SIMULATION AND OPTIMIZATION OF AN EXISTING ETHYLBENZENE DEHYDROGENATION REACTOR

SIMULATION AND OPTIMIZATION OF AN EXISTING ETHYLBENZENE DEHYDROGENATION REACTOR

By

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<u>SCOPE AND CONTENTS</u>: The main purpose of this research was to find, from a simulation of an existing reactor under rather heavy constraints, how upon removal of these limitations the same reactor could be operated more economically and efficiently. An accurate, simplified model of the process was developed and used in the design of single and double bed reactors with very consistent results. A better understanding of the process variables, reactions and constraints was obtained by extrapolation of the model within reasonable bounds.

The usefulness of a multivariable search technique applied to a relatively complicated process was proven. Such techniques as Pontryagin's Maximum Principle[1] and dynamic programming[2] become unwieldy for processes involving many state variables. An engineer can quickly grasp the ideas of multivariable search methods whereas it is difficult to understand the above more elaborate techniques without much study. This report may be particularly useful to plant-process engineers who seek a practical optimum-seeking method.

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1. ABSTRACT

A mathematical model has been put together in order to simulate the dehydrogenation of ethylbenzene to styrene in an ideal, adiabatic reactor. The model includes five associated side reactions along with the main one. The differential equations describing the process are integrated by the fourth order Runge-Kutta-Gill method[3] on an IBM 7040 digital computer. Various parametric studies are presented.

A cost function ($GAINED/HOUR) was chosen and for numerous combinations of process variables, subjected to actual and fictitious sets of constraints, the single bed reactor was optimized. Knowledge and experience gained from these studies was applied to the design of a double bed reactor with steam addition at the entrance of each bed. Again, the two-bed situations were optimized. In all optimization studies, a multivariable search technique, that of Rosenbrock[4], was used; slight modifications were necessary for handling constraints.

The problem of catalyst aging has not been investigated since insufficient data were available. All work carried out is for constant hydrocarbon feed rate and composition at a moment in the life of the catalyst.

All results are consistent and show that the single existing reactor can be operated more efficiently if the present plant constraints can be surmounted. The model can be used for the design of new reactors of a type similar to the existing one.

2. PROCESS DESCRIPTION

2.1 A Typical Plant

The production of styrene from benzene and ethylene consists of three basic steps:

(1) ethylbenzene synthesis from benzene and ethylene

(2) ethylbenzene dehydrogenation

(3) styrene separation

Very simply, the overall process may be represented by the flow diagram of Figure 1.

Of the three steps, our only concern is the ethylbenzene dehydrogenation unit. It is assumed that the styrene finishing columns can cope with all exit compositions of the reactor and so, little improvement can be made here. The alkylation section could perhaps be operated more efficiently but that too is not our concern, since little is known of the exact nature of the ethylbenzene synthesis[5]. There is more information about the reactions which take place in the dehydrogenation reactor[6], although which of the numerous postulated ones (see section 4.2) really occur is open to question. We will forego all monetary gains made in reduction of recycle stream rates and will concentrate only on increasing the yield ($GAINED/HOUR) of the reactor. Figure 2 shows the area of concern.

Our tool will be a mathematical model whose parameters have been derived from a single case. This model will be used for extrapolating the process variables over reasonable ranges,

FIGURE 1

OVERALL PROCESS

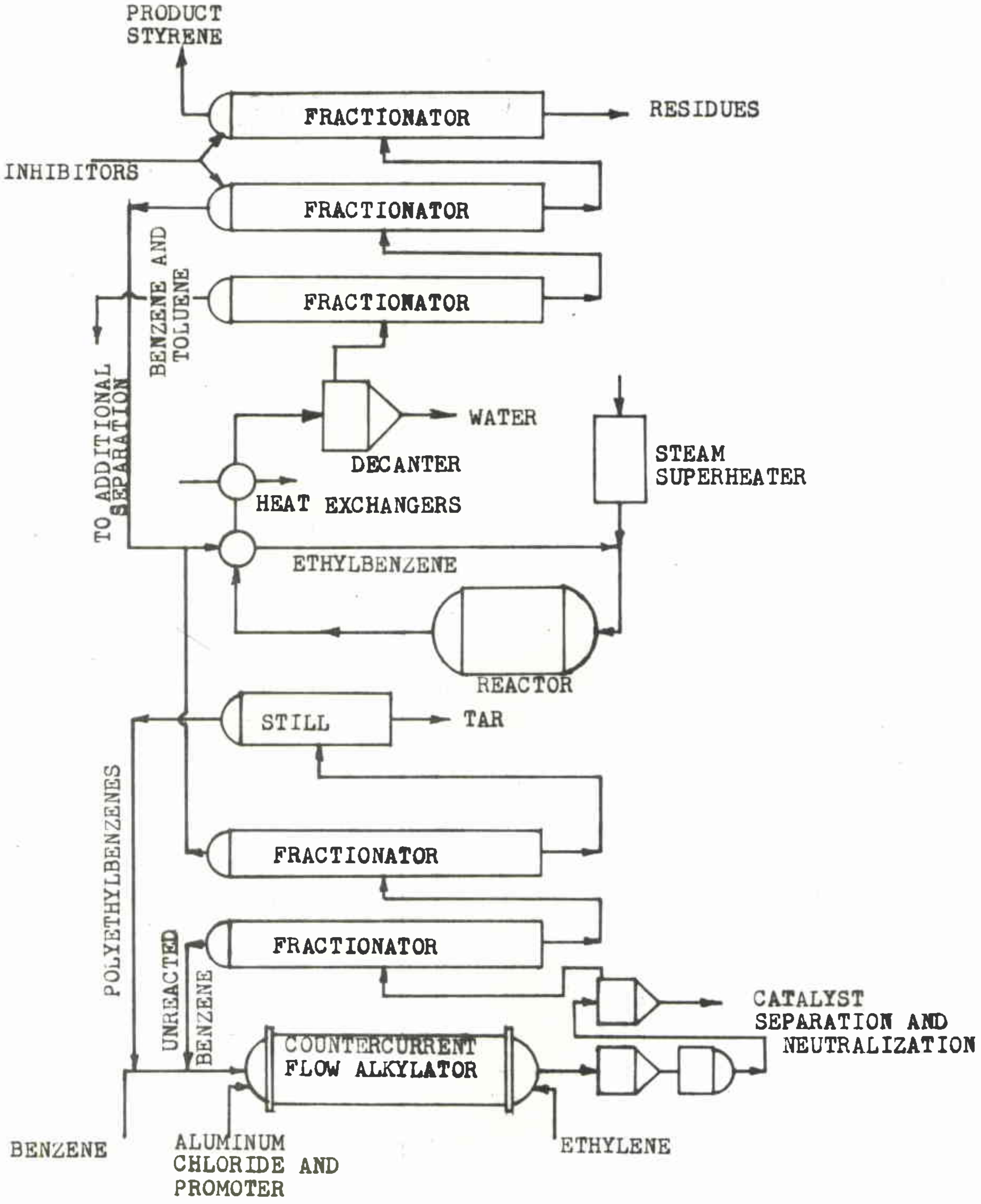
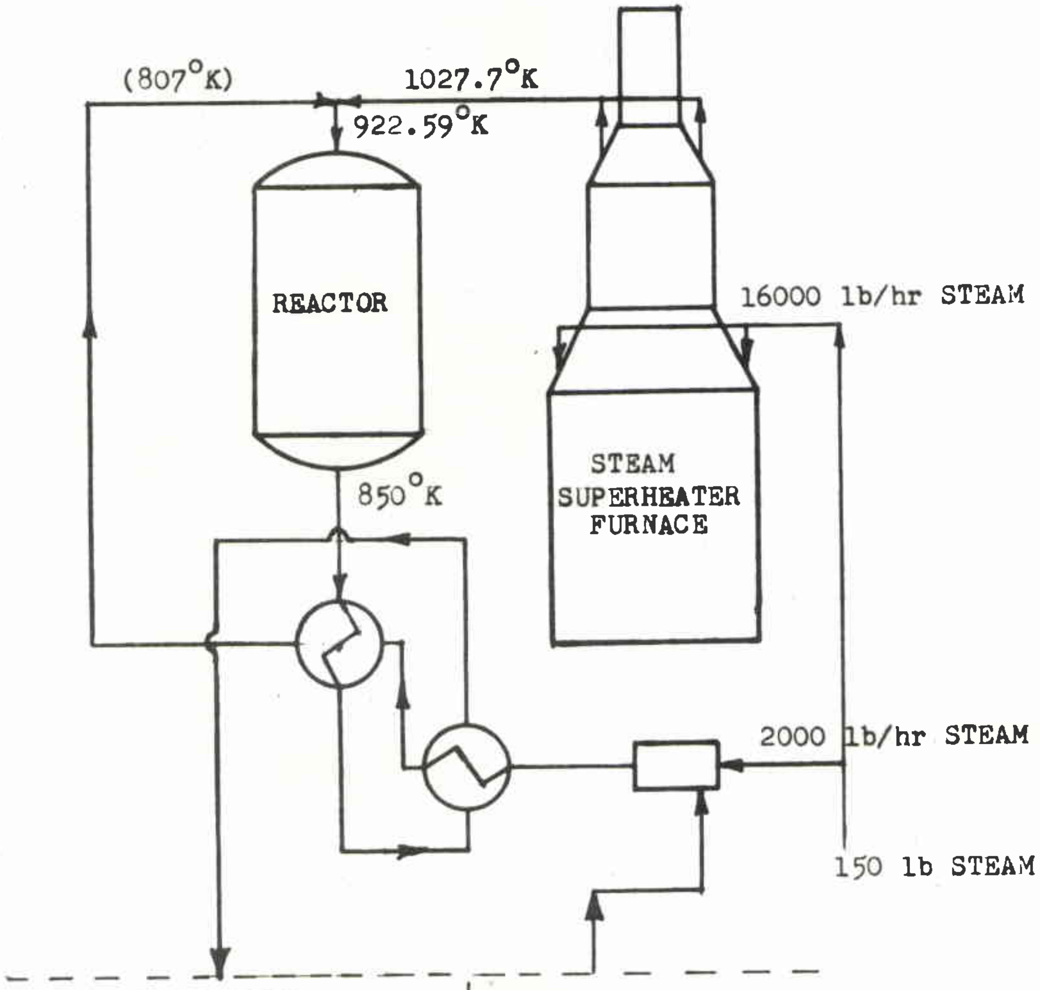


FIGURE 2

THE REACTOR SYSTEM AND APRIL CASE FLOWS



LIQUID PRODUCT

	ACTUAL	MODEL
ETHYLBENZENE	4551.22	4550.58
STYRENE	3573.76	3573.64
TOLUENE	412.02	412.02
BENZENE	258.25	257.53
H_2O	?	17802.21

FEED FROM ALKYLATOR

	ACTUAL = MODEL
ETHYLBENZENE	8630.73
STYRENE	153.45
TOLUENE	178.74
BENZENE	18.54

GASES

	MOLE %		
	ACTUAL	MODEL	lb/hr (MODEL)
HYDROGEN	83.54	85.918	96.41
METHANE	2.80	2.905	26.13
ETHYLENE	3.18	1.337	21.01
CARBON DIOXIDE	9.28	9.733	240.46
CARBON MONOXIDE	0.04	.107	1.70
OTHERS	1.16	0.0	0

NOTE: ALL FLOWS IN LB/HR.
DATA IN PARENTHESIS IS PECULIAR TO MODEL ONLY

thus showing trends comparable to those found from pilot plant studies or extensive plant factorial design runs. Since our plant is operating at a capacity limited by constraints, an EVOP search[7] is impossible. A model seems to be the most practical of all possibilities available.

2.2 Basic Principles

The equilibrium constant, K_p, for the main endothermic reaction increases with temperature:

$$K_P = f(T) = \frac{N_S \cdot N_{H2} \cdot P}{N_{EB} \cdot N_T}$$

where N_S = moles styrene   T = temperature

N_{H2} = moles hydrogen   P = total pressure

N_T = total moles = $N_{EB} + N_{H2} + N_S + N_I$

N_{EB} = moles ethylbenzene N_I = moles inert

High styrene yield is favoured by a low pressure or an increase in the relative amount of the inert compound (N_I) which may be either benzene or steam, the latter being more commonly used. Steam is normally added in the ratio of 2.6 lb./lb. of hydrocarbon[5] giving about 15 moles of steam per mole of ethylbenzene. The total pressure is about 1.4 atmospheres[5] while the reactor inlet temperature of the mixed feed varies around 600°C.-630°C. With no steam at 630°C., the equilibrium conversion is around 30%; while with inert a conversion of 85% can be obtained[5]. The steam also provides the heat required to raise the hydrocarbons up to the required temperature. It also suppresses carbon formation. Direct heating leads to ethylbenzene decomposition.

In achieving a respectable conversion of the main reaction, by-product formation (i.e. benzene, toluene) must be kept at a minimum. Were it not for by-products, it would be best to operate at a very high temperature since the equilibrium conversion and the reaction rate of the main reaction are then highest. Unfortunately, the by-products' rate of formation increases very quickly with temperature and so, a convenient operating temperature represents a compromise between the main reaction and by-product reactions systems. A selective dehydrogenation catalyst is used so that more rapid formation of styrene is possible at lower temperatures with a minimum of side reactions.

2.3 Polymer Plant Setup

At Polymer Corporation in Sarnia, Ontario, the reactor is now being operated at a sub-optimal mass velocity because of limitations in

(i) pressure drop
(ii) furnace capacity
and (iii) condenser capacity.

This combination of constraints has forced operation at a hydrocarbon flow of 9000 lb./hr. with a total steam flow not exceeding 18000 lb./hr. at 1050°K. The furnace can give more steam at a lower temperature but the product condenser system cannot handle the increased throughput. The actual steam to hydrocarbon ratio is 2.0 lb./lb. while 2.6 lb. per lb. is desirable. The reactor inlet pressure is about 2.3 atmospheres (absolute); 1.4 atmospheres[5] is normal but unattainable. It appears that these constraints impose severe restrictions on the operation of the plant. Extrapolation of the operating variables with the model to values beyond these constraints should show considerable overall improvement.

3. MODEL DEVELOPMENT

3.1 Simplifications and Assumptions

Numerous assumptions pertaining to the ideality of the reactor or to the simplification of calculations were made. These are listed below.

(1) Plug flow was assumed.

(2) The reactor was thought to be operating close to adiabatic conditions and hence this assumption was used throughout. Variables such as the overall heat transfer coefficient and the ambient temperature have been eliminated, thus reducing the variables considered in optimization studies to those relevant only to the process.

(3) The pressure and temperature rates of change with bed depth have been updated outside the integration in order to reduce the number of calculations required by each pass through the model. Only the material balances have been integrated according to the fourth order Runge-Kutta-Gill method. Each increment has a constant pressure and temperature over it. The temperature has also been included inside the integration and a comparison is offered in Section 6.4. The model does not suffer from these simplifications.

(4) Since this study deals with an optimization technique that requires numerous passes through the model, it was necessary to keep the calculation time per pass as low as possible. Certain suspected possible side reactions, which

would have improved the accuracy of the model, were therefore omitted (Section 3.2). The six reactions chosen appear to be adequate and any improvement by addition of further reactions would only be offset by the extra time required for computation.

(5) The catalyst efficiency, although in reality varying with both time and bed depth, has been considered to be constant. The nature of the data available (Section 4) has necessitated this assumption. Efficiency factors are tied up in the frequency factors, making it impossible to obtain absolute values.

(6) It was assumed that none of the aromatic rings would decompose. A discussion of this is found in Section 4.3. This assumption enabled the calculation of an overall material balance between the feed and liquid product-gas product streams.

(7) The choice of activation energies for the reactions may be open to question since some of the values apply to different catalysts and reacting systems. Sections 3.3 and 5.4 elaborate on these activation energies.

Other assumptions are relevant to particular cases only and these will be discussed as they arise in following sections of the report.

3.1 Basic Reactions

Research (References 5, 6, 13) shows that the following reactions could occur simultaneously in the reactor:

(1) $EB \longrightarrow STY + H_2$

(2) $EB \longrightarrow BZ + C_2H_4$

(3) EB + H_2 —> TOL + CH_4

(4) EB + H_2 —> BZ + C_2H_6

(5) TOL + H_2 —> BZ + CH_4

(6) STY + H_2 —> BZ + C_2H_4

(7) STY —> BZ + C_2H_2

(8) STY —> $C_6H_5C_2H + H_2$

(9) $C_6H_5C_2H + H_2O$ —> $C_6H_5CO(CH_3)$

(10) C_2H_6 —> $C_2H_4 + H_2$

(11) C_2H_4 —> $C_2H_2 + H_2$

(12) C_2H_2 —> $H_2 + 2C$

(13) $C + 2H_2O$ —> $CO_2 + 2H_2$

(14) $\frac{1}{2}C_2H_4 + H_2O$ --> $CO + 2H_2$

(15) $CH_4 + H_2O$ —> $CO + 3H_2$

(16) $CO + H_2O$ —> $CO_2 + H_2$

LEGEND

EB = ethylbenzene
STY = styrene
TOL = toluene
BZ = benzene

Apart from the main reaction (1) and two main side reactions (2, 3) very little is known about the lesser side reactions (4 to 16). It is generally accepted[6] that reactions 1-3 constitute the most important ones. Any of the reactions 4 through 16 may be combined with the basic three.

The plant feed, liquid product and gas product analyses (Table 1) showed that almost all of the liquid product could be described by ethylbenzene, styrene, benzene and toluene while most of the product gas could be attributed to hydrogen (83 mole %) and carbon dioxide (10 mole %). If these six compounds can be accounted for, the model would be representative of the plant situation. Methane and ethylbene would also be traced.

Which set of reactions of the sixteen presented will be most representative? Since no acetylene was detected in the products, reactions involving this component (7, 11, 12) have been excluded from consideration. Also the carbon deposition and removal reactions (12, 13) are neglected since we are concerned with the reactor at a given catalyst age. That is, the amount of carbon in the system will be constant. The acetophenone reactions (8, 9) have also been excluded since this compound was not detected in the hydrocarbon liquid and gas products. It could be that due to a relatively high solubility, this compound has dissolved in the water (condensed steam) and so has escaped the analysis which were carried out.

It is important that the model not only be representative but that it involve as few of the above equations as possible in order to keep computation time to a minimum.

Preliminary models based on three (1, 2, 3), four (1, 2, 3, 4) and six (1, 2, 3,14, 15, 16) reactions were found to be inadequate for representation of the gas product although

TABLE 1

DATA AVAILABLE

(A) PROCESS VARIABLES

CASE	TOTAL HYDRO-CARBON FEED LB./HR.	STEAM RATE LB./HR.	INLET PRESSURE (ABS) ATMOSPHERE	STEAM TEMP. °K	MIXED FEED TEMPERATURE °K	EXIT TEMP. °K	TOTAL LIQUID PRODUCT LB./HR.
POLY-29	8393.24	15965.5	2.21	*	922.59	*	8167.43
APRIL	9000	18000	2.37	1027.73	922.59	866.36	8832.43
MAY	9000	18000	2.37	1021.50	922.0	866.0	8832.17
JUNE	9000	18000	2.37	1022.0	920.33	865.82	8832.19

(B) HYDROCARBON FEED BREAKDOWN

CASE	ETHYLBENZENE LB./HR.	ETHYLBENZENE WT.%	STYRENE LB./HR.	STYRENE WT.%	TOLUENE LB./HR.	TOLUENE WT. %	BENZENE LB./HR.	BENZENE WT.%	OTHERS LB./HR.	OTHERS WT.%
POLY-29	7939.12	94.589	108.13	1.288	329.41	3.924	16.58	.197	*	.0
APRIL	8630.73	95.704	153.45	1.702	178.74	1.982	18.54	.206	18.40	.204
MAY	8536.00	95.40	121.50	1.35	229.50	2.55	58.50	.65	4.50	.05
JUNE	8548.83	94.987	177.66	1.974	244.89	2.721	12.51	.139	16.11	.179

(C) LIQUID PRODUCT BREAKDOWN

CASE	ETHYLBENZENE LB./HR.	ETHYLBENZENE WT.%	STYRENE LB./HR.	STYRENE WT.%	TOLUENE LB./HR.	TOLUENE WT.%	BENZENE LB./HR.	BENZENE WT.%	OTHERS LB./HR.	OTHERS WT.%
POLY-29	3971.67	48.64	3520.38	43.15	531.43	6.50	213.17	2.61	*	-
APRIL	4551.22	51.53	3573.76	40.463	412.02	4.665	258.25	2.924	37.18	.421
MAY	4438.17	50.25	3603.52	40.80	481.35	5.45	295.88	3.35	13.25	.15
JUNE	4708.97	53.316	3441.29	38.963	433.48	4.908	213.47	2.417	34.98	.396

(D) GAS ANALYSIS

CASE	MOLE PER CENTS CO	N_2	CO_2	H_2	C_1	C_2^-	C_2°	C_3^-	C_3°
POLY-29	*								
APRIL	.04	.34	9.28	33.54	2.8	3.18	0.70	0.1	0.02
MAY	.30	-	8.4	84.8	2.8	2.8	0.60	0.1	(Σ = 0.2 →)
JUNE	(Σ = 1.42)		7.48	83.38	2.68	2.74	0.70	(	Σ = 1.6 →)

*.... unavailable

they could readily be made to account for the liquid product by a suitable choice of the rate equation frequency factors, explained in Section 3.3.

It was found that a combination of reactions 1, 2, 3, 14, 15 and 16 gave good results (Table 3) for both liquid and gas effluent streams. A further addition of reactions to these six would perhaps result in better answers, but at the expense of valuable computer time. Thus the chosen six reactions should suffice.

3.3 Reaction Rate Equations

The general rate expression used in the model has the form:

$r_i = k_i f(P_i)$

where r = lb.mole/(sec. lb. catalyst)

k_i = lb.mole/(sec. lb. catalyst atmos.^{n})

$= EXP(- \Delta E_i/RT + A_i)$[**]

ΔE_i = Activation energy in calories/gm.mole

A_i = frequency factor exponent

R = 1.987 calories/gm.mole $^{\circ}K$

T = $^{\circ}K$

K_p = equilibrium constant (reaction 1 below)[*]

P_T = total pressure in atmospheres

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[*] Appendix 1

[**] Appendix 2 and 3

TABLE 3

MODEL RESULTS

(A) PRODUCT DISTRIBUTIONS (LB./HR.)

COMPONENT	CASE POLY-29	APRIL	MAY	JUNE
Ethylbenzene	3975.12	4550.58	4436.00	4713.31
Styrene	3517.13	3573.64	3600.45	3446.27
Hydrogen	89.35	96.41	95.02	95.42
Ethylene	18.52	21.01	24.88	10.25
Benzene	209.51	257.53	291.52	215.63
Toluene	526.13	412.02	478.45	442.29
Methane	22.91	26.13	28.02	15.73
Ethane	0.0	0.0	0.0	0.0
Acetylene	0.0	0.0	0.0	0.0
Ethynylbenzene	0.0	0.0	0.0	0.0
Steam	15810.66	17802.21	17815.84	17798.39
Carbon Monoxide	1.43	1.70	1.83	1.79
Carbon Dioxide	188.16	240.46	223.69	245.06
Carbon	0.0	0.0	0.0	0.0

TABLE 3 - Continued

(B) TYPICAL GAS ANALYSIS - COMPARISON BETWEEN PLANT AND MODEL FOR APRIL CASE

COMPOUND	MODEL LB./HR.	MODEL LB.MOL./HR	MODEL MOL. %	PLANT MOL. %
H_2	96.41	48.20	85.918	83.54
C_2H_4	21.01	.75	1.337	3.18
CH_4	26.13	1.63	2.905	2.80
CO	1.70	.06	0.107	0.04
CO_2	240.46	5.46	9.733	9.28
OTHERS	0	0	0	1.16
			Σ = 100.00	Σ = 100.00

(C) CONVERSIONS OF REACTIONS (X_F)

REACTION NUMBER	CASE POLY-29	APRIL	MAY	JUNE
1	.43772 E 00	.40397 E 00	.41305 E 00	.38976 E 00
2	.33028 E-01	.37634 E-01	.36885 E-01	.32292 E-01
3	.28551 E-01	.31145 E-01	.33411 E-01	.26607 E-01
14	.40808 E-02	.46211 E-02	.41925 E-02	.44701 E-02
15	.79711 E-03	.90337 E-03	.95565 E-03	.11622 E-02
16	.48202 E-02	.54637 E-02	.50828 E-02	.55683 E-02

TABLE 3 - Continued

(D) TEMPERATURES, PRESSURES

DATA	CASE POLY-29	APRIL	MAY	JUNE
Inlet Temperature (°K)	922.59	922.59	922.00	920.33
Outlet Temperature (°K)	845.53	850.76	849.58	850.98
Inlet Pressure (Atmos.)	2.21	2.37	2.37	2.37
Outlet Pressure (Atmos.)	2.13	2.29	2.29	2.29

REACTION NUMBER	REACTION	EQUATION
1	$EB \longrightarrow STY + H_2$	$r_1 = k_1 \cdot (P_{EB} - \frac{P_{STY} \cdot P_{H2}}{K_p})$
2	$EB \longrightarrow BZ + C_2H_4$	$r_2 = k_2 \cdot P_{EB}$
3	$EB + H_2 \longrightarrow TOL + CH_4$	$r_3 = k_3 \cdot P_{EB} \cdot P_{H_2}$
14	$H_2O + \frac{1}{2}C_2H_4 \longrightarrow CO + 2H_2$	$r_{14} = k_{14} \cdot P_{H_2O} \cdot (P_{C_2H_4})^{\frac{1}{2}}$
15	$H_2O + CH_4 \longrightarrow CO + 3H_2$	$r_{15} = k_{15} \cdot P_{H_2O} \cdot P_{CH_4}$
16	$H_2O + CO \longrightarrow CO_2 + H_2$	$r_{16} = \frac{P_T}{T^3} \cdot k_{16} \cdot P_{H_2O} \cdot P_{CO}$

As shown, only the main reaction has been considered to act in reverse. The other five do not approach equilibrium in the extent of the 1st and hence only their forward reaction rate is dealt with $^{(6,i)}$. Slight error is introduced here but it should be quite insignificant. All six reactions are assumed to occur on the catalyst surface.*

3.4 Material Balances

The material balance equations are now written according to the plug flow assumption. Conversions (X_i) are expressed as the mole fraction of ethylbenzene (Reactions 1, 2, 3) or steam (Reactions 14, 15, 16) reacted.

* References may be found in Appendix 2.

REACTION NUMBER	MATERIAL BALANCE
1	$E \frac{dX_1}{dZ} = r_1 . A . \rho_B$
2	$E \frac{dX_2}{dZ} = r_2 . A . \rho_B$
3	$E \frac{dX_3}{dZ} = r_3 . A . \rho_B$
14	$W \frac{dX_{14}}{dZ} = r_{14} . A . \rho_B$
15	$W \frac{dX_{15}}{dZ} = r_{15} . A . \rho_B$
16	$W \frac{dX_{16}}{dZ} = r_{16} . A . \rho_B$

Nomenclature

E = initial lb. moles ethylbenzene per sec.

W = initial lb. moles steam per sec.

A = reactor cross-sectional area ($Ft.^2$)

r_i, i = 1, 3 & 14, 16 reaction rate expressions (3.3)

Z = reactor bed depth (Ft.)

ρ_B = catalyst bulk density ($Lb./Ft.^3$)

X = mole fraction of E or W converted

Note: Material balance calculations for a 2-Bed reactor system are to be found in Appendix 7.

