THE TRANSIENT BEHAVIOR
OF
AN ETHANE DEHYDROGENATION FURNACE

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By

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SCOPE AND CONTENTS : The thermal dehydrogenation of ethane in the box-type furnaces of the Polymer Corporation is analyzed and the transient behavior of the furnaces has been simulated. Also a simple optimization cyclic operation has been obtained by maximizing the objective function, average ethylene produced per day.

In the transient model the optimization technique of the direct search method of Hooke and Jeeves was used. The Euler and Runge-Kutta third-order numerical integrations, and interpolation techniques were utilized to solve a set of eleven differential equations encountered in the model.

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1. ABSTRACT

This report deals with the mathematical model of the transient behavior of an existing ethane dehydrogenation furnace which is composed of two main sections: a preheating convection section and a radiant-heated section. The correlation of pressure drop with time has been found from the available data. The fractional carbon deposition and the multiplier coefficient of a pressure drop equation have been determined by the direct search optimization technique of Hooke and Jeeves.

An optimal policy for the cyclic operation of the furnace was determined by considering plant temperature profile and hydrocarbon/steam ratio as parameters for maximizing average ethylene produced per day. The effect of temperature profile on the distribution of carbon deposited along the reactor was also predicted and discussed.

2. INTRODUCTION

In recent years many workers have focused attention upon ethylene as an important raw material due to the current expansion of the petrochemical industry. Steam pyrolysis of light hydrocarbons (ethane, propane, butanes) is a major process for the production of ethylene (30), and naphtha cracking for ethylene has also been developed (32, 33, 34). For improving the production of ethylene, the kinetics and mechanisms of thermal cracking, simulation and optimal control of an existing furnace, and furnace design have been widely studied by applying a digital or an analog computer.

The kinetics and mechanisms of the thermal decomposition of ethane at high temperature have been investigated (10, 11, 12, 13, 14, 15, 16, 25). They have shown that the reaction mechanism appears to be a free radical chain process. However, the rate equations describing the formation of the intermediate and final products have not been resolved yet. The chemical reactions and rate expressions proposed by Snow and Schutt (3) have been applied for simulation work (1, 2). Similar simplified reaction schemes have been proposed for propane, butane, and mixed light hydrocarbons prolyses (9, 23, 26, 29).

The study of a pyrolysis furnace is logically divided into two parts, the tubular reactor and the furnace. The main purpose in creating a simulation model is to be able to predict the correct trends of plant behavior with reasonable accuracy when either the controllable or uncontrollable variables are changed. The simulation of an existing ethane dehydrogenation furnace has been discussed by Petryschuk and Johnson (1, 2), and Shah (9); their mathematical models have also been programmed on a digital computer. Lichtenstein (4) simulated propane dehydrogenation for a pilot plant on an analog computer. All these simulation studies are built by matching the available data from the plants.

For the design problem, the design of the tubular reactor consists of selecting the proper diameter and total length of tubes needed to produce the required conversion at some assumed heat flux. The papers by Fair and Rase (21), Calderbank (20), Andrews and Pollock (22), and Lichtenstein (4) have been concerned more with tubular reactor design. Karbosky et al (31) and Loftus et al (17) discussed the design of the furnace which included selection of tube material, arrangement of the tubes, and the design of the convection and radiant sections. An emperical technique for predicting heat transfer in the combustion chamber of the radiant section was proposed by Labo and Evans (35) early in 1939. Later, Hottel and Cohen (36, 37) developed a zoning technique for computing heat transfer in the combustion chamber which provides a sound basis for developing a mathematical model that will permit furnace design to meet requirements of heat flux level and distribution without violating constraints on maximum metal or refractory temperature. The optimization and on-line computer control of thermal cracking were discussed by Parson et al (19), Roberts and Laspe (18), Calderbank (20), and Shah (9).

This report is a continuation of Petryschuk's work (1, 2) for the ethane dehydrogenation. The reaction scheme and rate equations proposed by Snow and Schutt, and the frequency factors (of rate equations) determined by Petryschuk are used. The optimization technique developed by Hooke and Jeeves (6, 7) has been utilized. Here the transient study is dealing with the tubular reactor only.

3. DESCRIPTION OF THE FURNACE

The ethane dehydrogenation furnaces under consideration are the direct-fired furnaces which are situated in the Light Ends Recovery Unit, Polymer Corporation, Sarnia, Ontario. Two box-type furnaces operate in parallel and process the bottoms stream from an ethane-ethylene distillation column.

Each furnace consists of a convection section where the ethane feed is preheated from approximately 200°F to about 1200°F and a radiant section where the tubes are exposed to direct fire heating and the reactions occur. The convection section is a cross-flow, counter-current heat exchanger with 1150 ft^2 of heat transfer area and 1050 ft tube length. The radiant section is composed of a hair-pin coil with about 480 ft^2 of heat transfer area and four zink burners as heat source. The coil is made of type 316 stainless steel with inside diameter 3.875 inches and it is constructed of 24 tubes each 17 ft in length and having return bends 4 ft in length; the latter are located outside the furnace wall and well insulated. The two sections are separated by a brick-wall. Figure 1 is a simple scheme of the furnace.

Plant temperatures are logged at seven points on the tube-side and at three points for flue gas. The inlet and outlet pressures of the reacting gas stream are also known. Recently a differential

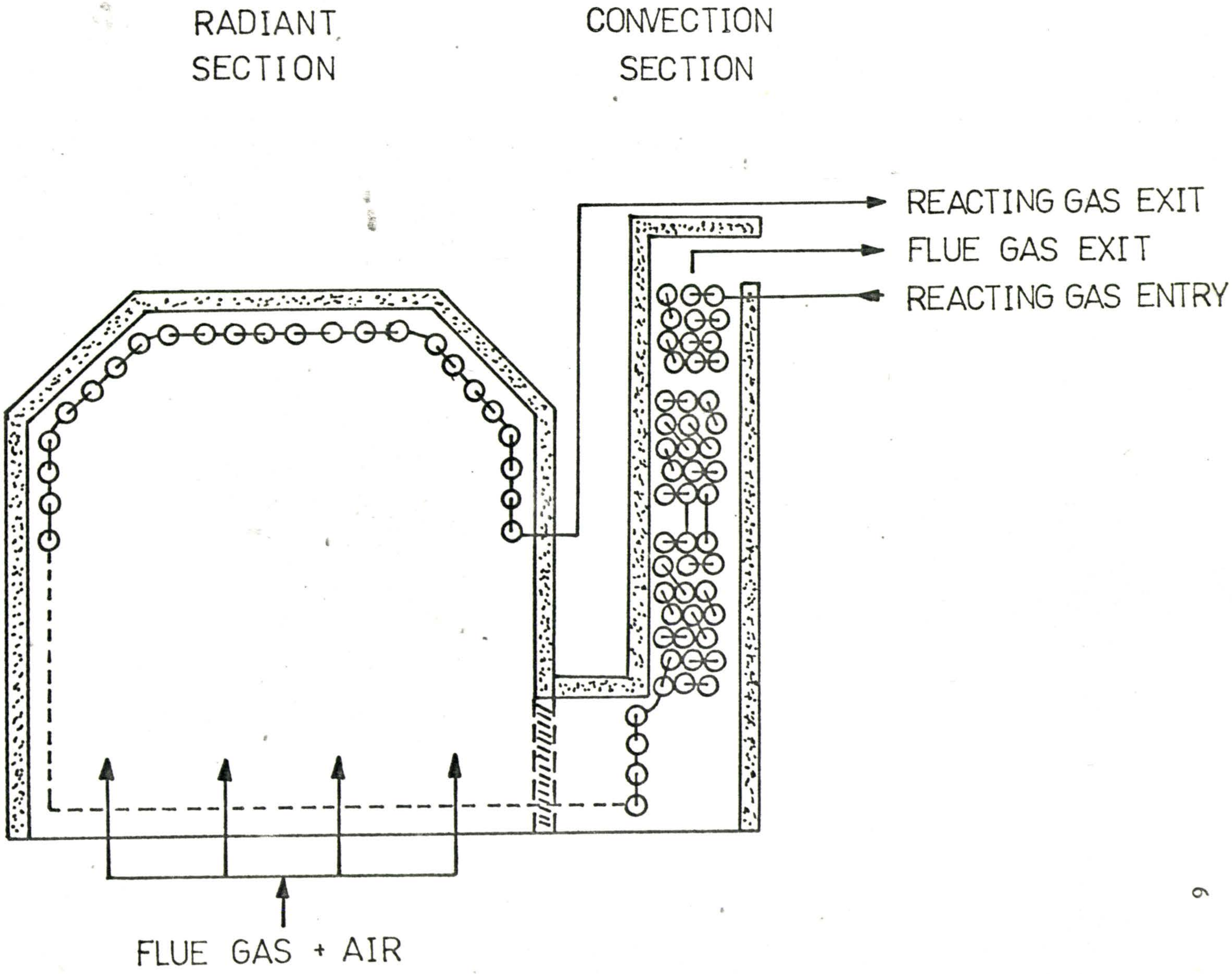

FIGURE 1 SIMPLE SCHEME OF A BOX-TYPE ETHANE DEHYDROGENATION FURNACE

pressure gauge has been installed for measuring the pressure drop vs. run time.

4. PLANT DATA AVAILABLE

Five sets of plant data are available in which four sets are mixed ethane-propane feed; only one set is suitable for this transient behavior study of ethane dehydrogenation and is shown in Table 1. Unfortunately the plant data available for temperature profile vs tube length and concerning feed rate variation are not as detailed as one would desire. Several assumptions will be made for the model because of the limited and incomplete data.

It is expected that this study will continue and that new data being obtained from the Corporation at the time of writing of the report will be analyzed using the methods discussed and illustrated in the following pages.

TABLE 1 FEED, TEMPERATURE AND PRESSURE OF FURNACE B301
(March 16 - April 23, 1966)

Date	Length	Feed Flow Rates		Temperatures		Pressures	
		Ethane	Steam	Inlet	Outlet(a)	Inlet	Outlet
		M lb/day	M lb/day	°F	°F	psig	psig
March 16	1	65.0	36.12	240	1520	61.0	13.7
17	2	103.5	48.00	251	1527	62.0	13.8
18	3	103.8	44.64	251	1527	62.0	13.6
19	4	128.4	27.60	226	1528	62.0	13.7
20	5	119.7	27.36	235	1528	62.0	13.7
21	6	130.0	24.50	215	1530	62.0	13.7
22	7	154.9	13.03	190	1532	62.75	13.7
23	8	123.9	36.00	216	1530	64.0	13.7
24	9	147.7	11.45	175	1533	66.0	13.8
25	10	153.8	9.60	172	1529	65.5	13.8
26	11	167.2	10.08	175	1535	65.75	13.8
27	12	143.8	16.15	200	1535	66.0	13.9
28	13	162.8	9.91	161	1530	69.7	14.0
29	14	140.2	18.07	193	1532	65.6	14.0
30	15	118.3	32.16	237	1535	65.9	14.0
31	16	118.0	33.12	239	1535	66.7	13.9
April 1	17	117.7	25.20	225	1530	67.0	13.7
2	18	154.9	10.80	179	1537	69.0	13.7
3	19	139.9	19.20	210	1539	68.0	13.7
4	20	123.8	24.96	220	1537	64.4	14.0
5	21	121.4	27.05	225	1527	68.0	14.0
6	22	117.8	29.76	230	1525	67.4	13.7
7	23	124.0	35.62	220	1525	66.0	13.9
8	24	145.7	11.40	187	1522	67.0	13.8
9	25	151.2	9.60	167	1522	68.0	13.8
10	26	156.6	9.60	167	1523	72.0	13.7
11	27	122.1	26.40	210	1525	69.3	13.9
12	28	141.1	17.40	220	1520	71.0	14.0
13	29	138.8	16.80	204	1521	71.5	14.0
14	30	140.1	9.60	173	1525	75.2	14.0
15	31	142.3	11.64	179	1526	71.2	13.9
16	32	NA(b)	15.60	190	1525	72.75	14.0
17	33	NA	12.00	184	1525	73.0	13.9
18	34	NA	10.80	179	1527	76.0	14.0
19	35	NA	19.20	204	1525	74.1	13.0
20	36	NA	19.20	210	1525	74.0	12.6
21	37	NA	17.28	200	1525	76.8	13.0
22	38	NA	15.36	198	1525	72.5	13.0
23	39	55	13.44	225	1525	72	13.0

(a) Temperature fourth tube from outlet

(b) This day was omitted in day count on log sheet.

5. TRANSIENT BEHAVIOR OF THE DEHYDROGENATION FURNACE

5.1 Purpose

Hydrocarbon pyrolysis processes can not be operated under the steady-state conditions because carbon is deposited on the tube walls during the operation. This causes the pressure drop to increase with increasing time. This unsteady-state operation leads to plant shut-downs for cleaning the carbon deposited inside the reactor after an operating run. In the present study a regression analysis of the available plant data has been carried out for finding a correlation of pressure drop with time. The mechanism of carbon formation and deposition is a complex transport and kinetic phenomena. The fractional carbon deposition has, as yet, not been solved; previous work on design or simulation (1, 2, 3, 4, 9) has usually assumed a constant fraction (approximately 0.1). The mathematical model presented in this section will determine the fraction carbon deposition and the multiplier of pressure drop equation (this will explain in Sec. 5.5) simultaneously on a digital computer by the optimization technique of Hooke and Jeeves, and using Euler and Runge-Kutta third-order numerical integrations, and interpolation techniques to solve the differential equations encountered.

5.2 Assumptions of the Model

The model equations will be described and derived for this transient study in the following sections. Because of the limitation of data and the need to simplify the problem for application of computer techniques and for saving computer time, several assumptions have to be made as follows:

(1) The velocity profile is flat at any cross-section along the reactor.

(2) There is radial uniformity of composition and temperature.

(3) No diffusion along a flow path exists.

(4) The carbon is assumed to coat the tube walls uniformly around the circumference at any point.

(5) The ideal gas law is valid for the reacting gas at high temperature and low pressure.

(6) The plant temperature profile in convection section is linear and the profile in radiant section is assumed to be a smooth curve.

(7) No reactions occur in convection section.

(8) The form of the pressure drop equation is that proposed by Hougen and Watson.

The assumptions (1), (2) and (3) constitute the plug-flow reactor model in which each element of gas passes through the reactor as a plug, unaffected by the preceding or following elements. It has to be noted that even the shape of inside tube will be changed due to carbon deposition. The plug-flow assumptions still be assumed to hold.

It is realized that there is a "saw-tooth" temperature profile in the radiant section caused by the insulated return bends as in the model proposed by Petryschuk and Johnson (1, 2). Since this model would require considerably more computer time, assumption (6) was made for the present studies.

There are also assumptions involved in the physical property treatment which will be introduced later.

5.3 Chemistry Description

The apparent over-all chemical reactions and expressions for the dehydrogenation of ethane proposed by Snow and Schutt (3) are used in this model study. The chemical reactions are:

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 \qquad (1)$$

$$C_2H_4 + 2H_2 \rightleftarrows 2CH_4 \qquad (2)$$

$$C_2H_4 \rightarrow 0.25\ C_4H_6 + 0.125\ C_4H_8 + 0.125\ C_4H_{10} + 0.125\ H_2 \qquad (3)$$

$$C_2H_4 \rightarrow 0.333\ C_6H_6 + H_2 \qquad (4)$$

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad (5)$$

$$C_2H_4 \rightarrow 2C + 2H_2 \qquad (6)$$

$$C_2H_4 + C_2H_6 \rightarrow 0.952\ C_3H_6 + 0.381\ C_3H_8 + 0.62\ H_2 \qquad (7)$$

The empirical rate expressions written for these reactions are as follows:

$$r_1 = \frac{k_1 P}{n_t} \left(n_{C_2H_6} - \frac{n_{C_2H_4}\, n_{H_2}\, P}{K_1\, n_t} \right) \qquad (8)$$

$$r_2 = \frac{k_2 P}{n_t} \left(\frac{n_{C_2H_4} P}{n_t} \sqrt{n_{C_2H_6} n_{H_2}} - \frac{n_{CH_4}}{K_2} \right) \qquad (9)$$

$$r_3 = k_3 \, r_1 \, P \quad (10)$$

$$r_4 = \frac{k_4 P^2}{n_t^{\,2}} \, n^2_{C_2H_4} \quad (11)$$

$$r_5 = \frac{k_5 \, P}{n_t^2} \, n^2_{C_2H_4} \quad (12)$$

$$r_6 = \frac{k_6 \, P^2}{n_t^2} \, n^2_{C_2H_4} \quad (13)$$

$$r_7 = \frac{k_7}{k_1} \, r_1 \quad (14)$$

where k_i = reaction rate constant

n_i = moles of ith component per mole of feed

n_t = gas flow, total moles per mole of feed

P = total pressure of reacting gas stream, atm.

r_j = rate of jth reaction, moles converted/(sec.)(cu.ft.)

The rate constants of these rate equations and the frequency factors are shown in Table 2, where one set of frequency factors proposed by Petryschuk and Johnson (1, 2) are used and k_{70} is set equal to zero. Actually there are only six reactions being used. The equilibrium constants proposed by Snow and Schutt (3) for dehydrogenation of ethane are:

$$K_1 = 3.31 \times 10^{-7} \, e^{0.00778T}$$

$$K_2 = 1.0$$

where T is temperature of reacting gas, °R.

