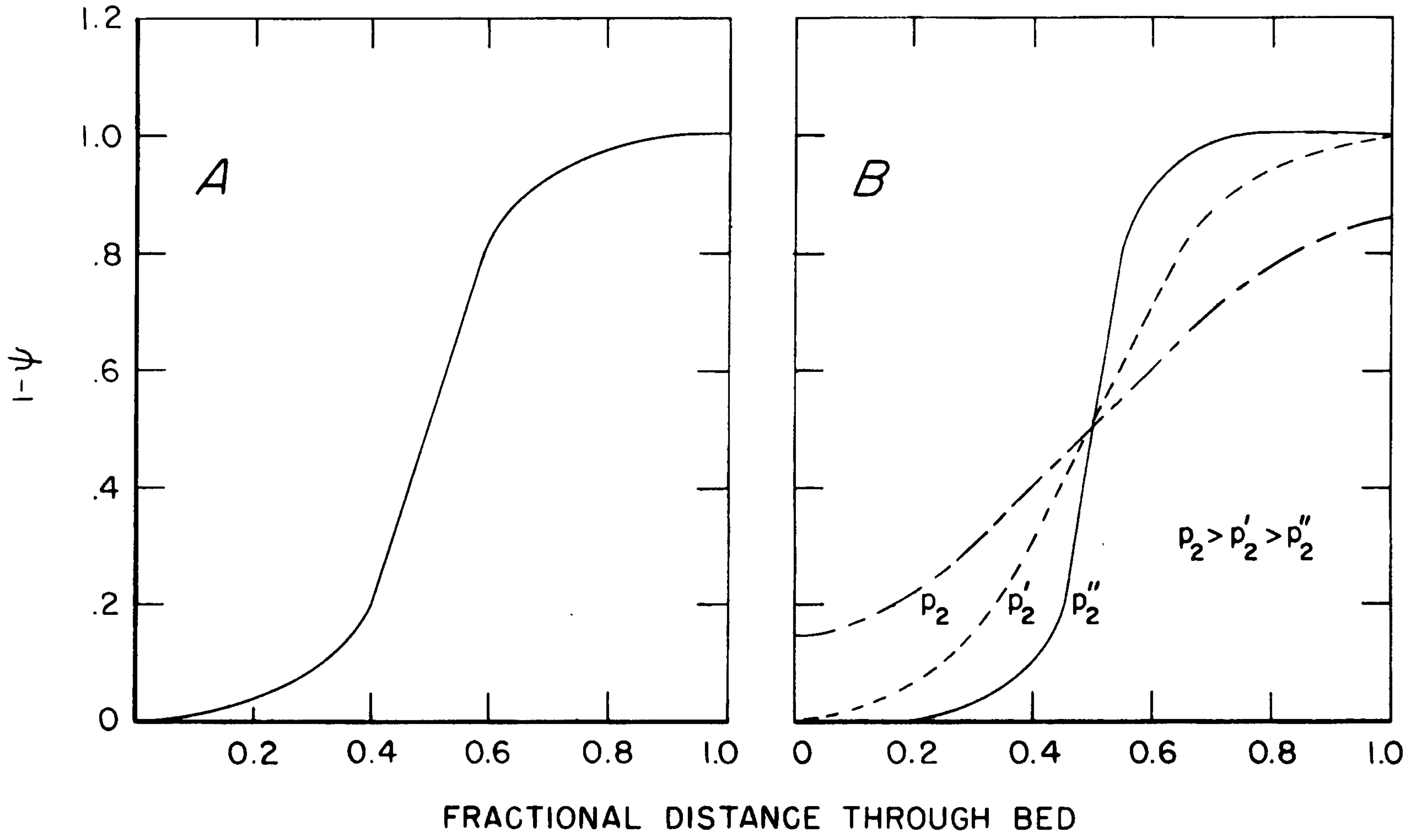

Figure 2. - Activity profiles for a fixed bed reactor

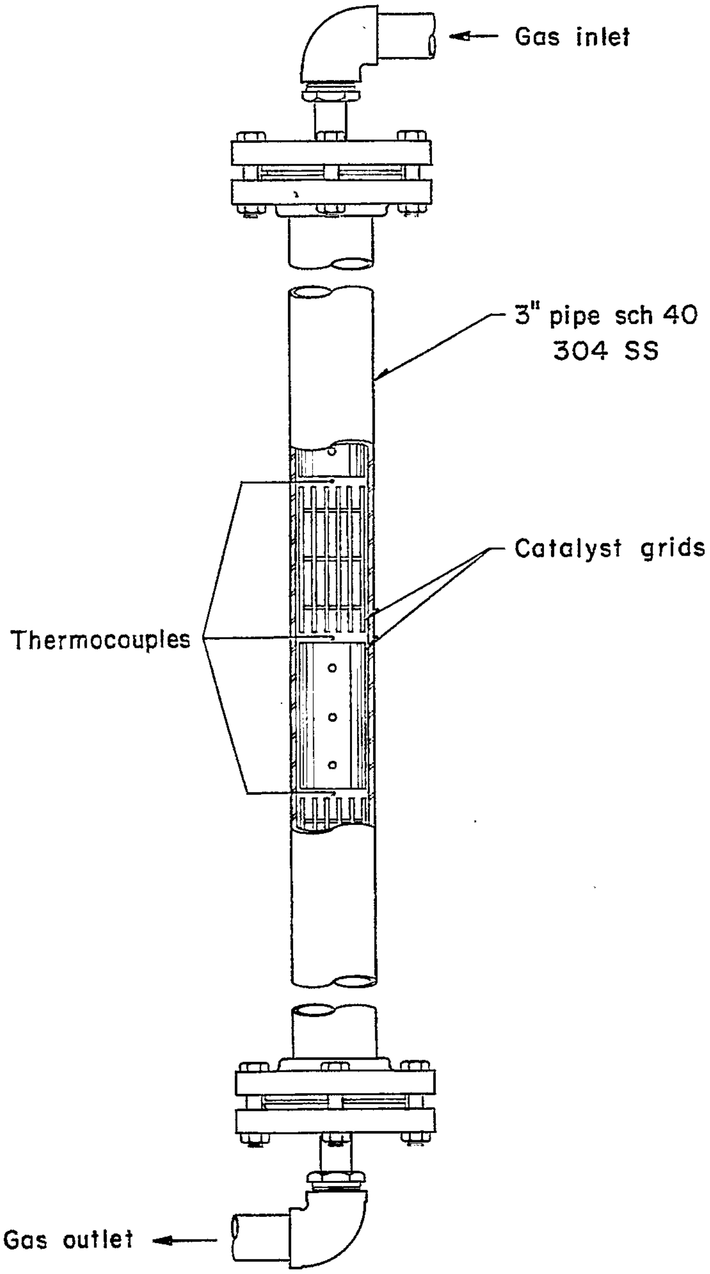

Figure 3. - Hot-gas-recycle methanation reactor

90° with respect to each other. The catalyst bed was contained in a 3-inch schedule 40 stainless steel pipe. The system was designed for approximately 10/1 recycle to fresh feed ratio so as to allow a 100° C temperature rise in the catalyst bed with inlet gas being 300° C and exit gas being 400° C. The reactor was operated at a space velocity of approximately 20 J (1 J = 1 scfh CO + H_2 per square foot of catalyst surface). The reactor was on stream for 1300 hours at which point in time the CO in the product stream was about 1 mole percent. Gas stream temperatures were measured at 6-inch intervals throughout the catalyst bed except in the central region of the bed where temperature probes were placed every 12-inches. Gas stream compositions were measured at the inlet, 1/4 and 3/4 of the distance through the catalyst bed, and at the exit of the reactor.

The model outlined in the previous section has, essentially, three parameters that must be obtained from experimental data; $A_{initial}$, p_1 and p_2. k_c and h, the mass and heat transfer coefficients, respectively, may be estimated from the correlation shown in figure 1 and the activation energy, E, is taken to be 1.25×10^4 Btu/lb mol (17). Ideally, $k_{initial}$ can be determined from data obtained early in the run when deactivation of the catalyst bed is negligible using a technique similar to that described in an earlier publication (26). Likewise, the ratio p_1/p_2 may be estimated by measuring the 'velocity' of the reaction zone as it moves down the reactor. Data of the type illustrated in figures 4 and 5 are suitable for this measurement. Profiles of the rate of heat liberated per unit catalyst area, which is proportional to the global reaction rate, are shown in figure 4 for different times on stream. These curves were calculated from the derivative of the experimental temperature profiles (see (27)). This leaves only p_1 or p_2 to be fitted to experimental temperature profile data by trial and error.

Unfortunately, it is difficult to maintain constant operating conditions with no interruptions throughout an experiment that may last for thousands of hours. Figure 5 is a plot of the arithmetic mean position of the reaction zone, $\overline{x}$, as a function of time on stream. The graph indicates several unscheduled shut-downs which were caused by power-outages or repair to equipment. During a shut-down, the reactor is purged and maintained in a 50 to 100 psig hydrogen environment, which accounts for the partial recovery of the catalyst activity after an interruption. An analytical solution to the poisoning model such as that given in the previous section cannot account for this type of change in the catalyst activity. Figure 5 also indicates that the concentration of poison in the feed may not have remained constant over the entire run since the slope of the line segments between consecutive shut-downs differ.