3.5 Energy Balance

Over a reactor section dZ, the energy balance may be written:*

$$- E \sum_{i=1}^{3} \frac{dX_i}{dZ} \cdot \Delta H_i - W \sum_{i=14}^{16} \frac{dX_i}{dZ} \cdot \Delta H_i - U(T-T_s) \frac{4\alpha}{D}$$

$$= \sum_{j=1}^{14^{*}} n_j C_{p_j} \cdot \frac{dT}{dZ}$$

Under adiabatic conditions the third term of the L. H. S. disappears leaving

$$\frac{dT}{dZ} = \frac{-E \sum_{i=1}^{3} \frac{dX_i}{dZ} \cdot \Delta H_i - W \sum_{i=14}^{16} \frac{dX_i}{dZ} \cdot \Delta H_i}{\sum_{j=1}^{14} n_j C_{p_j}} = \frac{N}{D}$$

When treating dT as a finite difference (i.e. when T is not included in the Runge-Kutta Integration), we may write

$$\Delta T = \frac{N. \Delta Z}{D}$$

$$T_i = T_{i-1} - \Delta T$$

* 14 compounds were considered

3.6 Pressure Drop

The rate of change of pressure with bed depth is found by the Ergun Equation[9].

$$\frac{dP}{dZ} = \frac{V_o(1-\epsilon)}{D_p \epsilon^3} \left(\frac{150\mu(1-\epsilon)}{D_p} + 1.75 V_o \rho_g \right) \frac{1}{144(14.7) g_c} = R$$

* Nomenclature may be found on page 19A

NOMENCLATURE USED IN ENERGY BALANCE

E	Initial lb. moles ethylbenzene per sec.
W	Initial lb. moles steam per sec.
X_i	Mole fraction of E or W converted
Z	Bed depth - (Ft.)
ΔH	Heat of Reaction (BTU/Lb.Mol.)
U	Reactor Surroundings heat transfer coefficient (BTU/sec.ft.^{2} $^\circ$K)
T	Reactor Temperature at bed depth Z ($^\circ$K)
T_s	Ambient temperature ($^\circ$K)
Ƶ	Reactor cross sectional area (Ft.^{2})
D	Reactor diameter (Ft.)
n	Component flow rate Lb.mol./sec.
C_p	Component heat capacity =(BTU/Lb.mol $^\circ$K)

Treating P over a finite difference we get

$$\Delta P = R \times \Delta Z$$

$$P_i = P_{i-1} - \Delta P$$

Note: In all runs mentioned in this report, the Ergun equation was missing the V_o of the turbulent flow contribution to pressure drop. The equation actually used reads

$$\frac{dP}{dZ} = \frac{V_o(1-\epsilon)}{D_p\epsilon^3}\left(\frac{150\mu(1-\epsilon)}{D_p} + 1.75\rho_g\right)\frac{1}{144.g_c.14.7}$$

where $\epsilon = 0.35$.

When the equation is used in the correct form, $\epsilon = .445$ must be used in order to simulate the observed plant pressure drop. Both pressure drop equations give the same results for all extremes of variables met in the parameter and optimization searches. Appendix 15 compares the two equations and shows that we may have complete confidence in the reported search optima.

Nomenclature

P = atmospheres

V_o = superficial velocity (Ft./Sec.)

ϵ = voidage fraction

Z = bed depth (Ft.)

D_p = catalyst particle diameter (Ft.)

ρ_g = gas density (Lb./ft.^{3})

Nomenclature -Continued

μ = viscosity of mixture*

= .03 x 6.72 x 10^{-4} (Lb./ft.sec.)

g_c = 32.2 (Lb. mass x ft./lb. force x sec.^2)

14.7 = lb./in.^2 atmos.

144. = $\text{in.}^2/\text{ft.}^2$

Reactor Inlet Pressure - Visual observation of the 29 cases comprising the POLY-29 case (4.1 and 5.3) indicated that inlet pressure seemed to be a linear function of the total molar flow. The following expression resulted:

$$P = 1.046 + .00122 \times S$$

where P = atmospheres

S = Lb. moles/hour in total mixed feed stream.

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* FOUST, S. F. et al, Principles of Unit Operations, Wiley, p. 557 (1962). A constant value of μ was used, i.e. μ of water vapour at high temperatures.

3.7 Heats of Reaction

The heats of reaction are expressed as linear functions of temperature over the range of temperature considered. In general,

$$\Delta H_i = a + bT$$

where ΔH = cal./gm.mole

T = $^\circ K$

a and b values:

REACTION NUMBER	a	b	REFERENCE* NUMBER
1	28843	1.09	1
2	25992	-1.90	1
3	-12702	-3.15	1
14	19602	2.11	2
15	50460	3.96	2
16	-10802	2.50	2

* References are given following 3.8

3.8 Heat Capacities

Heat capacities are expressed as quadratic functions of temperature. The relation $d(\Delta H)/dT = C_p$, implies that ΔH should be in cubic form to be consistent with a quadratic C_p function. However little error is introduced by the linear ΔH assumption (Appendix 4).

$$C_p = a + bT + cT^2$$

where:

C_p = Cal./gm.mole°C. or BTU/lb.mole°F.

T = °K

Table of C_p Values

PROGRAM COMPOUND NUMBER	COMPONENT	a	b x 10^{-3}	c x 10^{-6}	RREFERENCE NUMBER
1	Ethylbenzene	2.23	110.	-36.7	4
2	Styrene	4.07	97.7	-33.1	4
3	Hydrogen	6.947	-0.2	.481	3
4	Ethylene	2.83	28.601	- 8.726	3
5	Benzene	-4.09 **	77.621	-26.426	3
6	Toluene	.576	93.493	-31.227	3
7	Methane	3.381	18.044	- 4.3	3
8	Ethane *	2.247	38.201	-11.049	3
9	Acetylene*	7.331	12.622	- 3.889	3
10	$C_6H_5C_2H$ * (ethynylbenzene)	3.47	91.9	-31.4	4
11	Steam	7.256	2.298	.284	3
12	Carbon Monoxide	6.42	1.665	- .196	3
13	Carbon Dioxide	6.214	10.396	- 3.545	3
14	Carbon *	4.10	1.02	0	3

* These compounds do not appear in the model

** See Appendix 14

References for ΔH and C_p formulae

REFERENCE NUMBER	REFERENCE
1	WENNER, R. R., and E. C. DYBDAL, Chem. Eng. Prog. Vol. 44, No. 4. 275 (1948) - their values were taken from A. P. I. 44

REFERENCE NUMBER	REFERENCE
2	Calculated from Smith and Van Ness C_p data. - Same reference as 3.
3	SMITH, and VAN NESS, "Introduction to Chemical Engineering Thermodynamics", McGraw-Hill (1959).
4	BOUNDY, R. H. and R. F. BOYER, Styrene, Its Polymers, Copolymers and Derivatives, Reinhold (1952). C_p in form $a + bT + cT^2$ was regressed from C_p vs. T data in this text.

3.9 Calculation

The six material balances, with $X_i = 0$, at the reactor entrance, have been solved simultaneously with the Fourth Order Runge-Kutta-Gill method of integration. Temperature and pressure have been dealt with by holding them constant over each integration step; they are updated at the end of every such increment.

A complete Fortran IV listing of the model is given in Appendix 5.

4. DATA

4.1 Data Available

It is necessary to discuss the data available and to point out some of their shortcomings. Polymer had run a factorial design with twenty-nine steady-state situations (to be referred to as Poly-29) in order to find a regression equation to describe the reactor. Only the information shown in Table 1 under Poly-29 was recorded. Mean values of all 29 cases are shown. Neither gas analysis, nor reactor exit temperature, nor any internal reactor temperature was available.

In April, May and June, 1966, data were taken representing mean conditions for periods of 1 to 5 days operation (Table 1). The gas compositions (Mole %) are only useful for determining the relative amount of each gaseous compound since absolute amounts could not be calculated. Although the reactor exit temperatures were taken, still no internal values were known. The model was created without knowledge of the reactor temperature profile.

Only in late June and August, 1966, were temperature profiles taken. These profiles (Table 2) are discussed in Section 5.7 and indicate that the real situation is close to an adiabatic one. The exact location of the thermocouples in the bed is shown in Figure 3 depicting the reactor. The temperature profiles of Table 2 are compared to the model

TABLE 2

TEMPERATURE PROFILE DATA

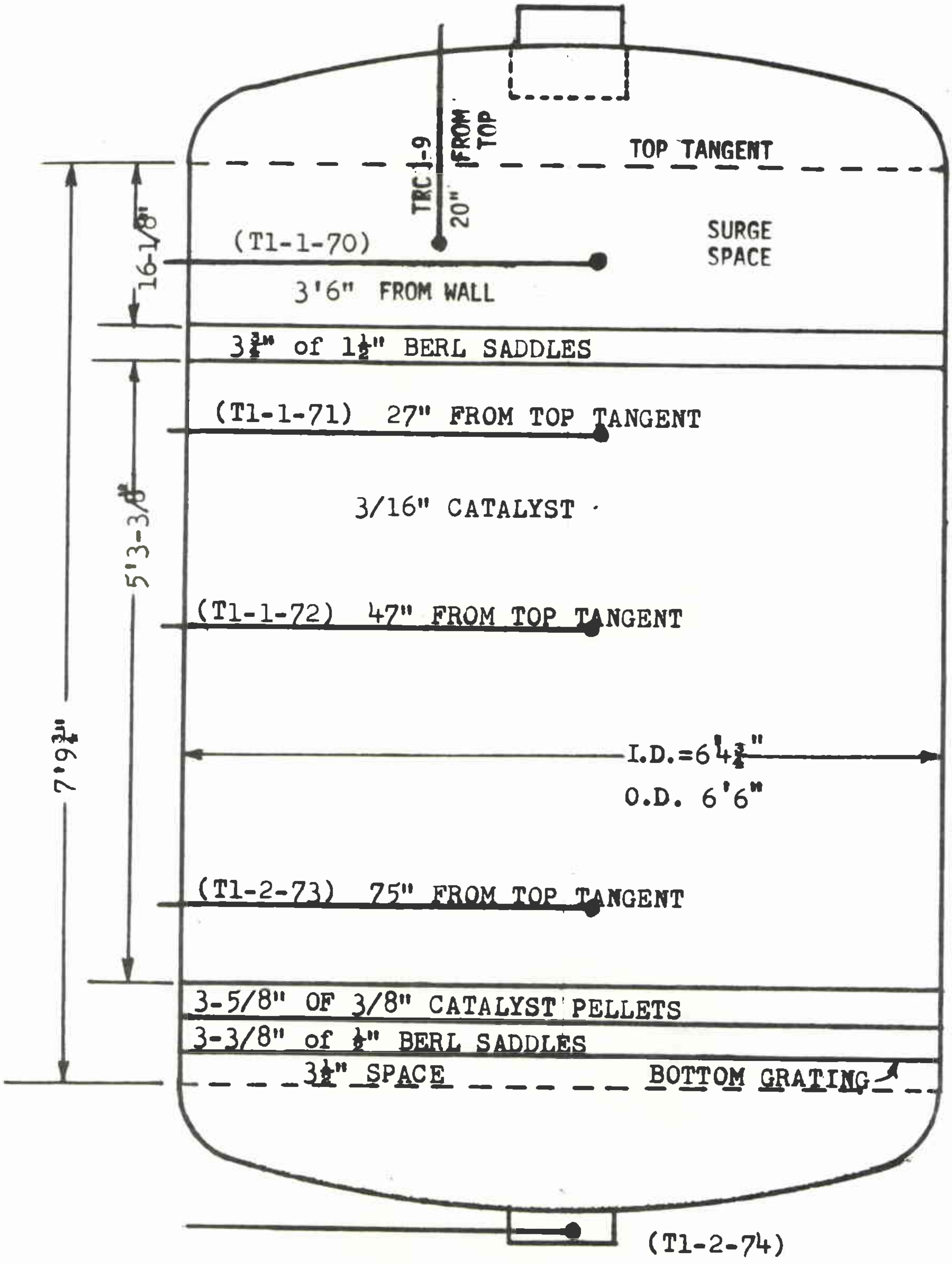
CASE	TRC-9 °K	TI-1-70 °K	TI-1-71 °K	TI-1-72 °K	TI-2-73 °K	TI-2-74 °K
JUNE[x]	920.33	928.56[y]	916.96	882.16	872.36	867.56
AUGUST	919.80	908.8[y]	911.00	869.00	854.80	850.60
BED DEPTH Z (FT.)	0.0	0.0	0.5	2.18	4.52	5.5833

Notes: x - The JUNE temperature profile data was not taken at the same time as the June case of Table 1.

y - The values of temperature at TI-1-70 seem erratic and have been discarded.

FIGURE 3

REACTOR CLOSE UP



profile in Section 5.7, Figure 12.

4.2 Project Limitations

Because available data were limited, the full potential of the project could not be realized. The catalyst has a useful life of about two years at the end of which it must be changed due to fouling. Since the data spanned a period of only three months, the decline of efficiency with time and bed depth could not be observed. It was impossible to determine the overall, long term optimum operating policy. A best operating policy could only be obtained for an instant in the catalyst's life, ignoring its possible acceleration of loss of efficiency.

All optimization studies were made on the April case, i.e. a moment in the life of the catalyst. Simply then, the data do allow a model of the reactor where the frequency factors must be changed according to the case being run.

In summary, it is possible to establish a temporary optimum operating policy, keeping in mind that this choice may not be beneficial to the long term optimum policy. With data covering the entire span of catalyst life, the long term policy can be found by the inclusion of time-dependent factors to depreciate the catalyst efficiency.

4.3 Treatment of Data - Simplifications

The absolute (lb./hr.) flows of liquid product and product gas were not available nor could the amount of gas be related to the amount of liquid since the gas analysis was in mole %. Assumptions had to be made in order to get the absolute flows of the product streams. It was assumed that the feed and liquid product wt. % analysis (by gas chromatograph) were precise. Also, as shown by the choice of reactions (3.2), it was assumed that none of the aromatic nuclei would decompose, and that all the aromatic compounds would appear only in liquid product. Thus it was possible to carry out a material balance on the aromatic ring compounds.

A ratio, R, the lbs. feed/lb. liquid product, was used to facilitate calculations. For a reasonable choice of R, a typical calculation (for the April case) went as follows:

R = 1.05 Basis = 9000 lb. total hydrocarbon feed

$$\text{Liquid Product Flow} = 9000 \times \frac{100}{105} = 8571.67 \text{ lb./hr.}$$

COMPOUND	LB./HR.	LB.MOL./HR.	
Ethylbenzene	8571.67 x .51530 = 4416.85	39.694	
Styrene	8571.67 x .40463 = 3468.25	31.830	
Toluene	8571.67 x .04665 = 399.86	2.400	$\Sigma = 37.201$
Benzene	8571.67 x .02924 = 250.62	2.971	
Others *	8571.67 x .00421 = 36.09	-	

For this case if we assume conservation of aromatic nuclei we have an inconsistency, since 39.694 moles of ethylbenzene have reappeared as only 37.201 moles of styrene, toluene and benzene. Each mole of ethylbenzene decomposed should reappear as a mole of these three products.

By interpolation between a few such calculations, it was found that for a value of R = 1.019(10), 38.428 lb. mols. lb. mols. of ethylbenzene reappeared as 38.444 lb. mols.

of styrene, toluene and benzene. For this case the total liquid product was 8832.43 lb./hr.; 167.57 lb./hr. of the original 9000 lb./hr. feed had gone in one form or another to the product gas stream. Thus the expected liquid product stream breakdown becomes:

COMPOUND	LB./HR.	LB.MOL./HR.	
Ethylbenzene	8832.43 x .51530 = 4551.22	38.428	
Styrene	8832.43 x .40463 = 3573.76	32.843	
Toluene	8832.43 x .04665 = 412.02	2.532	$\Sigma = 38.444$
Benzene	8832.43 x .02924 = 258.25	3.069	
Others*	8832.43 x .00421 = 37.18	-	

* Note that in the model this small fraction of components has been omitted.

Further assumptions regarding the gas stream had to be made. Associated with the liquid products of reactions 1, 2 and 3 there is a definite amount and composition of gas (CH_4, C_2H_4, H_2). Reactions 14 to 16 would be used, by choosing appropriate rates, so that the final gas mole per cent analysis of the model would approach the reported values. The total weight of gas per hour depends on the amount of reaction (of 14 - 16) required to bring the model analysis close to that of the existing product gas.

5. TESTING OF MODEL

The subsections 5.1 to 5.6, to follow, either point out that the model is fundamentally sound or give the results of parametric studies which show that the model reacts as expected to changes in the process variables. Due to its importance, the comparison of the model temperature profile with the actual is discussed separately in section 5.7.

5.1 Frequency Factor Searches

Frequency factors were found by carrying out a search (to be described in Section 7) on their exponents (i.e. A_i of $EXP(-\Delta E_i/RT + A_i)$). As exponents were changed according to this search technique, a response function of the form

$$\text{Response} = \sum\left(\text{Expected Amount Component } i - \text{Model Amount Component } i\right)^2$$

was minimized. The values of A_i giving the least response were those used in the final model; each case required its own set of frequency factors (see Appendix 3). All sets of frequency factors were found for fifty equal size integration steps.

The response included the four major hydrocarbons (ethylbenzene, styrene, toluene and benzene) only, even though the frequency factors involved in the search represented all six reactions. By changing the A_i of reactions 14 to 16, the hydrogen, ethylene and methane amount were adjusted and thus indirectly these exponents controlled reactions 1 to 3, and so, the response. In each case the product gas amount and composition is as reasonable as can be expected. Model results for the April, May, June and Poly-29 cases are given in Table 3; these compare favourably with the expected reactor outputs of Table 1.

Plots of conversion versus the reactor bed depth for all reactions are given for the April case in Figure 4.

5.2 Runge-Kutta Step Size Studies

An intensive survey was carried out on the integration step sizes, keeping in mind that speed as well as accuracy was required. Typical results of such a study for two variables, the mixed feed temperature and steam rate to a single reactor, are shown in Table 4. The four major hydrocarbons are traced to convergence by increasing the number of integration steps. Over the range of steam rate (5000 - 30000 lb./hr.) and inlet temperature (922 - 1010°K) studied, the following restrictions on step size must be adhered to:

RESTRICTION	NUMBER OF INTEGRATION STEPS
$T < 960^\circ K$	50
$T \leq 960^\circ K$ & $S > 22000$	100
$960^\circ K < T < 985^\circ K$	100
$985^\circ K < T < 1010^\circ K$	150

where T = mixed feed temperature (°K)
S = steam rate (lb./hr.)

FIGURE 4

X_i VERSUS Z FOR APRIL MODEL RESULTS

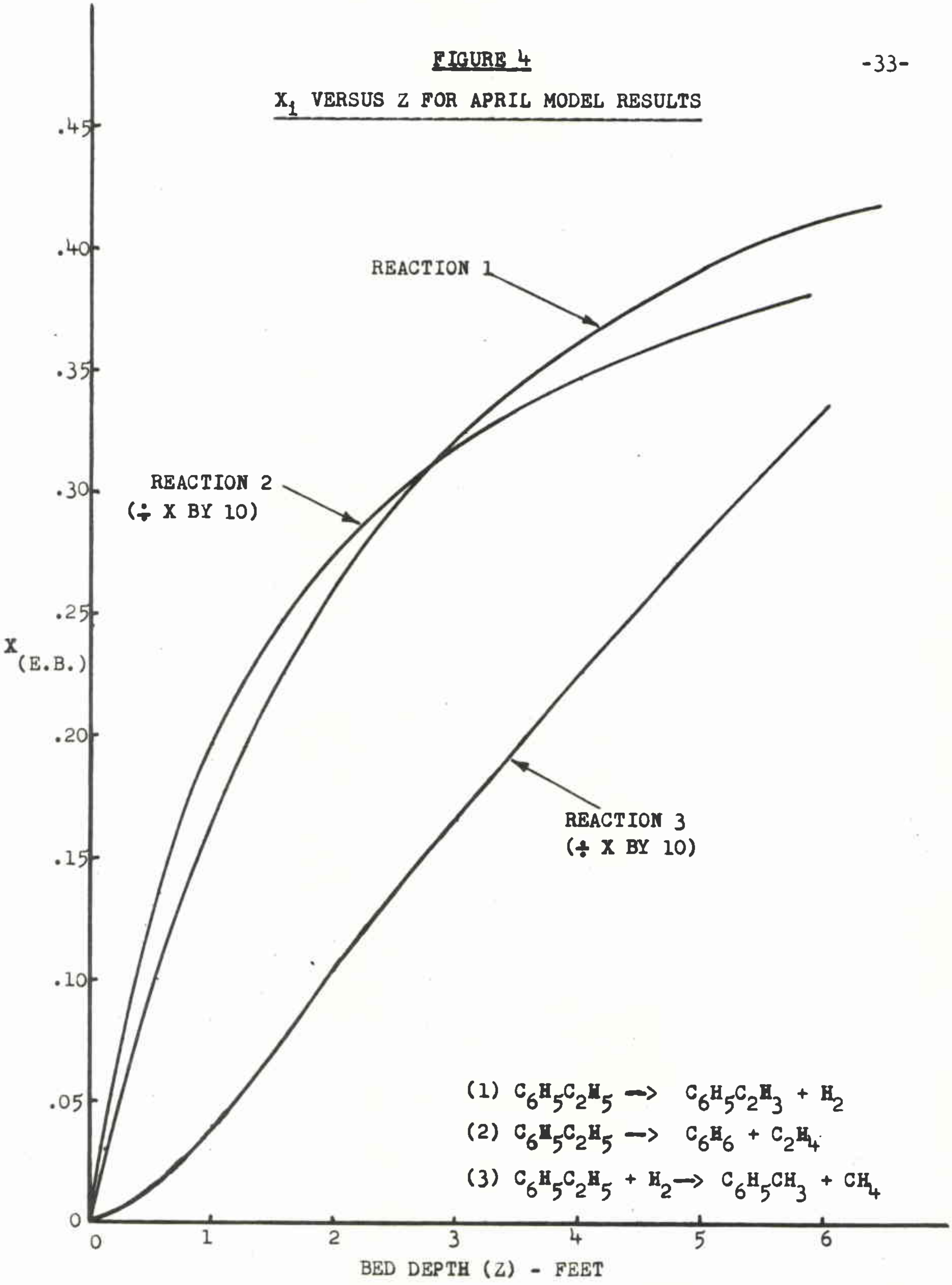
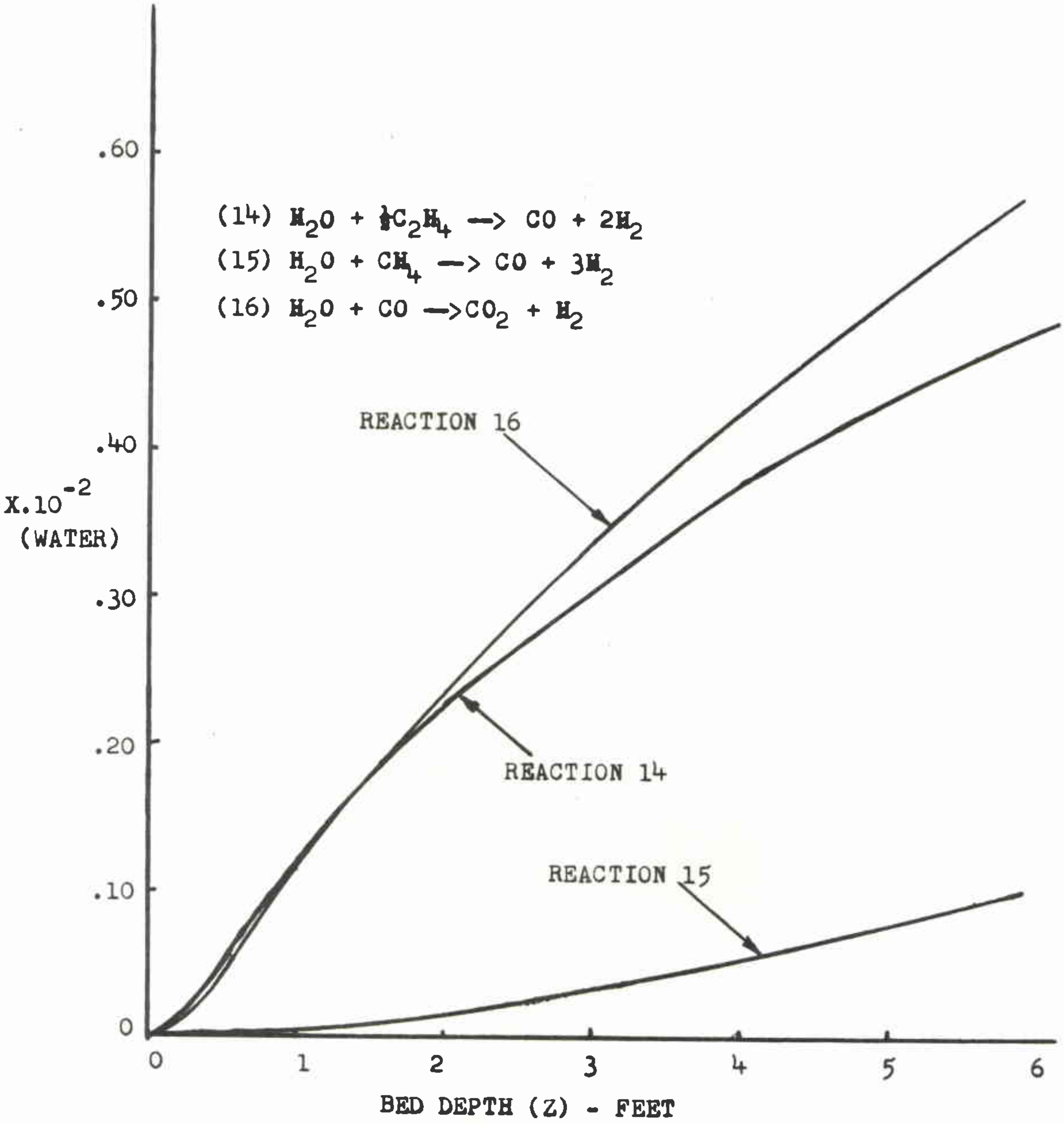


FIGURE 4 - CONTINUED

X_1 VERSUS Z FOR APRIL MODEL RESULTS



(14) $H_2O + \frac{1}{2}C_2H_4 \longrightarrow CO + 2H_2$

(15) $H_2O + CH_4 \longrightarrow CO + 3H_2$

(16) $H_2O + CO \longrightarrow CO_2 + H_2$

TABLE 4

SAMPLE RUNGE-KUTTA STEP SIZE SURVEY

Basis: Standard April Case (Table 3)

Steam rate = 18000 lb./hr. (Similar surveys were conducted for other steam rates and temperatures)

MIXED FEED TEMP. °K	NUMBER OF INTEGRATION STEPS	REACTOR OUTLET TEMP. °K	ETHYL-BENZENE LB./HR.	STYRENE LB./HR.	TOLUENE LB./HR.	BENZENE LB./HR.
EXPECTED —> (Values taken from Table 1C)						
922.59	50	?	4551.22	3573.76	412.02	258.25
922.59	25*	852.38	4981.18	3173.85	454.40	204.64
922.59	50**	850.76	4550.58	3573.64	412.02	257.53
922.59	100	850.91	4559.13	3570.29	410.59	254.97
922.59	150	850.96	4561.97	3569.17	410.11	254.12
922.59	500	851.03	4565.95	3567.59	409.44	252.95
960.00	25*	-				
960.00	50	870.77	3575.78	4049.48	562.88	489.97
960.00	100	870.91	3583.40	4051.19	560.81	484.82
960.00	150	870.97	3586.44	4052.09	559.96	482.64
985.00	25*	-				
985.00	50*	884.53	2980.44	4227.18	680.27	695.19
985.00	100	884.09	2970.67	4214.55	681.55	710.78
985.00	150	884.16	2973.60	4218.15	680.42	706.87
1010.00	25*	-				
1010.00	50*	898.55	2426.74	4282.06	821.01	942.10
1010.00	100	897.10	2410.63	4231.16	808.97	1002.34
1010.00	150	897.19	2413.32	4238.85	807.70	995.67

* The integration results are not smooth and/or there are negative concentrations of compounds.