TABLE 2 REACTION RATE CONSTANTS

(Reaction rate constants were proposed by Snow and Schutt (3) and k_{io} values were proposed by Petryschuk and Johnson (1, 2))

Reaction	Rate Constant	k_{io} Value
1	$k_1 = \frac{k_{1o}}{T} e^{-\frac{64500}{T}}$	5.3×10^{14}
2	$k_2 = k_{2o} e^{-\frac{49140}{T}}$	5.9×10^{7}
3	$k_3 = k_{3o}$	0.008
4	$k_4 = k_{4o} e^{-\frac{59120}{T}}$	2.2×10^{9}
5	$k_5 = k_{5o} e^{-\frac{54040}{T}}$	3.0×10^{7}
6	$k_6 = k_{6o} e^{-\frac{44100}{T}}$	4.51×10^{4}
7	$k_7 = k_{7o} e^{-\frac{83160}{T}}$	0.0

5.4 Mass Balance

Referring to Figure 2 the mass balance for a single component i can be expressed as:

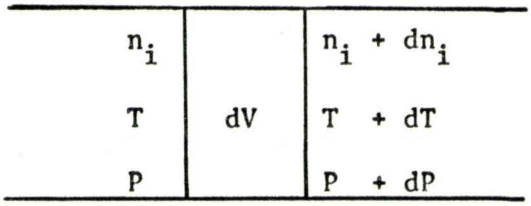

FIGURE 2 An element of a tubular reactor

$$F \frac{dn_i}{dV} = \sum_{j=1}^{s} a_{ij} \gamma_j \qquad j = 1, 2, \cdots, 5 \tag{15}$$

where F = feed rate, moles per second

V = volume of reacting gas, cu.ft.

a_{ij} = stoichiometric ratio of jth reaction

s = number of reactions

n_i = moles of ith component per mole of feed

and

$$dV = \left(\frac{\pi D^2}{4} \right) dz \tag{16}$$

where D = tube inside diameter, ft.

z = tube length, ft.

Substituting Equation (16) into (15) the result is

$$\frac{dn_i}{dz} = \left(\frac{\pi D^2}{4F} \right) \sum_{j=1}^{s} a_{ij} r_j \tag{17}$$

where the stoichiometric ratio of the reaction, a_{ij}, is positive when the ith component is product, negative for reactant.

By applying Equation (17) the mass balance for each component in the model can be written as:

$$\frac{dn_{H_2}}{dz} = B\,(r_1-2r_2+0.125\,r_3+r_4+r_5+2r_6) \quad (18)$$

$$\frac{dn_c}{dz} = 2Br_6 \quad (19)$$

$$\frac{dn_{CH_4}}{dz} = 2Br_2 \quad (20)$$

$$\frac{dn_{C_2H_2}}{dz} = Br_5 \quad (21)$$

$$\frac{dn_{C_2H_4}}{dz} = B(r_1-r_2-r_3-r_4-r_5-r_6) \quad (22)$$

$$\frac{dn_{C_2H_6}}{dz} = -Br_1 \quad (23)$$

$$\frac{dn_{C_4H_6}}{dz} = 0.25\,Br_3 \quad (24)$$

$$\frac{dn_{C_4H_8}}{dz} = 0.125\,Br_3 \quad (25)$$

$$\frac{dn_{C_4H_{10}}}{dz} = 0.125\,Br_3 \quad (26)$$

$$\frac{dn_{C_6H_6}}{dz} = 0.333\,Br_4 \quad (27)$$

where $B = \Pi D^2/4F$.

The component steam is considered as an inert gas because CO and CO_2 are not observed by analyzing the products in this plant. Possibly the steam-carbon reactions discussed by Shah (9) may occur in operation, in this case steam will reduce carbon deposition.

5.5 Momentum Balance

The pressure drop calculation for circular tubes is conventionally expressed by the Fanning equation (5):

$$\frac{d\,P'}{dz} = \frac{2fG^2}{g_c D_i \rho} \tag{28}$$

where P' = total pressure of reacting gas stream, psi

z = tube length, ft

f = dimensionless friction factor

G = mass velocity per unit cross-sectional area, lbs/(ft^2)(sec).

g_c = gravitational constant = 32.2 ft/(sec^2)

D_i = internal diameter, inches

ρ = density of reacting gas, lbs/cu.ft.

A modified form of the Fanning equation applicable in the region of Reynolds numbers above 100,000 from Hougen and Watson (5) is:

$$\frac{d\,P'}{dz} = \frac{0.0235}{D_i^{\,4.8}} \left(\frac{W}{1000} \right)^{1.8} \left(\frac{\mu^{0.2}}{\rho} \right) \tag{29}$$

where dP'/dz = pressure drop per foot of tube, psi/ft

D_i = internal diameter, inches

W = mass flow rate, lbs/hr

μ = viscosity of reacting gas, micropoises

ρ = density of reacting gas, lbs/cu.ft

Both Equation (28) and (29) have been used by many investigators $^{(1, 2, 3, 4, 21, 22, 27, 29)}$ on the simulation and design of a dehydrogenation furnace. Equation (29) is used in this transient model, it has to be adjusted by a multiplier to compensate for the irregular roughness due to carbon deposition and the number of return bends existing in the reactor.

The reacting gas viscosity is calculated from the reduced correlation of Hougen and Watson $^{(5)}$:

$$\ln \mu_r^{0.2} = -0.1208 + 0.1354 \ln T_r \tag{30}$$

$$\mu_r = \mu / \mu_c \tag{31}$$

$$\mu_c = \sum_{i=1}^{n'} y_i \mu_{ci} \tag{32}$$

$$T_r = T / T_c \tag{33}$$

$$T_c = \sum_{i=1}^{n'} y_i T_{ci} \tag{34}$$

where μ_r = reduced viscosity of reacting gas

μ_c = critical viscosity of reacting gas, micropoises

μ_{ci} = critical viscosity of ith component, micropoises

T_r = reduced temperature of reacting gas

T_c = critical temperature of reacting gas, ^oR

T_{ci} = critical temperature of ith component, ^oR

y_i = mole fraction of ith component

n' = number of components

and the gas density is evalueated by the ideal gas law.

$$\rho = \frac{MP}{RT} \tag{35}$$

$$M = \sum_{i=1}^{n'} y_i M_i \tag{36}$$

where M = average molecular weight of reacting gas

M_i = molecular weight of ith component

R = gas constant

P = total pressure of reacting gas, atm.

T = temperature of reacting gas, °R

ρ = density of reacting gas, lbs/cu.ft.

The physical properties of each component for the model calculation are shown in Table 3.

TABLE 3 PHYSICAL PROPERTIES

(Ref. (5), p.873 and Ref. (43), p.744)

Component	Molecular weight	Critical Temperature	Critical Viscosity
	lbs per lb-mole	^{o}R	Micropoise
Hydrogen	2.016	59.94	34.7
Carbon	12.00	0.00	0.0
Methane	16.04	343.26	159.0
Acetylene	26.04	557.10	237.0
Ethylene	28.05	508.32	215.0
Ethane	30.07	549.72	210.0
Propylene	42.08	657.00	233.0
Propane	44.09	666.00	228.0
Butadiene	54.10	768.00	220.0
Butylene	56.10	752.50	250.0
Butane	58.12	765.32	239.0
Benzene	78.11	1012.68	312.0
Steam	18.00	1165.0	495.0

5.6 Coke Formation

Coke is probably formed inside the reactor as a secondary reaction from ethylene. The local rate of this reaction is influenced by temperature and by the extent of primary decomposition of ethane to ethylene. The reacting gas velocity and temperature across the cross-section of the tube is not uniform, in fact. Possibly most of the coke formation occurs in a film, or layer of retarded flow, near the walls, and a part of carbon will deposit on the tube wall to form a carbon ring. If the temperature distribution around the circumference of the tubes is uniform, the rates of reactions may be uniform in the radial direction. Then it may be reasonable to assume that the carbon coating is uniform on the tube wall at any cross-section. The calculation of coke thickness derived by Lichtenstein (4) is utilized:

$$d = \frac{D_i}{2} (1 - e^{-mt}) \qquad (37)$$

where $m = \phi r_c M_c / 2 \rho_c$

d = coke thickness, inches

t = time, hour

ρ_c = carbon density, lbs/cu.ft.

ϕ = fractional carbon deposition

M_c = carbon molecular weight

r_c = rate formation of carbon

Equation (37) can be easily applied to calculate the inside diameter which decreases with run length for the reacting gas stream.

5.7 Regression Analysis of Plant Data

The digital computer and regression analysis in evaluating plant data can become a valuable aid in process control. A practical analytical procedure that may be used to obtain a maximum of information from plant operating data has been suggested by Fisher (38). A quick method for the choice of non-linear transformations in the analysis of data by restricting the possible transformations to the "simple family" has been discussed by Dolby (39). Here the library subroutine "MLTREG" which is based on the stepwise method of M.A. Efroymson (40) for multiple regression analysis in the Computer Center, McMaster University, has been used for analyzing the plant operating data available from Polymer Corporation.

From Equation (28) we know that the gas-flow rate influences the pressure drop. The data of pressure drop, gas-flow rate, and run length in Table 1 are correlated. For this transient study the dependent variable in terms of $\Delta P/F_1^n$ (where n is a fractional power), and the independent variable θ are to be found the best way by regression analysis. The result and discussion will be presented in the next section.

5.8 Results and Discussions

For the regression analysis of plant operating data, if we have a theoretical basis, it is usually easy to produce a suitable theoretical or semi-theoretical correlation. Otherwise we have to try several possible transformations, generally a simple linear correction as

$$y = a + b\theta + c\theta^2 + d\theta^3 + \cdots \tag{38}$$

is first considered. If the linear correlation is less significant the quick method suggested by Dolby (39) can be used to find the possible transformation for non-linear systems.

First, the linear correction is considered in this study. Equation (38) becomes

$$\frac{\Delta P}{F_1^n} = a + b\theta + c\theta^2 + d\theta^3 + \cdots \tag{39}$$

where ΔP = pressure drop, psi

F_1 = feed rate, thousand lbs/day

θ = time, days

According to the criterion of multiple regression analysis, if the multiple correlation coefficient is closer to unity, probably the result is fitted better to the data. Hence the best fit is in the form of

$$\frac{\Delta P}{F_1^{0.3}} = 10.3852 + 0.0756407\ \theta \tag{40}$$

in which the multiple correlation coefficient is equal to 0.88972. Next the possible transformation in the form of

$$\frac{\Delta P}{F_1^n} = a + b\ (\ c + \theta)^d \tag{41}$$

is considered. The best fit of the transformation is

$$\frac{\Delta P}{F_1^{0.3}} = 10.5603 + 0.00635283\ (4.75 + \theta)^{1.65} \qquad (42)$$

and the multiple correlation coefficient is 0.89470. The results of these two corrections are plotted in Figure 3.

The mathematical model includes a set of eleven differential equations to be solved. In the convection section the Euler method of integration technique is used to calculate pressure variation with the assumptions that no reaction has occurred and that the temperature profile is linear; the temperature of gas stream can be calculated by linear interpolation with known inlet and outlet temperatures. In the radiant section the third-order Runge-Kutta method is used, the reacting gas temperature is calculated by forward, central and backward interpolation with the known temperature profile being used. The optimization technique of direct search by the method of Hooke and Jeeves is used to find the values of the fractional carbon deposition and the multiplier of pressure drop equation by minimization of a sum of squares. Two cases have been studied:

(i) Minimization of a sum of squares of pressure drop differences between model and plant data.

(ii) Minimization of a sum of squares of pressure drop differences between model and the one from Equation (42).

The results of these two cases are:

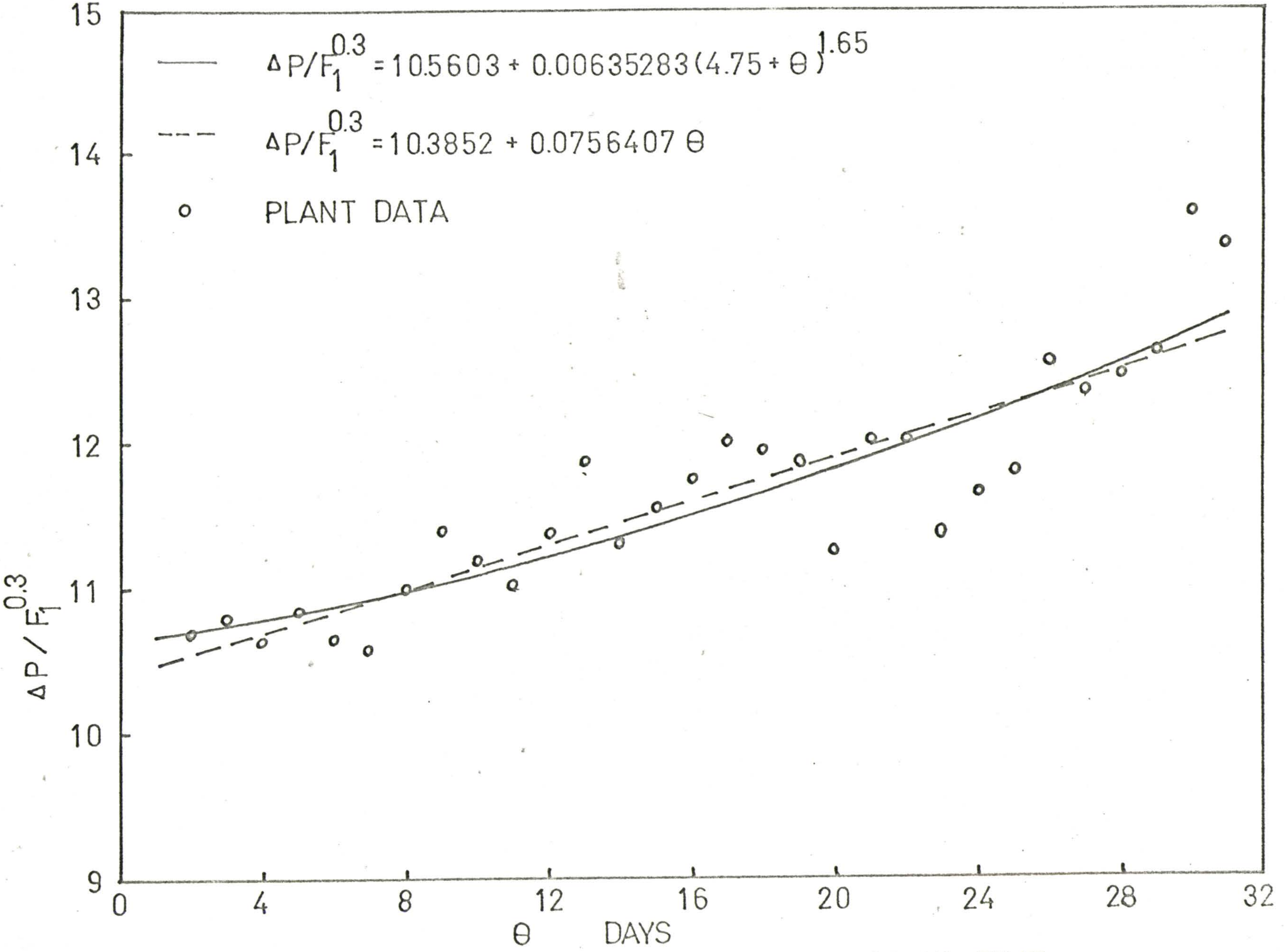

FIGURE 3 CORRELATION CURVES OF PRESSURE DROP VS TIME
(PLANT DATA HAVE BEEN TABULATED IN TABLE 1)

Case	Fractional Carbon Deposition	Multiplier
1	0.130	0.85937
2	0.135	0.84125

In the regression analysis both linear and non-linear correlations show that the value of the powers of feed rate, n, is 0.3. In accordance with the criterion of multiple regression analysis, the non-linear form, Eq. (42), is better than the linear correlation, Eq. (40). Also it can be seen clearly by investigating Eq. (29), that the pressure drop does not increase linearly with decreasing inside diameter due to non-uniform distribution of carbon deposition along the tube. In this result we still can not guarantee that this correlation can represent the operating conditions because the data available for this analysis is a short run. Also regression analysis of plant data is a continuous process. After the initial regression has been obtained, it should be revised with new data, and then statistically compared with the previous regression to determine if there has been any significant change in the process.

By the comparison of the fractional carbon deposition and the multiplier in both cases, these two values seem to compensate each other. It is similar to the previous work by Petryschuk and Johnson (1, 2) for steady-state study, ϕ is assumed to be 0.1 and the multiplier has been calculated to be greater than unity. It is the author's opinion that case (i) is preferred because case (ii) is based on the result of regression analysis which can not be identified perfectly.

The computer algorithms and programs are presented in Appendices.

6. CASE STUDIES

6.1 Purpose

The maximization of average ethylene produced per day is to be considered as an objective function to determine the cyclic operation of the furnace. In these case studies the total feed rate is assumed to be 150 thousand pounds per day (from the plant data the average feed rate is 156.68 thousand pounds per day, and the average hydrocarbon/steam ratio is 6.03), the inlet temperature is 700°F. The inlet pressure is calculated from Equation (42) which is the correlation from the regression analysis of plant data. The hydrocarbon/steam ratio and plant temperature profile are considered as parameters.

The distribution of carbon deposition along the reactor depends greatly on the plant temperature profile. The effect of temperature profile on coke profile (coke thickness vs tube length) will be discussed by selecting different shapes of the temperature profiles.