No attempt was made to account for the changes in activity due to shutdowns throughout the run. A larger value of p_1 was used, however, in the range $0 \leq t \leq 207$ hours than for times in the range $t > 207$ hours in order to account for the apparent more rapid initial deactivation rate early in the run. This is tantamount to an increased poison concentration in the feed stream early in the run and violates the set of boundary conditions (equations 14). At 207 hours on stream the hot-gas-recycle compressor was overhauled. Prior to this time it is possible that the catalyst was exposed to higher concentration of oil vapor from the compressor. Equations 11 and 13 were solved numerically yielding a solution of a form similar to equation 15. A fit of the model to experimental data, using an activation energy 1.25×10^4 Btu/lb mol yielded the values $A_{initial} = 1.09 \times 10^6$, $p_1 = 0.0114$

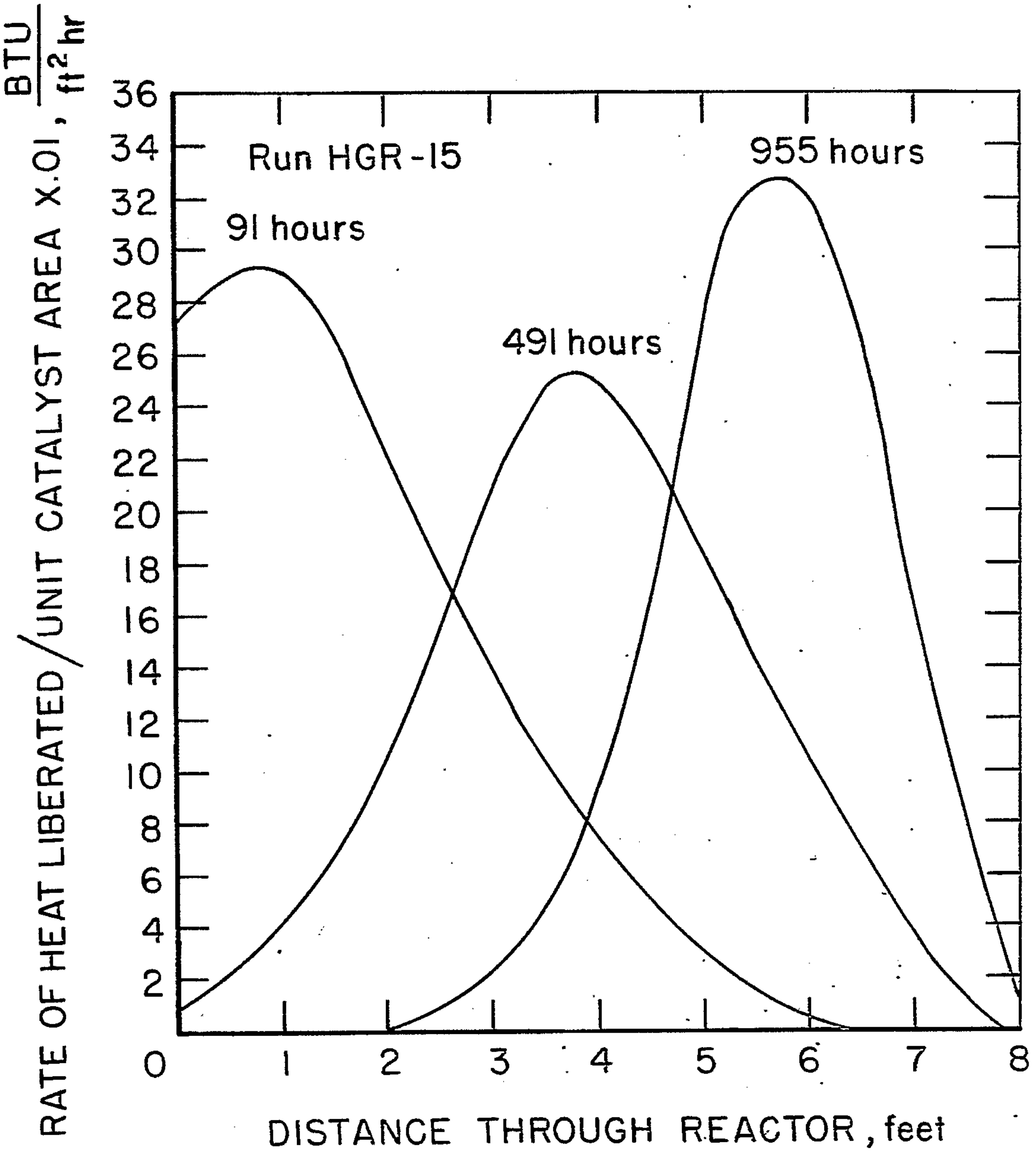

Figure 4. - Heat liberation profiles for different times on stream

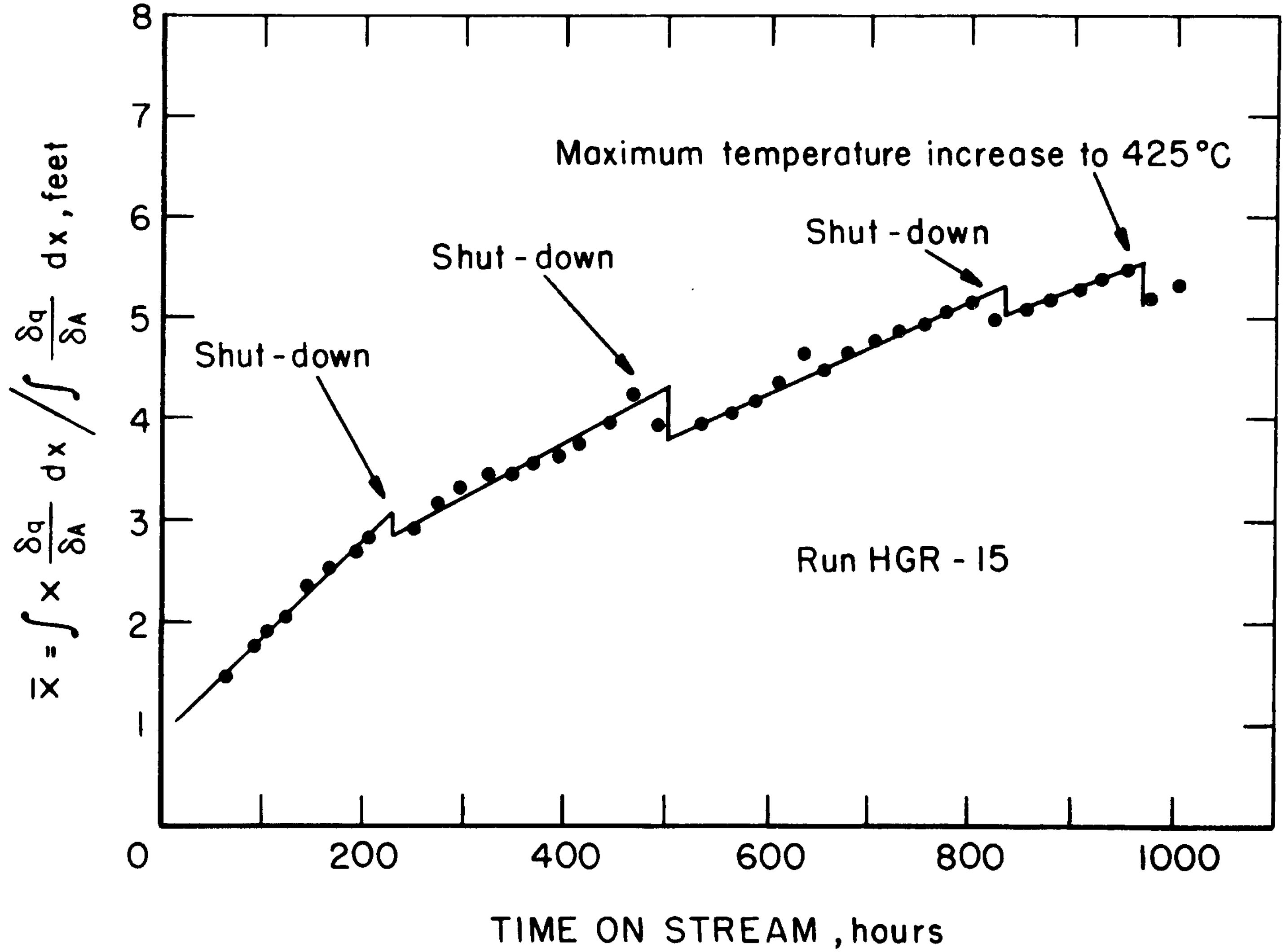

Figure 5. - Times dependence of the mean position of the reaction zone

and 0.00625, and $p_2 = 0.2$. Typical comparisons of the model predictions with experimental data are shown in figures 6 and 7. Figure 6 illustrates the fit of calculated gas temperature profiles to experimentally measured temperatures for several different times on stream. Figure 7 compares the calculated and observed CO concentrations as functions of distance through the reactor and time on stream.

Figure 8 demonstrates a computer simulation of the experimental run (HGR-15) for the first 1150 hours. Agreement between model and experiment is seen to be remarkably good. At 950 hours the temperature rise through the catalyst bed was increased to 125° C. Figure 8 indicates that the model responded to this change in parameter rather well. Figure 9 is a comparison of calculated catalyst temperature with experimental and calculated gas temperatures at 347 hours on stream. The maximum temperature difference between catalyst and gas is approximately 20° C. The relative catalyst activity is also plotted to indicate the extent of catalyst deactivation at this time on stream.

SUMMARY

The deactivation of Raney nickel catalyst in an ERDA methanation reactor has been quantified in a mathematical model. The model assumes an independent poisoning mechanism with an irreversible Langmuir-Hinshelwood type of expression for the rate of formation of adsorbed poison on the catalyst.