** The frequency factors (A_i of ($e^{-\Delta E_i/RT + A_i}$)) were chosen at this condition.

Similar checks were required for the two-bed situations. Slight modifications were made to the number of steps to account for pressure, steam rate, and bed length changes; these may be found in the two-bed model associated with the optimization programme. (Appendix 11).

Although the integration has not quite converged to steady values (Table 4) at 50 steps when compared to 100, 150 and 500 steps (at 922.59°K), it was decided to use the values of A_i found from 50 steps. The slight loss in accuracy is more than compensated for in the savings in calculation. Since these A_i were found for 50 steps, the model is more accurate at 50 steps than at a greater number, the truncation error has been compensated for by the choice of A_i.

5.3 Poly-29 Cases

The twenty-nine runs (4.1) which make up the mean Poly-29 case were each calculated by the model with the frequency factors of the mean case. For these cases, the mixed feed temperatures varied between 917°K and 928°K, the steam rate was between 14780 and 17220 lb./hr., and hydrocarbon feed rates ran from 7000 to 9000 lb./hr. Inlet pressures also varied from about 2.05 atmos. to 2.35 atmos. Mean deviations from the expected amount of the four main hydrocarbons were:

Ethylbenzene	42.49 lb./hr.
Styrene	19.16 lb./hr.
Toluene	0.21 lb./hr.
Benzene	(1.91) lb./hr.

where (n) means less than expected.

The mean error is less than 1% for each compound.

Results of the 29 cases are given in Appendix 6 where the simulation and actual product rates for the four major hydrocarbons are compared.

5.4 Effects of Varying ΔE_1, The Activation Energy

In Section 3.3 we found frequency factors (A_i) to complement values of ΔE_i taken from the literature.

Because of the uncertainty[11] of the value of the activation energy of the main reaction, several runs with different ΔE_1 were made. Frequency factor exponents (A_1) were adjusted accordingly so that the sum $(- \Delta E_1/RT + A_1)$ remained as close to that obtained over the whole temperature (T) range for the value of ΔE_1 actually used (Appendix 2).

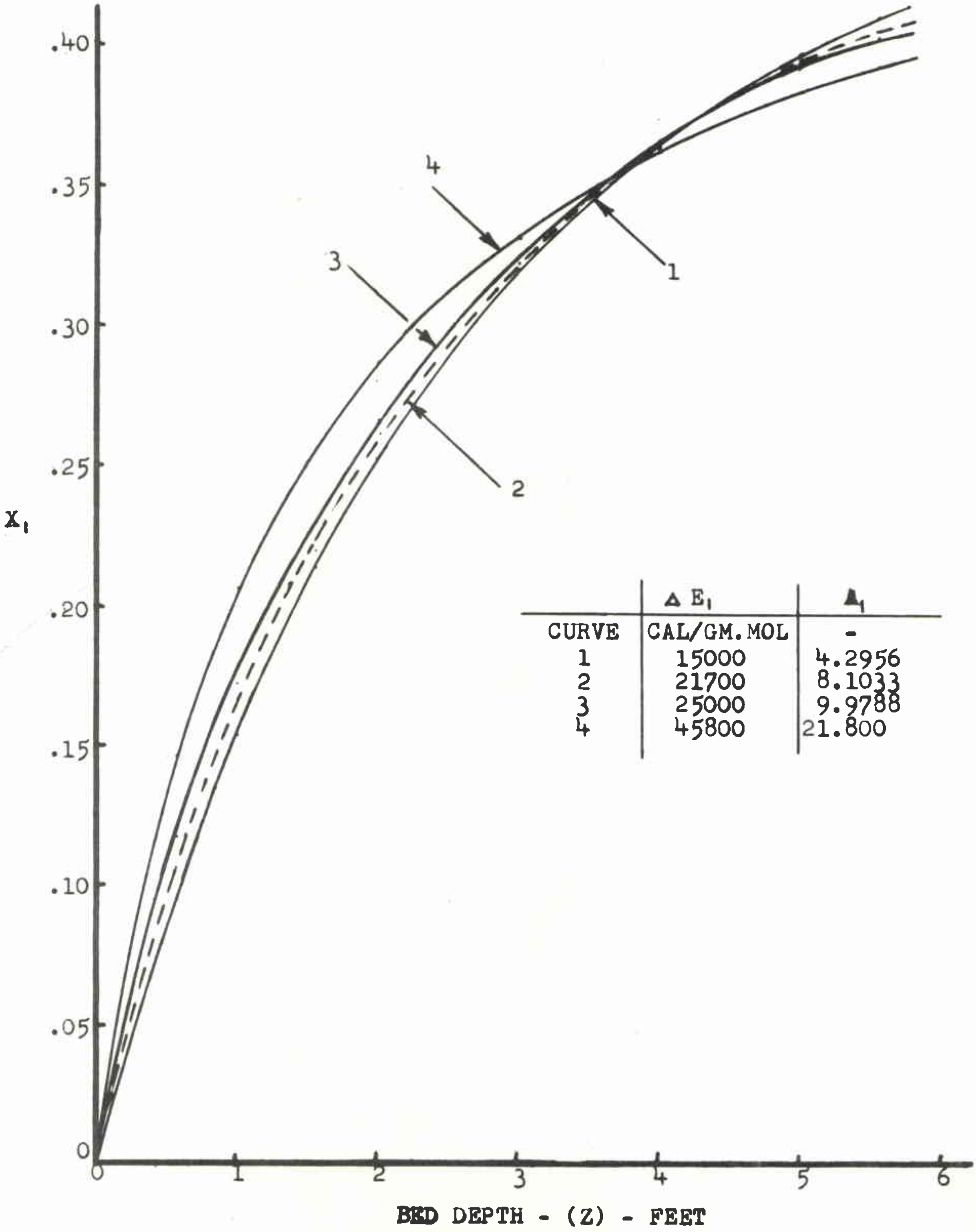
A_1 was chosen for a temperature around the arithmetic mean of the reactor inlet and outlet temperatures. All ΔE_i and A_i for reactions 2, 3, 14, 15 and 16 remained as for the April case (Appendices 2 and 3). The results are shown in Figure 5.

One can immediately conclude that it is possible to compensate for a poor value of ΔE_1 by the variation of A_1. Better A_1's, for each ΔE_1 of Figure 5, can be found since those used are only crude first approximations.

This work was carried out without knowledge of the

FIGURE 5

VARIATION OF ΔE_1, COMPENSATION WITH CHANGE IN A_1



	ΔE_1	A_1
CURVE	CAL/GM.MOL	-
1	15000	4.2956
2	21700	8.1033
3	25000	9.9788
4	45800	21.800

temperature profile. It is evident that the conversion profiles for ΔE_1 equal 15000, 21800, and 25000 cal./gm.mol. are similar to each other but quite different from that at 45800[12] cal./gm.mol. No choice of A_1 will make the "45800" curve assume the general shape of the other three. Since the main reaction dominates the temperature profile, knowledge of this profile should indicate which X vs. Z curve, and hence which ΔE_1, A_1 combination is appropriate. In Section 5.7, it is seen that the value of $\Delta E_1 = 21800$ cal./gm.mol. is a good choice.

Serious error could result should an extrapolation be carried out (i.e. on bed length), if the value of ΔE of any of the reactions is far from the correct one. For reactions 2, 3 and 14 to 16 a similar situation exists and although some ΔE values for these reactions were found over different catalysts and conditions, it is felt that an error in these ΔE_i has been compensated for by an appropriate choice of A_i.

5.5 Parameter Studies

Parametric studies were carried out only on major process variables such as steam rate, mixed feed temperature and inlet pressure. In all cases to follow, the April case of Table 1 has been used as basis. The relationships found in these studies are to be of aid in visualizing just how the process variables are interdependent in the optimization studies to follow.

(1) Variation of Mixed Feed Temperature - In Figure 6 the rapidly increasing rate of formation of the by-products, benzene and toluene, becomes apparent as the mixed feed temperature is raised. The loss in chemical value to by-products cannot be made up by the formation of more styrene in the equilibrium limited main reaction and an optimum temperature of operation is found. This optimum comes at 948.5°K, i.e. Figures 18 and 19 show the mixed feed temperature (M.F.T.) and Gain($/HR.) in value of the chemicals as a function of the steam temperature and flow rate. This relationship is derived in Section 8.1.1.

Wherever graphs mention conversion (X_i), we may convert to get the lb./hr. flow rates quite easily. For example at 900°K as mixed feed temperature in Figure 6 we get:

STYRENE RATE = Amt. formed in reaction + initial

$$= 8630.73 \times .35813 \times \frac{104.14}{106.16} + 153.45$$

$$= 3185.54 \text{ lb./hr.}$$

TOLUENE RATE

$$= 8630.73 \times .021844 \times \frac{92.13}{106.16} + 178.74$$

$$= 342.36 \text{ lb./hr.}$$

(2) Variation of Steam Rate Only - In Figure 7 only the rate of steam flow has been changed. Inlet pressure remains at 2.37 atmospheres and the temperature of the mixed feed is always 922.59°K as in the April case. Results are most meaningful around a steam rate of 18000 lb./hr.

(3) Variation of Steam Rate and Inlet Pressure is a Function of Molar Flow Rate - Here, as steam rate was varied, the inlet pressure was treated as a linear function of the total molar flow (i.e. P = (a + b x total moles/hr.)). A comparison of Figure 8 with Figure 7 shows crude relationships between inlet pressure and the conversions, X_i, at fixed steam rate and inlet temperature.

(4) Variation of Mixed Feed Temperature Over a Large Range With a steam rate of 18000 lb./hr. and inlet pressure of 2.37 atmospheres, runs were made at different inlet temperatures and compared to the April case. Figures 9 and 10 offer X_i vs. Z plots for the three main reactions at various mixed feed temperatures. The rapid rate of increase of by-products is contrasted to the relatively slow rate of increase of styrene formation.

(5) Variation of Inlet Pressure Only - Only inlet pressure has been varied for the April case (steam rate = 18000 lb./hr., T.M.F. = 922.59°K). It is evident that a pressure greater than 2.37 atmospheres does not aid the main reaction conversion. Reaction 3 (second order) is seriously affected by an increase in pressure and since the overall conversions of reactions 1 and 2 remain approximately constant, a lower operating pressure is suggested. Figure 11 complements Figures 7 and 8 and all three should be looked at together for relationships dealing with pressure and steam rate.

FIGURE 6

VARIATION OF MIXED FEED TEMPERATURE - APRIL CASE

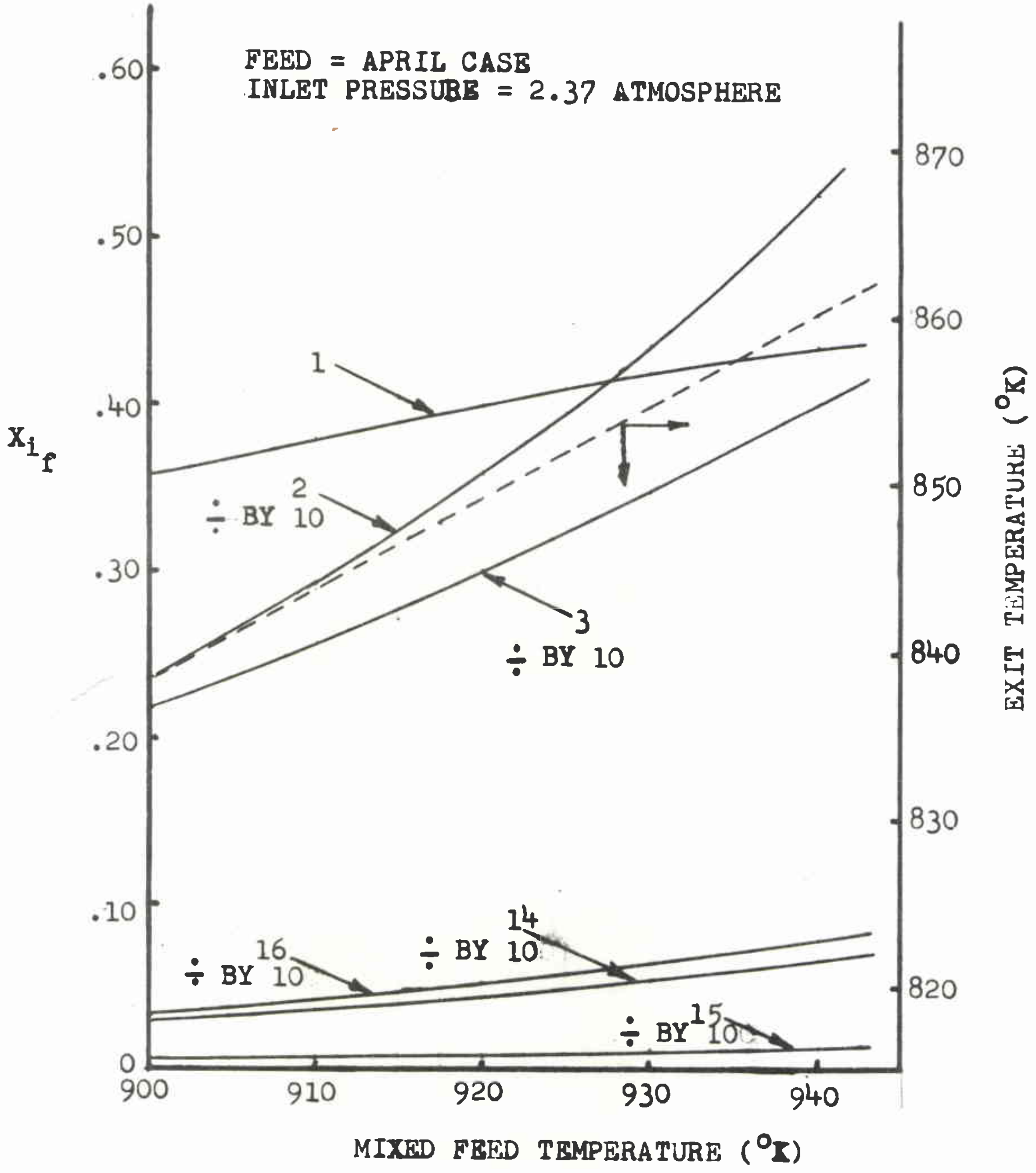


FIGURE 7

VARIATION OF STEAM RATE ONLY

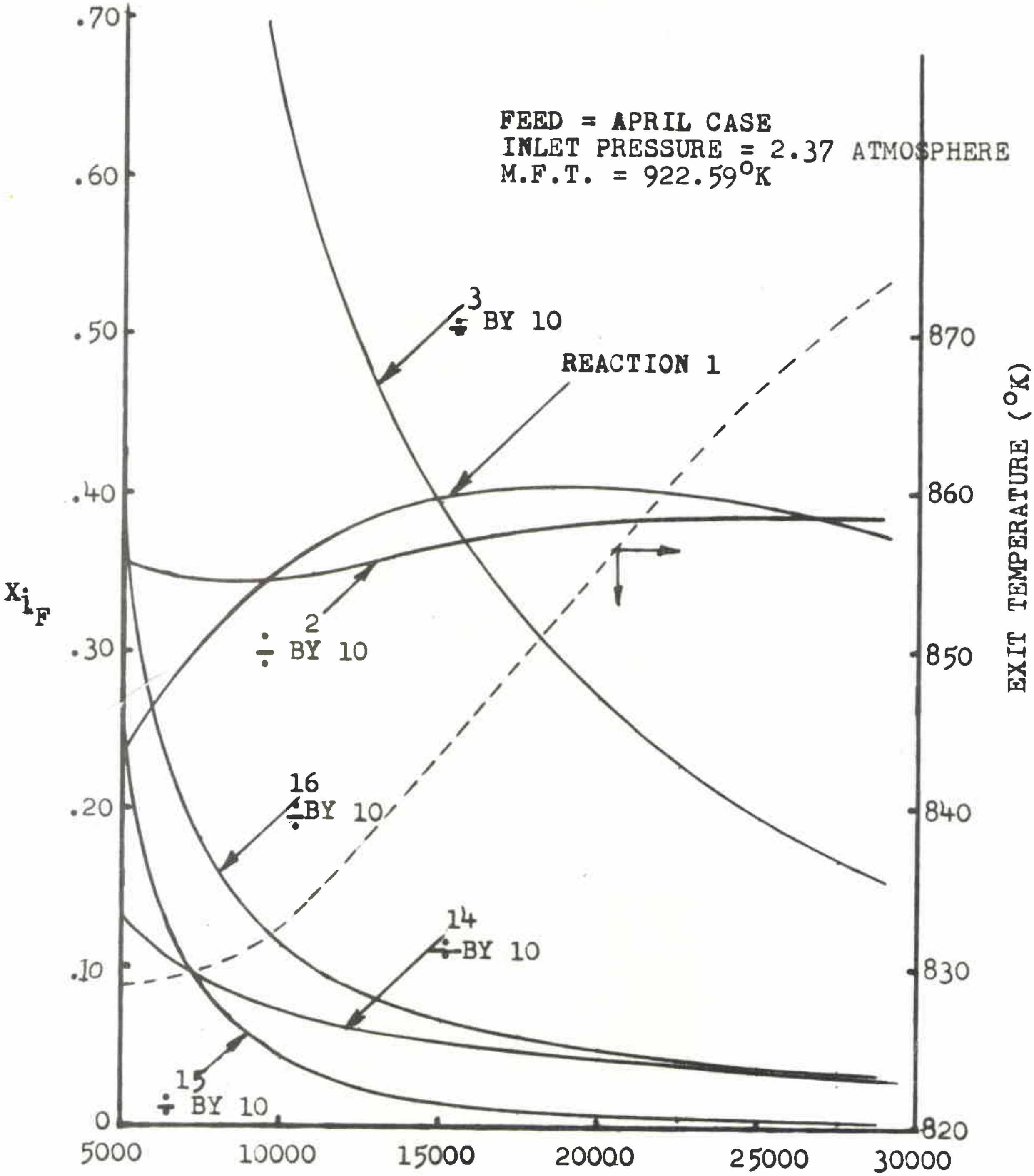


FIGURE 8

VARIATION OF STEAM RATE AND INLET PRESSURE IS A FUNCTION OF MOLAR FLOW RATE

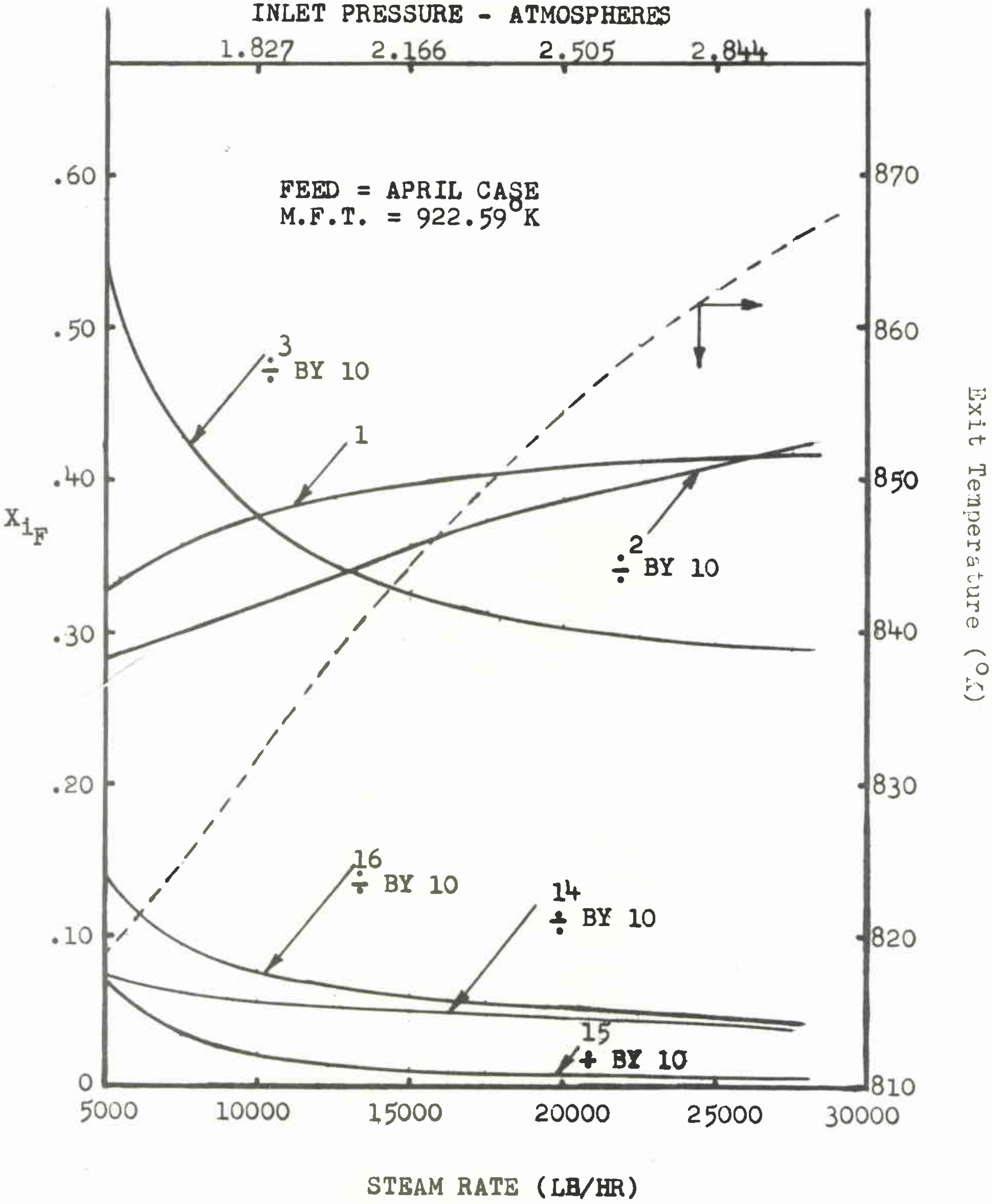


FIGURE 9

X VERSUS Z - MAIN REACTION - VARIOUS M.F.T.

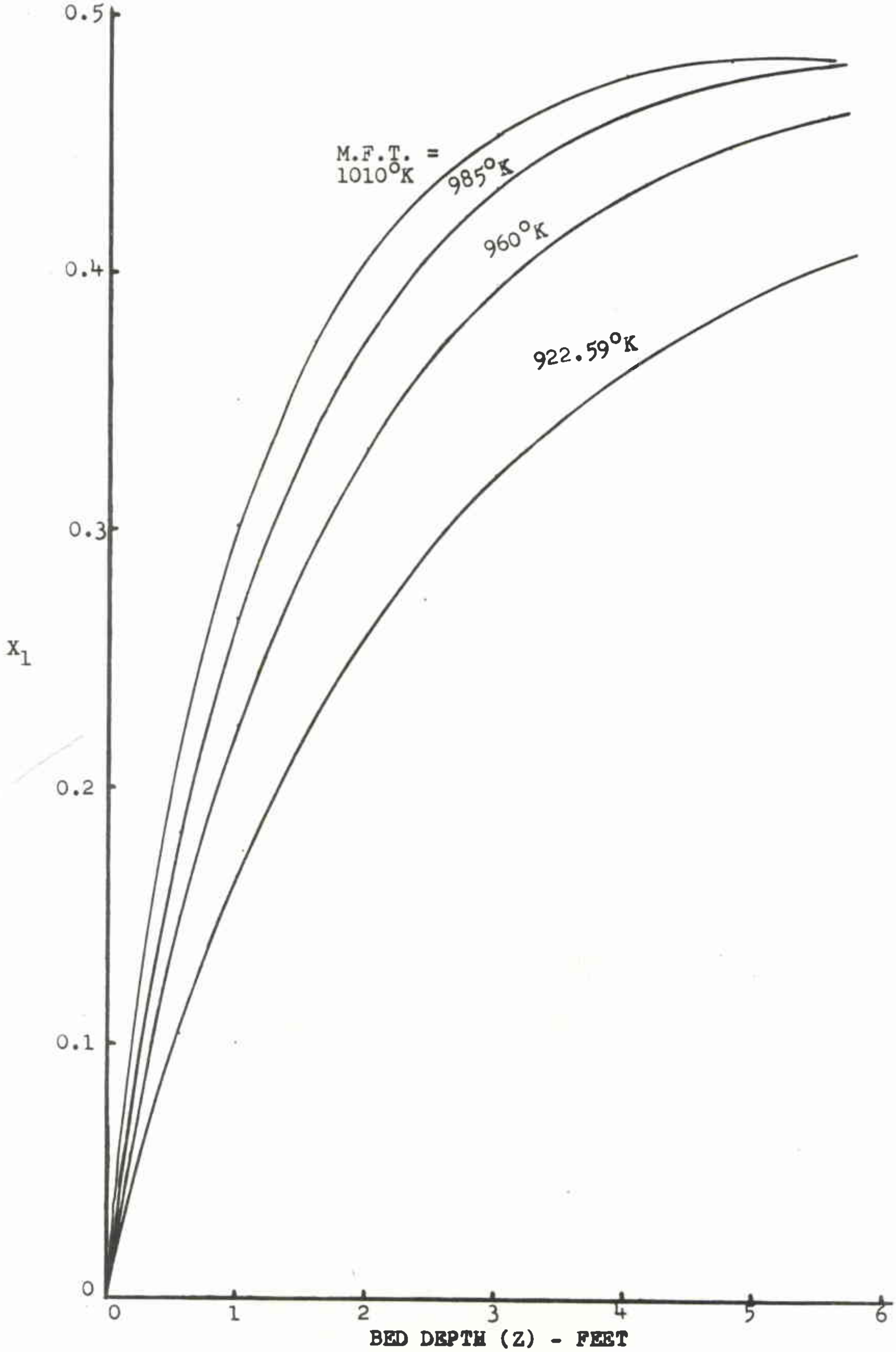


FIGURE 10

X VERSUS Z - SIDE REACTIONS - VARIOUS M.F.T.