6.2 Temperature Profiles

In this study there are five cases (five temperature profiles) concerned as shown in Figure 4 in which case 1 is the base one used in the transient model, and corresponds to the plant run. Case 2 is a generally higher temperature. Case 3 is higher

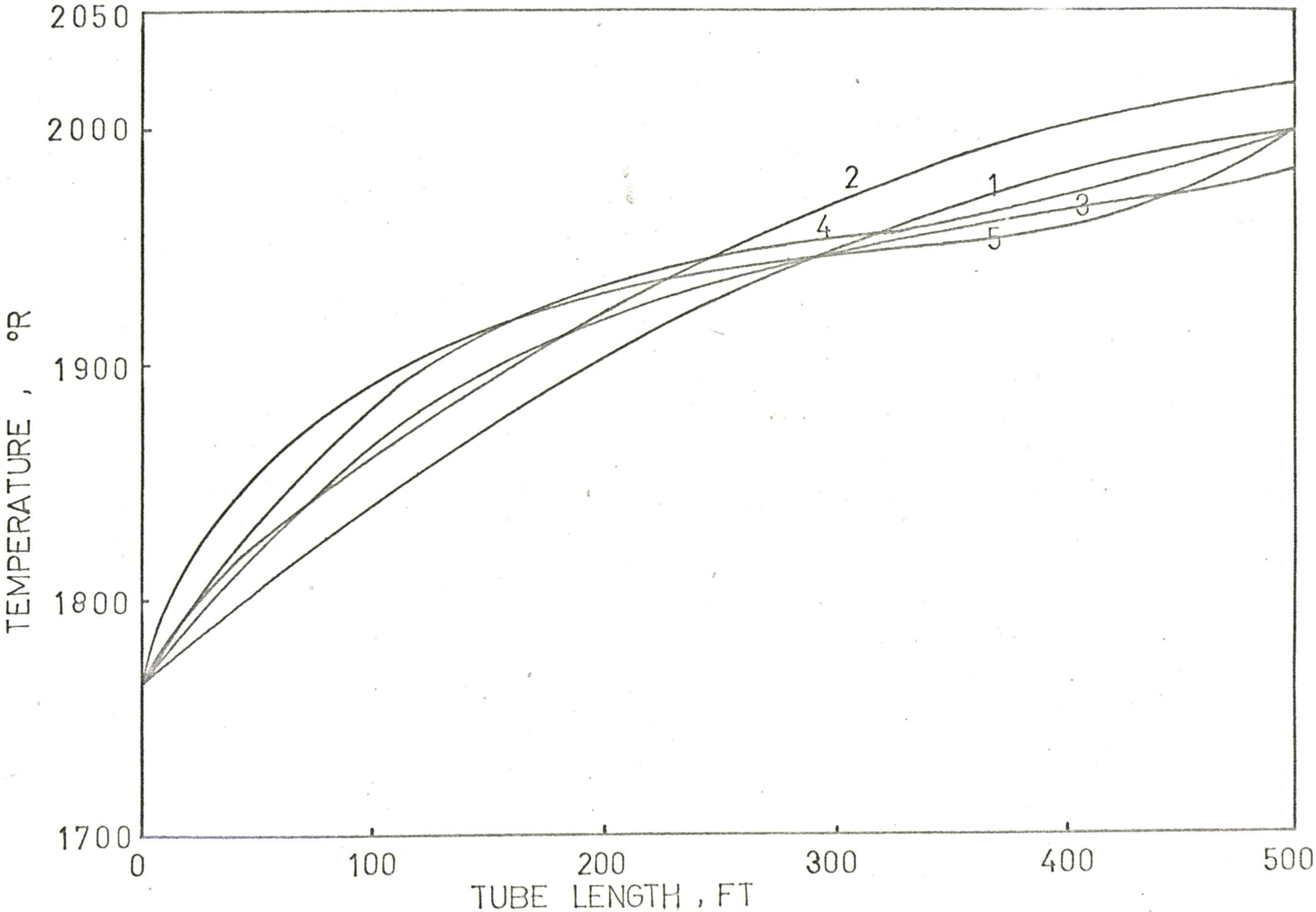

FIGURE 4 TEMPERATURE PROFILES FOR CASE STUDIES

initially and lower finally. Case 4 is higher initially, and Case 5 is still higher initially and have flat central profiles. For each case several values of hydrocarbon/steam ratio (3, 4, 5, 6, 7, 8) have been tested, the cases without steam feed are also compared.

For determining the optimal operating cycles per year (365 days/year) to maximize the average ethylene produced per day we define

$$t_c = t_o + t_s \tag{43}$$

$$S = \frac{R'}{t_c} = \frac{R'}{t_o + t_s} \tag{44}$$

where t_o = operating time per cycle, days

t_s = time of shut-down for cleaning, days

t_c = total time for one cycle, days

R' = total ethylene produced per cycle, thousand pounds

S = average ethylene produced per day, thousand pounds per day

and the optimal operating cycles can be calculated from the equation

$$C = \frac{365}{t_{c\ max}} \tag{45}$$

where C = optimal operating cycles per year

$t_{c\ max}$ = total time for one cycle in which S is maximum, days

Here t_s is assumed to be one day.

The effect of temperature profile on coke profile based on hydrocarbon/steam ratio being six for each case of five temperature profiles has been studied.

TABLE 4 TEMPERATURE PROFILES FOR CASE STUDIES

Distance ft	Case (temperature in ^{o}R) 1	2	3	4	5
0	1765.00	1765.00	1765.00	1765.00	1765.00
20	1781.37	1801.37	1790.00	1795.00	1818.00
40	1797.16	1817.16	1810.00	1820.00	1843.00
60	1812.37	1837.37	1830.00	1844.00	1864.00
80	1827.00	1847.00	1849.00	1865.00	1880.00
100	1841.04	1861.04	1865.00	1883.00	1893.00
120	1854.51	1874.51	1880.00	1898.00	1903.00
140	1867.39	1887.39	1892.50	1911.00	1912.00
160	1879.69	1899.69	1902.50	1920.00	1919.00
180	1891.41	1911.41	1911.00	1929.00	1925.00
200	1902.55	1922.55	1919.00	1935.00	1930.00
220	1913.11	1933.11	1925.00	1940.00	1935.00
240	1923.08	1943.08	1931.00	1944.00	1939.00
260	1932.48	1952.48	1935.00	1948.00	1942.50
280	1941.29	1961.29	1942.00	1951.00	1945.00
300	1949.52	1969.52	1947.00	1953.00	1948.00
320	1957.17	1977.17	1951.00	1956.00	1950.50
340	1964.24	1984.24	1956.00	1959.00	1952.50
360	1970.72	1990.72	1959.00	1962.00	1955.00
380	1976.63	1996.63	1963.00	1967.00	1957.00
400	1981.95	2001.95	1968.00	1971.00	1960.00
420	1986.69	2006.69	1970.00	1975.00	1965.00
440	1990.85	2010.85	1972.00	1980.00	1970.00
460	1994.43	2014.43	1975.00	1986.00	1977.50
480	1997.43	2017.43	1979.00	1992.50	1987.50
500	1999.84	2019.84	1982.50	2000.00	2000.00

6.3 Results and Discussions

Table 4 or Figure 4 represents the temperature profiles used for these case studies in which the temperature range for these reactions based on the Case 1 is 1765 ∿ 2000°R in all cases except Case 2. The optimal operating days and the maximum average ethylene yield, and the optimal operating cycles are shown in Table 5 and 6 respectively for each case at different hydrocarbon/steam ratio. From Table 5 we can see that the optimal days and the maximum yield increase with increasing hydrocarbon/steam ratio. Case 2 will produce more ethylene by comparing with the others because thermal dehydrogenation is endothermic. One must insure that the operation temperature does not cause the tube walls to become overheated. By considering the other four cases, Case 4, is the best one to produce more ethylene.

The profile of carbon layer thickness inside the reactor calculated from the model is approximate and somewhat erratic, but it is convenient to plot smooth curves as shown in Figures 6 through 10 for all cases at different hydrocarbon/steam ratios. From these figures the shape of coke profiles (coke thickness vs tube length) are almost the same in the cases without steam feed, although the coke profiles are different at low hydrocarbon/steam ratio (3∿8) for different temperature profiles.

Through these case studies we hope to suggest improved operating conditions for an ethane dehydrogenation furnace. The average ethylene yield vs time at hydrocarbon/steam ratio of six of Figure 5 shows that all the curves become very flat after 20 days operation.

TABLE 5 OPTIMAL OPERATING DAYS AND MAXIMUM YIELD

HCSR	CASE									
	1		2		3		4		5	
	OOD	AEPPD	OOD	AEPPD	OOD	AEPPD	OOD	AEPPD	OOD	AEPPD
3	29	50.94	33	55.31	30	49.03	30	51.20	30	50.07
4	29	53.17	37	57.73	30	51.19	31	53.41	30	52.24
5	30	54.57	40	59.29	30	52.54	33	54.81	31	53.61
6	30	55.53	42	60.39	31	53.47	34	55.79	32	54.56
7	31	56.24	43	61.20	31	54.15	36	56.50	33	55.26
8	32	56.78	43	61.83	32	54.67	37	57.06	34	55.79
∞	41	60.90	43	66.54	40	58.59	50	61.40	47	59.93

HCSR - Hydrocarbon/steam Ratio

OOD - Optimal Operating Days

AEPPD - Average Ethylene Produced Per Day

TABLE 6 OPTIMAL OPERATING CYCLES

HCSR	CASE				
	1	2	3	4	5
3	12.17	10.74	11.77	11.77	11.77
4	12.17	9.61	11.77	11.41	11.77
5	11.77	8.90	11.77	10.74	11.41
6	11.77	8.49	11.41	10.43	11.06
7	11.41	8.30	11.41	9.86	10.74
8	11.06	8.30	11.06	9.61	10.43
∞	8.69	8.26	8.90	7.16	7.60

Hence one may operate a furnace more economically with a long run length. The maximum coke thickness, and pressure drop vs cumulated ethylene product are shown in Figures 11 and 12 respectively. Figure 13 represents calculated coke profiles after 50 days' operation. Figure 14 shows the correlations of maximum coke thickness at any point along the furnace, pressure drop, cumulated ethylene production and operating days for all cases at hydrocarbon/steam ratio of six. In real plants the termination of the run will be governed by the pressure drop, and from these plots we can predict and compare the total amount of ethylene product, maximum coke thickness and operating days for a run with the constraint of pressure drop at different temperature profiles. It is presumed that the case with higher maximum coke thickness will be higher pressure drop, but this may not really be true as shown in Figure 14. For example the maximum coke thickness of Case 1 is thicker than that of Case 4, but the pressure drop of the former is less than that of the latter. In Figure 13 we can see that the area under curve 4 is greater than that of curve 1, i.e., the amount of carbon deposition of the former is greater than that of the latter. Hence, both the maximum coke thickness and the amount of carbon deposited influence the pressure drop.

Consequently, the pressure drop increases with increasing the production of ethylene. At the temperature range of reactions $1765 \sim 2000^{0}R$, Case 4 is preferred to produce more ethylene, and Case 3 is preferred to run the furnace longer. The results of these case studies suggest that best operation corresponds to achieving as uniform a carbon deposit as possible, so that the safe tube skin temperature is not exceeded anywhere along the length at long run times with the restriction of the pressure drop. The optimal hydrocarbon/steam ratio will be involved in cost study.

Commercially it is more realistic to consider the net profit as an objective function rather than the production of ethylene. Hence, the best way to find the optimal operating conditions of a furnace is to use optimization techniques such as, maximum principle, dynamic programming, optimum seeking method etc. by maximizing the net profit. The net profit can be defined as the cost of ethylene and by-products minus the cost of raw material, utilities, operation and maintenance, and fixed charge.