Additional experiments must be performed to test the capability of the model to predict reactor performance under dimensional scale-up and different operating conditions such as total system pressure and space velocity. The largest source of uncertainty in the model is the accuracy of the heat and mass transfer correlations. Reynold's number for run HGR-15 fall in the range 4000 to 5000, and the literature cautions against the use of the j-factor correlation for Reynold's number less than 10,000. The transfer correlations used in the model are appropriate for turbulent flow through circular conduits. These correlations may be extended to conduits of other shapes provided the circular diameter is replaced by an effective diameter given by four times the hydraulic radius. The hydraulic radius is defined as the crossection area divided by the wetted perimeter. Extensions of these correlations to non-circular conduits frequently involve errors of up to 20 to 30 percent.

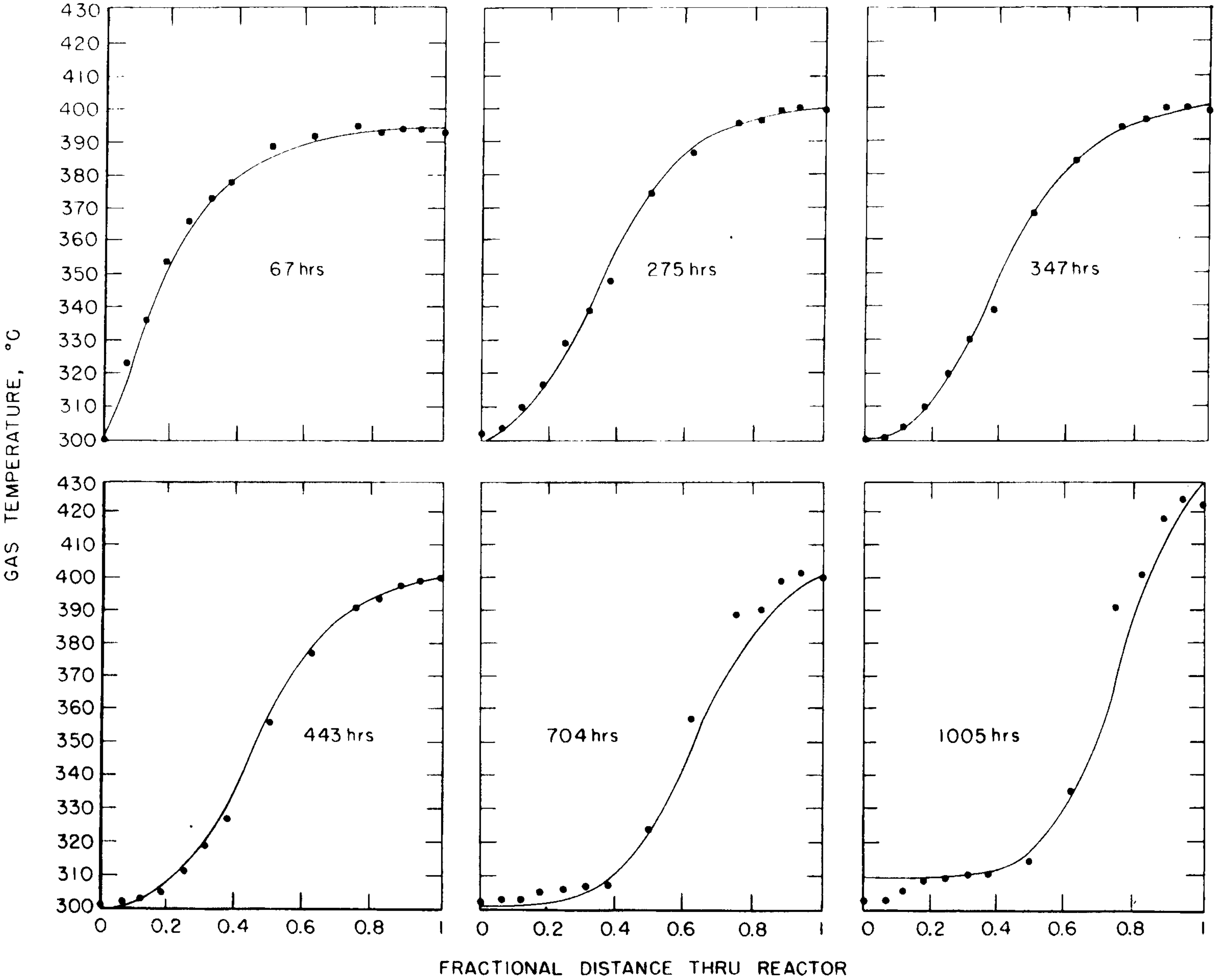

Figure 6. - Gas temperature profiles for different times on stream, model (———), experimental (●)