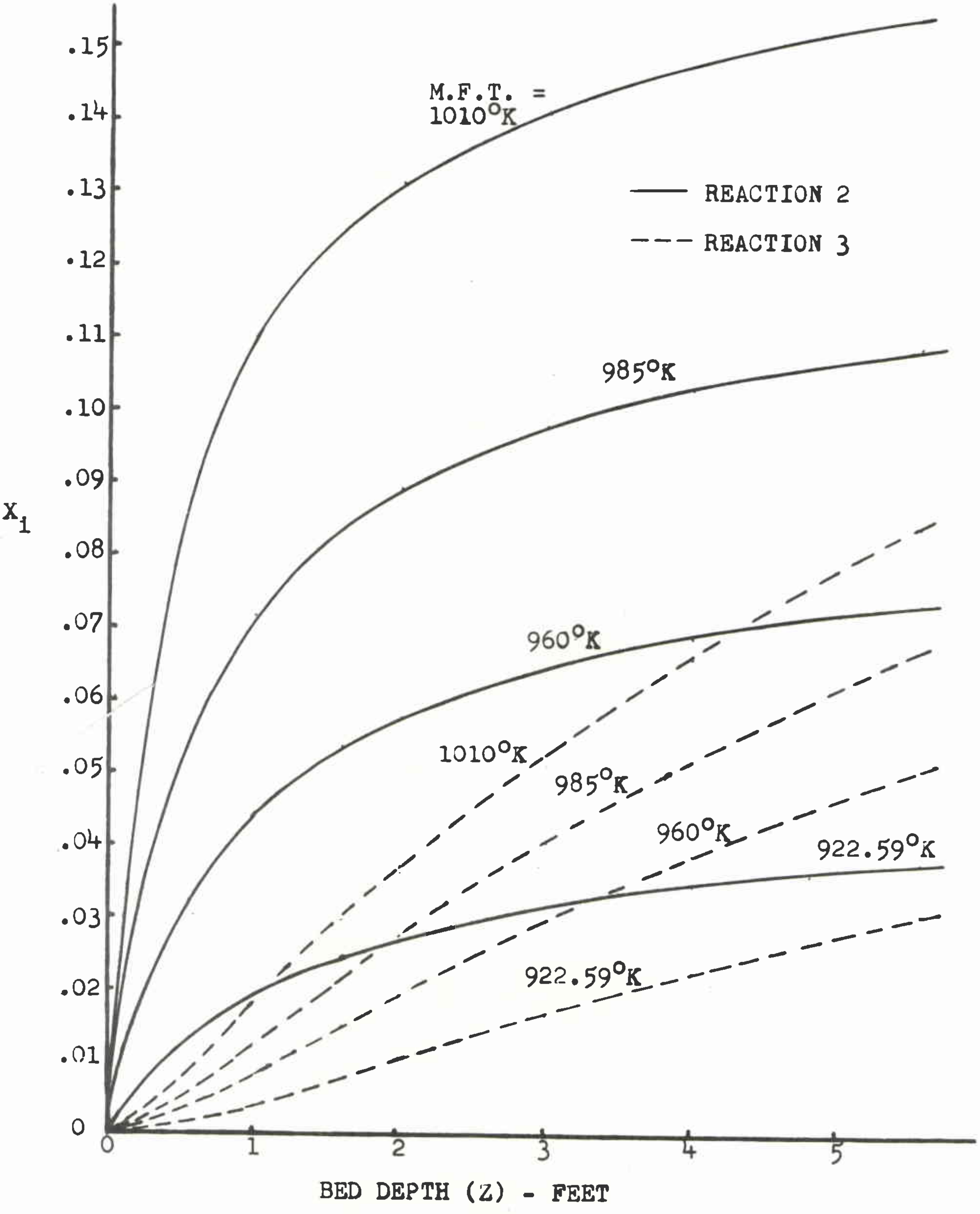
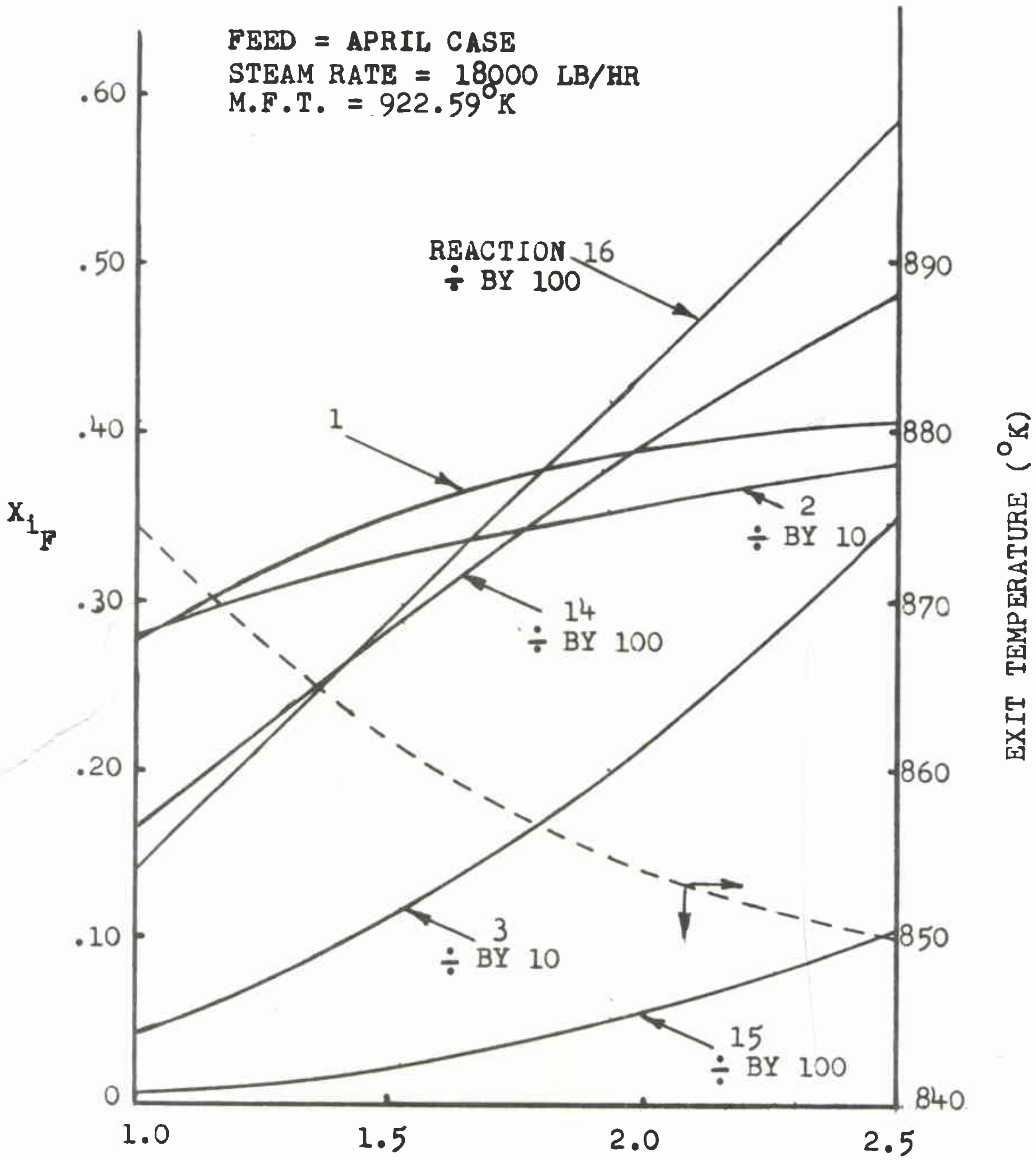


FIGURE 11

VARIATION OF INLET PRESSURE ONLY



INLET PRESSURE - ATMOSPHERE

5.6 Reliability of Model

It is difficult to assess the worth of the model without having proven it at different conditions (at the same catalyst age) from those for which it was conceived. The problem arises that since the plant presently operates at maximum capacity (shown later by optimization studies), limited by constraints, there is no room for changes in the process variables without incurring a loss of production. Although the Poly-29 case differs from those of April, May and June, the catalyst age is also different and therefore they cannot be compared.

The twenty-nine cases comprising the Poly-29 case (Table 1) were run with the frequency factors obtained from this mean case (5.3). The reproducibility of each case was excellent (Appendix 6). Any discrepancies can be explained by the use of a mean set of frequency factors which represent a period of about three months of the catalyst life.

A quick glance at the X_i vs. Z plots of the April case (Figure 4) shows that the reactions behave as expected[5]. The main reaction rate slows down as the reverse reaction becomes important and the ethylbenzene concentration falls. Benzene (reaction 2) production falls off with decreasing ethylbenzene. The third reaction is slow at first, since hydrogen must first be produced so that it may occur. Initially the rate increases due to a high concentration of both hydrogen and ethylbenzene and then falls off as ethylbenzene concentration drops. A decrease of temperature in the reactor slows down all three reactions (Figures 6, 9 and 10).

Reactions 14 and 15 depend on the ethylene of reaction 2 and methane of reaction 3, respectively. Since ethylene is produced immediately, reaction 14 proceeds from the reactor mouth at almost constant rate. Reaction 15 lags reaction 3 which itself must wait for hydrogen and hence is very slow at first; the rate increases as more methane becomes available. Carbon dioxide is produced immediately in reaction 16 from the carbon monoxide of reactions 14 and 15, thus accounting for the very low monoxide analysis. In reactions 14 - 16 the steam concentration remains almost constant.

When the inlet temperature is raised from 900°K to 940°K (Figure 6), the conversion of the main reaction increases from about 0.36 to 0.435 at a decreasing rate. However, reactions 2 and 3 proceed at increasing rates from 0.0235 to 0.0525, and 0.022 to 0.040, respectively. Overall conversions of reactions 14 - 16 depend on reactions 2 and 3 and they increase much quicker than does that of the main reaction and hence, at higher temperatures, any gain in production of styrene is offset by much higher production of the by-products, benzene and toluene.

It would appear that the model is adequate and represents the plant reactor quite well. Optimization studies, which follow, will further demonstrate the model's consistency and ability to show the correct[5] direction of change to be chosen for plant variables in order that the optimum be reached.

5.7 Discussion of Temperature Profiles

The model was founded solely on conversions of the various reactions and on the assumption that the reactor was operating adiabatically. Internal reactor temperatures were unavailable. A temperature profile would have given an excellent indication of the extent of the main reaction at any reactor bed depth.

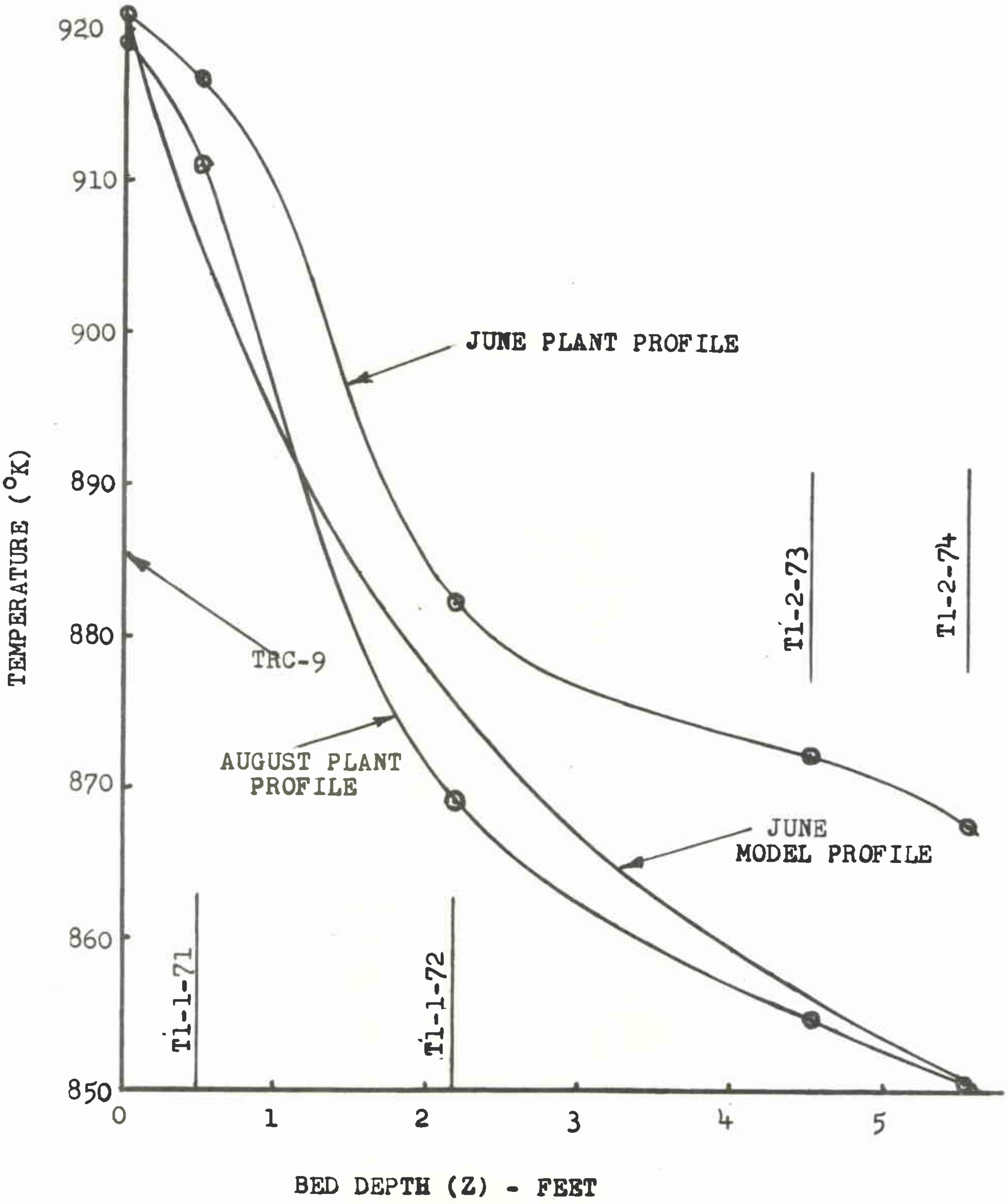
Two temperature profiles were received in late June and in August (Table 2). The former (Figure 12) lies consistently above the model profile. It was assumed that some malfunction in the measuring device had caused such a consistent shift.

A check of the thermocouples and the measuring device was well warranted. The resulting August profile (Figure 12) does not vary by more than $5^{o}K$ from the calculated June profile, and this is well within the possible error of thermocouples operating at the temperatures involved. The matching of calculated and actual temperature profiles lends much confidence to model extrapolations, etc. The exit temperatures which had been recorded for all cases of Table 1 were assumed to have errors similar to that of the June profile and thus were given no weight in determination of the worth of the model.

Since the TI-1-70 (temperature measuring devices are referred to by the Polymer Corporation nomenclature) temperature readings were erratic, they were discarded altogether; the reactor inlet temperature of the plant profiles was thus taken from TRC-9, as it had been for the various model cases of Table 1.

FIGURE 12

COMPARISON OF CALCULATED TEMPERATURE PROFILE WITH ACTUAL



6. PREPARATION FOR OPTIMIZATION STUDIES

6.1 Choice of the Cost Function

A cost function which was representative of the process chemical values only was established for the purpose of the optimization studies. It measured the gain in dollars per hour of all chemicals with an allowance for steam cost. The gain function accounts for:

(1) the overall gain in value of the aromatic chemicals

(2) the fuel value of any by-product gases

(3) the cost of steam required.

i.e. Gain/Hr. = Gain due to Styrene + Gain due to Fuel Gases
- Steam Cost - Loss due to Toluene and Benzene

Table 5 lists the values of the chemicals involved in the cost function, while Appendix 8 gives calculations leading to the final gain equation.

In optimization studies conducted later, where the bed depth was a variable, the cost of the extra catalyst required was included in the cost function. The catalyst was depreciated at $0.05937/Hr./Ft. of extra bed (i.e. greater than 5.5833 Ft.). Inclusion of this added cost had little effect on the overall gain function.

TABLE 5

VALUE OF CHEMICALS

CHEMICAL	VALUE	REFERENCE CODE
Ethylbenzene	.06 \$/lb.	C
Styrene	.105 \$/lb.	A
Toluene	.0185 \$/lb.	E
Benzene	.037 \$/lb.	A
Hydrogen	.03 \$/lb.	B
Methane	.012 \$/lb.	B
Ethylene	.011 \$/lb.	B
Steam	.01182 + .0000646 T (T = $^{\circ}$K) \$/100 lb.	D

References for Cost Function

Code

A	Canadian Chemical Processing, April, 1966
B	Based on standard heating value of \$.50/10^6 B.T.U.
C	Estimated in-plant value of ethylbenzene. The loss in value if it goes to by-products is approximately equal to the gain if styrene is produced (on a pound basis).
D	Estimated equation gives reasonable costs i.e. T = 800°K cost = \$0.0635/100 lb. T = 1000°K cost = \$0.0764/100 lb. Compare to Perry Chemical Engineers Handbook, 4th edition, 9-46, 26-28.
E	Real value/2, i.e. \$.037/lb./2, real value taken from reference A. Since this is an in-plant, impure by-product stream this assumption seems reasonable. It must still be treated or used in benzene production.

6.2 Costs Not Included in the Cost Function

There are numerous other costs associated with the optimization studies. It may be found that a reactor with a longer bed may be required, or it may be necessary to build a steam superheating furnace of larger capacity. In the case of a longer bed, a new reactor shell, supporting framework, etc., must be built and its cost must be accounted for. Loss of production from plant shutdowns due to construction must be noted. A new composition of the liquid product stream may dictate changes in the existing distillation columns. Changes to the cost function would be stepwise in nature.

Such costs, however, are fixed initial costs and these can easily be determined after we see how much of a gain is possible from the chemicals involved. A considerable gain may call for new equipment; a slight gain may not. Any of these fixed costs can be depreciated on an hourly basis and then readily combined with the Gain function. If the forecast is still reasonably profitable, the proposed changes should be carried out. Operating and maintenance costs can be assumed constant for present and proposed operating conditions.

Careful consideration of the limitations of the model should be taken. Perhaps the main flaw is the inability of the model to account for the effect of operating temperature on the overall catalyst life. It may turn out that twice as many shutdowns to change catalyst, which itself is relatively inexpensive, will be necessary. Thus shutdown time will be

FIGURE 13

COMPARISON OF REGRESSION EQUATION FOR GAIN WITH MODEL

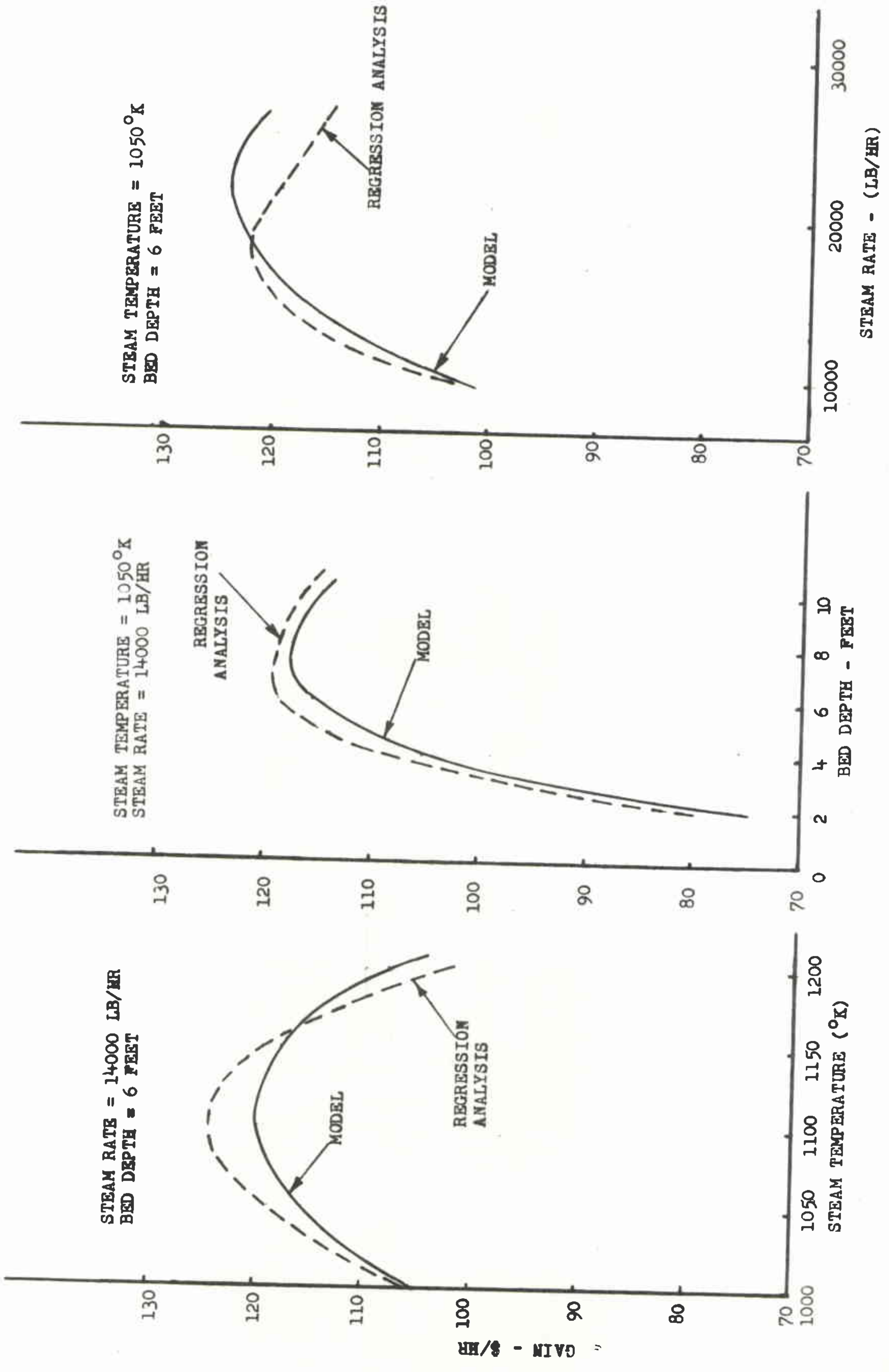
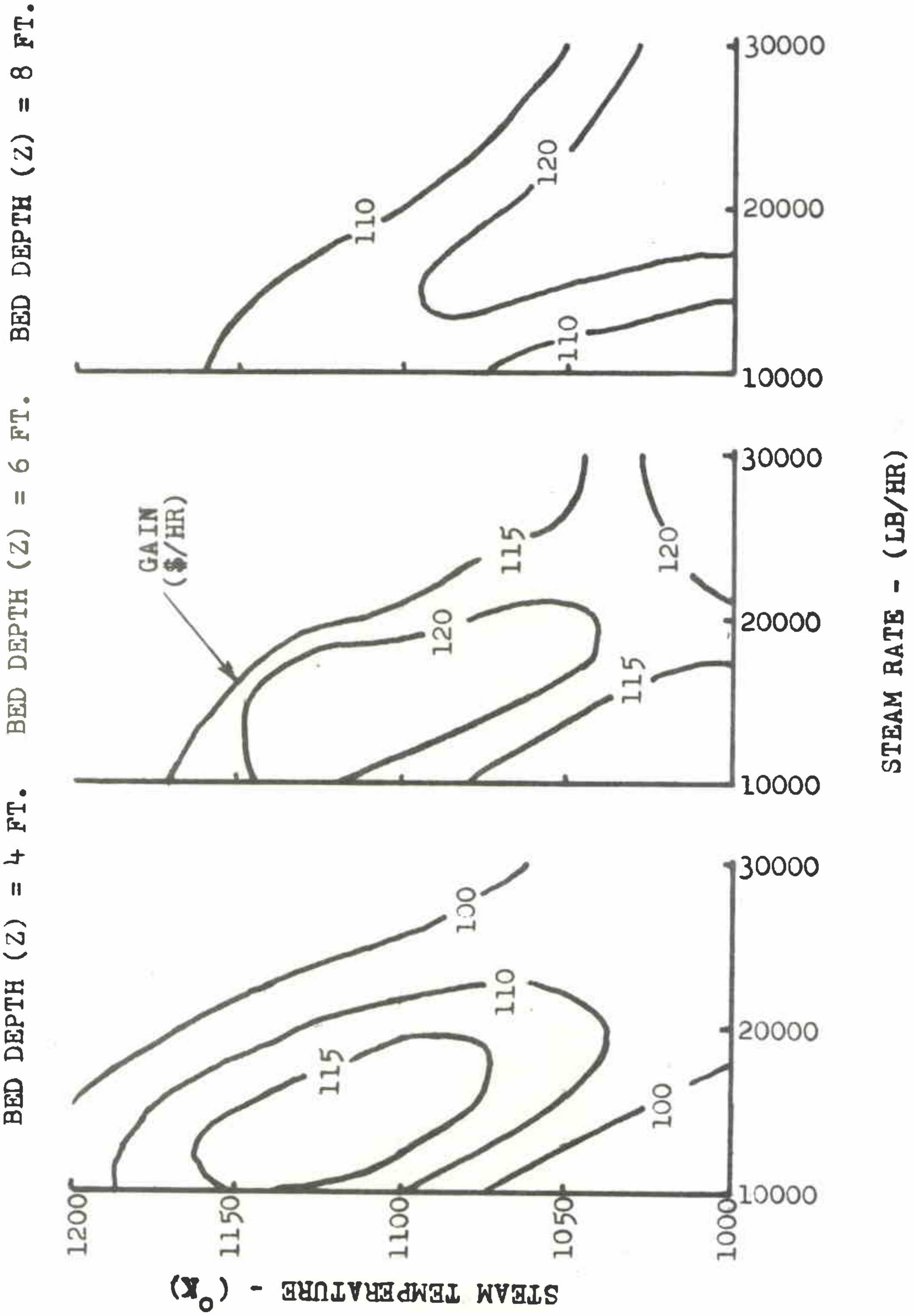


FIGURE 14

MAP OF GAIN RESPONSE FOR REGRESSION EQUATION



costly from the view of catalyst cost, labour, and loss of production. Numerous variables are involved here and the problem will be discussed again in sections dealing with the optimization of various proposed situations.

6.3 Regression Analysis Studies

An attempt was made to relate the Gain function to three major process variables for the single bed case. A 3 x 5 (125 points) factorial experiment covering the ranges indicated below was run off.

Steam Temperature.......1000 - 1200°K
Steam Rate ....10000 - 26000 lb./hr.
Bed Length ....2 - 10 feet.

The mixed feed temperature is related to the steam temperature (8.1) and it varied from 875°K to 1057°K. Inlet pressure was a function of the total molar flow rate of mixed feed (3.6) and thus constituted another hidden variable. The hydrocarbon feed was always that of the April case (Table 1).

It had been hoped to use the regression equation as the response in optimization studies and in so doing, save considerable time in calculation since the model would no longer be required. Unfortunately such an attempt failed. The regression equation is given in Appendix 9 and it is compared to the model in Figure 13. Figure 14 maps out the regression gain function; the response surface, although inaccurate, is similar to that generated by situation 2-ii (Appendix 13) and hence of interest.

The results of the multivariable searches (to be explained in 8) are given in Table 6.

TABLE 6

OPTIMIZATION OF REGRESSION EQUATION

SEARCH BEGAN			SEARCH ENDED			GAIN
STEAM TEMP. °K	STEAM RATE LB./HR.	Z FT.	STEAM TEMP. °K	STEAM RATE LB./HR.	Z FT.	$/HR.
1100	10000	3.	1106	14079	5.74	124.27
1125	10000	7.	1106	14078	5.74	124.28
1050	26000	8.	1000	30000	10	147.88

Here there is a breakdown of the cost function as in situation 2ii-4 (Appendix 12 and 13). The search has run up against constraints in all variables.

More points are needed if the regression equation is to be representative of the model or the area encompassed by the regression should be reduced. For a given plant situation, a regression expression could be useful[13], but since the situation in these studies was always different, such equations would not be beneficial. More computer time may be required to find the regression equation than the optimum.

6.4 Time Studies

The rate of change of temperature with distance ($\Delta T/\Delta Z$) which was arrived at from the energy balance (3.5) has been handled outside the integration, i.e. the temperature over each integration step has been considered to be constant. This simplification allows a saving of about 15% in computation time over a similar case with the temperature inside the integration. The question arises - if the temperature is included in the integration, would it be possible to reduce the number of steps so that there is an overall saving in time? Runs of both types were made at various step sizes. The April case was used and comparisons are offered in Table 7.

No advantage was found when the temperature was included in the integration. Convergence to steady values came quicker, but in approximately the same number of steps so that computation time remained greater.