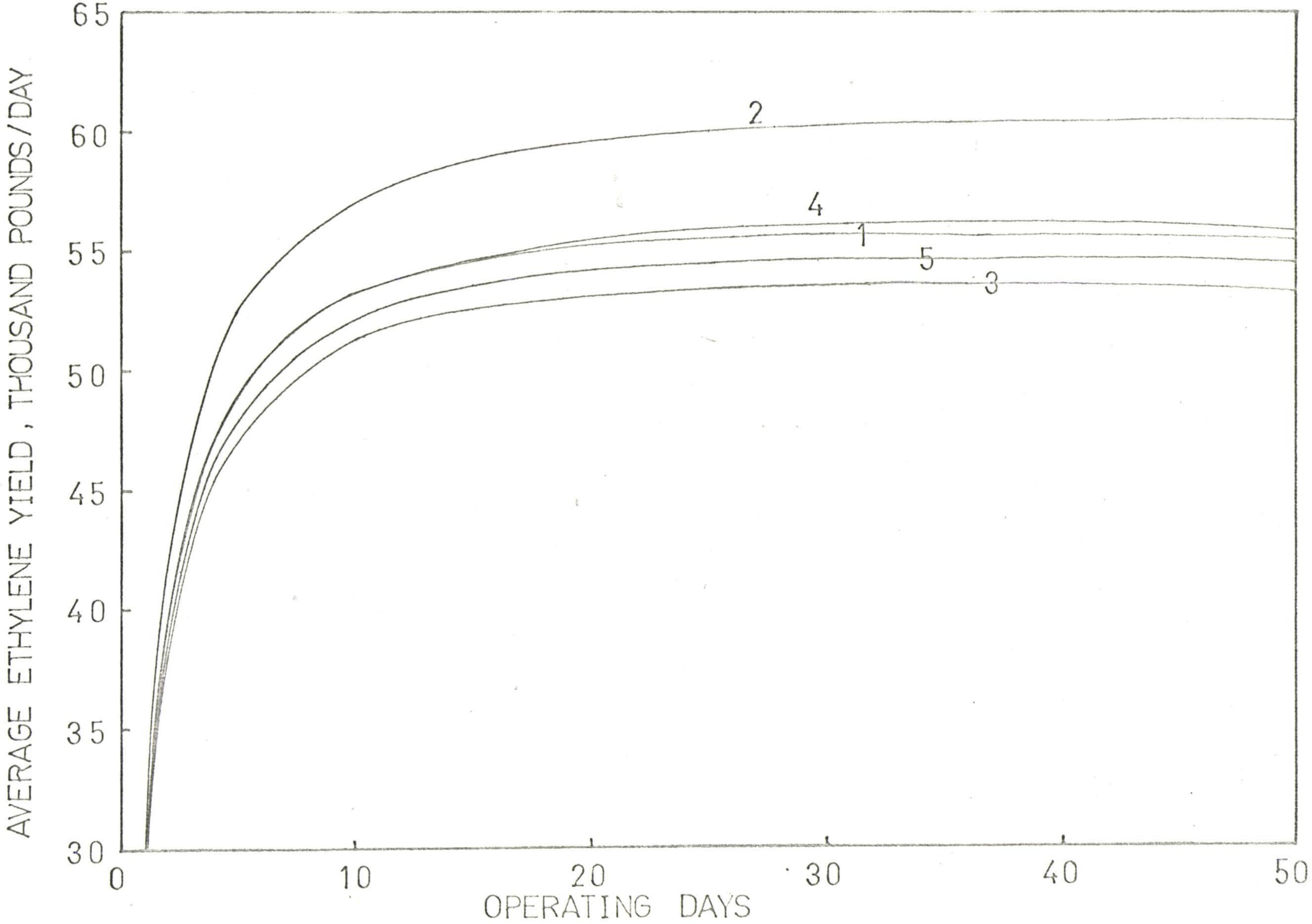

FIGURE 5 AVERAGE ETHYLENE YIELD VS TIME AT HYDROCARBON/STEAM RATIO OF 6

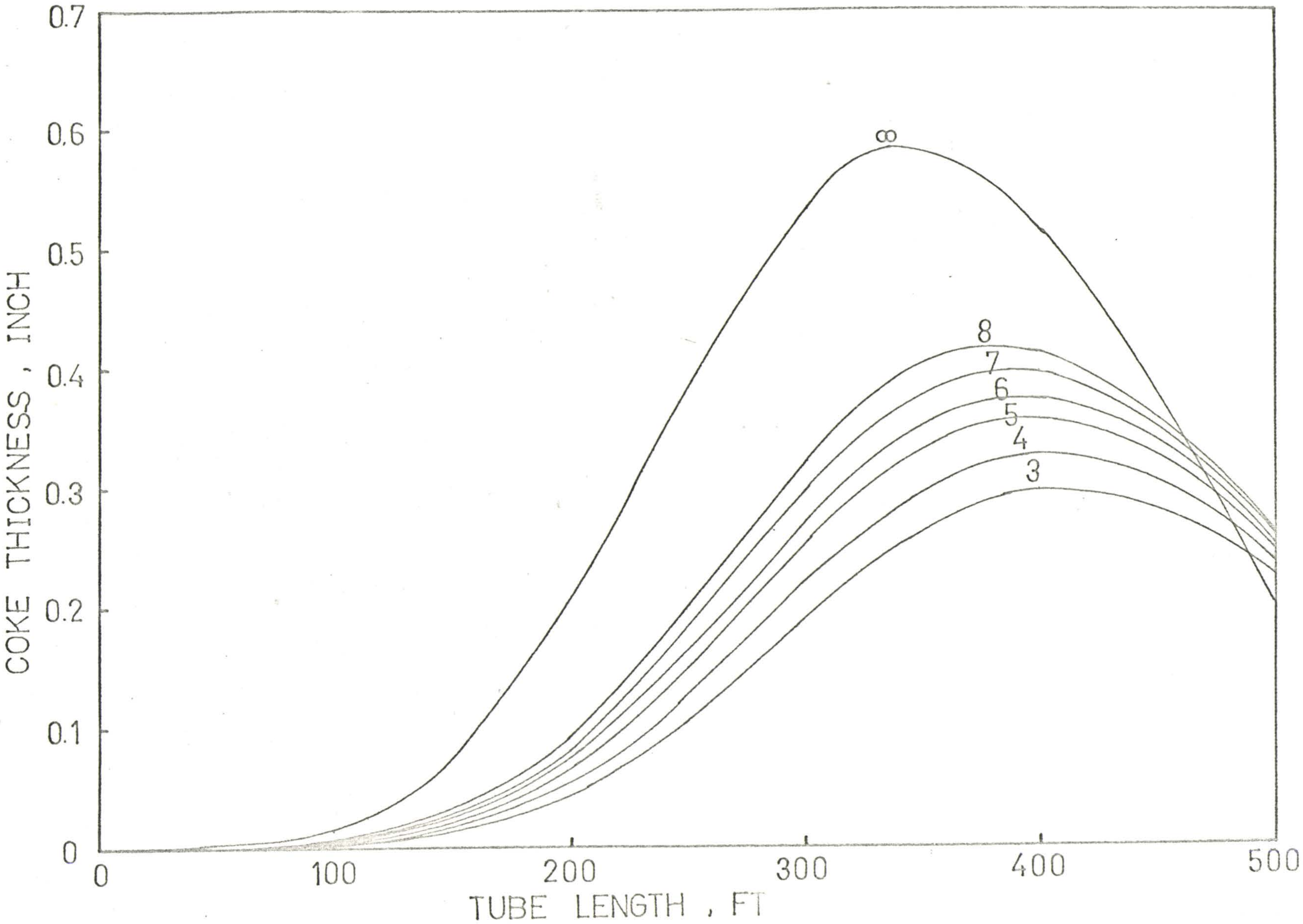

FIGURE 6 COKE PROFILES AT DIFFERENT HYDROCARBON/STEAM RATIO FOR CASE 1

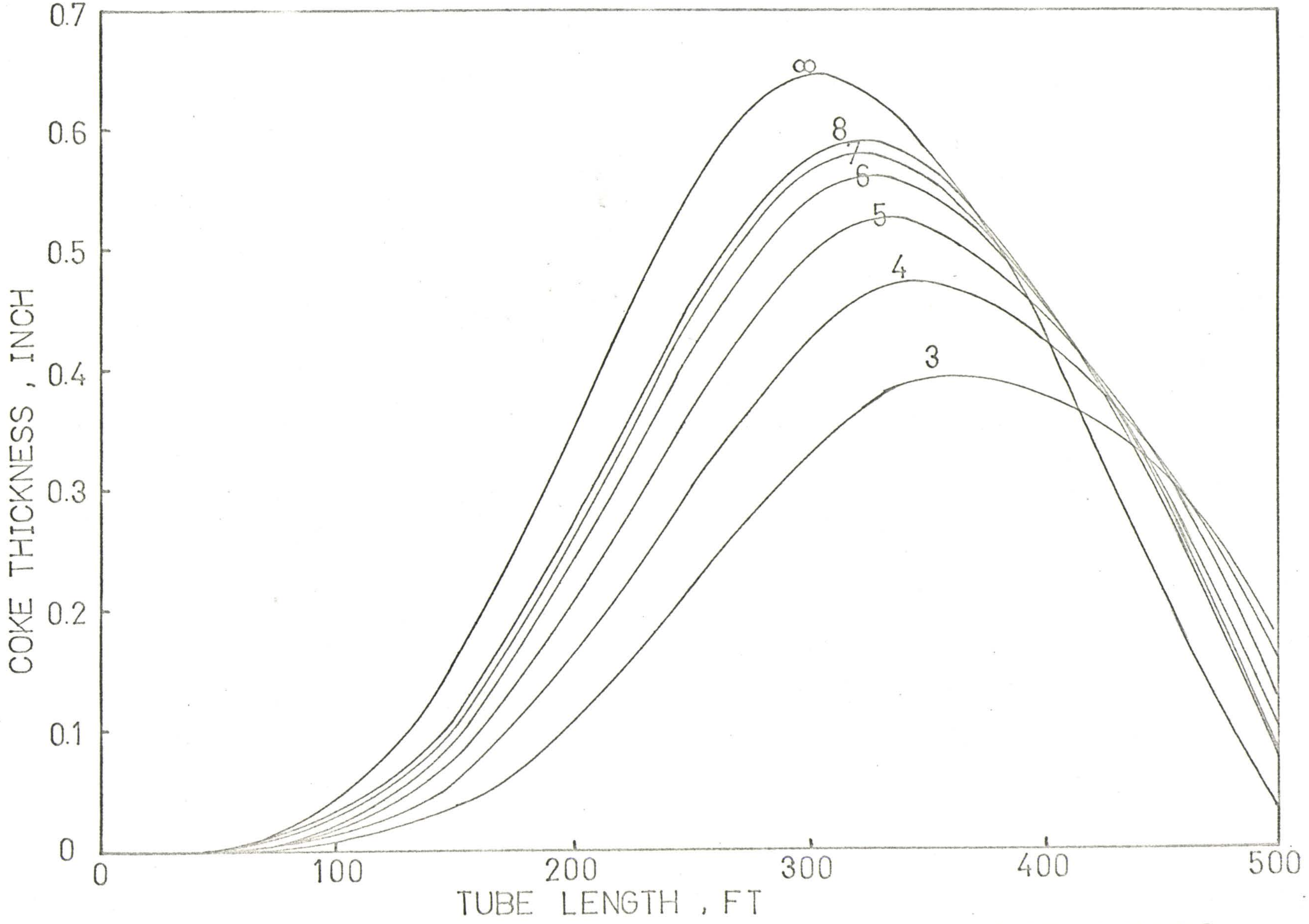

FIGURE 7 COKE PROFILES AT DIFFERENT HYDROCARBON/STEAM RATIO FOR CASE 2

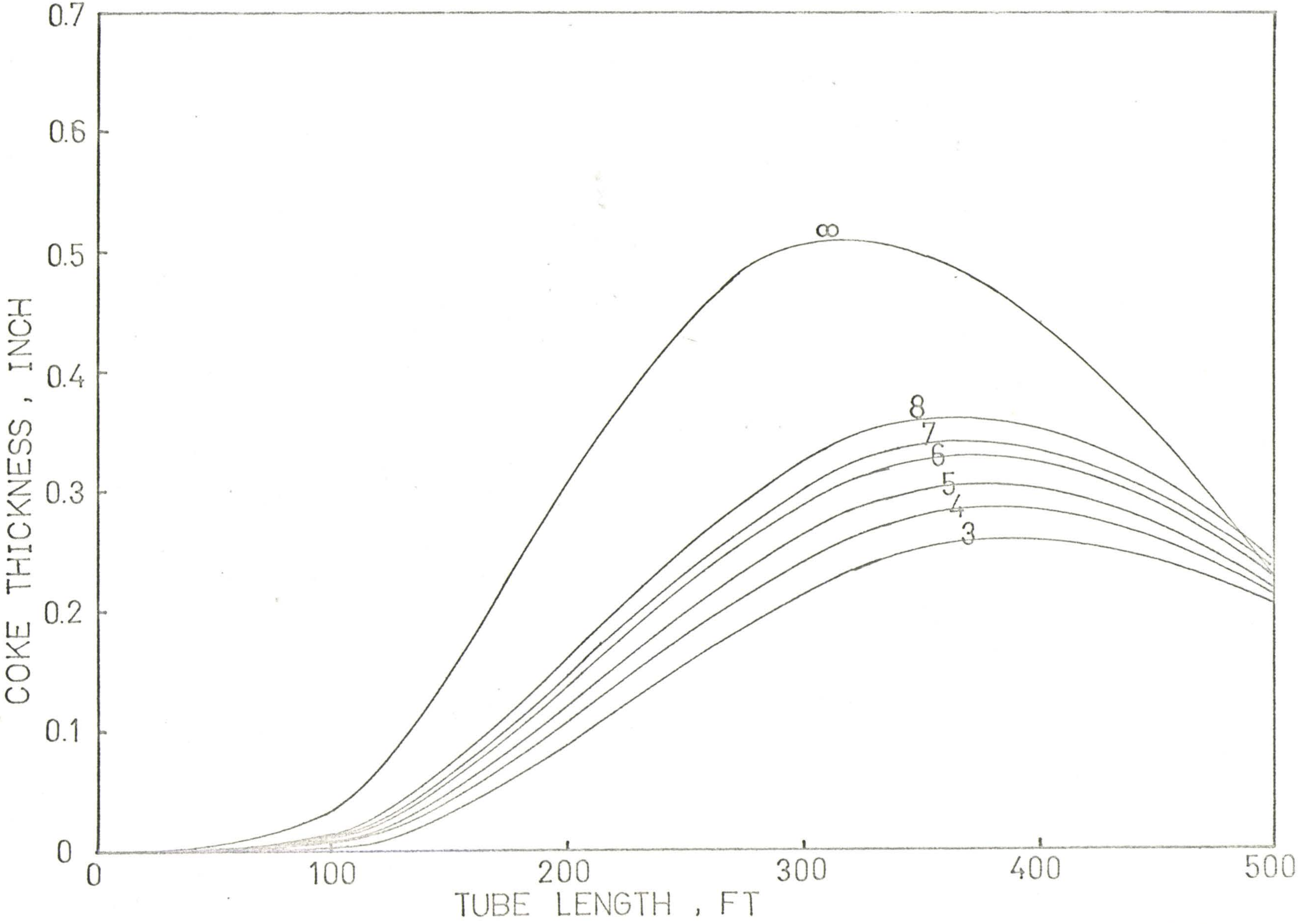

FIGURE 8 COKE PROFILES AT DIFFERENT HYDROCARBON/STEAM RATIO FOR CASE 3

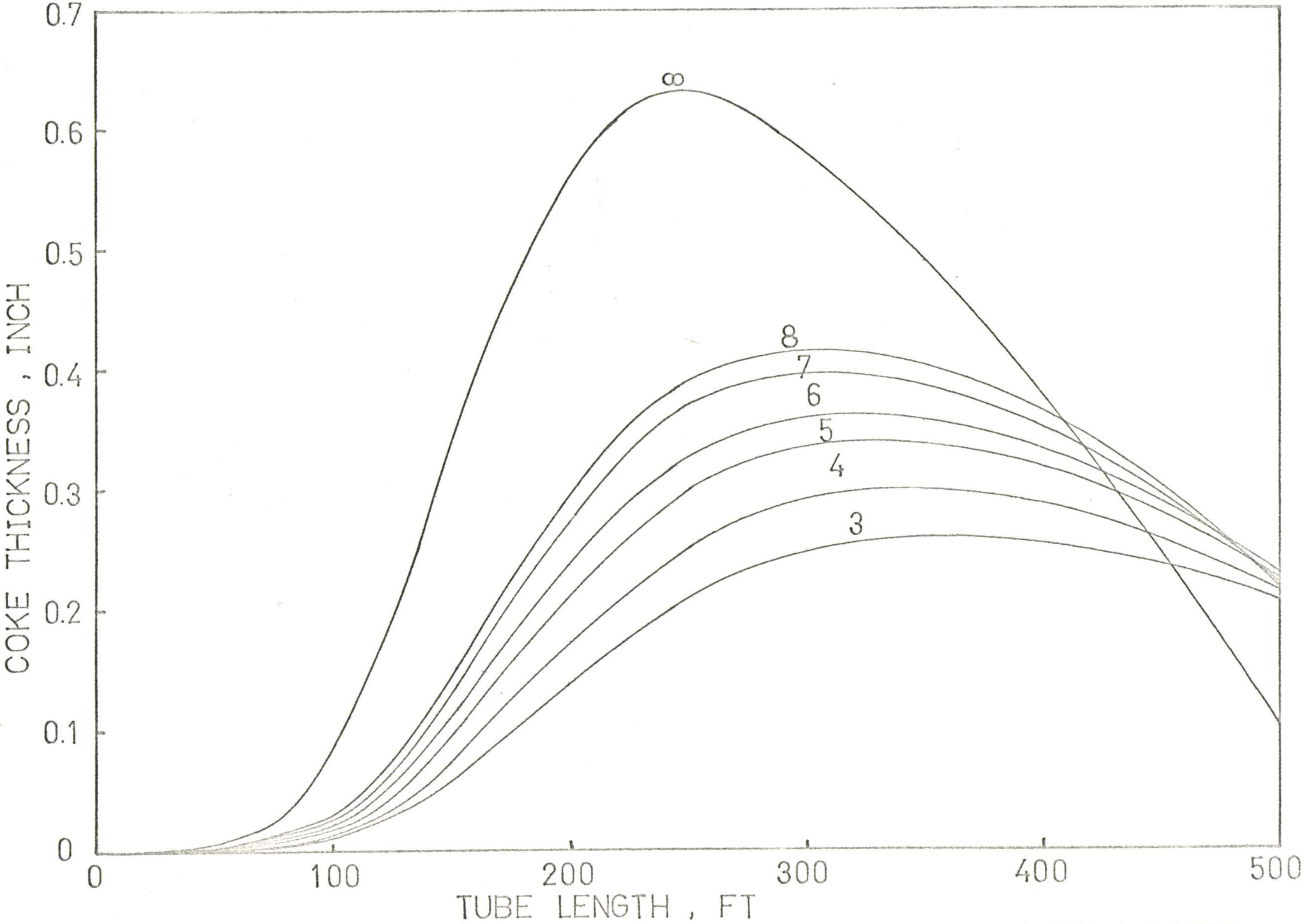

FIGURE 9 COKE PROFILES AT DIFFERENT HYDROCARBON/STEAM RATIO FOR CASE 4

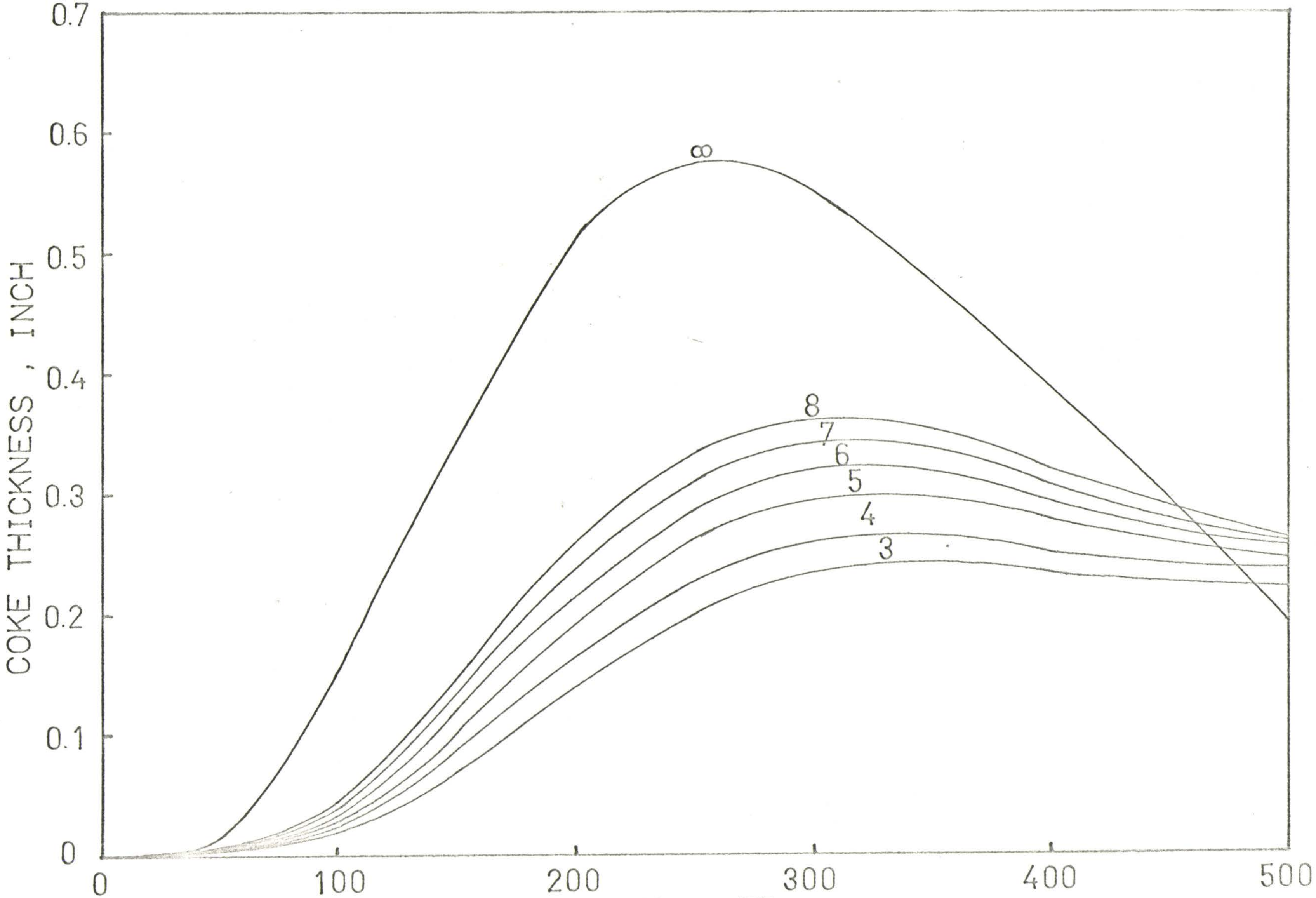

FIGURE 10 COKE PROFILES AT DIFFERENT HYDROCARBON STEAM RATIO FOR CASE 5

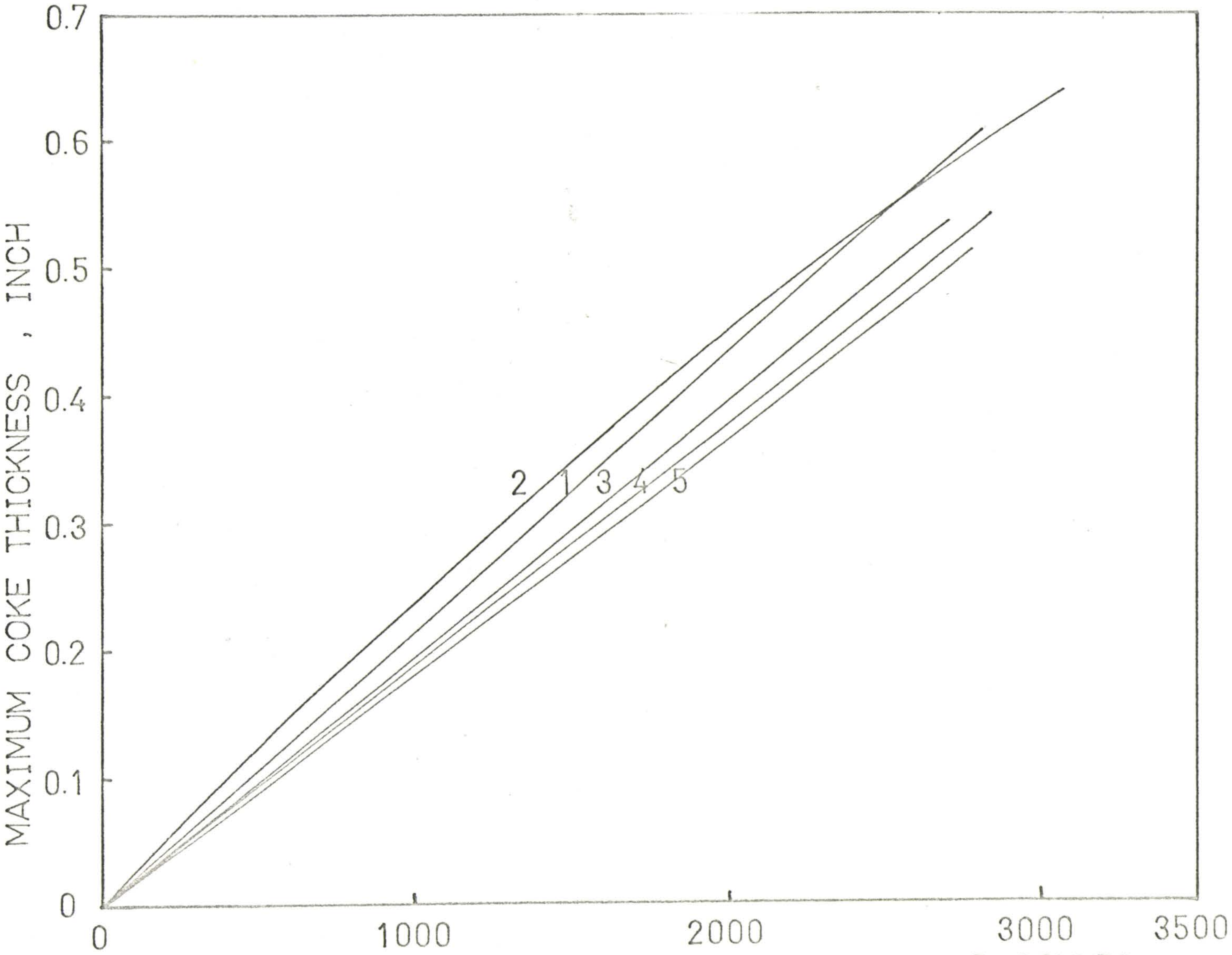

FIGURE 11 MAXIMUM COKE THICKNESS VS CUMULATED ETHYLENE PRODUCT AT HYDROCARBON/STEAM RATIO OF 6

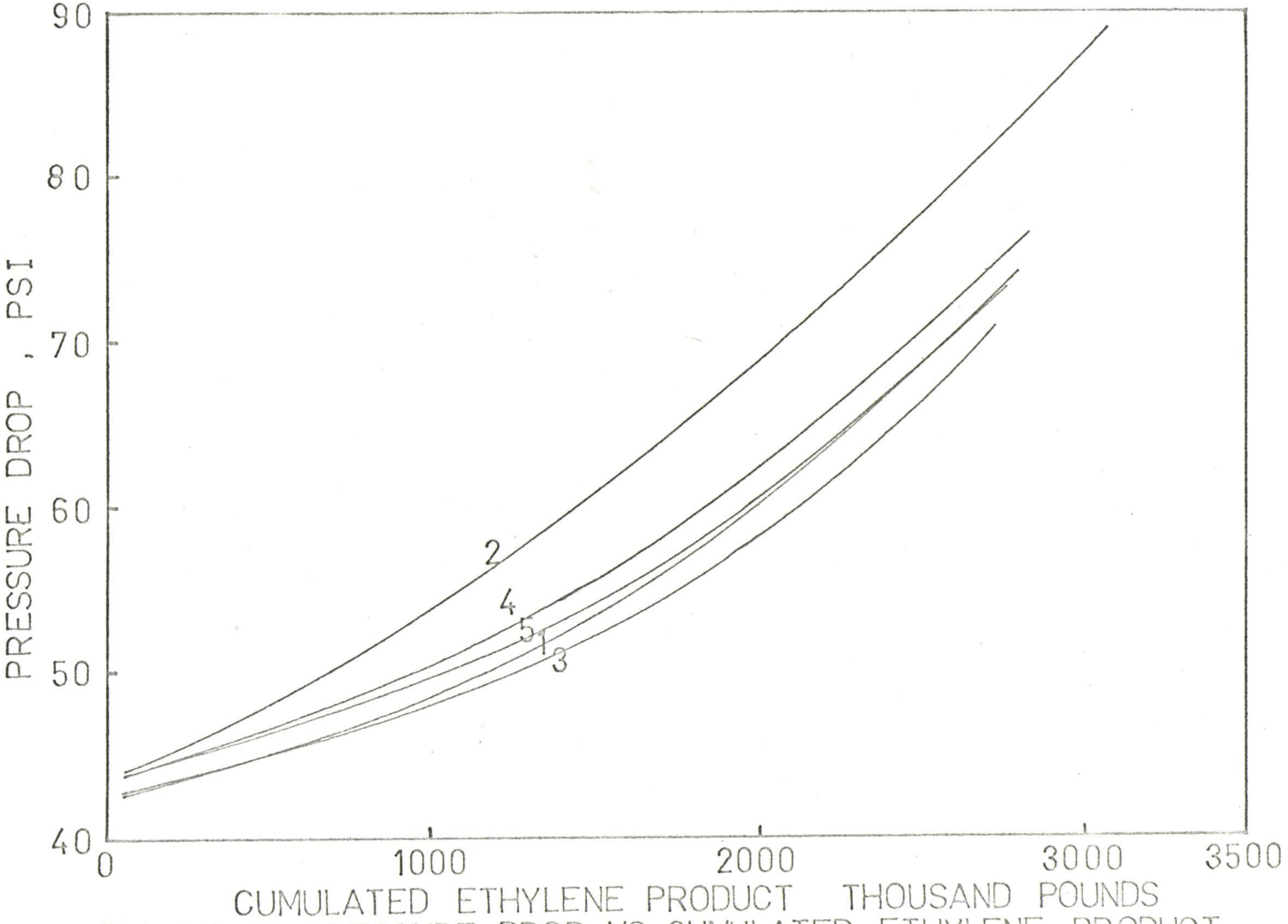

FIGURE 12 PRESSURE DROP VS CUMULATED ETHYLENE PRODUCT AT HYDROCARBON/STEAM RATIO OF 6

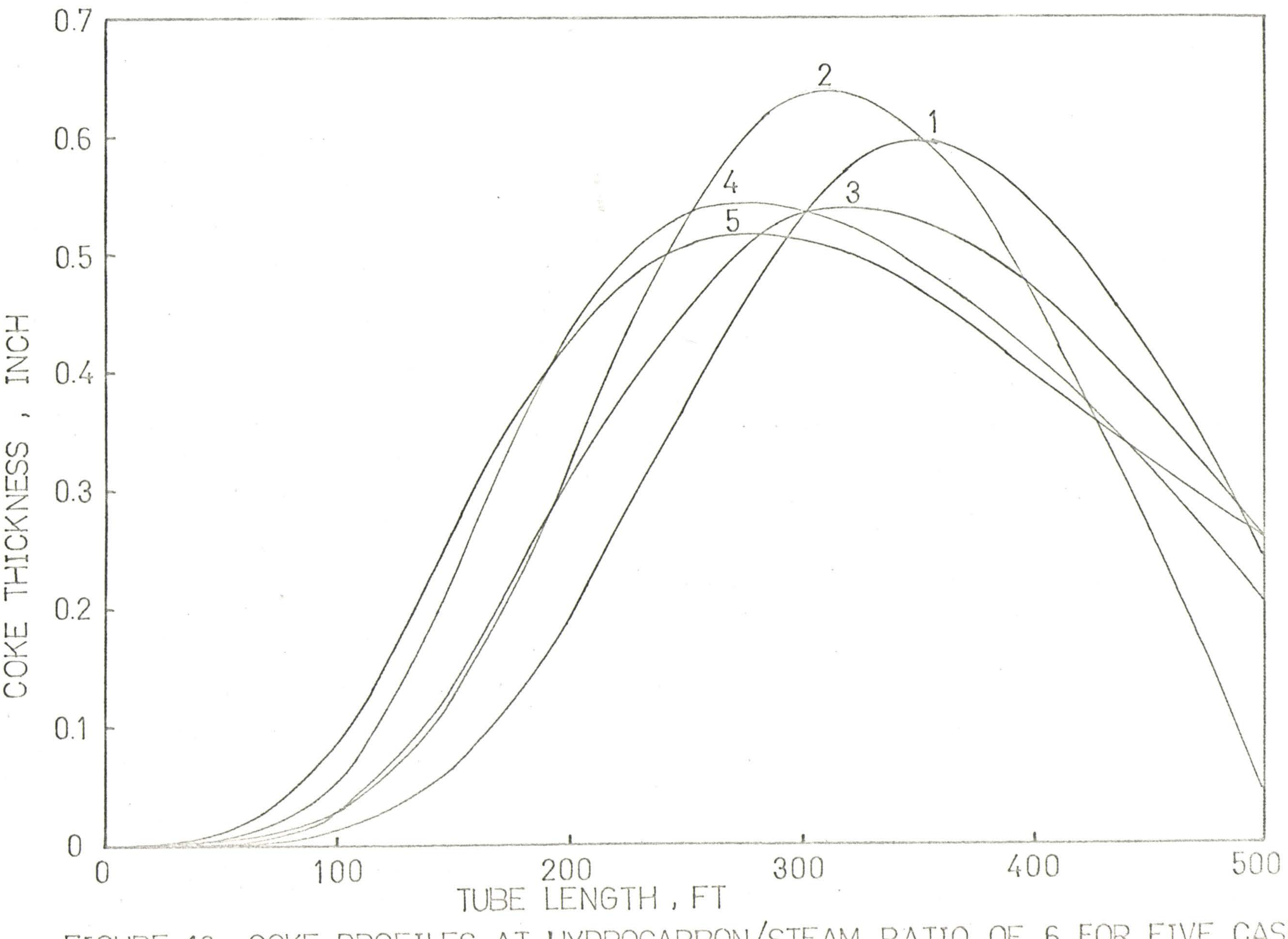

FIGURE 13 COKE PROFILES AT HYDROCARBON/STEAM RATIO OF 6 FOR FIVE CASES

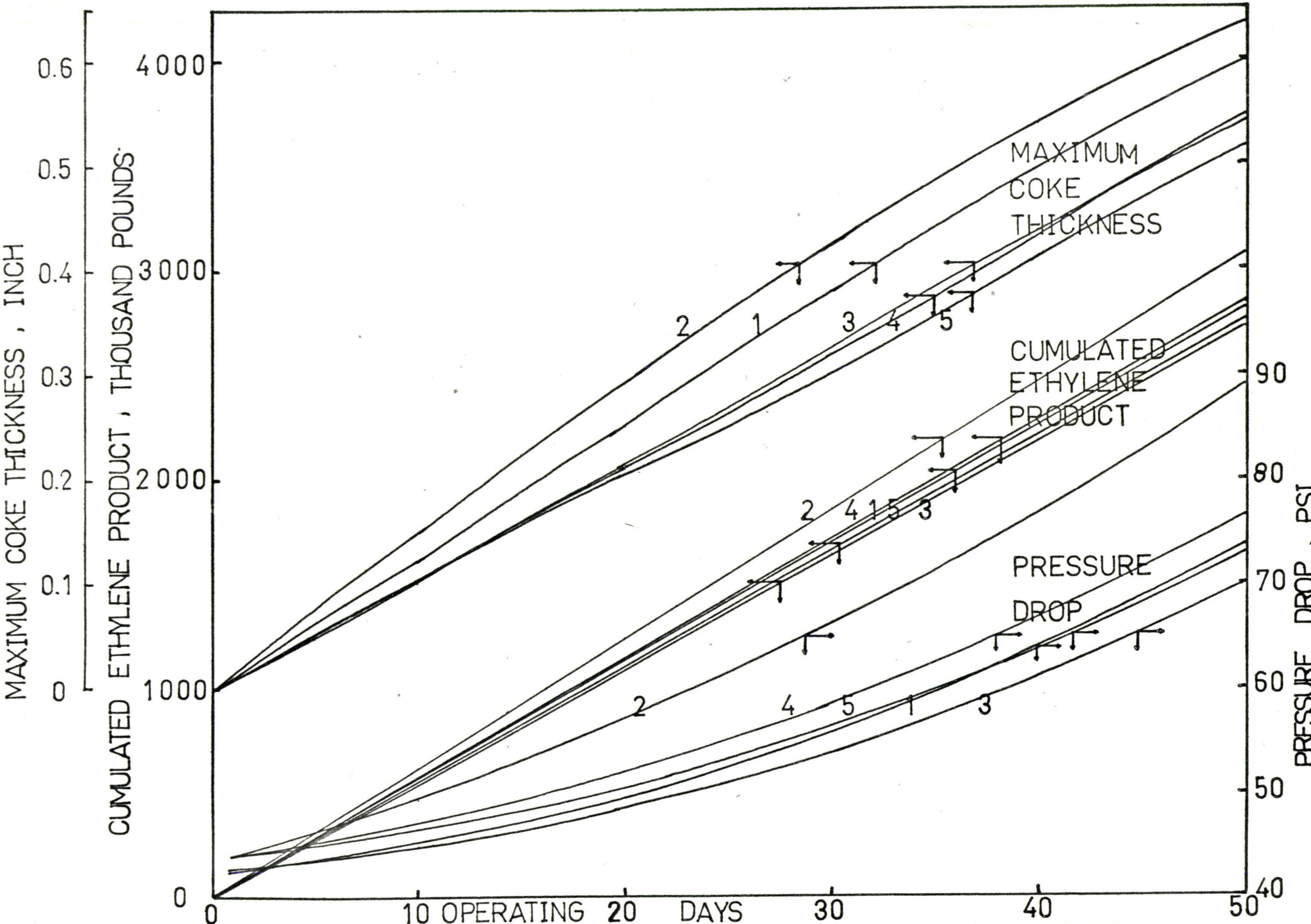

FIGURE 14 MAXIMUM COKE THICKNESS, CUMULATED ETHYLENE PRODUCT, AND PRESSURE DROP VS OPERATING DAYS

7. FUTURE WORK

7.1 Optimization

In the practical world we are interested in optimizing, that is in finding the most economical way to operate such furnaces. Many optimization techniques have been developed by mathematicians and statisticians. These techniques commonly used are: direct method of calculation, classical differential calculus method, Lagrangian multiplier method, the calculus of variations, experimental search method, linear and nonlinear programming, dynamic programming and the maximum principle. Among these mathematical optimization methods, dynamic programming developed by Bellman and the maximum principle derived by Pontryagin are probably the two most successful. Recently these two techniques and linear programming have been widely used in industries for the economical studies.

The further study of a cracking furnace will compare and extend these mathematical optimization methods involving the maximization of net profit.

7.2 Decoking Process

The carbon deposition inside the tubular reactor of a pyrolysis furnace causes a shut-down of the furnace for cleaning the tubes. There are two kinds of processes to do this job: the mechanical and burning processes, the latter has been widely adopted by a number of oil and polymer companies to burn the carbon out of the tubes with steam and air (41).

The burning process has the following advantages: (i) the very clean job produced, (ii) speed of cleaning (six to ten hours normally is sufficient) and (iii) no need to use a polisher or to remove more than a few random-selected heater-plugs for inspection of the job unless a complete tube inspection is desired. The disadvantage of this process is that the furnace must be carefully watched all during the burning process to be sure that the tubes do not get too hot and lose their heat treatment.

The decoking process with steam and air is accomplished by three mechanisms:

(i) Shrinking and cracking the coke loose by heating the tubes from the outside, with steam flow blowing the coke from the coil.