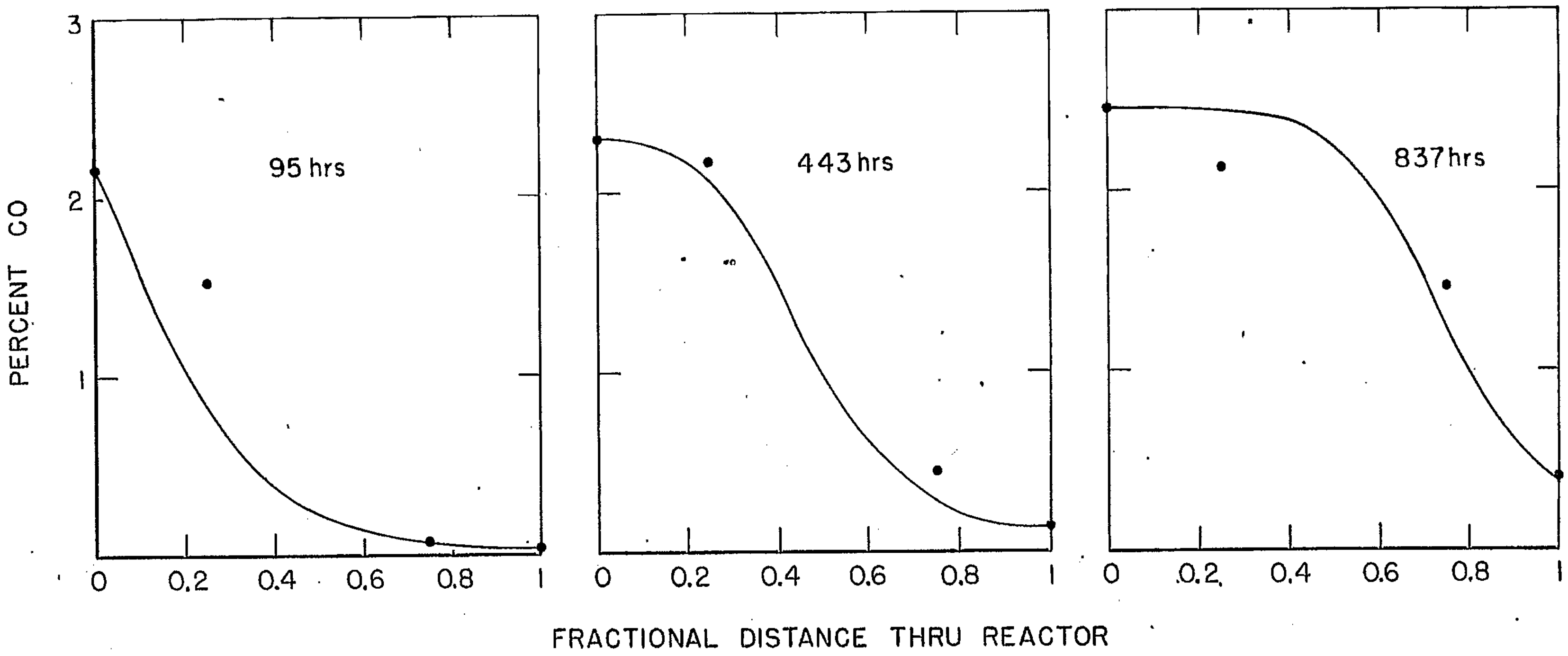

Figure 7. - CO concentration profiles for different times on stream, model (———), experimental (●)