TABLE 7

TEMPERATURE OUTSIDE VS. TEMPERATURE INSIDE THE INTEGRATION

(A) TEMPERATURE OUTSIDE

NUMBER OF STEPS	OUTLET TEMP. °K	ETHYLBENZENE LB./HR.	STYRENE LB./HR.	TOLUENE LB./HR.	BENZENE LB./HR.
50	850.76	4550.58	3573.64	412.02	257.53
40	850.71	4547.42	3574.99	412.54	258.40
35 *	851.32	4577.32	3559.94	408.82	250.85
30 *	854.09	4705.16	3466.17	407.31	228.40

(B) TEMPERATURE INSIDE

NUMBER OF STEPS	OUTLET TEMP. K	ETHYLBENZENE LB./HR.	STYRENE LB./HR.	TOLUENE LB./HR.	BENZENE LB./HR.
50	851.06	4567.18	3567.18	409.28	252.49
40	851.06	4567.02	3567.28	409.31	252.51
30	model breaks down completely				

* Reaction 16 is slightly unstable during intial integration steps.

Other integration techniques could not be tried since it was necessary to go on to the optimization studies. Third-order Runge-Kutta, or predictor-corrector methods might have allowed a saving in computation time with the same accuracy.

7. METHOD OF OPTIMIZATION

7.1 The General Method

A multivariable search technique, that of Rosenbrock[4], was chosen to seek out the optimum operating conditions of proposed plant situations. The method is advantageous because it not only finds the optimum conditions of well-behaved response surfaces, but also is able to follow sharply defined ridges quickly and efficiently.

Basically, the programme employs the GRAM-SCHIMDT Orthogonalization[4] and [14] to adjust the direction of the search to follow the ridge. This is, in reality, a flexible method of steepest ascent[15]. Initially, for convenience, the directions of search are parallel and perpendicular to the coordinate system. Each variable is perturbed in turn and a corresponding response is obtained.

An accelerator is used after a success (higher value of the response if seeking a maximum) has been found in one direction. The step length in that direction becomes α ($\alpha > 1$) times the former step length on the next testing of that variable. Similarly, upon recording a failure, the search returns to the beginning of the step, carries on with the other variables, and on returning to the variable registering the failure, it multiplies the former failure step length by β ($-1 < \beta < 0$), and so searches in the opposite direction for that variable.

When at least one failure has been found for each variable, a stage has been completed, and the search halts. Then, using the initial and final base-points of the stage just completed, it evaluates new search directions by the orthogonalization process. When successive responses differ by a preset value a predetermined number of times, the entire search ends, hopefully at the optimum.

Figure 15 shows the beginning of a Rosenbrock search over two variables, X and Y, whose response is a profit which we seek to maximize.

At point A, a response of $1.60 is obtained. When we perturb X by 1 unit (i.e. ¢ = 1), the new higher response ($1.72) becomes the temporary base point. After a similar success in Y, we advance X by α times ¢ (here $\alpha \times 1$ or α), and again register a success ($2.70). On continuing, similar successes in Y and X, bring us to a response of $3.01. When the change in Y is again accelerated, since the last change in Y had been successful, we find a profit of only $2.62 and so we have a failure for Y. The search returns to the point of the last success ($3.01) and perturbs X by $\alpha \times (\alpha^2)$ or α^3 to a response of $3.03. Since the last change in Y resulted in a failure we now change Y by $\beta(\alpha^2)$, in the opposite direction to the previous Y movement. From point B, we get a failure ($1.21) by advancing X by α^4 and since we now have at least one failure per variable, we come to the end of the first stage (point B).

The next search begins in directions parallel and perpendicular to the vector joining A and B (determined by orthogonalization), the initial and final base points of the first stage. The first two probes result in failures, i. e. \$3.10 and \$3.08, and so, we search in the opposite direction (due to registering successive failures for all variables on initial changes). A similar pattern brings us to point C and the next directions of search parallel and perpendicular to the line BC. The search procedes in such stages toward the combination of X and Y yielding the maximum profit.

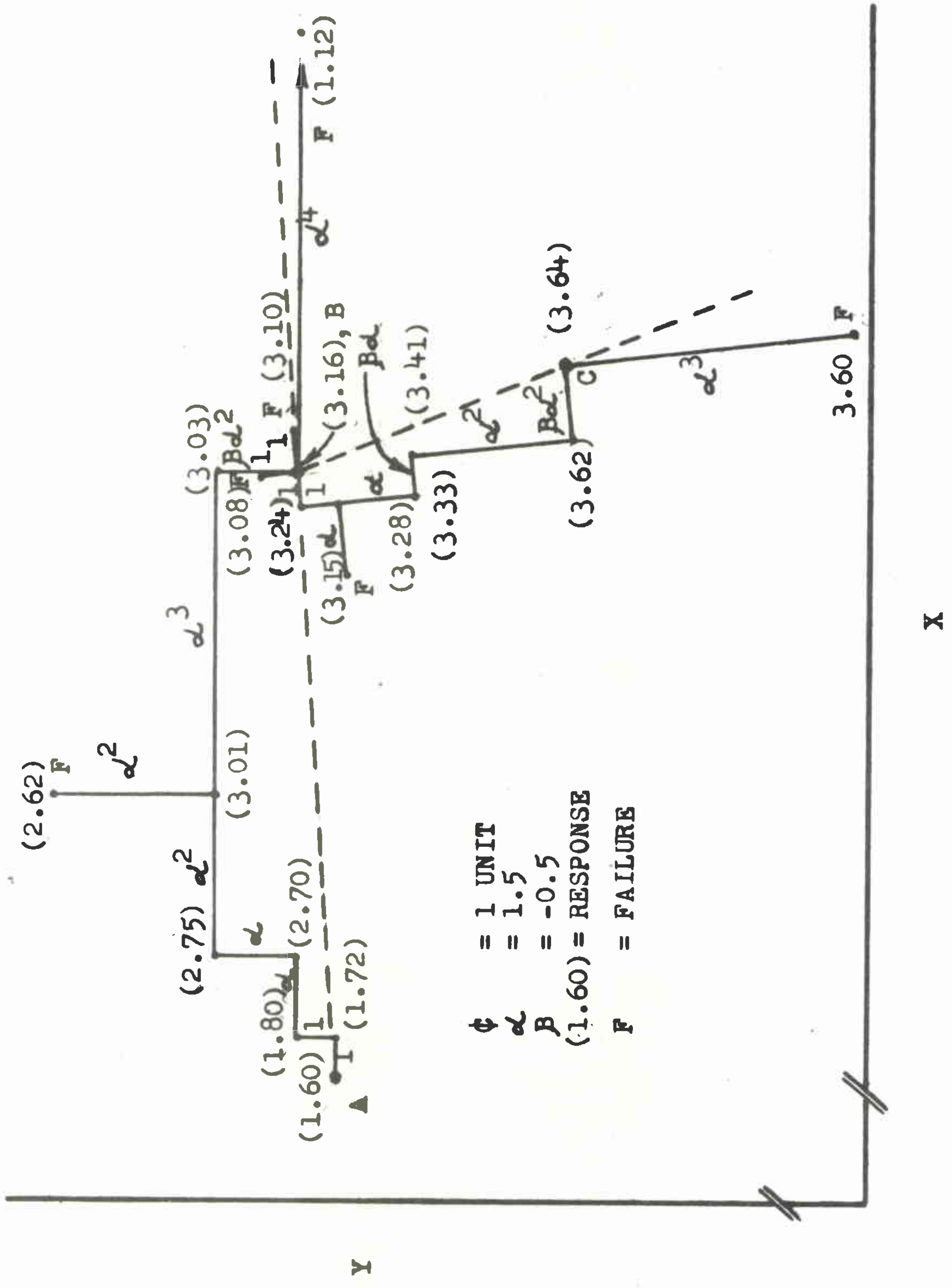
Rosenbrock's programme has been used for various purposes in this report. In order to find the frequency factors, an initial set (A_i of EXP(- $\Delta E_i/RT + A_i$)) was chosen and a search was conducted on these values. The response for these searches has already been discussed (5.1).

Later, in optimization searches, variables such as the steam temperature (i.e. this is proportional to the mixed feed temperature), steam rate, bed length, etc., were searched. The effect of changes, carried out by the search programme, on the Gain response (6.1) was of interest here. Naturally, those values of variables giving the maximum Gain represented the optimum.

This search method has limitations. The degree of acceleration and deceleration (i.e. α and β), is subject to human choice. Certain values of α and β may work well for one situation and poorly for another. In most cases, an $\alpha = 2.$ and $\beta = -.5$ were found to be adequate. The choice of the initial

FIGURE 15

ILLUSTRATION ROSENBROCK SEARCH



step (¢) is important too. Perhaps as one approaches the optimum, the initial step should be reduced after each stage (i.e. ¢ = 0.95 x ¢). Another method of reduction may have proved more successful.

In order to save time and facilitate programming, the variables were scaled so that all were of the same order of magnitude. An example of scaling is shown below:

VARIABLE	MODEL RANGE	SEARCH SCALED RANGE
Steam temperature	1000 - 1200°K	1000 - 1200
Steam flow rate	0- 30000 Lb./Hr.	0 - 3000
Bed length	0 - 10 Ft.	0 - 1000

Thus a common ¢, α, and β could be used for all variables of a search.

Highlights of the programme are illustrated in a logic flow chart in Appendix 10. An application of the technique is given in Appendix 11 where a 2-bed, 5 variable situation is optimized.

7.2 Handling of Constraints

Only linear constraints are found in these optimization studies and although the methods used to handle them are not written in general form, they can be readily adjusted to deal with non-linear constraints. Two types of constraints were met and these were dealt with in different ways. A constraint of the type $X_1 + X_2 \leq M$ was handled by the "mirror image" method described below while constraints of the form $X \leq M$ were dealt with the "high failure" technique. It was relatively easy to integrate both types of constraints into the search programme.

The High Failure Method For $X \leq M$ - At certain times a constraint of this type was placed on the steam temperature, bed length, inlet pressure and steam rate. Whenever the search yielded a value of the variable in question greater than that permitted (i.e. M) the response was set to a very high value (when seeking a minimum) and the model was bypassed. A failure was recorded and the search would continue as described in 7.1 (Figure 16A).

It was necessary to improvise the search programme here because on some occasions (Figure 16B) the search would come to a quick halt. When the directions of search were made parallel and perpendicular to the original axes, and so likewise to the constraint, the search could proceed along the constraint very efficiently. Successive failures in all variables would trigger this rotation back to the original search directions.

The Mirror Image Method ($X_1 + X_2 \leq M$) - Constraints of the type $X_1 + X_2 \leq M$ were found when the total available steam rate (also total bed depth) to two beds was limited and an appropriate X_1, X_2 distribution was sought. The search proceeds normally until the variables X_1 and X_2, together, exceed their constraint (M). Instead of recording the response of this situation, new values of X_1 and X_2 are found by taking their mirror image about the constraint. All other variables remain as they were and the response is then recorded (Figure 17A). The search continues with the former values of X_1 and X_2. A very searchable response surface is generated.

The method has drawbacks in situations where the response contours are almost parallel to constraints (Figure 17B), or where the contours are wavy (Figure 17C), or where they are convex toward the constraint (Figure 17D). It must be mentioned that difficulties such as these exist in any event, mirror image or not. The situation where the optimum lies within the constrained region is easily handled by the technique since the search on the variables may either be direct or indirect with reflection into the permissible area (Figure 17E).

A good knowledge of the nature of the response surface is helpful. Verification of whether or not the optimum has been reached may be obtained by running numerous searches, each beginning at an extremity of the variables so that most of the region has been traversed.

The high failure method was not used for handling $X_1 + X_2 \leq M$ constraints since it was not considered practical to calculate directions of search along these constraints. In essence, it was easier to incorporate the mirror image treatment into the programmes.

FIGURE 16

CONSTRAINTS - HIGH FAILURES FOR X ≤ M

FIGURE 16A - HIGH FAILURE METHOD

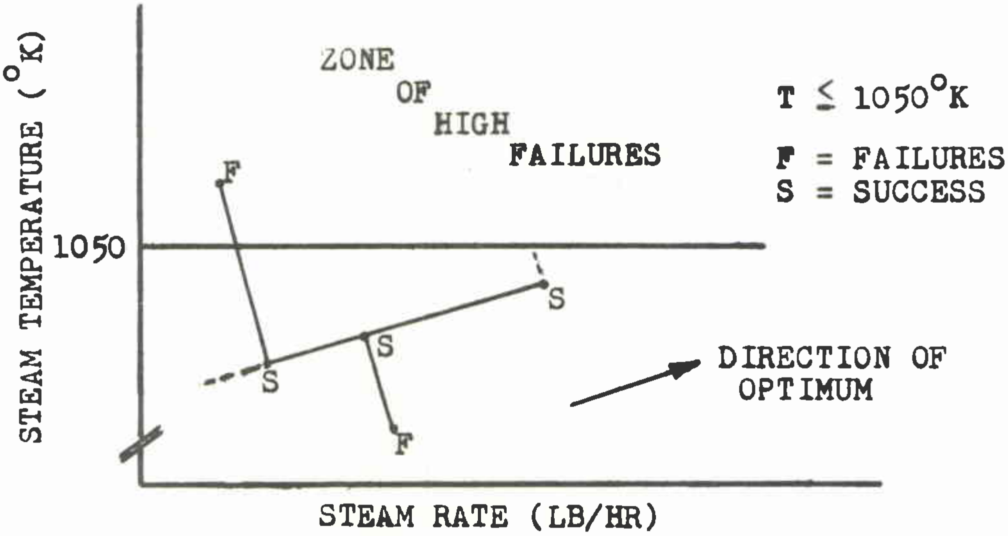


FIGURE 16B - IMPROVISATION TO ROSENBROCK FOR HIGH FAILURE METHOD

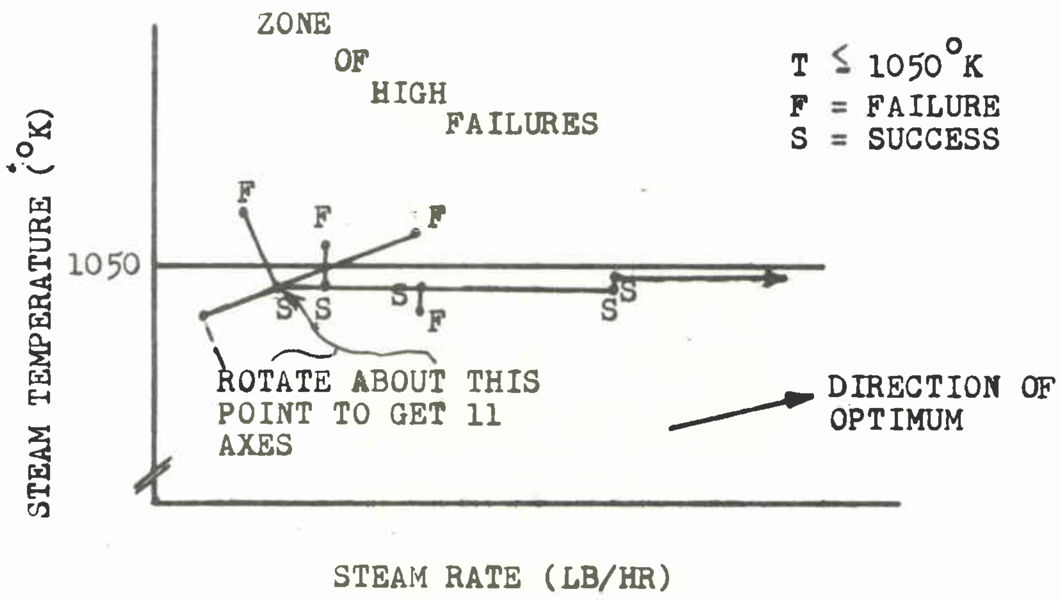
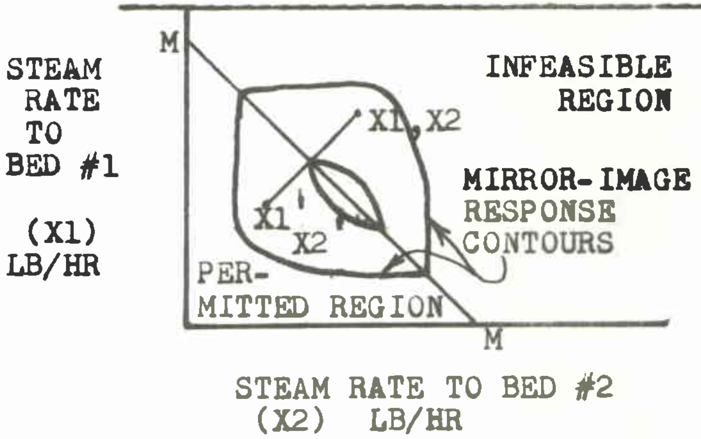


FIGURE 17

CONSTRAINTS - MIRROR IMAGE FOR X1 + X2 ≤ M

FIGURE 17A - GENERAL MIRROR IMAGE METHOD X1 + X2 ≤ M

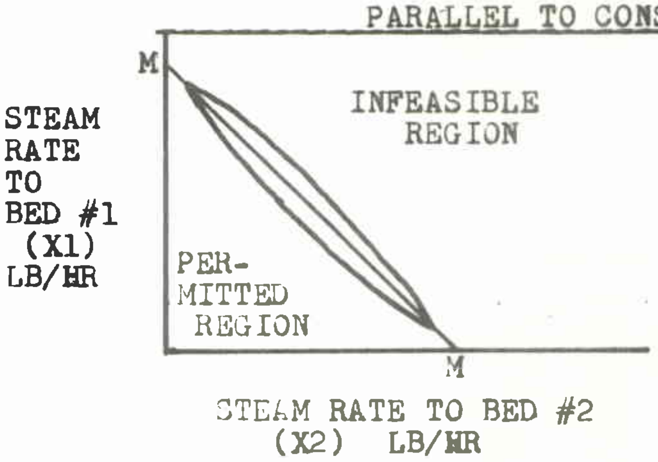


COMMENTS

(1) X1, X2 OF SEARCH BECOME X1', X2' IN THE RESPONSE FUNCTION

(2) RESPONSES WITH X1, X2 AND X1', X2' ARE THE SAME; HENCE SEARCH TENDS TO CONSTRAINT.

FIGURE 17B - RESPONSE CONTOURS APPROXIMATELY PARALLEL TO CONSTRAINT

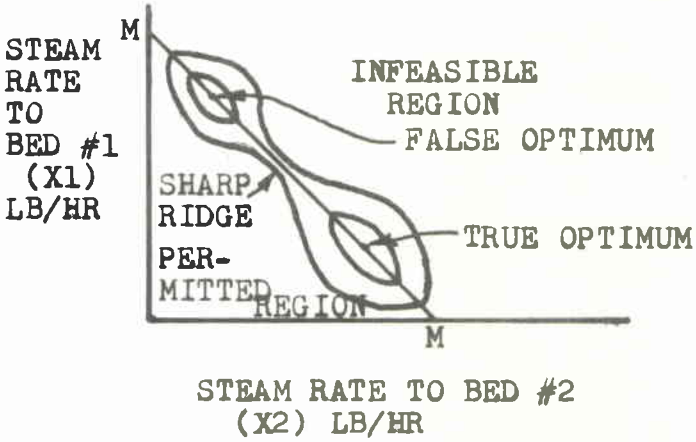


COMMENTS

(1) A VERY STEEP RIDGE IS CREATED AND IT WILL TAKE A LONG TIME TO ARRIVE AT THE OPTIMUM

(2) IF THE CONTOURS ARE PARALLEL TO THE CONSTRAINT, THE SITUATION IS DEGENERATE

FIGURE 17C - WAVY RESPONSE CONTOURS ALONG CONSTRAINT

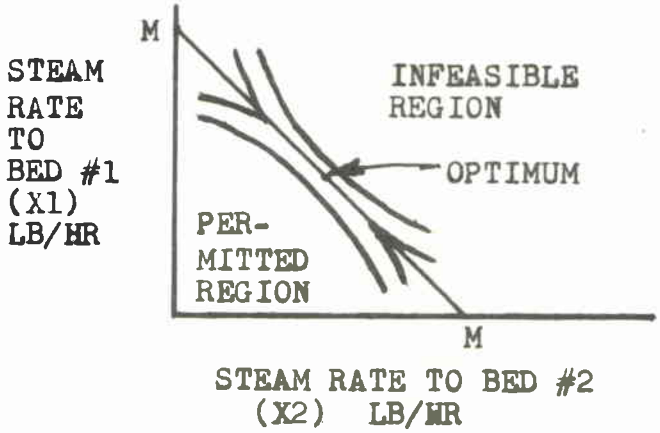


COMMENTS

(1) CAN ONLY FIND THE TRUE OPTIMUM BY RUNNING A SERIES OF SEARCHES BEGINNING AT DIFFERENT POINTS

(2) THE SEARCH MAY HAVE DIFFICULTY AT SHARP RIDGES

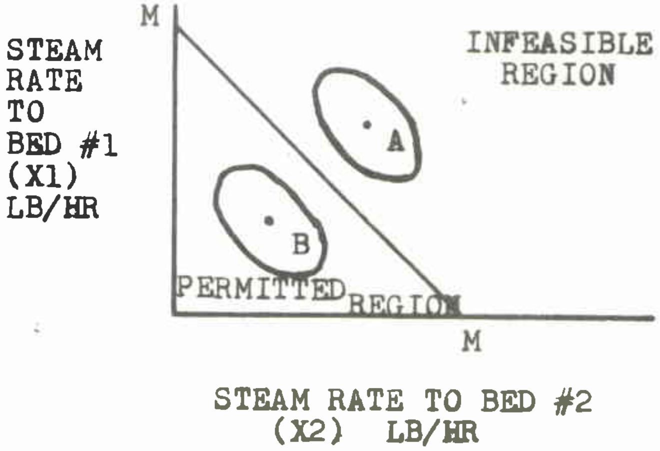
FIGURE 17D - RESPONSE CONTOURS ARE CONVEX TOWARD CONSTRAINT



COMMENTS

(1) ANY SEARCH INITIAL POINT WILL LEAD TO THE OPTIMUM

FIGURE 17E - OPTIMUM LIES INSIDE THE CONSTRAINT



COMMENTS

(1) SEARCHES (VALUES OF X1,X2) MAY END UP IN THE AREA AROUND A OR B. IN EITHER CASE, THE OPTIMUM IS FOUND

8. OPTIMIZATION AND DESIGN STUDIES

Mild and extreme searches over process variables for both the single bed (8.1) and the double bed reactor systems (8.2) are carried out below. All trends, behavior of the Gain function with changes in variables, etc., have been noted and the knowledge obtained has been applied to the more practical problem of changing the present single bed into a double bed without requiring major changes in existing equipment (8.2 and 8.3).

8.1 Design and Optimization of a Single Bed

8.1.1 Aims, variables and constraints

The model of the April plant situation will be extrapolated for the major process variables (i.e. mixed feed temperature, steam flow rate and bed length). Each combination of variables would be run under two sets of constraints. The actual plant limitations allowing a maximum steam rate of 18000 lb./hr. and a maximum steam temperature of 1050°K would be tested. These values would become 30000 lb./hr. and 1200°K respectively in more severe extrapolations. The suspected optimum operating condition for the single bed is thought to lie at a steam to hydrocarbon ratio of 2.6 lb./1 lb.[5], i.e. at about 23400 lbs. steam/hr. for the April hydrocarbon feed rate.

Since the limitation on temperature is expressed in terms of the steam temperature, it was decided to use this quantity as a variable instead of the mixed feed temperature. 2000 lb./hr. of the total steam flow (April case) is mixed with the pure hydrocarbon feed stream for preliminary heating (we shall refer to this resulting stream as the HS stream). The remaining steam (16000 lb./hr.) is mixed with the HS stream at the reactor entrance. Although the states of the 2000 lb./hr. steam and the 16000 lb./hr. superheated steam are different, it was assumed that both streams were at the temperature of the steam leaving the superheater (Figure 2). It was calculated that in order to have a mixed feed temperature of 922.59°K for a steam (exit superheater) temperature of 1027.7°K, the HS stream must be at 807°K. This overall assumption was necessary since nothing was known of the pure feed condition prior to mixing with the 2000 lb./hr. steam. In all runs for both the single and double beds, it was assumed that the temperature was 807°K, no matter what the temperature of the superheated steam was. To this stream is added the remaining steam and the mixed feed temperature results. Figure 18 shows the relationship between the steam temperature, mixed feed temperature and steam rate.

The inlet pressure for a single bed remained a function of the total molar hourly flow rate (3.5). An upper limit of 10 feet was placed on the bed length.

8.1.2 Reactor situations studied

This section illustrates the various combinations of variables and constraints studied for single and double bed reactors. Each such combination is classified by a situation number. Complete results of each optimization are found in Appendices 12 and 13, and these may be related to this section by the situation numbers. Appendix 12 gives the values of the process variables at the beginning and the end of a search, along with the corresponding optimum value of the Gain function ($/Hr.). Appendix 13 shows more complete results at the optimum condition for each situation. Duplicate runs are represented by case numbers.

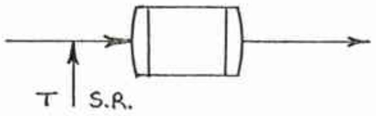
For convenience, all combinations of variables and constraints for both single and double beds are included together. These situations are illustrated below.

Legend: For Reactor Situations Studied

QUANTITY NAME	DESCRIPTION OF VARIABLE
T	Steam temperature (^{o}K)
S.R.	Steam flow rate, single bed (Lb./Hr.)
Z	Bed length, single bed (Ft.)
P	Inlet pressure (Atmos.)
S.R.1	Steam flow rate to 1st bed (Lb./Hr.)
S.R.2	Steam flow rate to 2nd bed (Lb./Hr.)
Z1	Bed length, 1st bed (Ft.)
Z2	Bed length, 2nd bed (Ft.)

8.1.2 Reactor situation studies

(1) Single bed - 2 variables



Situation
Number

CONSTRAINTS

	T	S.R.
(i)	≤ 1050	≤ 18000
(ii)	≤ 1200	≤ 30000

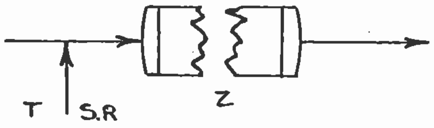
FIXED PARAMETERS

$Z = 5.5833$ Ft.

VARIABLES

T
S.R.
$P = a + b(S.R.)$* (see 3.5)

(2) Single bed - 3 variables



CONSTRAINTS

	T	S.R.	Z
(i)	≤ 1050	≤ 18000	≤ 10
(ii)	≤ 1200	≤ 30000	≤ 10

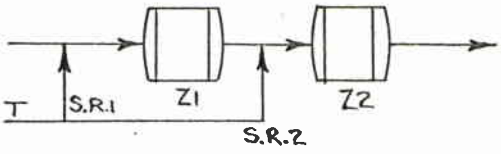
FIXED PARAMETERS

None

VARIABLES

T
S.R.
Z
$P = a + b(S.R.)$*

(3) Double Bed - 3 variables



CONSTRAINTS

(i)	T	$(S.R.1 + S.R.2) \leq$
(i)	≤ 1050	18000
(ii)	≤ 1200	30000
(iii)	≤ 1200	18000

FIXED PARAMETERS

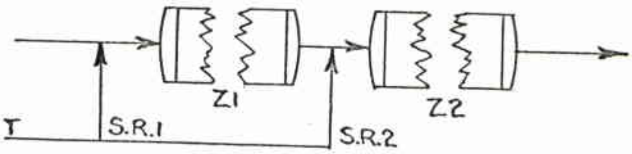
$P = 2.37$ atmos.
$Z_1 = Z_2 = 2.79165$ Ft.
= one-half present single bed length

VARIABLES

T
S.R.1
S.R.2

* Note - The inlet pressure (P), unless constant is an indirect variable since it is a function of S.R., the steam flow rate.