(ii) Chemical reaction of hot coke with steam whereby carbon monoxide, carbon dioxide and hydrogen are produced.

(iii) Chemical reaction between coke and oxygen of the air to produce carbon monoxide and dioxide.

During the decoking process air is continuously fed into the steam, or air is used only intermittently. The general method of the decoking process described in the literature (41) follows:

(i) Steam is introduced through the tubes, the burners are lit, and the temperature of the furnace is brought to

1150^o - 1300^oF. Air is introduced occasionally to induce a heavy spalling of coke, and is cut off as soon as the spalling proceeds satisfactorily.

(ii) The flow of steam, or steam and air, is alternated through the coil every 30 to 45 minutes until coke burning is complete. Each burning with air and steam is accompanied by a blowing-out operation with steam only during which a reddish ash is discharged from the furnace.

Sufficient steam is passed through the tube bank to give a steam inlet pressure of 60 - 125 psig with atmospheric discharge, depending on the size of the furnace and the number of tubes in series. When rather coarse coke particles are being discharged in large quantities, the quantity of steam is reduced to decrease the velocity of these particles and their "sand blasting" effect.

It may be possible to confirm the fractional carbon deposition predicted by the transient model if in the period of decoking the total amount of carbon removed can be measured. If the reactions of carbon with air and steam were complete, the total amount of carbon deposited could be calculated easily with known the concentration of carbon dioxide vs time by analyzing effluent gas. Actually the mechanism of decoking is not a simple one, the principal governing reactions of carbon with steam proposed by Haslam et al (42) are

$$C + H_2O = CO + H_2 \tag{46}$$

$$C + 2H_2O = CO_2 + 2H_2 \quad (47)$$

$$C + CO_2 = 2CO \quad (48)$$

$$CO + H_2O = CO_2 + H_2 \quad (49)$$

hence the possible compositions of effluent gas are oxygen, nitrogen, hydrogen, carbon monoxide and dioxide. In addition, some of the carbon particles may be blown out and be carried away with the quench water without ever being oxidized. There is no attempt made to achieve complete oxidation of carbon in the tubes because it may overheat the reactor. If a complete analyzed data (which also includes carbon particles and steam) is available, the total amount of carbon deposited still can be evaluated. A decoking model concerning solid-gas mass transfer with chemical reaction may be involved in further study.

7.3 Mixed Feed Processes

In commercial operation for the production of ethylene, the feedstock is nearly always a mixture of light hydrocarbons. But the production of ethylene from ethane-propane is practiced in most commercial plants now.

Schutt (29) treated the dehydrogenation of ethane-propane mixture as first-order reactions in the design work, the mechanism and rates of second - and third-order reactions were neglected. The chemical reactions are described as,

$$C_2H_6 \rightleftarrows C_2H_4 + H_2 \quad (50)$$

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \qquad (51)$$

$$C_3H_8 \rightleftarrows C_3H_6 + H_2 \qquad (52)$$

$$2C_3H_8 \rightleftarrows 2C_2H_6 + C_2H_4 \qquad (53)$$

Similarly Buell and Weber (23) used the same reactions without the last one for the furnace design study.

All these workers dealt with the primary reactions only for their design problem, but for the simulation of an ethane-propane dehydrogenation furnace the secondary reactions have to be considered due to coke formation. The chemical reactions and rate equations proposed by Snow and Schutt (3) for ethane dehydrogenation and proposed by Myers and Watson (26) for propane dehydrogenation may possibly be combined for the simulation study of ethane-propane dehydrogenation.

8. CONCLUSION

In the previous work on the design or simulation of a dehydrogenation furnace the fractional carbon deposition was assumed to be a constant value. The transient model presented in this report demonstrates a possible way to determine fractional carbon deposition by applying the direct search method of Hooke and Jeeves. The value of the fractional carbon deposition in the transient model and the correlation of pressure drop vs time by the multiple regression analysis are all obtained from the available plant data which is limited for a short run. It is necessary to have a long run data for predicting the transient behavior of a long run operation.

A cracking furnace may operate more economically if the carbon layer is flatter and the pressure drop is lower. Through these case studies it has been shown that the shape of temperature profile of Case 3 is preferred to the criteria of the termination of the run with constraint on the pressure drop. In this case the furnace may operate longer if the temperature profile can be controlled by adjusting heat flux in the combustion chamber. The cracking process without steam feed shows too much carbon deposited on a high peak shape in all cases which are to be prohibited. Steam has such a function of reducing coke formation, to determine the best hydrocarbon/steam ratio will involve the cost study by applying mathematical optimization methods to maximize the net profit for keeping constant either on total feed rate or on ethane feed rate.

9. NOMENCLATURE

a_{ij} - stoichiometric ratio of ith reaction

C - optimal operating cycles per year

d - coke thickness, in.

D - tube inside diameter, ft.

D_i - tube inside diameter, in.

f - friction factor

F - feed rate, lb.moles/sec.

g_c - gravitational constant, 32.2 ft/sec^2

G - mass velocity, lbs/(ft^2)(sec)

k_i - reaction rate constant, lb.moles/(sec.)(cu.ft)(atm) for a first-order reaction, lb.moles/(sec.)(cu.ft)(atm^2) for a second-order reaction

K_i - equilibrium constant for dehydrogenation of ethane, atm

M - average molecular weight of reacting gas

M_i - molecular weight of ith component

M_c - carbon molecular weight

n' - number of components

n_i - moles of ith component / mole of feed

n_t - gas flow, total moles/mole of feed

P - total pressure of reacting gas, atm.

P' - total pressure of reacting gas, psi

r_j - rate of jth reaction, moles converted/(sec)(cu.ft.)

r_c - rate formation of carbon

R - gas constant, 0.73 (atm)(cu.ft.)/(mole)(^{o}R)

R' - total ethylene produced per cycle, thousands of pounds

s - number of reactions

S - average ethylene produced per day, thousands of pounds per day

t - time, hour

t_c - total time for one cycle, days

$t_{c\ max}$ - total time for one cycle in which S is maximum, days

t_o - operating time per cycle, days

t_s - time of shut-down for cleaning, day

T - temperature of reacting gas, ^{o}R

T_c - critical temperature of reacting gas, ^{o}R

T_{ci} - critical temperature of ith component, ^{o}R

T_r - reduced temperature of reacting gas

V - volume of reacting gas, cu.ft.

W - gas-flow rate, lbs/hr.

y_i - mole fraction of ith component

z - tube length, ft.

μ - viscosity of reacting gas, micropoises

μ_c - critical viscosity of reacting gas, micropoises

μ_{ci} - critical viscosity of ith component, micropoises

μ_r - reduced viscosity of reacting gas

ρ - density of reacting gas, lbs/cu.ft.

ρ_c - carbon density, lbs/cu.ft.

ϕ - fractional carbon deposition

θ - time, days

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APPENDICES

Appendix I Discussions on Computer Techniques

II Simplified Algorithms and Computer Programs.

I. DISCUSSIONS ON COMPUTER TECHNIQUES

There are two computer programs in this report. One for the transient model which consists of a main program, HAJCFR, and a subprogram, REACTR; and the other for case studies, CZSEST. The program HAJCFR is used for the minimization of the least squares deviation by the direct search method of Hooke and Jeeves, REACTR calculates pressure vs time by numerical integration and interpolation methods. CZSEST calculates optimal operating conditions for all five cases at different hydrocarbon/steam ratio.

The direct search method of Hooke and Jeeves is a sequential type of search in which the new trials are based on the past outcomes. The procedure for this computational method is as follows:

(1) Establishing a pattern:

- (a) Choose a base point to begin the search.
- (b) Test both directions of each independent variable near the base.
- (c) If the test is successful, keep the new point as a base point; if not, keep the old one.

(2) Pattern moves:

- (d) By drawing a vector from the original base point through the new one, a temporary head is located beyond the new base point.

- (e) Test each independent variable near this temporary point.
- (f) Check whether the new response is nearer the optimum or not. If it is, repeat this procedure; if not, go back to the previous best point.

(3) Ridge tactics:

- (g) There is no improvement in procedure (2), shortening the step-size. In this case if a better point can be found, the search repeats as procedure (1) and (2).

(4) Ending the search:

- (h) The search terminates when the step sizes fall below a preselected minimum.

A more detail description of this search technique is referred to (6, 7)

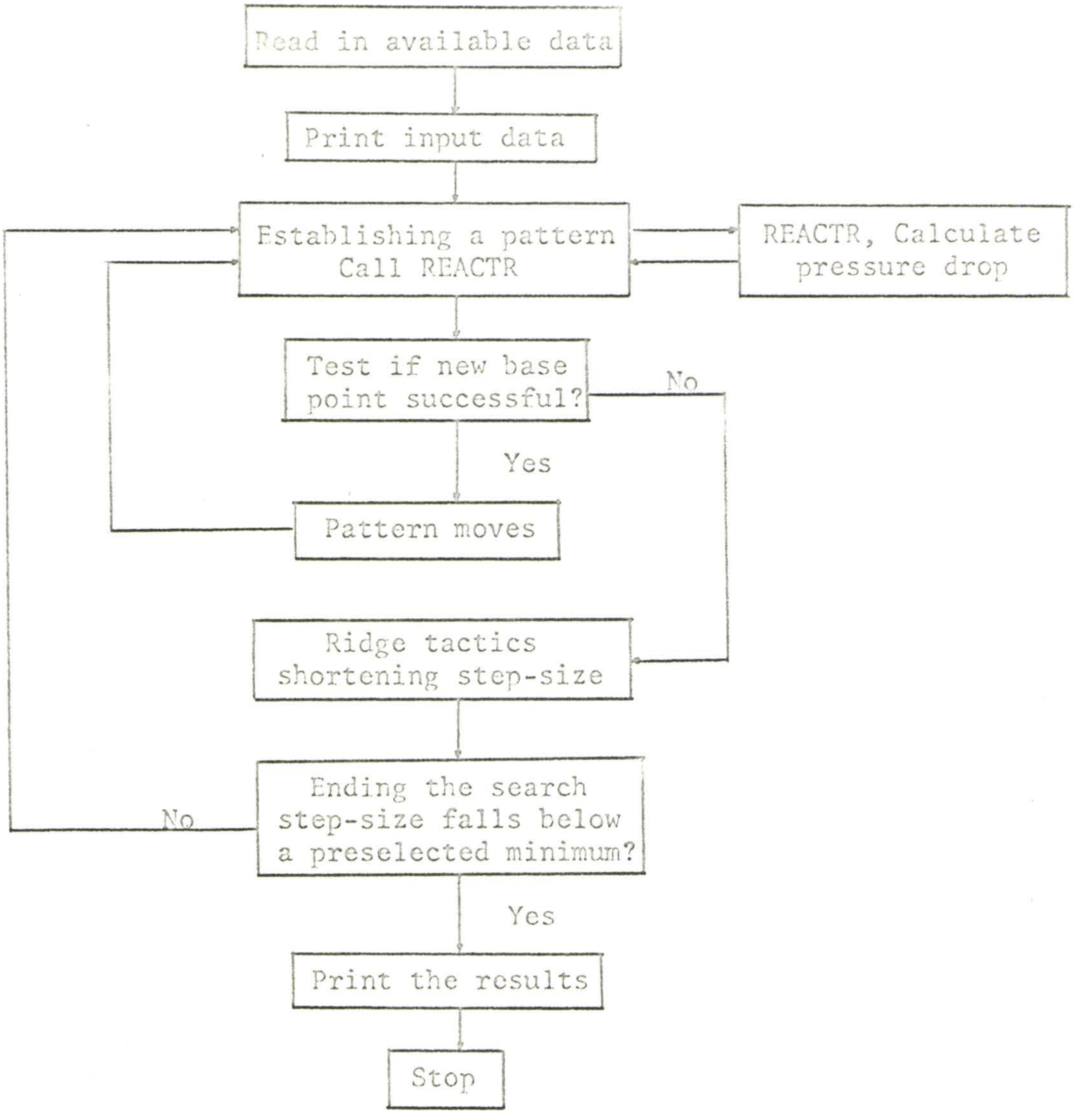
In the convection section the Euler method is used to calculate the pressure drop and linear interpolation is used to calculate the gas temperature. In the radiant section a set of eleven differential equations are solved by the third-order Runge-Kutta method and the temperature of reacting gas is calculated by forward, central and backward interpolation.

The computer time to run a set of data is 4 minutes by using the third-order Runge-Kutta method and 4.5 minutes by using the forth-order Runge Kutta method. The deviation of pressure drop calculated by these two methods is less than one percent. Also it will take long computer time (over 100 minutes) to run the transient model. Hence the third-order Runge-Kutta method can be adopted without losing its accuracy, in addition to reduce computer time.

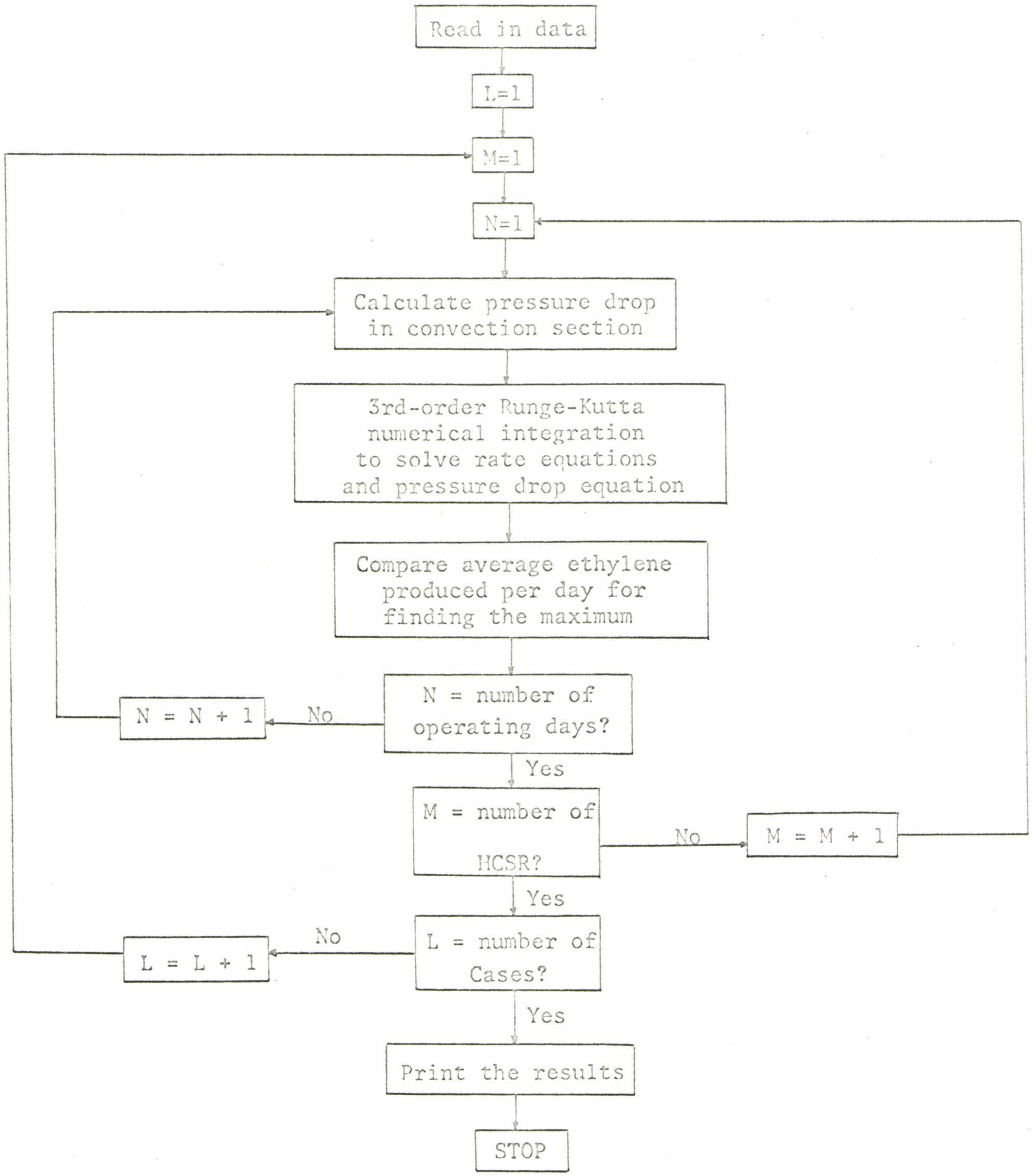
Equation (42), the correlation of pressure drop vs time is obtained by the multiple regression analysis of the short-run data. In the statistical viewpoint this correlation can apply in this limited time range, it may or may not be good over this range which will depend on the trend of the correlation. This correlation has been used to calculate inlet pressure in case studies, but it has been found that the outlet pressure calculated is lower than the plant criteria (11 ∿ 15 psig) after 50 days operation. Hence all cases are limited to 50 days operation.