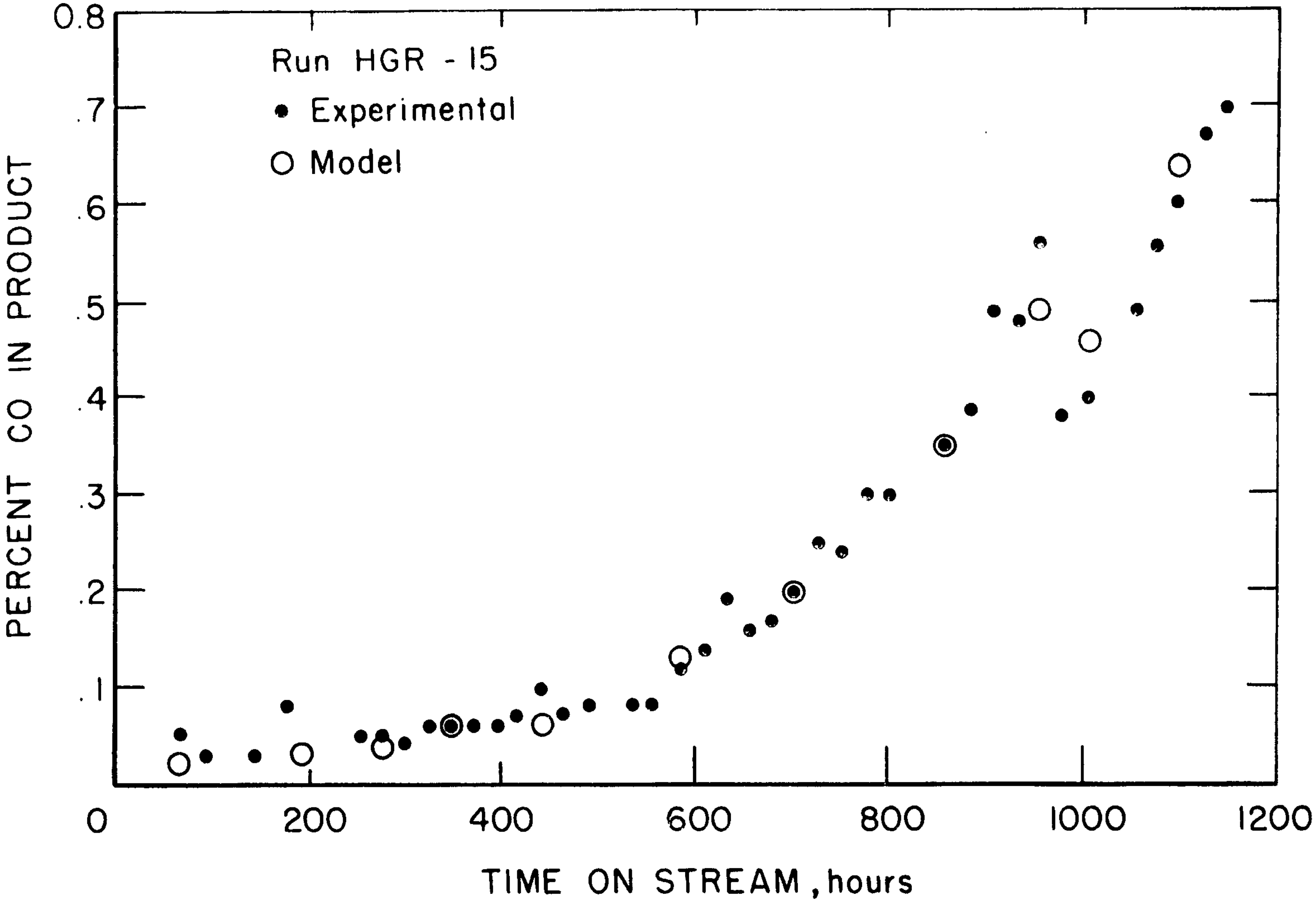

Figure 8. - CO concentration in the product stream as a function of time

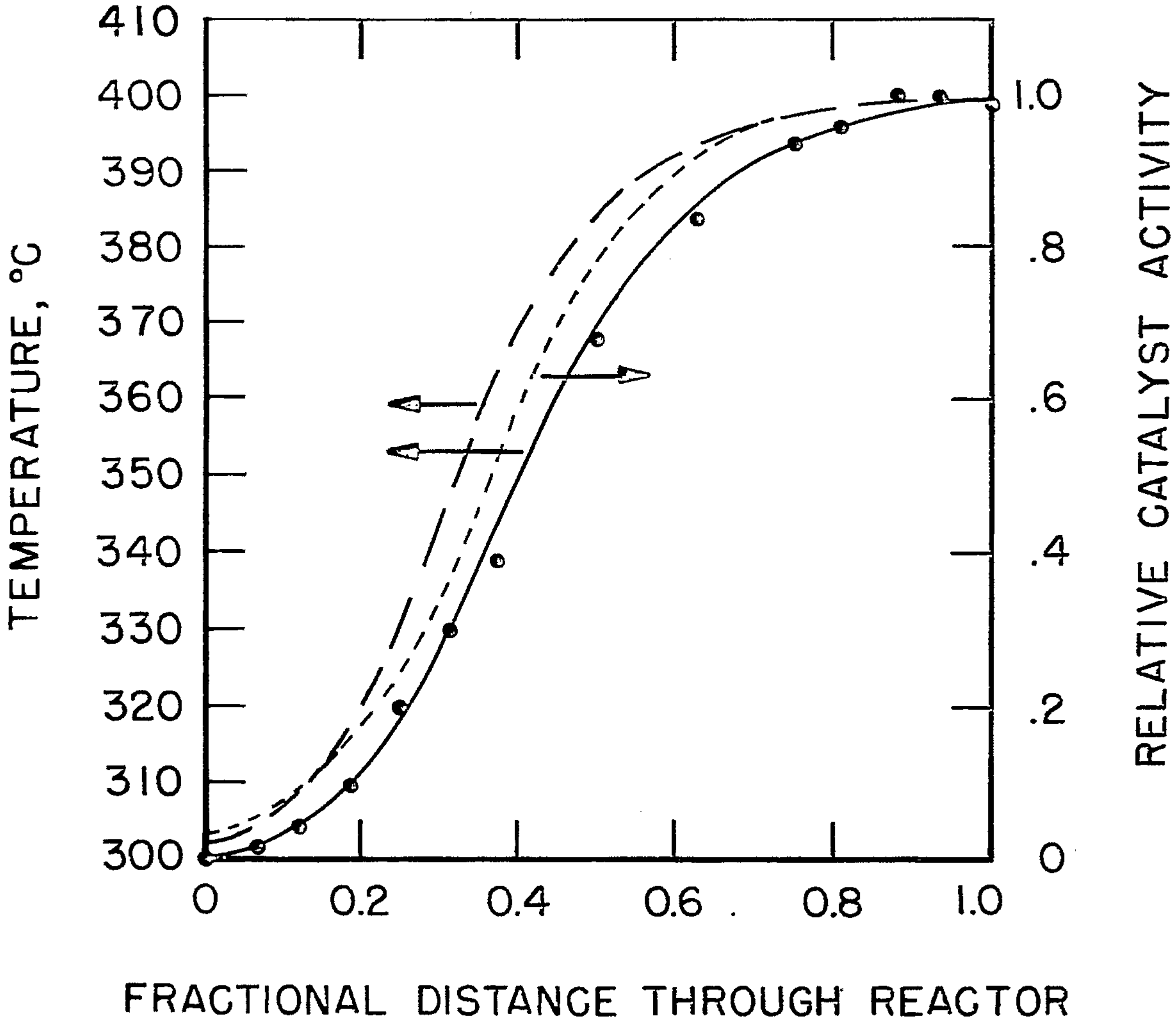

Figure 9. - Comparison of catalyst activity (-----) and gas (—●—) and catalyst (—— ——) temperature profiles

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APPENDIX

For given operating conditions, the deactivation front of the general shape as indicated in figure 2-A moves through the catalyst bed as the time on stream increases. The shape of the catalyst activity profile as a function of θ and λ is given by

$$1-\psi = 1 - (1-e^{-\theta})/(1 + e^{-\theta}(e^{N_P\lambda}-1)). \qquad \text{(A-1)}$$

In order to calculate the velocity of the deactivation front, it is convenient to define the time dependence of some characteristic point on the activity profile. One such point is the point of inflection, defined by

$$\frac{\partial^2\psi}{\partial\lambda^2} = 0 \qquad \text{(A-2)}$$

Thus, taking the necessary partial derivatives of ψ with respect to λ we have

$$\frac{\partial\psi}{\partial\lambda} = \frac{-e^{-\theta}(1-e^{-\theta})N_P e^{N_P\lambda}}{(1 + e^{-\theta}(e^{N_P\lambda}-1))^2} \qquad \text{(A-3)}$$

and

$$\frac{\partial^2\psi}{\partial\lambda^2} = \frac{N_P^2\, e^{-\theta}e^{N_P\lambda}\,(1-e^{-\theta})\left[2e^{-\theta}e^{N_P\lambda}-(1+e^{-\theta}(e^{N_P\lambda}-1))\right]}{(1 + e^{-\theta}(e^{N_P\lambda}-1))^3} \qquad \text{(A-4)}$$

Hence from equation A-2 one has

$$1 + e^{-\theta}(e^{N_P\lambda_I}-1) = 2e^{-\theta}e^{N_P\lambda_I}\ , \qquad \text{(A-5)}$$