(4) Double bed - 5 variables



FIXED PARAMETERS

$P = 2.37$

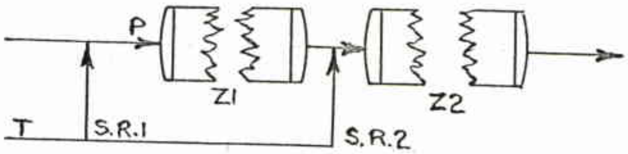
VARIABLES

T
S.R.1
S.R.2
Z1
Z2

CONSTRAINTS

	$T \leq$	$(S.R.1 + S.R.2) \leq$	$Z1, Z2 \leq$
(i)	1050	18000	10
(ii)	1200	30000	10

(5) Double Bed - 6 variables



FIXED PARAMETERS

None

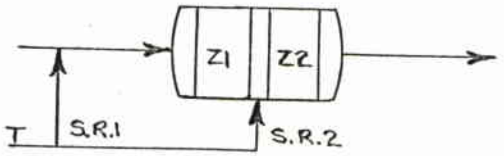
VARIABLES

T
S.R.1
S.R.2
Z1
Z2
P

CONSTRAINTS

	$T \leq$	$(S.R.1+S.R.2) \leq$	$Z1, Z2 \leq$	P
(i)	1050	18000	10	2-2.5
(ii)	1200	30000	10	2-2.5

(6) Single bed converted to 2 beds; 5 variables



FIXED PARAMETERS

$P = 2.37$

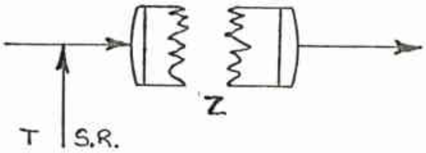
VARIABLES

T
S.R.1
S.R.2
Z1
Z2

CONSTRAINTS

	$T \leq$	$(S.R.1+S.R.2) \leq$	$(Z1+Z2) \leq$
(i)	1050	18000	5.5833
(ii)	1027.7	18000	5.5833
(iii)	1200	18000	5.5833
(iv)	1050	30000	5.5833
(v)	1200	30000	5.5833
(vi)	1027.7	30000	5.5833

(7) Single bed - 1 variable



FIXED PARAMETERS

P = 2.37
S.R. = 18000
T = 1027.7

CONSTRAINTS

	Z≤
(i)	10

VARIABLE

Z

8.1.3 Discussion of Results

A single reactor of the type investigated, operates at a Gain of $117.31/Hr. (Appendix 12, Standard April Case): Polymer operates three of these. A search (situation 1,i)* with the steam temperature varying up to 1050°K and the steam rate permitted to reach 18000 lb./hr. at a fixed bed depth of 5.5833 feet showed that each reactor could yield $120.45. This is a rather insignificant gain, especially so when one considers that the catalyst may age quicker due to the increased coke caused by higher mixed feed temperature (M.F.T.). As steam temperature rose from 1027.7°K (April case) to 1049.98°K, the M.F.T. moved from 922.59°K to 934.76°K (Figure 18).

When constraints were lifted (situation 1,ii), it was found that the optimum values of the steam temperature and flow rate were 1062.08°K and 22140 lb./hr. respectively, with a

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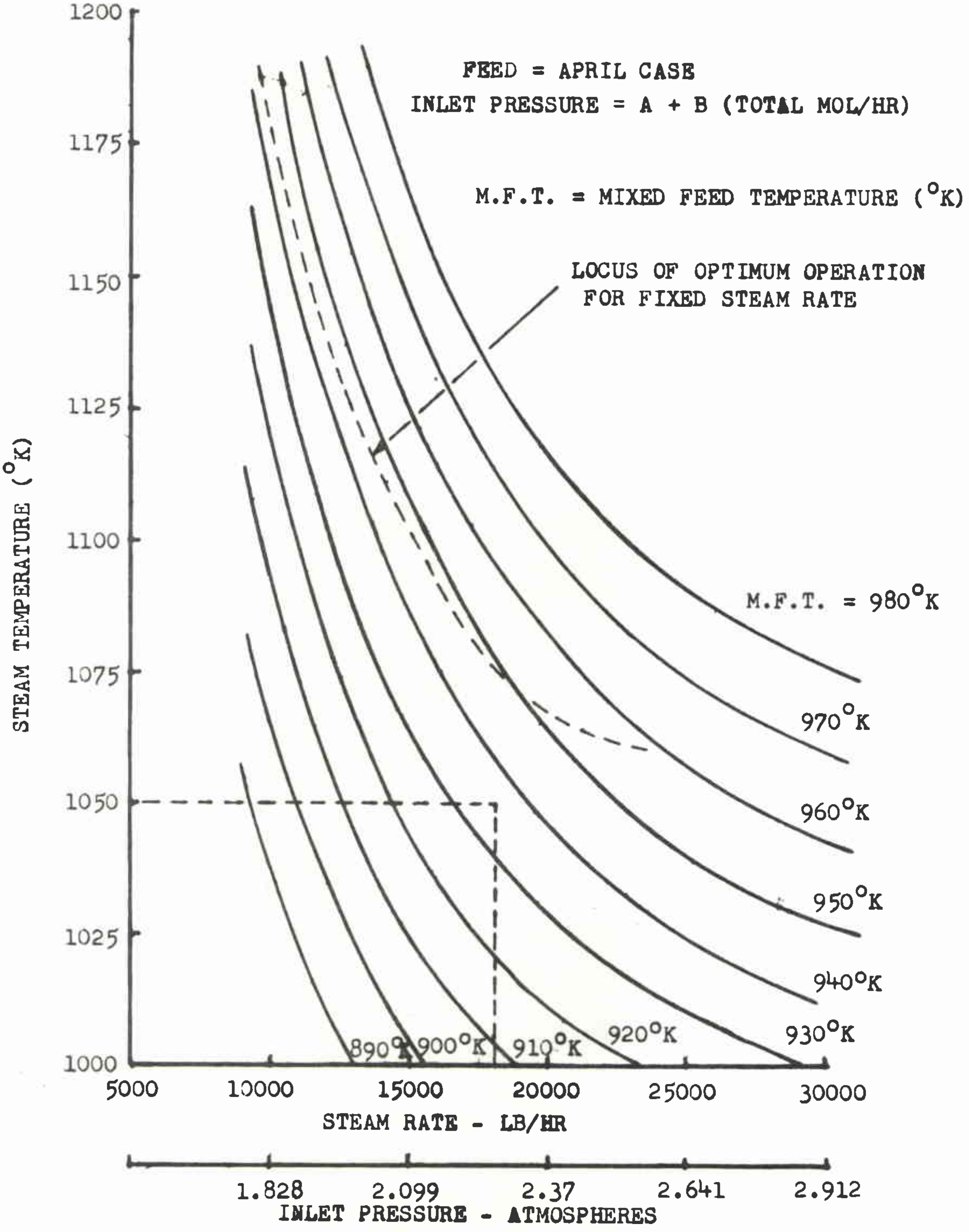
* Whenever situation numbers are noted, please refer to Appendix 12, then 13 if more information is desired.

FIGURE 18

RELATIONSHIP BETWEEN MIXED FEED TEMPERATURE, STEAM TEMPERATURE, AND STEAM RATE



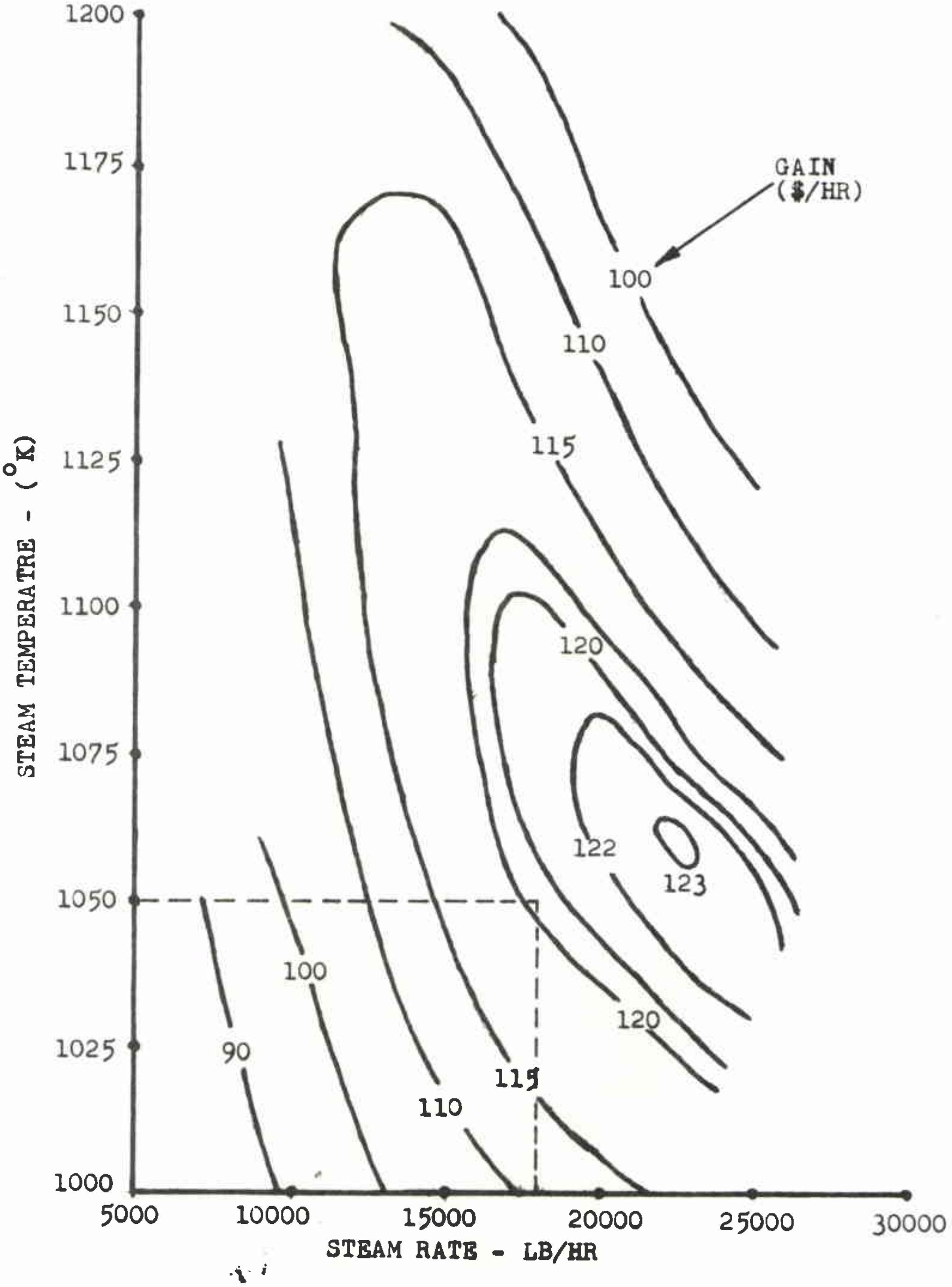
corresponding Gain of \$123.10 per hour. Although the mixed feed temperature of 956°K indicates more severe carbon buildup, it is thought that the higher steam rate would tend to cancel out the effect of higher temperature. The steam to hydrocarbon ratio is about 2.46 Lb./Lb. as compared to the present 2.0 Lb./Lb. This finding agrees well with the value of 2.6 Lb./Lb. cited by Boundy and Boyer[5] but it must be noted that conditions (i.e. temperature, pressure) differed. Figure 19 shows how the response (GAIN/HR.) varies with steam temperature and flow rate at a fixed bed depth of 5.5833 Ft.

When bed length was included as a variable (situation 2,i) with present plant constraints on steam temperature and flow rate, a gain of \$124.66/Hr. was realized at a bed depth of approximately 8.15 feet. Situation 7,i is analogous to the April case; only the bed length has been varied. At 8.27 feet the reactor yields \$122.80/Hr. indicating again that a longer bed improves the GAIN. A longer bed is desirable if present plant constraints cannot be removed. The only change in the cost function for cases where bed depth is also a variable was the inclusion of a penalty of approximately \$.059 per foot of extra bed per hour allowing for the cost of extra catalyst.

It seems that the cost function breaks down when all plant constraints are removed (Situation 2,ii). Depending on where the search begins, we find two optima separated by a saddle point. The optimum represented by a steam temperature of 1044.18°K, a steam rate of 19874 Lb./Hr., and a bed depth

FIGURE 19

RESPONSE ($/HR) AS A FUNCTION OF STEAM TEMPERATURE AND FLOW RATE. (SINGLE BED)



of 7.45 feet has a reasonable gain of $125.95/Hr. The other optimum condition is reached at values of the variables tending towards those expected for an ideal reactor, i.e. low temperature, high steam rate and long length. This apparent failure can be explained quite simply: the cost function does not include penalties for larger furnaces, larger reactors, etc., (6.2). The Gain of $130.98/Hr., can be adjusted algebraically to account for such extra costs.

Figure 20 shows how the Gain behaves at various bed depths, around the local optimum of cases 1, 2, and 3 of Situation 2,ii.

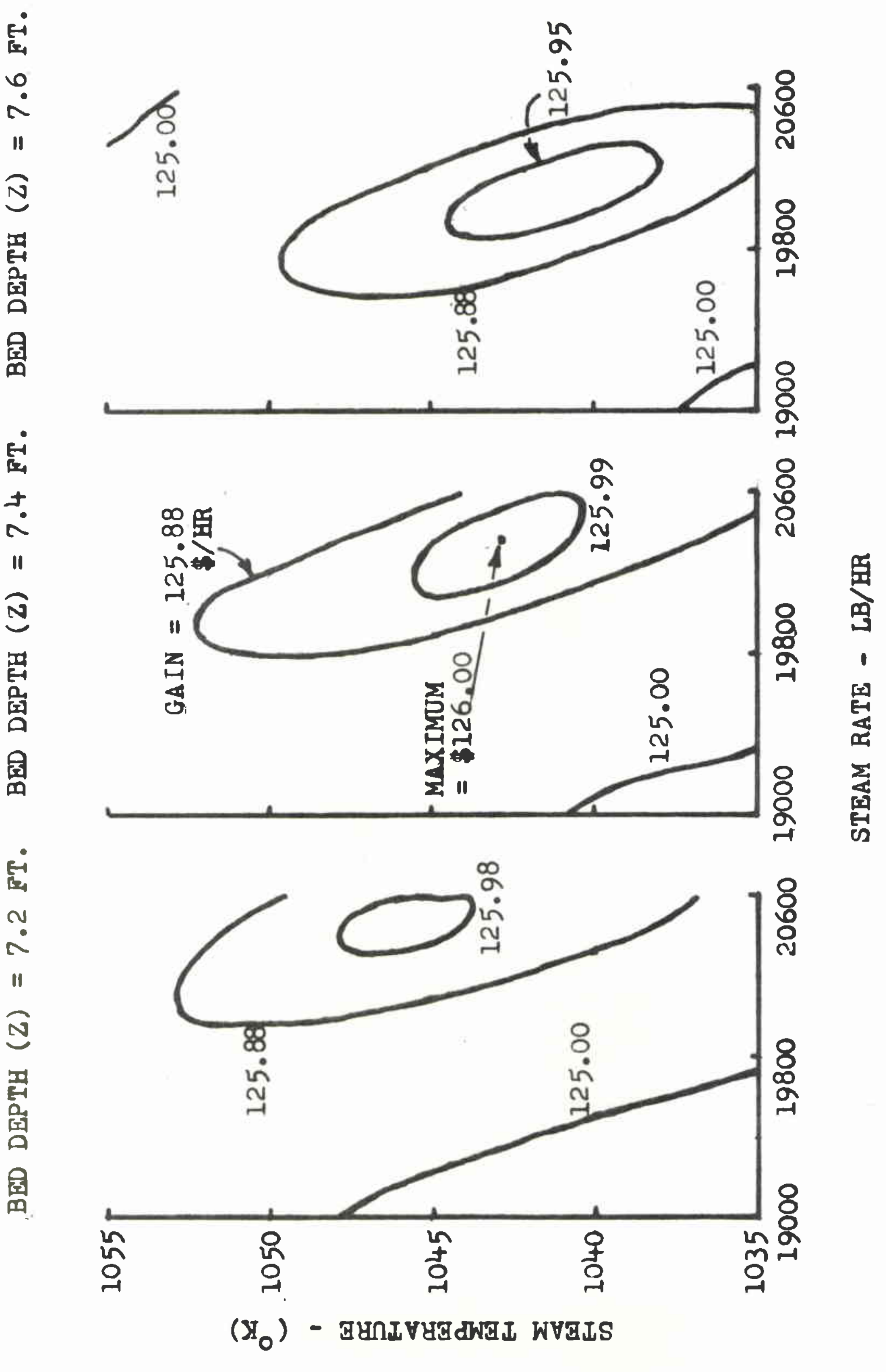
8.1.4 Conclusions

It appears that the cost function (GAIN/HR.) is representative of the changes that occur in the reactor when the process parameters are varied over reasonable ranges around present operating conditions. Each time a constraint is removed, the GAIN increases, indicating consistency of the model.

The GAIN/HR. may be very simply improved by increasing the bed depth. The reactor has a large dead space above the bed and the addition of about one foot of catalyst should do no harm. A secondary advantage could also result. Since the catalyst is known to coke up from the reactor entrance down toward the bed interior, the reactor could be operated efficiently for a longer time due to the extra catalyst at the end of the bed. Fewer shutdowns would be required to remove spent catalyst.

FIGURE 20

3 VARIABLE RESPONSE AS A FUNCTION OF STEAM TEMPERATURE AND FLOW RATE AT FIXED BED DEPTHS



Due to the large capital cost of installing a new furnace and losses incurred during shutdown time, it would seem that the lengthening of the bed would be economically more feasible than increasing the steam flow rate and temperature.

8.2 Design and Optimization of a Double Bed

8.2.1 Aims, variables and constraints

Much greater improvements in GAIN are found when the jump is made from a single to a double bed. The constraints used in this section remain similar to those used for the single bed studies (8.1). A two bed system offers certain advantages. Initially, when rates of formation of some by-products are low due to lack of reactants (i.e. H_2 for reaction 3 (see 3.2)) and the reverse rate of the main reaction is negligible, steam is mainly required for its heat. In the second bed, steam provides a means for the dilution of reactants which are vital to reactions 2, 3, 14, 15 and 16. The rate of benzene formation (reaction 2) is reduced only linearly with steam added, but that of toluene is cut more drastically due to the second order nature of reaction 3. The temperature increase, of course, affects both of these reactions. The rate of reverse reaction in reaction 1 is reduced more than the forward rate. Figure 21 compares the conversion profiles of reactions 1, 2 and 3 under similar constraints for a single bed (situation 1,i) and a double bed (situation 6,i).

The HS stream (8.1.1) was again given a temperature of 807°K for all superheated steam temperatures. The only major difference between the one and two bed models was in the treatment of inlet pressure. For single beds this had been a function of the molar flow rate (3.6). In the two bed situation, this simplification was no longer valid since if most of the steam enters the second bed, the inlet pressure of the first bed would be so low that results of the 1 and 2 bed set-ups could not be well interpreted. It was decided to keep the inlet pressure fixed at 2.37 atmospheres for all runs where it was not a variable. This would enable relatively good comparisons with the single bed runs. The exit pressure of the first bed was considered as the inlet pressure of the second bed, no matter how the steam was introduced between beds.

The variables to be searched would consist of the:

(1) steam temperature
(2) steam flow rate to Bed 1
(3) steam flow rate to Bed 2
(4) bed length, Bed 1
(5) bed length, Bed 2
(6) inlet pressure.

Searches run with various combinations of these are illustrated in section 8.1.2 under "Reactor Situations Studies".

Complete results for each situation (3,i to 5,ii) are found in the Appendix sections 12 and 13.

8.2.2 Discussion of Results

In situations 3i, 3ii and 3iii the steam temperature and steam distribution were varied, subject to the constraints indicated with the illustrations (8.1.2). The depth of each bed was set at one half that of the existing single bed. Searches were conducted from within the permissible region (3i, 1A, 1B) or along the steam rate constraint (3i, 1, 2, 3) and it seems that both methods are comparable. For present plant constraints (3i, 1B and 3i, 1, 2) a GAIN of \$123.28/Hr. is attained. This represents quite an improvement over the \$120.45 gain of the single bed under similar constraints (1i, 1, 2). The steam stream at 1049.98°K, must be split with 12830 Lb./Hr. going to the first bed, and 5170 Lb./Hr. to the second.

Situations 3iii, 1, 2 and 3iii, 1A are run with steam temperature $\leq$ 1200°K and the smaller steam rate constraint of 18000 Lb./Hr. The steam distribution is now 8700 Lb./Hr. to the first bed and 9300 Lb./Hr. to the second, at 1162°K. When compared to 3i, 1 the mixed feed temperature to the first bed has risen only slightly from 911.17°K to 921.24°K. The gain per hour has jumped to \$134.97.

Bed lengths were varied along with steam temperature and flow rates in situations 4i and 4ii. As the severity of the constraints imposed is reduced, the GAIN increases appropriately, again showing that the model is consistent. It would perhaps be best to consult Appendices 12 and 13 in order to compare the numerous situations studies.

When the inlet pressure (P) is varied ($2.0 \leq P \leq 2.5$ atmos.), the final search value is always 2.0 atmos. Situations

5i and 5ii can be compared to 4i and 4ii for the effect of change of pressure but the validity of these results can be questioned owing to an apparent breakdown of the cost function. Trends, however, must be regarded as being correct, i.e. a comparison of 5i, 1 and 4i, 1 shows that a lower inlet pressure is desirable. This is confirmed by Boundy and Boyer[5] who state that a typical reactor bed operates at 1.2 to 1.4 atmospheres.

8.2.3 Conclusions

Whenever all three basic variables, i.e. steam temperature, steam flow rates and bed lengths are varied over large ranges, the cost function seems to break down (situations 4ii, 5ii). The search halts on one or several of the constraints and algebraic adjustments allowing for costs not included (6.2) must be made if these answers are to have more meaning.

Very realistic gains are found when constraints force operations near present plant operation conditions (3i, 3ii, 3iii). In order to exploit the area close to present constraint limitations, it was decided to run a series of double bed situations (6i to 6vi) with the constraint that the sum of the bed-lengths be $\leq$ 5.5833 feet (April).

When the constraints were set at 1050°K for steam temperature and 18000 Lb./Hr. for total steam rate, it was found that most of the steam must be added to the first reactor (3i, 1, 2). If steam temperature can reach 1200°K (3iii, 1, 2) at the same steam rate, 8729 Lb./Hr. and 9271 Lb./Hr. steam at 1162°K are fed to beds 1 and 2, respectively. At lower temperatures the greater part of the steam is added to the first bed mainly for its heating ability; dilution effects are not really required until the reverse reaction rate of the main reaction and the hydrogen concentration for reaction 3 become important. At higher steam temperatures less steam is required by the first bed, i.e. approximately the same mixed feed temperature is maintained, but dilution effects are less. The steam added to the second bed is important for both its heating and dilution effects.

8.3 Application of Two-Bed System to Present Reactor

8.3.1 Proposed changes explained

The present single bed is about 6'2" in total length and has a surge space of about 17" between the top of the bed and the upper reactor tangent line (Figure 3). It should be possible to split the bed with a space of about 6" into which steam can be added. About 4 to 5 inches, on either side of the split, must be allowed for Berl saddles, steel grating, etc. This change reduces the surge space to about 6 inches. If steam can be evenly mixed in the 6 inch split and the flow in the first bed is not disrupted, then we have a very feasible, simple change in design. Numerous situations (6i to 6vi) have been studied to determine whether the proposed change is economically sound.

In all runs the search involves five variables; steam temperature, the steam rate to each bed, and the length of each bed. The sum of the bed depths was not allowed to exceed the present single bed length so that a comparison of situations 1i, 1ii with 6i to 6vi would be realistic. The constraints peculiar to each situation are described in section 8.1.2.

A review of the results of these searches (Appendices 12 and 13) indicates that it is possible to improve the present operation. For example, the comparison of 6i with 1i, where the only difference is in the number of beds, shows that a GAIN of $120.45/Hr. is obtained from the single bed while $124.99/Hr. results from the two bed system. Although styrene conversion is almost exactly the same (Figure 21), the major part of the extra gain results due to much lower benzene production, caused by an overall lower operating temperature. A similar comparison exists between situation 6ii, 2 and the April case, where it is seen that there is very little to be gained if the present (April) operating conditions are applied to a two bed system.

8.3.2 Discussion of results

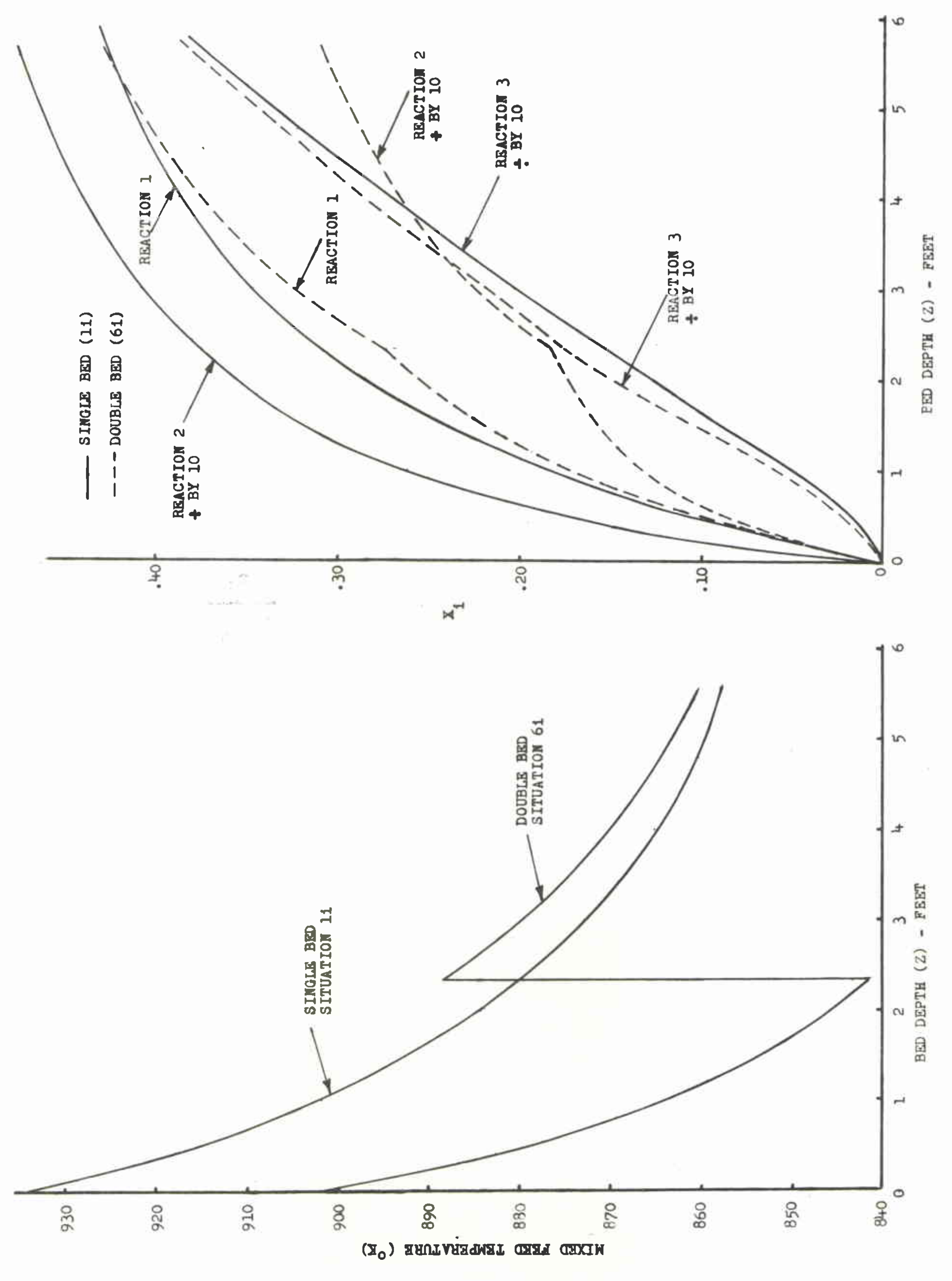
The largest GAINS are to be made with a larger furnace (situations 6iii to 6vi) but it must be remembered that allowance for this is not included in the cost function so that the actual GAINS should be closer to those possible with present constraints (6i, 6ii).