II. SIMPLIFIED ALGORITHMS

1. Transient Behavior of Ethane Dehydrogenation Model (HAJCFR)



2. Case Studies of an Ethane Dehydrogenation Furnace



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$JOB            003130 M LI
$IBJOB          DECK
$IBFTC HAJCFR   DECK
C-------------------------------------------------------------------------
C
C
C      TRANSIENT BEHAVIOR OF ETHANE DEHYDROGENATION MODEL
C
C
C-------------------------------------------------------------------------
C
C
C THIS IS A MINIMIZATION PROGRAM FOR MULTI-VARIABLES SEARCH. THE DIRECT
C SEARCH METHOD OF HOOKE AND JEEVES IS USED THE MINIMIZATION TECHNIQUE
C IS TO FIND THE LEAST SQUARES DEVIATION
C NP-------NO. OF PARAMETERS
C NB-------NO. OF OBSERVATIONS
C NS-------NO. OF SHORTEN
C NT-------NO. OF TESTS
C TC(I)---CRITICAL TEMPERATURE
C VC(I)---CRITICAL VISCOSITY
C WM(I)---MOLECULAR WEIGHT
C DIAMI---INSIDE DIAMETER OF CLEAN TUBE
C TLEN----TUBE LENGTH IN RADIANT SECTION
C CRHO----CARBON DENSITY
C STEPNO--NO. OF INTEGRATION STEP-SIZE
C AF(I)---PARAMETERS OT BE FOUND
C         AF(1) - FRACTION OF CARBON DEPOSIT
C         AF(2) - MULTIPLIER IN EMPERICAL EQUATION OF PRESSURE DROP
C DZL-----INTERVAL OF TUBE FOR STORAGING TEMPERATURE
C NTD-----NO. OF TEMPERATURE DATA POINTS
C ZL(I)---DISTANCE ALONG THE TUBE
C T(I)----TEMP. PRLFILE ALONG THE TUBE
C F(I,J)--FEED,M/DAY
C DAY(I)--DAY
C PIN(I)--INLET PRESSURE OF CONVECTION SECTION
C TOL-----TOLERANCE OFR MINIMIZING OBJECTIVE FUNCTION
C SP(I)---STEP-SIZE OF AF(I) PERTURBATION
C XPF(I)--PLANT DATA OF PRESSURE DROP
C STPSIZ--NO. OF INTEGRATION STEP-SIZE IN CONVECTION SECTION
C TUBEL---TUBE LENGTH IN CONVECTION SECTION
C DIAMIC--INSIDE DIAMETER OF THE TUBE IN CONVECTIONSECTION
      COMMON NT,NB,TC(15),VC(15),WM(15),DIAMI,TLEN,CRHO,SIEPNO,AF(10)
      COMMON DZL,NTD,ZL(100),T(100),F(200,16),DAY(200),PIN(200)
      COMMON SF(200,15),SDAY(200),SPIN(200),SP(10),XPF(200),PF(200)
      COMMON DIAMIC, TUBEL,STPSIZ,FEED,FEEDM,FED(15),FM(15),XF(15),X(15)
      COMMON XN(15),DXN(15),CM(15),Q(15),QA(15),TGAS,PGAS,TIN(200)
      COMMON TOUT(200),DIAMII(100),DELP(200),STIN(200),STOUT(200)
      COMMON K1
      DIMENSION Y(10),C(10),Z(10)
      READ(5,503) NP,NB,NS,NT,K1
      READ(5,501) (TC(I),I=1,11)
      READ(5,501) (VC(I),I=1,11)
      READ(5,501) (WM(I),I=1,11)
      READ(5,501) DIAMI,TLEN,CRHO,STEPNO
      READ(5,501) DIAMIC,TUBEL,STPSIZ
      READ(5,501) (AF(I),I=1,NP)
      READ(5,511) DZL,NTD
      READ(5,501) (ZL(I),T(I),I=1,NTD)
      READ(5,501) ((F(I,J),J=1,16),I=1,NB)
      READ(5,501) (DAY(I),PIN(I),I=1,NB)
      READ(5,501) TOL,(SP(I),I=1,NP)
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```
      READ(5,501) (XPF(I),I=1,NB)
      READ(5,501) (TIN(I),TOUT(I),I=1,NB)
C
C  STORING INITIAL CONDITION
C
      DO 899 I=1,NB
      DO 898 J=1,11
  898 SF(I,J)=F(I,J)
  899 CONTINUE
      DO 897 I=1,NB
      SDAY(I)=DAY(I)
  897 SPIN(I)=PIN(I)
      DO 825 I=1,NB
      STIN(I)=TIN(I)
  825 STOUT(I)=TOUT(I)
      JJ=0
      KS=0
      TM=0.0
C
C  STORING PREVIOUS VALUES OF PARAMETERS
C
      DO 896 I=1,NP
  896 Y(I)=AF(I)
C
C  PRINT INPUT DATA
C
      WRITE(6,599) (AF(I),I=1,NP)
      WRITE(6,598) (SP(I),I=1,NP)
      WRITE(6,597) TOL
      WRITE(6,596) NP
      WRITE(6,595) NB
      WRITE(6,594) (XPF(I),I=1,NB)
C
C  CALCULATION OF OBJECTIVE FUNCTION
C
  895 JJ=JJ+1
      IF(JJ.GT.NT) GO TO 894
      KCOUNT=0
      CALL  REACTR
      SUM=0.0
      DO 893 I=1,NB
  893 SUM=SUM+(XPF(I)-DELP(I))**2
C
C  ESTABLISHING A PATTERN
C
      B=SUM
      DO 892 I=1,NP
      A=SUM
      IF(JJ.EQ.1)  D=SUM
      AF(I)=AF(I)+SP(I)
      CALL  REACTR
      SUM=0.0
      DO 891 J=1,NB
  891 SUM=SUM+(XPF(J)-DELP(J))**2
      C(I)=SUM
      IF(C(I).LT.D) GO TO 890
      AF(I)=AF(I)-2.*SP(I)
      CALL  REACTR
```

```
      SUM=0.0
      DO 889 J=1,NB
  889 SUM=SUM+(XPF(J)-DELP(J))**2
      C(I)=SUM
      IF(C(I).LT.D) GO TO 890
      AF(I)=AF(I)+SP(I)
      C(I)=A
      KCOUNT=KCOUNT+1
      GO TO 892
  890 D=C(I)
  892 CONTINUE
      WRITE(6,593) JJ,(AF(I),C(I),I=1,NP),B,KS
      IF(KS.GE.NS) GO TO 894
      IF(KCOUNT.GE.NP) GO TO 888
      TM=B
      DO 887 I=1,NP
  887 Z(I)=AF(I)
C
C PATTERN MOVES
C
      DO 886 I=1,NP
  886 AF(I)=2.*AF(I)-Y(I)
      DO 885 I=1,NP
  885 Y(I)=Z(I)
      GO TO 895
C
C BACK TO PREVIOUS BASE SHORTEN SP AND EATABLISH A NEW PATTERN
C
  888 KS=KS+1
      DO 884 I=1,NP
  884 AF(I)=Y(I)
      DO 883 I=1,NP
  883 SP(I)=SP(I)/2.
      GO TO 895
  894 WRITE(6,592) (AF(I),I=1,NP)
      WRITE(6,591) (SP(I),I=1,NP)
      WRITE(6,590) D
      K1=1
      CALL  REACTR
  501 FORMAT(8F10.5)
  503 FORMAT(10I5)
  511 FORMAT(F10.5,I5)
  599 FORMAT(1X,33H INITIAL VALUES OF PARAMETERS ARE,/20X,2F20.5/)
  598 FORMAT(1X,54H INITIAL VALUES OF STEP-SIZE OF AF(I) PERTURBATION AR
     1E,/20X,2F20.5/)
  597 FORMAT(1X,43H TOLERANCE OF MINIMUM OBJECTIVE FUNCTION IS,/20X,F20.
     15/)
  596 FORMAT(1X,20H NO. OF PARAMETERS =,I5/)
  595 FORMAT(1X,20H NO. OF DAYS       =,I5/)
  594 FORMAT(1X,11H PLANT DATA,/20X,10F10.5//)
  593 FORMAT(1X,I5,5F20.5,I5/)
  592 FORMAT(1X,31H FINAL VALUES OF PARAMETERS ARE,/20X,2F20.5/)
  591 FORMAT(1X,52H FINAL VALUES OF STEP-SIZE OF AF(I) PERTURBATION ARE,
     1/20X,2F20.5/)
  590 FORMAT(1X,39H MINIMUM VALUE OF OBJECTIVE FUNCTION IS,F20.5/)
      STOP
      END
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$IBFTC REACTR  DECK
      SUBROUTINE REACTR
C THIS PROGRAM CALCULATES PRESSURE DROP INSIDE THE FURNACE BY USING
C THIRD-ORDER RUNGE KUTTA METHOD,EULER METHOD AND FORWARD,CENTRAL,AND
C BACKWARD INTERPOLATION.
      COMMON NT,NB,TC(15),VC(15),WM(15),DIAMI,TLEN,CRHO,STEPNO,AF(10)
      COMMON DZL,NTD,ZL(100),T(100),F(200,16),DAY(200),PIN(200)
      COMMON SF(200,15),SDAY(200),SPIN(200),SP(10),XPF(200),PF(200)
      COMMON DIAMIC, TUBEL,STPSIZ,FEED,FEEDM,FED(15),FM(15),XF(15),X(15)
      COMMON XN(15),DXN(15),CM(15),Q(15),QA(15),TGAS,PGAS,TIN(200)
      COMMON TOUT(200),DIAMII(100),DELP(200),STIN(200),STOUT(200)
      COMMON K1
      DO 655 I=1,NB
      DO 654 J=1,11
  654 F(I,J)=SF(I,J)
  655 CONTINUE
      DO 653 I=1,NB
      DAY(I)=SDAY(I)
  653 PIN(I)=SPIN(I)
      DO 826 I=1,NB
      TIN(I)=STIN(I)
  826 TOUT(I)=STOUT(I)
      NSTEP=STEPNO+0.001
      DZ=TLEN/STEPNO
      DO 293 I=1,NSTEP
  293 DIAMII(I)=DIAMI
      NOB=0
      DO 652 I=1,NB
      FEED=0.0
      FEEDM=0.0
      DO 2 J=1,11
      FED(J)=F(I,J)*1000./24.
      FM(J)=FED(J)/WM(J)
      FEED=FEED+FED(J)
    2 FEEDM=FEEDM+FM(J)
      DO 3 J=1,11
    3 XF(J)=FM(J)/FEEDM
      DO 6 J=1,10
    6 XN(J)=XF(J)
      DO 7 J=1,11
    7 X(J)=XF(J)
C CALCULATE PRESSURE DROP IN CONVECTION SECTION BY EULER METHOD
      NSTPS=STPSIZ+0.001
      DL=TUBEL/STPSIZ
      PGAS=PIN(I)/14.7
      CL=0.0
      DO 22 JK=1,NSTPS
  700 TGAS=TIN(I)+CL*(TOUT(I)-TIN(I))/TUBEL
      IF(CL.EQ.TUBEL) GO TO 777
      AMWW=0.0
      DO 41 J=1,11
   41 AMWW=AMWW+WM(J)*XF(J)
      RHOO=AMWW*PGAS/TGAS/0.73
      TCMIXX=0.0
      VCMIXX=0.0
      DO 42 J=1,11
      TCMIXX=TCMIXX+XF(J)*TC(J)
   42 VCMIXX=VCMIXX+XF(J)*VC(J)
      TRR=TGAS/TCMIXX
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```
      VR11=-0.1208+0.1354*ALOG(TRR)
      VRR=EXP(5.*VR11)
      VISCC=VCMIXX*VRR
      FDD=(FEED/1000.)**1.8
      VISOO=VISCC**0.2
      DP=-AF(2)*0.0235*FDD*VISOO/RHOO/(DIAMIC**4.8)/14.7
      PGAS=PGAS+DL*DP
      CL=CL+DL
      IF(CL.EQ.TUBEL) GO TO 700
   22 CONTINUE
  777 WRITE(6,555) CL,TGAS,PGAS
      Z=0.0
      WRITE(6,504) Z,TGAS,PGAS,(X(J),J=1,11)
C THIRD-ORDER RUNGE KUTTA INTEGRATION
      DO 11 K=1,NSTEP
      XN(11)=PGAS
      KK=1
      GO TO 600
   51 DO 61 IJ=1,11
      CM(IJ)=DZ*DXN(IJ)
   61 XN(IJ)=XN(IJ)+CM(IJ)/2.
      Z=Z+DZ/2.
      KK=2
      GO TO 600
   52 DO 62 IJ=1,11
      Q(IJ)=DZ*DXN(IJ)
      QA(IJ)=Q(IJ)
   62 XN(IJ)=XN(IJ)+2.*Q(IJ)-1.5*CM(IJ)
      Z=Z+DZ/2.
      KK=3
      GO TO 600
   54 DO 64 IJ=1,11
      Q(IJ)=DZ*DXN(IJ)
   64 XN(IJ)=XN(IJ)+(7.*CM(IJ)-8.*QA(IJ)+Q(IJ))/6.
      GO TO 900
C CALCULATION OF TEMPERATURE ALONG THE TUBE
C 5 POINTS FORMULA OF FORWARD,CENTRAL,AND BACKWARD DIFFERENCE INTERPOLATION
  600 N=1
      IF(Z.LT.ZL(N+1)) GO TO 299
      N=2
      IF(Z.LT.ZL(N+1)) GO TO 299
      IF(Z.EQ.500.) GO TO 295
  297 N=N+1
      IF(N.GE.(NTD-1)) GO TO 296
      IF(Z.LT.ZL(N+1)) GO TO 298
      GO TO 297
C FORWARD DIFFERENCE INTERPOLATION
  299 DTGAS=(T(N+4)-4.*T(N+3)+6.*T(N+2)-4.*T(N+1)+T(N))*(Z-ZL(N))/DZL
      GO TO 300
C CENTRAL DIFFERENCE INTERPOLATION
  298 DTGAS=(T(N+2)-4.*T(N+1)+6.*T(N)-4.*T(N-1)+T(N-2))*(Z-ZL(N))/DZL
      GO TO 300
C BACKWARD DIFFERENCE INTERPOLATION
  296 N=N+1
      DTGAS=(T(N)-4.*T(N-1)+6.*T(N-2)-4.*T(N-3)+T(N-4))*(Z-ZL(N))/DZL
  300 TGAS=T(N)+DTGAS
      GO TO 294
  295 TGAS=T(NTD)
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```
C CALCULATION DENSITY OF GAS MIXTURE
  294 AMW=0.0
      DO 4 J=1,11
    4 AMW=AMW+WM(J)*X(J)
      RHO=(AMW*XN(11)/TGAS)/0.73
C CALCULATION VISCOSITY OF GAS MIXTURE
      TCMIX=0.0
      VCMIX=0.0
      DO 5 J=1,11
      TCMIX=TCMIX+X(J)*TC(J)
    5 VCMIX=VCMIX+X(J)*VC(J)
      TR=TGAS/TCMIX
      VR1=-0.1208+0.1354*ALOG(TR)
      VR=EXP(5.*VR1)
      VISC=VCMIX*VR
C CALCULATION OF TOTAL MOLES PER MOLE OF FEED
      XNT1=0.0
      DO 8 J=1,10
    8 XNT1=XNT1+XN(J)
      XNT=XNT1+XF(11)
C CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS
      EK1=3.31E-7*EXP(0.00778*TGAS)
      EK2=1.0
      RK1=5.3E14*EXP(-64500./TGAS)/TGAS
      RK2=5.9E07*EXP(-49140./TGAS)
      RK3=0.008
      RK4=2.2E09*EXP(-59120./TGAS)
      RK5=0.3E08*EXP(-54040./TGAS)
      RK6=4.51E04*EXP(-44100./TGAS)
C CALCULATION DERIVATIVE OF EACH COMPONENT AND PRESSUR DROP
      RR=(XN(11)*XN(5)/XNT)**2
      R1=RK1*XN(11)*(XN(6)-XN(5)*XN(1)*XN(11)/(EK1*XNT))/XNT
      R2=RK2*XN(11)*(XN(5)*XN(11)*SQRT(XN(6)*XN(1))/XNT-XN(3)/EK2)/XNT
      R3=RK3*R1*XN(11)
      R4=RK4*RR
      R5=RK5*RR/XN(11)
      R6=RK6*RR
C CALCULATION THICKNESS OF COKE
      THETA=12.
      VK=3600.*AF(1)*R6*WM(2)/CRHO
      EVK=EXP(-VK*THETA)
      DETA=DIAMII(K)*(1.-EVK)/2.
      DI=DIAMII(K)-2.*DETA
      IF(DI.LT.0.0) GO TO 1000
      BETA=(900.*3.1416*DI**2/FEEDM)/144.
      DXN(1)=BETA*(R1-2.*R2+0.125*R3+R4+R5+2.*R6)
      DXN(2)=BETA*2.*R6
      DXN(3)=BETA*2.*R2
      DXN(4)=BETA*R5
      DXN(5)=BETA*(R1-R2-R3-R4-R5-R6)
      DXN(6)=BETA*(-R1)
      DXN(7)=BETA*0.25*R3
      DXN(8)=BETA*0.125*R3
      DXN(9)=BETA*0.125*R3
      DXN(10)=BETA*0.333*R4
C PRESSURE DROP
      FD=(FEED/1000.)**1.8
      VISO=VISC**0.2
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```
      DXN(11)=-AF(2)*0.0235*FD*VISO/RHO/(DI**4.8)/14.7
      GO TO (51,52,54),KK
  900 PGAS=XN(11)
      TMOLE=0.0
      DO 9 J=1,10
    9 TMOLE=TMOLE+XN(J)*FEEDM
      TMOLES=TMOLE+FM(11)
      DO 10 J=1,10
   10 X(J)=XN(J)*FEEDM/TMOLES
      X(11)=FM(11)/TMOLES
      CARTHK=2.*DETA+(DIAMI-DIAMII(K))/2.
      DIAMII(K)=DIAMI-2.*CARTHK
      IF(NOB.NE.(NB-1)) GO TO 11
      WRITE(6,507) Z,DETA,DIAMII(K),CARTHK
   11 CONTINUE
      DELP(I)=PIN(I)-14.7*PGAS
      NOB=NOB+1
      WRITE(6,504) Z,TGAS,PGAS,(X(J),J=1,11)
      WRITE(6,508) DAY(I),DELP(I)
  652 CONTINUE
      IF(K1.EQ.0) GO TO 650
      WRITE(6,504) Z,TGAS,PGAS,(X(J),J=1,11)
      GO TO 650
 1000 WRITE(6,505)
      GO TO 650
  504 FORMAT(1X,F6.1,2F10.3,13F8.5/)
  505 FORMAT(///58X,15HTUBE IS PLUGGED)
  507 FORMAT(30X,F10.2,10X,3E20.5/)
  508 FORMAT(1X,2F20.5/)
  555 FORMAT(1X,3F20.5/)
  650 RETURN
      END
$ENTRY