which may be reduced to

$$\lambda_I = \frac{1}{N_P}\ln\,(e^{-\theta}-1). \qquad \text{(A-6)}$$

λ_I is the value of λ corresponding to the inflection point at time $t = \theta/p_1$ Since $N_P\,\lambda = p_2\,a$

$$a_I = \frac{1}{p_2}\ln\,(e^{\theta}-1). \qquad \text{(A-7)}$$

The velocity of the inflection point is then given by

$$\frac{da_I}{dt} = \frac{1}{p_2}\,\frac{p_1\,e^{\theta}}{(e^{\theta}-1)}\ . \qquad \text{(A-8)}$$

For the deactivation rates encountered in this study, p_1 was on the order of 0.01, hence, for t of the order of a few hundred hours

$$\frac{e^{\theta}}{e^{\theta}-1} \longrightarrow 1$$

and

$$\frac{d\,a_I}{dt} \longrightarrow \frac{p_1}{p_2}\ . \qquad \text{(A-9)}$$

The slope of the deactivation front, at the point of inflection, may be calculated by substituting equation A-5 into equation A-3 yielding

$$\left.\frac{\partial\psi}{\partial\lambda}\right|_{\lambda=\lambda_I} = \frac{-e^{-\theta}N_p\ (1-e^{-\theta})(e^{\theta}-1)}{(1+e^{-\theta})((e^{-\theta}-1)-1))^2} \qquad \text{(A-10)}$$

$$= \frac{N_p}{2}\ (e^{-\theta}-1).$$

Since $N_p\lambda = p_2 a$,

$$\left.\frac{\partial\psi}{\partial a}\right|_{a=a_I} = \frac{N_p}{2}\ (e^{-\theta}-1)\ \frac{d\lambda}{da}$$

$$= \frac{N_p}{2}\ (e^{-\theta}-1)\ \frac{p_2}{N_p}$$

$$= \frac{p_2}{2}\ (e^{-\theta}-1). \qquad \text{(A-11)}$$

Using the same argument leading to equation (A-9),

$$\left.\frac{\partial\psi}{\partial a}\right|_{a=a_I} \longrightarrow\ -\ p_2/2$$

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