Situations 6iv, 6v and 6vi exhibit very flat response regions along the steam rate constraint. A close look at

FIGURE 21

COMPARISON OF SINGLE AND DOUBLE BED

CONVERSION AND TEMPERATURE PROFILES



cases 1 and 2 of 6iv shows that when the search is started from different locations a pseudo-optimum condition is found (Case 1). The first bed is the longer of the two and also requires more steam. At the real optimum (Case 2) the first bed is the shorter of two and now requires less steam. The distributions of bed depths and steam rates have the tendency to complement one another. The permissible ranges for these variables are large and one can operate close to the actual optimum quite easily. This pseudo-optimum where the search may terminate is explained in section 7.2.

9. OVERALL CONCLUSIONS

(1) A suitable model of actual plant conditions for the dehydrogenation of ethylbenzene has been developed. The model gives excellent results for the four major liquid product hydrocarbons (compare Table 1C with Table 3A) and a reasonably accurate gas product composition (Table 1D vs. 3B). Results are well within errors that can be attributed to flowmeters (1% is reasonable) or sample analysis techniques. The model and actual plant reactor temperature profiles do not differ by more than 4 or 5°K at any bed depth (Figure 12).

The model allows for optimization at fixed times in the catalyst life; it can be used for the designing of new reactors; and it can give considerable insight to the relative importance of these variables.

(2) Extrapolation of the model variables in parametric and in optimization studies has shown that the plant is being operated at sub-optimal conditions. This situation has resulted from increasing the hydrocarbon feed rate without being able to compensate by changing other process variables, i.e. mixed feed temperature, rate of steam addition, etc. Constraints (2.3) do not permit such changes. Although an increase in styrene production has resulted due to the increased hydrocarbon throughput, the existing situation is by no means optimal with respect to the possible hourly gain at the fixed hydrocarbon rate.

(3) Rosenbrock's multivariable search technique has proven to be a good method for seeking optimum operating conditions for this reactor system. Searches were carried out on situations having up to six variables. Computer time for each optimization was from 5 to 20 minutes (IBM 7040) with much of this being used up in the immediate vicinity of the optimum. About 60 to 200 passes of the model were required by each run.

(4) Optimization searches on the single bed (i.e. situation 1i) have shown that the process should be operated at a higher temperature and a higher steam rate (Figure 19). If, however, these variables cannot be raised, the bed length should be increased (situations 2i, 2ii and 7i). It is possible to add approximately one foot of extra catalyst for slight improvement (Figure 3); otherwise a furnace of greater capacity and/or a new reactor should be considered with a complete economic survey being conducted to determine the feasibility of such a plan.

(5) If it is feared that a higher operating temperature will greatly reduce the useful catalyst life due to coke build-up, the present April situation can be improved by the addition of more steam at the same temperature. By adding 22000 lb./hr. steam at 1027.7°K (Figure 18), the GAIN/Hr. would be increased from \$117.31 to approximately \$121 (Figure 19) for the 5.5833 foot bed depth. The mixed feed temperature rises slightly from 922.59°K to about 935°K. More steam should allow higher mixed feed temperatures since these two variables go hand in hand in removing and laying down carbon.

An EVOP[7] type of search is recommended when introducing variations in process variables. Optimization runs should give the proper direction in which to head. For the present single bed the goal of such slight changes in mixed feed temperature and steam rate should be the optimum area described by Figure 19.

(6) Adaption of the model to the design of a two-bed reactor has shown that considerable improvement is possible (situations 6i to 6vi) over a single bed employing an equal amount of catalyst. Unless the furnace capacity is increased, however, the extra gains will be small (situations 6i, 6ii).

The two-bed reactor allows lower operating temperatures (compare 1i and 6i or the April case with 6ii) presumably resulting in less coke being deposited. Of course, there will also be less steam for coke removal in the first bed; whether the lower temperature or lower steam rate controls coke laydown can only be estimated for the particular situation involved. Better results (6iii to 6vi) seem possible with a larger furnace.

(7) If economically feasible it is advisable that a two-bed (situation 6i) reactor with steam introduction between beds be set up. Present furnace and reactor limitations need not be exceeded in order to obtain a better gain/hr. If results compare with those predicted by the model, serious consideration should be given to increasing the present furnace capacity.

10. FUTURE WORK

The work of this report has been directed at predicting the improvement of the present plant operating situation. This has been accomplished satisfactorily with the limited data available. Temporary optimal policies have been found for various conditions. Due to the wide scope of the work certain sections of the report were passed by rather quickly and these may demand more thorough investigation. Areas in which more work can be done are listed for convenience:

(1) At some future date, should more data become available, the effect of operating conditions on catalyst life could be determined. All necessary data should be taken about once a month for the duration of the life (about 2 years) of a catalyst charge. It would then be possible to establish a crude relationship between operating temperature and steam to hydrocarbon ratio with catalyst efficiency on a time basis.

Data should be taken for new plants as soon as they go on stream. The full potential of a plant can be realized from an intensive initial study.

(2) The cost function (GAIN/HR.) could be expanded to include the items described in section 6.2 and a penalty for the effect of process variables on catalyst aging. Optimizations run on the cost function used in this report could be compared to those carried out on the more complete cost function. A

complete breakdown of the individual components of the total GAIN should be given.

(3) This report has only looked at one and two reactor situations. Although it is doubtful that a three bed reactor system would offer much improvement over the two bed situation, the three bed case should be examined.

Different means of heating the reacting mixture between beds could also be investigated.

(4) The general methods of this report can be applied to other reactor systems without requiring basic changes in the model programme structure or in the Rosenbrock search technique.

(5) The efficiencies (accuracy and time combined) of other integration methods such as third order Runge-Kutta or Predictor-Corrector could be compared with the fourth order Runge-Kutta Gill technique that was used.

(6) Other methods of optimization should also be tried since Rosenbrock's method may not be the most suitable for this system. Combinations of existing methods may be desirable. For example, a steepest ascent search[15] can be combined with Rosenbrock's method; the former quickly seeks out the general location of the optimum but fails on flat response surfaces where the latter is very effective.

The recent ideas of Fletcher and Powell[16] should also be considered.

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APPENDIX 1

CHOICE OF EQUILIBRIUM CONSTANT (K_p) EXPRESSION FOR MAIN REACTION

Two expressions for K_p as a function of temperature were found. Another, derived from first principles, was compared with these and since it gave K_p values intermediate between the two it was used in the rate expression (3.3).

An exposé of the expressions is given below.

(i) THE K_p EXPRESSIONS

EQUATION NUMBER	EQUATION FOR K_p	REFERENCE
1	$K_p = EXP(-15350/T + 16.12)$	G
2	$K_p = T^{.549}\ EXP(-14516/T + 11.41)$	H
3	$K_p = EXP(-\Delta F^o/RT)$	I

Note: (1) Equation 3 was used in the final model.
(2) References follow Appendix 3.

ABOVE NOMENCLATURE

$T = {}^oK$

$R = 1.987$ CAL/(GM.MOL. ^oK)

$\Delta F^o = (a + bT + cT^2)$ CAL/GM.MOL. (See Ref. I)

$a = 29311$

$b = -30.157$

$c = -.000524$

(ii) EQUATION 2 DERIVATION

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^o}{RT^2} = \frac{28843 + 1.09\ T}{RT^2}$$

(See 3.8 of main body for ΔH^o)

but at 956^oK, $K_p = 1$ (Ref. H)

$$\ln K_p = -\frac{14516}{T} + .549 \ln T + g$$

$$0 = -\frac{14516}{956} + .549 \ln 956 + g$$

$$g = 11.41$$

Therefore

$$\ln K_p = -\frac{14516}{T} + .549 \ln T + 11.41$$

$$K_p = T^{.549}\ \mathrm{EXP}(-14516/T + 11.41)$$

(iii) A COMPARISON OF VALUES OF K_p OF EQUATIONS 1, 2, 3

TEMPERATURE ^oK	K_p EQUATION 1	EQUATION 2	EQUATION 3
750	.125499 E-01	.134302 E-01	.136564 E-01
770	.220363 E-01	.225261 E-01	.228820 E-01
790	.365023 E-01	.368191 E-01	.373610 E-01
810	.589764 E-01	.587587 E-01	.595581 E-01
830	.931098 E-01	.917128 E-01	.928566 E-01
850	.143873 E 00	.140224 E 00	.141813 E 00
870	.217909 E 00	.210314 E 00	.212457 E 00
890	.323942 E 00	.309830 E 00	.312635 E 00
910	.473250 E 00	.448850 E 00	.452408 E 00
930	.680195 E 00	.640129 E 00	.644494 E 00
950	.962814 E 00	.899602 E 00	.904759 E 00

APPENDIX 2

ACTIVATION ENERGIES

REACTION NUMBER	ΔE CAL/GM.MOL.	REFERENCE NUMBER
1	21708	A
2	49675	B
3	21857	C
14	24838	D
15	15697	E
16	17585	F

Note: References follow Appendix 3

APPENDIX 3

FREQUENCY FACTORS I.E. (A_i OF EXP($-\Delta E_i/RT + A_i$))

These frequency factor exponents (A_i) were found by the Rosenbrock search technique described in (7.1). Section (5.1) of the main body discusses frequency factors.

FREQUENCY FACTORS FOR VARIOUS CASES

REACTION NUMBER	A_i FOR APRIL	A_i FOR MAY	A_i FOR JUNE	A_i FOR POLY-29
1	8.1033	8.1614	8.0272	8.2907
2	13.2392	13.2654	13.0719	13.2294
3	0.2961	0.4075	0.1219	0.2741
14	- 0.0724	- .1882	0.1129	- .1137
15	- 2.9344	- 2.9408	- 2.2596	- 3.0570
16	21.2402	21.1607	21.1493	21.3021
CATALYST AGE (HRS.)	8850	9700	10350	ABOUT 20000

REFERENCES TO APPENDICES 1, 2 AND 3.

REFERENCE NUMBER	REFERENCE
A	See Ref. H.
B	See Ref. H.
C	See Ref. H.
D	This value was estimated
E	AKERS, W. W., and CAMP, O.P., AICHE, No. 4, 471 (Dec. 1955). We assume the nature of the catalytic reaction to be the same, although the catalysts differ.
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I	F^o vs. T data was obtained from: BOUNDY AND BOYER, "STYRENE, Its polymers, Copolymers, and Derivatives", Reinhold (1952) A second order polynomial was fitted to the F^o vs T values (I.E. $\Delta F^o = a + bT + cT^2$)

APPENDIX 4

ΔH, LINEAR VS. CUBIC FUNCTION OF TEMPERATURE

A comparison between linear and cubic expressions of the heat of reaction (ΔH) as a function of temperature is offered for the main reaction. Similar results are obtained for the other five reactions. The cubic ΔH_1 equation was derived from

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta(nC_p)\, dT$$

where $\Delta(nC_p)$ is of the form $a + bT + cT^2$

All C_p data is as in the Table in 3.8 while ΔH_{298} for reaction 1 is 28,100 cal./gm.mole (Ref. 3, Sect. 3.8). At worst, as shown in the table below, an error of approximately 30 cal./gm.mol. on 30000 results.

ΔH_1 FROM LINEAR AND CUBIC EXPRESSIONS

TEMPERATURE (T) °K	$\Delta H_T = a + bT$ CAL./GM.MOL.	$\Delta H_T = \Delta H_{298^\circ} + \int_{298}^{T} \Delta(nC_p)\, dT$ CAL./GM.MOL
750	29660.50	29649.01
800	29715.00	29726.59
850	29769.50	29789.24
900	29824.00	29837.98
950	29878.50	29873.84
1000	29933.00	29897.83

We can conclude that although a linear expression for ΔH does not warrant quadratic C_p's, this simplification has done little harm. Much computation time has been saved.

APPENDIX 5

SINGLE BED ETHYLBENZENE DEHYDROGENATION MODEL

(1) Explaination of Major Terms

A(5), B(5), C(5)	Runge-Kutta constants. See Major Reference 3
H1, H2	Heat of reaction constants, i. e. $\Delta H_i = H1(i) + H2(i)xT.....(T = {}^oK)$
AAA, BBB, CCC	$\Delta F^o = 1000 \times (AAA + BBBxT + CCCxT^2)$ $= cal./gm.mol.$
C1, C2, C3	C_p coefficients, i. e. $C_p = (C1 + C2xT + C3xT^2)$ C_p in cal./gm.mol ${}^oK$
WTMOL	Compound molecular weights
AMTCMD	Compound flow rates - Lb./Hr.
AMTSEC	Compound flow rates - Lb.Mol./Sec.
RKK	$\Delta X / \Delta Z$, rate of change of conversion (mole fraction) with bed depth (Feet)
X	Mole fraction conversion
R	A of $EXP(- \Delta E/RT + A)$
Q	See Major Reference 3
DIAM	Bed diameter (feet)
ZLAST	Bed length (feet)
CATWT	Bulk density of catalyst ($Lb./Ft.^3$)
E	Bed voidage
DP	Catalyst particle diameter (feet)
NSTEP	Number of integration steps
TIN	Reactor and integration increment inlet temperature (${}^oK$)

PIN.................Reactor and integration increment inlet pressure (atmos.)

NRCT................Number of reactions

N...................Number of compounds

AVMLWT..............Mixed feed mean molecular weight

DENGAS..............Gaseous feed density Lb./Ft.^{3}

VO..................Feed superficial velocity (Ft./Sec.)

HEATIN..............Stream heat content (B.T.U./Lb.Mol.$^{\circ}$K)*

HEATRX..............Heat of reaction (B.T.U./Lb.Mol.)*

* Note: essentially we have these units. Unit conversion factors, i. e. 1.8°F/$^{\circ}$C. have been internally cancelled

(2) Model

A complete FORTRAN IV listing of the single bed model now follows. Terms that have not been defined above, are defined internally within the programme, which is set up in such a way that formulae verification should be a simple exercise.

```
$JOB            003201 JOHN SHEEL         100   010
$IBJOB          NODECK
$IBFTC
C    SIMULATION OF ETHYLBENZENE DEHYDROGENATION
C    RUNGE-KUTTA-GILL (4TH ORDER) PERFORMED ON REACTIONS
C    TEMP AND PRES ARE CHANGED ONCE FOR EVERY COMPLETE R-K-G INCREMENT
C    ADIABATIC - PLUG FLOW MODEL
C    FOLLOWING BASIC REACTIONS ONLY USED
C          C6H5C2H5 = C6H5C2H3 + H2
C          C6H5C2H5 = C6H6 + C2H4
C          H2 + C6H5C2H5 = C6H5CH3 + CH4
C          H2O + 1/2 C2H4 = CO + 2H2
C          CH4 + H2O = CO + 3H2
C          CO + H2O = CO2 + H2
C    COMPOUNDS AND CORRES NUMBERS ARE
C          1=EB       2=STY      3=H2       4=C2H4     5=C6H6     6=C6H5CH3
C          7=CH4      8=C2H6     9=C2H2     10=C6H5C2H            11=H2O
C          12=CO      13=CO2     14=C
      DIMENSION A(5),B(5),C(5),H1(16),H2(16),AAA(16),BBB(16),CCC(16),
     1C1(16),C2(16),C3(16),WTMOL(16),AMTCMD(16),AMTSEC(16),RKK(6,5),
     2Q(6,5),X(6,5),AMTLBM(16),R(6),ALL(14)
      READ(5,405)(R(I),I=1,6)
      READ(5,406) NSTEP,TIN
      READ(5,6)(AMTCMD(I),I=1,14)
      READ(5,11) DIAM,ZLAST,CATWT,Z,E,DP
      READ(5,10)(A(J),B(J),C(J),J=1,5)
      READ(5,2)(H1(I),H2(I),I=1,10)
      READ(5,3) AAA(1),BBB(1),CCC(1)
      READ(5,1)(C1(I),C2(I),C3(I),I=1,14)
      READ(5,4)(WTMOL(I),I=1,14)
  405 FORMAT(6F10.4)
  406 FORMAT(I4,F10.2)
    6 FORMAT(7F10.2)
   11 FORMAT(6F10.4)
   10 FORMAT(3F20.5)
    2 FORMAT(2E12.6)
    3 FORMAT(3E15.8)
    1 FORMAT(3E12.6)
    4 FORMAT(7F10.2)
C    ..................................................................
C    INITIALIZATION FOLLOWS
C    ..................................................................
C     PERMANENT STORAGE OF FEED IN ARRAY ALL, AMTCMD IS WORKING ARRAY
      DO 112 I=1,14
  112 ALL(I)=AMTCMD(I)
      NRCT=6
      N=14
      OFE=144.*14.7*32.2
      EEL=E*E*E
      AREA=3.1416*(DIAM/2.)**2
      EFF=AREA*CATWT
      U=0.03*6.72*1.0E-04
      H=ZLAST/FLOAT(NSTEP)
      DO 33 I=1,NRCT
      X(I,1)=0.0
      Q(I,1)=0.0
   33 RKK(I,1)=0.0
C          INITIAL FLOWS OF COMPONENTS IN FEED AND PARTIAL PRESSURES
C    ..................................................................
      DO 21 I=1,N
      AMTCMD(I)=ALL(I)
      AMTLBM(I)=AMTCMD(I)/WTMOL(I)
   21 AMTSEC(I)=AMTLBM(I)/3600.
      FEBO=AMTSEC(1)
      FSTYO=AMTSEC(2)
      FH2O=AMTSEC(3)
      FC2H4O=AMTSEC(4)
      FBZO=AMTSEC(5)
      FTOLO=AMTSEC(6)
      FCH4O=AMTSEC(7)
      FC2H6O=AMTSEC(8)
      FC2H2O=AMTSEC(9)
      FRC2HO=AMTSEC(10)
      FH2OO=AMTSEC(11)
      FCOO=AMTSEC(12)
      FCO2O=AMTSEC(13)
      FCO=AMTSEC(14)
      SUMMLS=0.0
      DO 22 I=1,N
   22 SUMMLS=SUMMLS+AMTSEC(I)
      PIN=1.046+.00122*(SUMMLS*3600.)
      SUMIN=SUMMLS-FEBO
C    FEED DENSITY,VELOCITY,AND AVE MOLECULAR WEIGHT
C    ..................................................................
      AVMLWT=0.0
      DO 24 I=1,N
   24 AVMLWT=AVMLWT+WTMOL(I)*AMTSEC(I)/SUMMLS
      DENGAS=PIN*AVMLWT/(1.314*TIN)
      VO=SUMMLS*(TIN*359./(273.*PIN))/AREA
C    ..................................................................
C    PRINT OUT CARDS FOLLOW BELOW
C    ..................................................................
      WRITE(6,53)
   53 FORMAT(1H1,10X,76H SIMULATION OF ETHYLBENZENE CONVERSION TO STYREN
     1E ASSUMING ADIABATIC REACTOR//11X,25H PROGRAMMED BY JOHN SHEEL)
      WRITE(6,52) TIN,PIN,ZLAST,H,AVMLWT,DENGAS,VO
   52 FORMAT(//////20X,20H INLET TEMPERATURE =,F10.3,6H DEG K/20X,17H IN
     1LET PRESSURE =,F13.3,4H ATM/20X,13H BED LENGTH =,F17.5,5H FEET/20X
     2,19H LENGTH INCREMENT =,F11.6,5H FEET/20X,23H AVERAGE MOLECULAR WT
     3 =,F7.3/20X,15H FEED DENSITY =,F15.6,7H LB/FT3/20X,23H SUPERFICIAL
     4 VELOCITY =,F7.4,7H FT/SEC)
      WRITE(6,408) NSTEP
  408 FORMAT(1H ,7H NSTEP=,I4)
      WRITE(6,407)(R(I),I=1,6)
  407 FORMAT(1H /22H FREQUENCY FACTORS ARE/6F15.4)
      WRITE(6,61)
   61 FORMAT(//////20X,16H COMPOUND NUMBER,5X,16H POUNDS PER HOUR,5X,
     117H MOLES PER SECOND)
      WRITE(6,62)(NN,AMTCMD(NN),AMTSEC(NN),NN=1,N)
   62 FORMAT(1H ,20X,I10,14X,F10.3,11X,F11.7)
      WRITE(6,44)
   44 FORMAT(1H1,3X,7H LENGTH,8X,6H TEMP ,8X,6H PRES ,8X,6H  X1  ,8X,
     16H  X2  ,8X,6H  X3  ,8X,6H  X4  ,8X,6H  X5  ,8X,6H  X6  )
      WRITE(6,45) Z,TIN,PIN,(X(I,1),I=1,NRCT)
   45 FORMAT(1H ,9E14.5)
C
C    ..................................................................
C    END OF  INITIAL PRINTOUT
C    END OF INITIALIZATION
C    ..................................................................
C
C    ..................................................................
C    RUNGE-KUTTA INTEGRATION BEGINS
C    ..................................................................
      DO 7 NSEC=1,NSTEP
      RST=(AAA(1)/TIN+BBB(1)+CCC(1)*TIN)*1000./1.987
      SST=EXP(-RST)
      FACEB=EFF/FEBO
      FACST=EFF/FH2OO
      EX1=EXP(-10925./TIN+R(1))
      EX2=EXP(-25000./TIN+R(2))
      EX3=EXP(-11000./TIN+R(3))
      EX4=EXP(-12500./TIN+R(4))
      EX5=EXP(-7900.0/TIN+R(5))
      EX6=EXP(-8850.0/TIN+R(6))
      EX66=PIN/(TIN*TIN*TIN)
C    BASIC RUNGE-KUTTA INTEGRATION
C    ..................................................................
      DO 100 J=2,5
      J1=J-1
      PEB=FEBO*(1.-X(1,J1)-X(2,J1)-X(3,J1))
      PSTY=FEBO*X(1,J1)+FSTYO
      PCO=FH2OO*(X(4,J1)+X(5,J1)-X(6,J1))+FCOO
      PCO2=FH2OO*X(6,J1)+FCO2O
      PH2O=FH2OO*(1.-X(5,J1)-X(6,J1)-X(4,J1))
      PCH4=FEBO*X(3,J1)+FCH4O-FH2OO*X(5,J1)
      PC2H4=FEBO*X(2,J1)+FC2H4O-FH2OO*0.5*X(4,J1)
      PH2=FEBO*(X(1,J1)-X(3,J1))+FH2O+FH2OO*(3.*X(5,J1)+X(6,J1)+2.*X(4
     1,J1))
      PTOTAL=FEBO*(1.+X(1,J1)+X(2,J1))+SUMIN+FH2OO*(2.*X(5,J1)+1.5*X(4
     1,J1))
      POST=PIN/PTOTAL
      RKK(1,J)=FACEB*EX1*POST*(PEB-PSTY*PH2*POST/SST)/3600.
      RKK(2,J)=FACEB*EX2*PEB*POST
      RKK(3,J)=FACEB*EX3*PEB*PH2*POST*POST
      RKK(4,J)=FACST*EX4*PH2O*SQRT(PC2H4*POST)*POST
      RKK(5,J)=FACST*EX5*PCH4*POST
      RKK(6,J)=EX66*FACST*EX6*PH2O*PCO*POST*POST
      DO 92 I=1,NRCT
      X(I,J)=X(I,J1)+H*(A(J)*(RKK(I,J)-B(J)*Q(I,J1)))
   92 Q(I,J)=Q(I,J1)+3.*(A(J)*(RKK(I,J)-B(J)*Q(I,J1)))-C(J)*RKK(I,J)
  100 CONTINUE
C    BASIC RUNGE-KUTTA INTEGRATION ENDS FOR MATERIAL BALANCES
C    ..................................................................
C
C    ..................................................................
C    CALCULATIONS TO UPDATE TEMPERATURE,PRESSURE,AND COMPOUND FLOWS
C    ..................................................................
      HEATIN=0.0
      DO 56 I=1,N
   56 HEATIN=HEATIN+AMTSEC(I)*(C1(I)+C2(I)*TIN+C3(I)*TIN*TIN)
      J=5
      AMTSEC(1)=FEBO*(1.0-X(1,J)-X(2,J)-X(3,J))
      AMTSEC(2)=FEBO*X(1,J)+FSTYO
      AMTSEC(3)=FEBO*(X(1,J)-X(3,J))+FH2O+FH2OO*(3.*X(5,J)+X(6,J)+
     12.0*X(4,J))
      AMTSEC(4)=FEBO*X(2,J)+FC2H4O-FH2OO*0.5*X(4,J)
      AMTSEC(5)=FEBO*X(2,J)+FBZO
      AMTSEC(6)=FEBO*X(3,J)+FTOLO
      AMTSEC(7)=FEBO*X(3,J)+FCH4O-FH2OO*X(5,J)
      AMTSEC(11)=FH2OO*(1.0-X(5,J)-X(6,J)-X(4,J))
      AMTSEC(12)=FH2OO*(X(5,J)-X(6,J)+X(4,J))+FCOO
      AMTSEC(13)=FH2OO*X(6,J)+FCO2O
      SUMMLS=0.0
      DO 50 I=1,N
   50 SUMMLS=SUMMLS+AMTSEC(I)
      HEATRX=0.0
      DO 57 M=1,3
   57 HEATRX=HEATRX+(X(M,5)-X(M,1))*FEBO*(H1(M)+H2(M)*TIN)
      DO 691 M=1,3
  691 HEATRX=HEATRX+(X(M+3,5)-X(M+3,1))*FH2OO*(H1(M+3)+H2(M+3)*TIN)
      TIN=TIN-HEATRX/HEATIN
      DPT=VO*(1.-E)/(EEL*DP)*(150.*U*(1.-E)/DP+1.75*DENGAS*VO)/OFE*H
      PIN=PIN-DPT
      AVMLWT=0.0
      DO 34 I=1,N
   34 AVMLWT=AVMLWT+WTMOL(I)*AMTSEC(I)/SUMMLS
      DENGAS=PIN*AVMLWT/(1.314*TIN)
      VO=SUMMLS*(TIN*359./(273.*PIN))/AREA
      DO 97 I=1,NRCT
      X(I,1)=X(I,5)
   97 Q(I,1)=Q(I,5)
      Z=FLOAT(NSEC)*H
      WRITE(6,45) Z,TIN,PIN,(X(I,1),I=1,NRCT)
    7 CONTINUE
C    ..................................................................
C    RUNGE-KUTTA INTEGRATION ENDS
C    ..................................................................
C
C    ..................................................................
C    FINAL PRINTOUT
C    ..................................................................
      DO 66 I=1,N
      AMTLBM(I)=AMTSEC(I)*3600.
   66 AMTCMD(I)=AMTLBM(I)*WTMOL(I)
      WRITE(6,63)
   63 FORMAT(1H1,20X,22H AT EXIT CONDITIONS...)
      WRITE(6,61)
      WRITE(6,62)(NN,AMTCMD(NN),AMTSEC(NN),NN=1,N)
      STOP
      END
$ENTRY
   8.1033   13.2392     0.2961     -.0724    -2.9344    21.2402
  50    922.59
 8630.73     153.45       0.00       0.00      18.54     178.74       0.00
    0.00       0.00       0.00   18000.00       0.00       0.00       0.00
  6.3875     5.5833      134.0        0.0      0.445   0.015306
                 .0                    .0                    .0
             .50000               2.00000                .50000
             .29289               1.00000                .29289
            1.70711               1.00000               1.70711
             .16667               2.00000                .50000
 .288430E 05 .109000E 01
```

```
 .259920E 05-.190000E 01
-.127020E 05-.315000E 01
 .196020E 05 .211000E 01
 .500460E 05 .396000E 01
-.108020E 05 .250000E 01
 .000000E 00 .000000E 00
 .000000E 00 .000000E 00
 .000000E 00 .000000E 00
 .000000E 00 .000000E 00
 0.29310942E 02-0.30157089E-01-0.52385439E-06
 .223000E 01 .110000E 00-.367000E-04
 .407000E 01 .097700E 00-.331000E-04
 .694700E 01-.200000E-03 .481000E-06
 .283000E 01 .286010E-01-.872600E-05
-.409000E 01 .776210E-01-.264260E-04
 .576000E 00 .934930E-01-.312270E-04
 .338100E 01 .180440E-01-.430000E-05
 .224700E 01 .382010E-01-.110490E-04
 .733100E 01 .126220E-01-.388900E-05
 .347000E 01 .919000E-01-.314000E-04
 .725600E 01 .229800E-02 .283000E-06
 .642000E 01 .166500E-02-.196000E-06
 .621400E 01 .103960E-01-.354500E-05
 .410000E 01 .102000E-02    0.0
    106.16    104.14      2.02     28.05     78.11     92.13     16.04
     30.07     26.00    102.00     18.00     28.01     44.01     12.00
$IBSYS

                                  CD TOT   0260
```

APPENDIX 6

POLY-29 CASES RUN WITH MEAN POLY-29 CASE FREQUENCY FACTORS

Notes: (1) Each case was run with inlet pressure varying linearly with total molar flow rate (3.6)

(2) Inlet conditions for each case vary in the ranges described in (4.1)

(3) Only the product flows of the main components are followed below.