                                   CD TOT   0208
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```
$JOB            003130 M LI
$IBJOB          DECK
$IBFTC CZSEST
C-----------------------------------------------------------------------
C
C     CASE STUDIES OF AN ETHANE DEHYDROGENATION FURNACE
C
C-----------------------------------------------------------------------
C
C     THE PROGRAM CALCULATES OPTIMAL OPFRATION CYCLES PER TEAR(365 DAYS)
C     BY MAXIMIZING AVERAGE ETHYLENE PRODUCED PER DAY
C     ASSUMPTIONS---CONSTANT FEED RATE
C                   TEMPERATURE PROFILE AND HYDROCARBON/STEAM RATIO AS
C                   PARAMETERS
C     HCSR-----------HYDROCARBON/STEAM RATIO
C     HCSR=0.0-------NO STEAM
C     NC2=0----------CONSTANT ETHANE FEED
      DIMENSION TC(15),VC(15),WM(15),AF(5),ZL(100),T(100),OPRCYL(20)
      DIMENSION FED(15),FM(15),XF(15),X(15),XN(15),DXN(15),CM(15)
      DIMENSION Q(15),QA(15),HCSR(20),TOW(365),C2APD(365),C2MAX(20)
      DIMENSION OPCYC(20),DAYTH(20),TOPW(20),NDMAX(20),DELP(365)
      READ(5,503) NB,NOHCSR,NOTP,NC2
      READ(5,501) (TC(I),I=1,11)
      READ(5,501) (VC(I),I=1,11)
      READ(5,501) (WM(I),I=1,11)
      READ(5,501) DIAML,TLEN,CRHO,STEPNO
      READ(5,501) DIAMIC,TUBEL,STPSIZ
      READ(5,501) (AF(I),I=1,2)
      READ(5,511) DZL,NTD
      READ(5,501) F,TIN,TOUT
      READ(5,501) (HCSR(I),I=1,NOHCSR)
      WRITE(6,801)
      NSTEP=STEPNO+0.001
      DZ=TLEN/STEPNO
      DO 499 II=1,NOTP
      READ(5,501) (ZL(I),T(I),I=1,NTD)
      WRITE(6,802) II
      WRITE(6,803)
      WRITE(6,804) (ZL(I),T(I),I=1,NTD)
      WRITE(6,822)
      DO 498 IM=1,NOHCSR
      WRITE(6,805)
      NHSR=HCSR(IM)
      WRITE(6,806) NHSR
      NOB=0
      TOTALW=0.0
      WRITE(6,815)
      DO 100 K=1,NB
      WRITE(6,824) K
      WRITE(6,816)
      DAY=K
      MD=0
  907 FEEDM=0.0
      DO 101 I=1,5
  101 FED(I)=0.0
      DO 102 I=7,10
  102 FED(I)=0.0
       IF(HCSR(IM).EQ.0.0) GO TO 9999
       IF(NC2.EQ.0) GO TO 384
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```
      FED(6)=(F*HCSR(IM)/(HCSR(IM)+1.))*1000./24.
      FED(11)=(F/(HCSR(IM)+1.))*1000./24.
      GO TO 9998
  384 FED(6)=F*1000./24.
      FED(11)=(F/HCSR(IM))*1000./24.
      GO TO 9998
 9999 FED(6)=F*1000./24.
      FED(11)=0.0
 9998 FEED=FED(6)+FED(11)
      DO 103 J=1,11
      FM(J)=FED(J)/WM(J)
  103 FEEDM=FEEDM+FM(J)
      DO 104 I=1,11
  104 XF(I)=FM(I)/FEEDM
      DO 105 I=1,10
  105 XN(I)=XF(I)
      DO 106 I=1,11
  106 X(I)=XF(I)
C CALCULATE INLET PRESSURE
      PIN=(10.5603+0.00635283*(4.75+DAY)**1.65)*(F**0.3)+28.7
      PGAS=PIN/14.7
C CALCULATE PRESSURE DROP IN CONVECTON SECTION BY EULER METHOD
      NSTPS=STPSIZ+0.001
      DL=TUBEL/STPSIZ
      CL=0.0
      DO 22 JK=1,NSTPS
  700 TGAS=TIN+CL*(TOUT-TIN)/TUBEL
      IF(CL.EQ.TUBEL) GO TO 777
      AMWW=0.0
      DO 41 J=1,11
   41 AMWW=AMWW+WM(J)*XF(J)
      RHOO=AMWW*PGAS/TGAS/0.73
      TCMIXX=0.0
      VCMIXX=0.0
      DO 42 J=1,11
      TCMIXX=TCMIXX+XF(J)*TC(J)
   42 VCMIXX=VCMIXX+XF(J)*VC(J)
      TRR=TGAS/TCMIXX
      VR11=-0.1208+0.1354*ALOG(TRR)
      VRR=EXP(5.*VR11)
      VISCC=VCMIXX*VRR
      FDD=(FEED/1000.)**1.8
      VISOO=VISCC**0.2
      DP=-AF(2)*0.0235*FDD*VISOO/RHOO/(DIAMIC**4.8)/14.7
      PGAS=PGAS+DL*DP
      CL=CL+DL
      IF(CL.EQ.TUBEL) GO TO 700
   22 CONTINUE
  777 Z=0.0
C THIRD-ORDER RUNGE KUTTA INTEGRATION
      DO 11 KM=1,NSTEP
      XN(11)=PGAS
      KK=1
      GO TO 600
   51 DO 61 IJ=1,11
      CM(IJ)=DZ*DXN(IJ)
   61 XN(IJ)=XN(IJ)+CM(IJ)/2.
      Z=Z+DZ/2.
```

```
      KK=2
      GO TO 600
   52 DO 62 IJ=1,11
      Q(IJ)=DZ*DXN(IJ)
      QA(IJ)=Q(IJ)
   62 XN(IJ)=XN(IJ)+2.*Q(IJ)-1.5*CM(IJ)
      Z=Z+DZ/2.
      KK=3
      GO TO 600
   54 DO 64 IJ=1,11
      Q(IJ)=DZ*DXN(IJ)
   64 XN(IJ)=XN(IJ)+(7.*CM(IJ)-8.*QA(IJ)+Q(IJ))/6.
      GO TO 900
C CALCULATION OF TEMPERATURE ALONG THE TUBE
C 5 POINTS FORMULA OF FORWARD,CENTRAL,AND BACKWARD DIFFERENCE INTERPOLATION
  600 N=1
      IF(Z.LT.ZL(N+1)) GO TO 299
      N=2
      IF(Z.LT.ZL(N+1)) GO TO 299
      IF(Z.EQ.500.) GO TO 295
  297 N=N+1
      IF(N.GE.(NTD-1)) GO TO 296
      IF(Z.LT.ZL(N+1)) GO TO 298
      GO TO 297
C FORWARD DIFFERENCE INTERPOLATION
  299 DTGAS=(T(N+4)-4.*T(N+3)+6.*T(N+2)-4.*T(N+1)+T(N))*(Z-ZL(N))/DZL
      GO TO 300
C CENTRAL DIFFERENCE INTERPOLATION
  298 DTGAS=(T(N+2)-4.*T(N+1)+6.*T(N)-4.*T(N-1)+T(N-2))*(Z-ZL(N))/DZL
      GO TO 300
C BACKWARD DIFFERENCE INTERPOLATION
  296 N=N+1
      DTGAS=(T(N)-4.*T(N-1)+6.*T(N-2)-4.*T(N-3)+T(N-4))*(Z-ZL(N))/DZL
  300 TGAS=T(N)+DTGAS
      GO TO 294
  295 TGAS=T(NTD)
C CALCULATION DENSITY OF GAS MIXTURE
  294 AMW=0.0
      DO 4 J=1,11
    4 AMW=AMW+WM(J)*X(J)
      RHO=(AMW*XN(11)/TGAS)/0.73
C CALCULATION VISCOSITY OF GAS MIXTURE
      TCMIX=0.0
      VCMIX=0.0
      DO 5 J=1,11
      TCMIX=TCMIX+X(J)*TC(J)
    5 VCMIX=VCMIX+X(J)*VC(J)
      TR=TGAS/TCMIX
      VR1=-0.1208+0.1354*ALOG(TR)
      VR=EXP(5.*VR1)
      VISC=VCMIX*VR
C CALCULATION OF TOTAL MOLES PER MOLE OF FEED
      XNT1=0.0
      DO 8 J=1,10
    8 XNT1=XNT1+XN(J)
      XNT=XNT1+XF(11)
C CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS
      EK1=3.31E-7*EXP(0.00778*TGAS)
```

```
      EK2=1.
      RK1=5.3E14*EXP(-64500./TGAS)/TGAS
      RK2=5.9E07*EXP(-49140./TGAS)
      RK3=0.008
      RK4=2.2E09*EXP(-59120./TGAS)
      RK5=0.3E08*EXP(-54040./TGAS)
      RK6=4.51E04*EXP(-44100./TGAS)
C CALCULATION DERIVATIVE OF EACH COMPONENT AND PRESSURE DROP
      RR=(XN(11)*XN(5)/XNT)**2
      R1=RK1*XN(11)*(XN(6)-XN(5)*XN(1)*XN(11)/(EK1*XNT))/XNT
      R2=RK2*XN(11)*(XN(5)*XN(11)*SQRT(XN(6)*XN(1))/XNT-XN(3)/EK2)/XNT
      R3=RK3*R1*XN(11)
      R4=RK4*RR
      R5=RK5*RR/XN(11)
      R6=RK6*RR
C CALCULATION THICKNESS OF COKE
      THETA = DAY*24.-12.
      VK=3600.*AF(1)*R6*WM(2)/CRHO
      EVK=EXP(-VK*THETA)
      DETA=DIAMI*(1.-EVK)/2.
      DI=DIAMI-2.*DETA
      IF(DI.LT.0.0) GO TO 1000
      BETA=(900.*3.1416*DI**2/FEEDM)/144.
      DXN(1)=BETA*(R1-2.*R2+0.125*R3+R4+R5+2.*R6)
      DXN(2)=BETA*2.*R6
      DXN(3)=BETA*2.*R2
      DXN(4)=BETA*R5
      DXN(5)=BETA*(R1-R2-R3-R4-R5-R6)
      DXN(6)=BETA*(-R1)
      DXN(7)=BETA*0.25*R3
      DXN(8)=BETA*0.125*R3
      DXN(9)=BETA*0.125*R3
      DXN(10)=BETA*0.333*R4
C PRESSURE DROP
      FD=(FEED/1000.)**1.8
      VISO=VISC**0.2
      DXN(11)=-AF(2)*0.0235*FD*VISO/RHO/(DI**4.8)/14.7
      GO TO (51,52,54),KK
  900 PGAS=XN(11)
      TMOLE=0.0
      DO 9 J=1,10
    9 TMOLE=TMOLE+XN(J)*FEEDM
      TMOLES=TMOLE+FM(11)
      DO 10 J=1,10
   10 X(J)=XN(J)*FEEDM/TMOLES
      X(11)=FM(11)/TMOLES
      WRITE(6,817) Z,DETA
   11 CONTINUE
      IF(MD.EQ.1) GO TO 906
      DELP(K)=PIN-14.7*PGAS
      NOB=NOB+1
      TW=X(5)*TMOLES*WM(5)*24./1000.
      TOTALW=TOTALW+TW
      TOW(K)=TOTALW
      OBS=NOB+1
      C2APD(K)=TOW(K)/OBS
      IF(K.NE.1) GO TO 909
      C2MAX(IM)=C2APD(K)
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      NDMAX(IM)=K
  909 IF(C2APD(K).LT.C2MAX(IM)) GO TO 100
      NTS=NDMAX(IM)
      C2TS=C2MAX(IM)
      C2MAX(IM)=C2APD(K)
      NDMAX(IM)=K
  100 CONTINUE
      WRITE(6,823)
      WRITE(6,807)
      WRITE(6,808) (K,C2APD(K),TOW(K),DELP(K),K=1,NB)
      GO TO 201
 1000 WRITE(6,809) K
      DAYTH(IM)=K
      GO TO 202
  201 WRITE(6,823)
      DAYTH(IM)=0.0
  202 M=NDMAX(IM)
      DAYS=M
      OPCYC(IM)=365./(DAYS+1.)
      TOPW(IM)=TOW(M)
      WRITE(6,810)
      WRITE(6,811) NDMAX(IM)
      WRITE(6,812) C2MAX(IM)
      WRITE(6,813) TOW(M)
      WRITE(6,814) OPCYC(IM)
      WRITE(6,815)
      WRITE(6,816)
      DAY=M
      MD=1
      GO TO 907
  906 WRITE(6,818)
  498 CONTINUE
      WRITE(6,819)
      WRITE(6,820) (HCSR(IM),NDMAX(IM),OPCYC(IM),C2MAX(IM),DAYTH(IM),IM=
     11,NOHCSR)
      WRITE(6,821)
  499 CONTINUE
      STOP
  501 FORMAT(8F10.5)
  503 FORMAT(10I5)
  511 FORMAT(F10.5,I5)
  504 FORMAT(1X,F6.1,2F10.3,13F8.5/)
  555 FORMAT(1X,3F20.5/)
  801 FORMAT(1H1,20(/),44X,43H CASE STUDIES OF AN ETHANE CRACKING FURNAC
     1E,4(/),60X,12H BY M. C. LI,4(/),56X,20H DEPT. OF CHEM. ENG.,4(/),6
     20X,12H AUGUST,1967/1H1)
  802 FORMAT(15(/),58X,11H CASE STUDY,I5/)
  803 FORMAT(5(/),1X,131(1H-)/43X,46H TEMPERATURE PROFILE ALONG THE TUBU
     1LAR REACTOR/1X,131(1H-)/)
  804 FORMAT(16X,10F10.2)
  805 FORMAT(/1X,131(1H*)/)
  806 FORMAT(3(/),50X,25H HYDROCARBON/STEAM RATIO=,I5,3(/),1X,131(1H-))
  807 FORMAT(8X,14HOPERATING DAYS,8X,33HAVERAGE ETHYLENE PRODUCED PER DA
     1Y,8X,33HTOTAL WEIGHT OF ETHYLENE PRODUCED,8X,13HPRESSURE DROP/39X,
     215HTHOUSAND POUNDS,26X,15HTHOUSAND POUNDS,22X,3HPSI/1X,131(1H-)//)
  808 FORMAT(13X,I4,23X,F10.5,29X,F15.5,18X,F10.5)
  809 FORMAT(//1X,131(1H-)/40X,26HTHE TUBE IS PLUGGED ON THE,I4,16HTH OP
     1ERATING DAY/1X,131(1H-))
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```
 810 FORMAT(1H1,/1X,131(1H-)/38X,55H THE OPTIMAL CONDITIONS BY MAXIMIZI
    1NG ETHYLENE PRODUCED/1X,131(1H-))
 811 FORMAT(//5X,22HOPTIMAL OPERATING DAYS,79X,I5,12X,4HDAYS)
 812 FORMAT(//5X,33HAVERAGE ETHYLENE PRODUCED PER DAY,63X,F10.5,16H THO
    1USAND POUNDS)
 813 FORMAT(//5X,33HTOTAL WEIGHT OF ETHYLENE PRODUCED,53X,F20.5,16H THO
    1USAND POUNDS)
 814 FORMAT(//5X,44HOPTIMAL OPERATION CYCLES PER YEAR (365 DAYS),52X,F1
    10.2,10X,6HCYCLES)
 815 FORMAT(//5X,32HCOKE FORMATION ALONG THE REACTOR,/)
 816 FORMAT(//40X,12HDISTANCE, FT,20X,15HTHICKNESS, INCH//)
 817 FORMAT(39X,F10.2,16X,E20.5)
 818 FORMAT(//1X,131(1H-)/1X,131(1H*))
 819 FORMAT(1H1,3(/),1X,131(1H-)/7X,4HHCSR,6X,22HOPTIMAL OPERATING DAYS
    1,6X,23HOPTIMAL CYCLES PER YEAR,6X,33HAVERAGE ETHYLENE PRODUCED PER
    2 DAY,6X,13HDAYTH PLUGGED/1X,131(1H-)//)
 820 FORMAT(4X,F7.1,15X,I5,20X,F9.4,25X,F10.5,21X,F7.1/)
 821 FORMAT(/1X,131(1H-),3(/),1X,131(1H*))
 822 FORMAT(/1X,131(1H-)/1H1)
 823 FORMAT(/1X,131(1H-))
 824 FORMAT(10X,14HOPERATING DAYS,I5//)
     END
$ENTRY
$IBSYS

                    CD TOT   0315
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