CASE NUMBER	ETHYLBENZENE LB./HR.	STYRENE LB./HR.	TOLUENE LB./HR.	BENZENE LB./HR.
POLY-29 MEAN CASE (See 4.1 & 5.3)				
Plant Results	3971.67	3520.38	531.43	213.07
Model Results	3975.12	3517.13	526.13	209.51
Deviation	3.45	(3.25)*	(5.30)	(3.66)
1	3836.36	3333.03	454.01	204.30
	3881.90	3322.18	458.91	186.97
	45.54	(10.85)	4.90	(17.33)
2	4325.23	3661.43	576.87	217.75
	4452.46	3590.60	583.23	208.23
	127.23	(70.83)	6.36	(9.52)
3	3727.07	3463.54	439.49	190.03
	3871.95	3371.25	418.55	186.91
	144.88	(92.29)	(20.94)	(3.12)
4	4391.96	3671.08	505.75	211.60
	4441.45	3660.63	522.10	209.08
	49.49	(10.45)	16.45	(2.52)

* Bracketed numbers mean that model gives this much less than plant.

CASE NO.	ETHYLBENZENE	STYRENE	TOLUENE	BENZENE
5	3449.44	3611.32	507.52	251.81
	3661.09	3462.56	485.55	220.25
	211.65	(149.76)	(21.97)	(31.56)
6	3978.94	3933.33	575.44	279.82
	4239.42	3751.75	581.44	240.55
	260.28	(181.58)	6.00	(39.27)
7	3409.37	3633.59	518.75	250.78
	3617.36	3512.65	471.97	226.10
	207.99	(120.94)	(46.78)	(24.68)
8	3802.32	4147.12	558.65	289.44
	4232.98	3835.90	498.09	243.23
	430.66	(311.22)	(60.56)	(46.21)
9	3782.58	3229.90	509.58	175.50
	3651.13	3367.60	503.62	209.90
	(131.45)	132.70	(5.96)	34.40
10	4367.98	3658.15	613.24	222.43
	4357.61	3724.06	621.21	228.84
	(10.37)	65.91	7.97	6.41
11	3994.34	3557.71	547.02	201.71
	4045.32	3508.69	566.71	212.44
	50.98	(49.02)	19.69	10.73
12	3965.56	3589.90	530.73	206.49
	3979.54	3576.24	549.66	226.54
	13.98	(13.66)	18.93	20.05
13	4304.25	3229.83	516.25	170.16
	4157.60	3449.88	549.75	186.86
	(146.65)	220.05	33.50	16.70
14	3798.31	3562.61	581.45	229.13
	3997.17	3546.32	572.60	209.49
	198.86	(16.29)	(8.85)	(19.64)
15	4074.19	3452.24	563.07	203.17
	4015.19	3538.38	565.13	214.21
	(59.00)	86.14	2.06	11.04
1A	3962.79	3120.15	499.22	169.77
	3840.27	3297.88	529.86	181.56
	(122.52)	177.73	30.64	11.79

CASE NO.	ETHYLBENZENE	STYRENE	TOLUENE	BENZENE
2A	4545.79 4502.34 (43.45)	3551.56 3617.33 65.77	493.15 517.67 24.52	215.75 197.98 (17.77)
3A	4057.14 3822.07 (235.07)	3037.83 3344.66 306.83	480.31 498.94 18.63	146.72 183.87 37.15
4A	3498.63 3267.25 (231.38)	2759.75 3046.91 287.16	401.85 379.00 (22.85)	162.38 172.52 10.14
5A	3636.71 3628.96 (7.75)	3346.86 3434.73 87.87	538.74 552.60 13.86	207.15 214.82 7.67
6A	4114.26 4271.82 157.56	3871.20 3768.04 (103.16)	554.79 536.23 (18.56)	267.58 236.47 (31.11)
7A	3533.59 3592.45 58.86	3427.80 3489.15 61.35	549.81 527.63 (22.18)	210.81 220.09 9.28
8A	4098.73 4220.14 121.41	3921.52 3828.17 (93.35)	561.74 519.98 (41.76)	278.21 242.15 (36.06)
9A	3616.56 3633.61 17.05	3312.57 3362.31 49.74	519.38 535.76 16.38	189.42 200.00 10.58
11A	4076.86 4039.03 (37.83)	3406.56 3502.21 95.62	561.44 582.13 20.69	199.51 210.35 10.84
12A	3948.07 3974.55 26.48	3502.56 3577.82 75.26	561.19 563.55 2.36	201.01 215.21 14.20
13A	4201.36 4143.44 (57.92)	3338.17 3449.76 111.59	530.12 557.64 27.52	174.78 193.51 18.73
15A	3936.71 4016.15 79.44	3534.38 3537.34 2.96	564.74 566.88 2.14	208.58 212.52 3.94

CASE NO.	ETHYLBENZENE	STYRENE	TOLUENE	BENZENE
1B	3775.22 3888.41 113.19	3367.80 3320.30 (47.50)	466.73 470.57 3.84	195.12 182.97 (12.15)

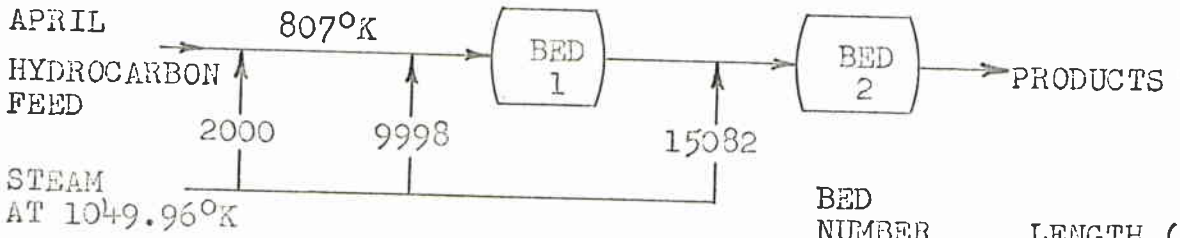
MEAN DEVIATION FOR 29 CASES RUN SEPARATELY AS ABOVE

	ETHYLBENZENE LB./HR.	STYRENE LB./HR.	TOLUENE LB./HR.	BENZENE LB./HR.
Deviation	42.49	19.16	0.21	(1.91)

APPENDIX 7

MATERIAL BALANCE - 2 BED SITUATION WITH STEAM ADDITION BETWEEN BEDS

(1) FLOW DIAGRAM (SITUATION 6iv, 2):



BED NUMBER	LENGTH (Z)
1	2.115 Ft.
2	3.469 Ft.

Note: Steam flows are in Lb./Hr.

(2) FEED BREAKDOWN:

COMPOUND	FEED RATE (APRIL CASE) LB./HR.	MODEL OPTIMUM PRODUCT RATE LB./HR.
Ethylbenzene	8630.73	3817.06
Styrene	153.45	4183.37
Hydrogen	0.0	117.47
Ethylene	0.0	26.55
Benzene	18.54	323.35
Toluene	178.74	431.56
Methane	0.0	25.69
Ethane	0.0	0.0
Acetylene	0.0	0.0
Ethynylbenzene	0.0	0.0
Steam	27080.0	26827.94
Carbon Monoxide	0.0	2.87
Carbon Dioxide	0.0	305.94
Carbon	0.0	0.0

(3) REACTION CONVERSIONS:

REACTION NUMBER	FINAL CONVERSION Mole Fraction of Initial Reactant	
1	.47598	......ethylbenzene
2	.047999	
3	.033754	
14	.0039293	.....steam
15	.00075934	
16	.0046207	

(4) STEAM BALANCE:

Steam in =27080 Lb./Hr.

REACTION NUMBER	WATER REACTED LB./HR.
14	27080 x .0039293 = 106.405
15	27080 x .00075934 = 20.563
16	27080 x .0046207 = 125.129
	Σ = 252.097 Lb./Hr.

Steam leaving reactor = 27080 - 252.10 = 26827.90 Lb./Hr.

(5) ETHYLBENZENE BALANCE:

Ethylbenzene in = 8630.73 Lb./Hr.

REACTION NUMBER	ETHYLBENZENE REACTED LB./HR.
1	8630.73 x .47598 = 4108.055
2	8630.73 x .047999 = 414.266
3	8630.73 x .033754 = 291.321
	Σ = 4813.642 Lb./Hr.

Ethylbenzene Unreacted = 8630.73 - 4813.64 = 3817.09 Lb./Hr.

(6) MAIN PRODUCTS

PRODUCT NAME	TOTAL COMPOUND (LB./HR.) = AMOUNT PRODUCED + AMOUNT IN FEED
Styrene	$4108.055 \times \frac{104.14}{106.16} + 153.45 = 4183.34$
Benzene	$414.266 \times \frac{78.11}{106.16} + 18.54 = 323.35$
Toluene	$291.321 \times \frac{92.13}{106.16} + 178.74 = 431.56$

APPENDIX 8

DEVELOPMENT OF COST FUNCTION

(1) AROMATIC RING COMPOUND VALUES:

Styrene Gain/lb. ($/Lb.)

$$= .105 - \frac{106.16}{104.14} \times .06 = + \$.044/\text{lb. styrene}$$

Toluene Gain/lb. ($/lb.)

$$= 0.0185 - \frac{106.16}{92.13} \times .06 = - \$.0508/\text{lb. toluene}$$

Benzene Gain/lb. ($/lb.)

$$= 0.037 - \frac{106.16}{78.11} \times .06 = - \$.0447/\text{lb. benzene}$$

Note: Unreacted ethylbenzene retains a value of $.06/lb.

(2) FUEL GAS COMPOUND VALUES:

COMPOUND	CALCULATION B.T.U./LB. x .50 x 10^{-6} $/B.T.U.	VALUE $/LB.
Hydrogen	61,020 x .50 x 10^{-6}	.0305
Methane	23,880 x .50 x 10^{-6}	.0119
Ethylene	21,640 x .50 x 10^{-6}	.0108

Hence:

Gain ($/Hr.) = (Lb./Hr. styrene x .044) - (Lb./Hr. Toluene x .0508)

- .... + (Lb./Hr. CH_4 x 0.012)

- Lb. steam/100 (.0118 + .0000646 x T)

where T = Steam Temperature ($^{\circ}K$)

Values of B.T.U./Lb. calculated from Smith and Van Ness, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, (1959)

APPENDIX 9

REGRESSION EQUATION

$$\text{Gain (\$/Hr.)} = A + BX_1 + CX_2 + DX_3 + EX_1X_2 + FX_1X_3 + GX_2X_3$$

$$+ HX_1X_2X_3 + IX_1^2 + JX_2^2 + KX_3^2 + LX_1^3 + MX_2^3 + NX_3^3$$

where:

P = inlet pressure = (1.046 + .00122 x S) Atmospheres
S = Lb. Mols. Mixed Feed/Hr.
X_1 = steam temperature...°K
X_2 = Steam rate....Lb/Hr.
X_3 = Bed depth.....Ft.

A = .20355438 E 04
B =-.88456704 E 01
C = .32631826 E-01
D = .27360542 E 02
E =-.13250333 E-04
F = .73207015 E-02
G = .37359278 E-02
H =-.35742527 E-05
I = .10436194 E-01
J =-.85542770 E-06
K =-.42597412 E 01
L =-.37617352 E-05
M = .12390612 E-10
N = .16721005 E 00

(Standard Error of Estimate)^2 = 17.58 on 111 degrees of freedom

APPENDIX 10

THE ROSENBROCK SEARCH PROGRAMME

(1) Explaination of Major Terms

NN....Number of variables to be searched

X.....Variable names

A.....Accelerating factor $A > 1.0$

BB....Decelerating factor $-1 < BB < 0$

C.....Initial perturbation of variable

R.....Storage of variable values at beginning of each stage

U.....Current value of perturbation of a variable

F.....Counts failures in search when search is parallel and perpendicular to axii

G.....Counts failures in search when search may be in any direction. In G and F when we register at least 1 failure per variable we come to the end of a stage.

L.....Exit from stage failure register.

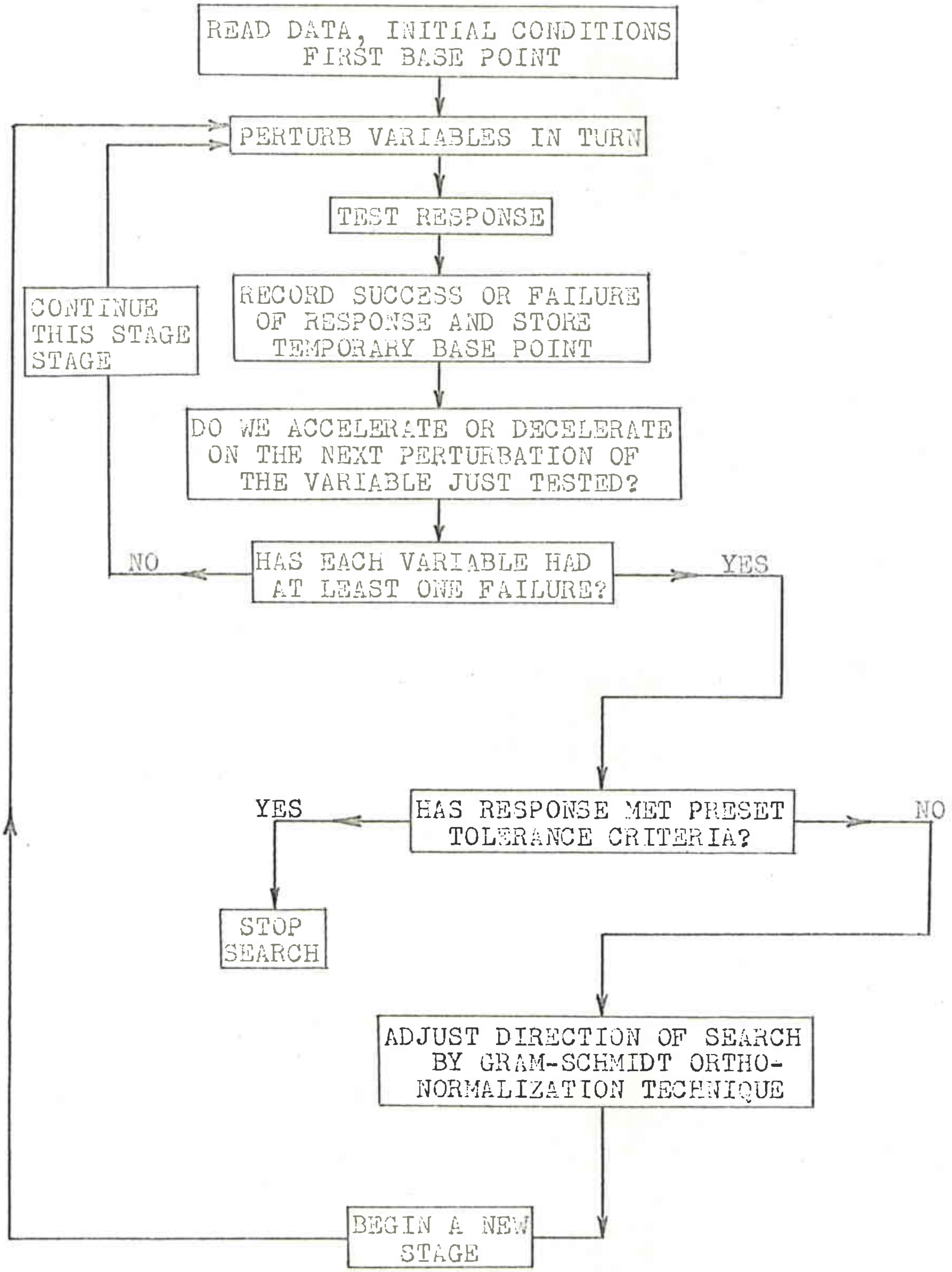
MM....Successive failure counter; if MM = NN, the search is returned to being parallel and perpendicular to the axii. (i. e. This is used for constraints of the type $X < XM$).

Y2....Current response of X, i. e. in the programme we minimize Y2 where Y2 = 1/HR GAIN where HR GAIN is the hourly gain we wish to maximize.

Y1....The best response to date. The programme stores the values of X(I) giving the optimum response Y1. By minimizing Y1 we maximize the GAIN in $/Hr.

LLL...When the condition, i. e. ABS (Y2 - Y1) < (some preset tolerance) has been met LLL times, we can stop the search.

K.....directs what sections of the programme are active.


READ DATA, INITIAL CONDITIONS
FIRST BASE POINT
PERTURB VARIABLES IN TURN
TEST RESPONSE
RECORD SUCCESS OR FAILURE OF RESPONSE AND STORE TEMPORARY BASE POINT
CONTINUE THIS STAGE STAGE
DO WE ACCELERATE OR DECELERATE ON THE NEXT PERTURBATION OF THE VARIABLE JUST TESTED?
NO
HAS EACH VARIABLE HAD AT LEAST ONE FAILURE?
YES
YES
HAS RESPONSE MET PRESET TOLERANCE CRITERIA?
NO
STOP SEARCH
ADJUST DIRECTION OF SEARCH BY GRAM-SCHMIDT ORTHO-NORMALIZATION TECHNIQUE
BEGIN A NEW STAGE
]

APPENDIX 11

OPTIMIZATION OF A TWO-BED SITUATION

The following programme combines the Rosenbrock Search with a two-bed model. Five variables (Steam temperature, Steam flow rates to beds 1 and 2 and the depths of Beds 1 and 2) are being searched with the goal of maximizing the GAIN FUNCTION ($/HR). The situation being studied is like situation 6i of Appendices 12 and 13.

Note that some array names had to be changed when the model was combined with the Rosenbrock Search programme. For example, the A(I) of the single bed model of Appendix 5 is now W(I), C(I) is now V(I) and so on.

```
$JOB            003201 JOHN SHEEL         100   01
$IBJOB          DECK
$IBFTC
C     ***************************************************************
C   SITUATION 6I .....DOUBLE BED REACTOR
C   OPTIMIZATION OF A 5 VARIABLE RESPONSE  IE. OF THE GAIN FUNCTION
C   IN $/HOUR OF AN ETHYLBENZENE DEHYDROGENATION REACTOR
C   MAXIMIZE $/HOUR GAINED BY METHOD OF ROSENBROCK
C     ***************************************************************
C
C     ..............................................................
C        INITIAL INFORMATION
C
C     ..............................................................
C   RUNGE-KUTTA GILL INTEGRATION PERFORMED ON MATERIAL BALANCES ONLY
C   TEMPERATURE AND PRESSURE ARE UPDATED ONCE FOR EVERY R-K-G STEP
C   ADIABATIC REACTORS USED
C   FOLLOWING BASIC REACTIONS ONLY USED
C        C6H5C2H5 = C6H5C2H3 + H2
C        C6H5C2H5 = C6H6 + C2H4
C        H2 + C6H5C2H5 = C6H5CH3 + CH4
C        H2O + 1/2 C2H4 = CO + 2H2
C        CH4 + H2O = CO + 3H2
C        CO + H2O = CO2 + H2
C   DATA INPUT EXPLANATION
C        1=EB      2=STY      3=H2      4=C2H4    5=C6H6    6=C6H5CH3
C        7=CH4     8=C2H6     9=C2H2    10=C6H5C2H          11=H2O
C        12=CO     13=CO2     14=C
C.....................................................................
      DIMENSION W(5),B(5),V(5),H1(16),H2(16),AAA(16),BBB(16),CCC(16),
     1C1(16),C2(16),C3(16),WTMOL(16),AMTCMD(16),AMTSEC(16),RKK(6,5),
     2Q(6,5),XX(6,5),AMTLBM(16),ALL(16),O(6)
      DIMENSION X(10),F(10),G(10),L(10),R(10),U(10)
      DIMENSION AA(10,10),E(10,10),PRODA(10,10),AB(10,10)
      COMMON ALL,AMTCMD,AMTLBM,WTMOL,AMTSEC,W,B,V,H1,H2,AAA,BBB,CCC,C1,
     1C2,C3,O,DIAM,CATWT,ZLAST,Z,EO,DP,Y2,NRR,K,HRGAIN,NN,U,E,NM,X
C   TIMSET ACTIVATES COMPUTER ACCOUNT CLOCK - STOPS SEARCH 20 SECONDS
C   BEFORE PERMITTED JOB TIME EXPIRES . IF SEARCH DOES NOT MEET
C   EXIT REQUIREMENTS
C.....................................................................
      CALL TIMSET(20)
      NN=5
C        PICK THE INITIAL BASE POINT
C   X(1) INCLUDES 2000 LBS PREHEATING STEAM , X(2) DOES NOT
C   X(1) = STEAM RATE  LB/HR  FOR BED NO. 1
C   X(2) = STEAM RATE  LB/HR  FOR BED NO. 2
C   X(3) = STEAM TEMPERATURE  DEG. KELVIN
C   X(4) = BED NO. 1 DEPTH - FEET
C   X(5) = BED NO. 2 DEPTH - FEET
C.....................................................................
      READ(5,111)(X(I),I=1,5)
      READ(5,400)(AMTCMD(I),I=1,14)
      READ(5,11) DIAM,ZLAST,CATWT,Z,EO,DP
      READ(5,401)(W(J),B(J),V(J),J=1,5)
      READ(5,2)(H1(I),H2(I),I=1,10)
      READ(5,402) AAA(1),BBB(1),CCC(1)
      READ(5,1)(C1(I),C2(I),C3(I),I=1,14)
      READ(5,403)(WTMOL(I),I=1,14)
  111 FORMAT(5F10.2)
  400 FORMAT(7F10.2)
   11 FORMAT(6F10.4)
  401 FORMAT(3F20.5)
    2 FORMAT(2E12.6)
  402 FORMAT(3E15.8)
    1 FORMAT(3E12.6)
  403 FORMAT(7F10.2)
C   INITIALIZATION FOLLOWS
C.....................................................................
      DO 404 I=1,14
      ALL(I)=AMTCMD(I)
      AMTLBM(I)=AMTCMD(I)/WTMOL(I)
  404 AMTSEC(I)=AMTLBM(I)/3600.
      WRITE(6,451)(LN,AMTCMD(LN),AMTLBM(LN),LN=1,14)
  451 FORMAT(1H ,10X,I12,2F19.6)
      WRITE(6,452)
  452 FORMAT(1H1)
      NRR=0
      O(1)=8.1033
      O(2)=13.2392
      O(3)=0.2961
      O(4)=-0.0724
      O(5)=-2.9344
      O(6)=21.2402
      LLL=0
      C=1.0
      NM=1
      K=0
      A=3.0
      BB=-0.5
      CALL SIMUL(X(1),X(2),X(3),X(4),X(5))
      Y1=Y2
      WRITE(6,70)(X(I),I=1,NN)
   70 FORMAT(1H0,20H FIRST BASE POINT IS/1H ,6F15.6/)
  120 DO 55 I=1,NN
   55 R(I)=X(I)
C     ..............................................................
C        RESETTING OF COUNTERS
C        RESET COUNTERS FOR EACH STAGE
C     ..............................................................
      DO 54 I=1,NN
      U(I)=C
      F(I)=0.0
      G(I)=0.0
   54 L(I)=0
      MM=0
      NM=1+NM
      IF(K.GE.1) GO TO 508
C     ..............................................................
C        INITIAL DO LOOPS FOR ROSENBROCK SEARCH PARALLEL AND
C        PERPENDICULAR TO THE AXII
C     ..............................................................
      DO 10 I=1,NN
      X(I)=X(I)+U(I)
      CALL SIMUL(X(1),X(2),X(3),X(4),X(5))
      WRITE(6,121)(X(LL),LL=1,NN),Y1,Y2,HRGAIN
  121 FORMAT(1H ,5F12.2,5X,4H Y1=,F12.5,4H Y2=,F12.5,2X,8H HRGAIN=,F8.3/
     1)
      IF(Y2-Y1)4,3,3
C        TREATMENT OF FAILURES
    3 Y1=Y1
      F(I)=F(I)+1.0
      L(I)=L(I)+1
      X(I)=X(I)-U(I)
      MM=MM+1
      IF(MM.EQ.NN) GO TO 12
      GO TO 10
C   CHANGE C=-C IF HAVE NN INITIAL SUCCESSIVE FAILURES
C.....................................................................
   12 C=-C
      GO TO 120
C        TREATMENT OF SUCCESSES
C.....................................................................
    4 Y1=Y2
      U(I)=A*C
   10 CONTINUE
      MM=0
   21 DO 15 I=1,NN
C        TREATMENT OF INITIAL FAILURES - ON FIRST MOVE
C.....................................................................
      IF(F(I).NE.1.0) GO TO 17
      U(I)=BB*C
      X(I)=X(I)+U(I)
      F(I)=0.0
      GO TO 19
C        TREATMENT OF ALL OTHER SUCCEEDING FAILURES
C.....................................................................
   17 IF(G(I).NE.1.0) GO TO 18
      X(I)=X(I)+U(I)
      G(I)=0.0
      GO TO 19
   18 X(I)=X(I)+U(I)
   19 CALL SIMUL(X(1),X(2),X(3),X(4),X(5))
      WRITE(6,121)(X(LL),LL=1,NN),Y1,Y2,HRGAIN
      IF(Y2-Y1)6,5,5
C        TREATMENT OF FAILURES
C.....................................................................
    5 Y1=Y1
      G(I)=1.0
      L(I)=L(I)+1
      MM=MM+1
      X(I)=X(I)-U(I)
      IF(MM.EQ.NN) K=0
      IF(MM.EQ.NN) GO TO 120
      IF(L(1).GE.1.AND.L(2).GE.1.AND.L(3).GE.1.AND.L(4).GE.1.AND.L(5).
     1GE.1) GO TO 24
      U(I)=BB*U(I)
      GO TO 15
   24 CONTINUE
      GO TO 71
C        TREATMENT OF SUCCESSES
C.....................................................................
    6 Y1=Y2
      MM=0
      U(I)=U(I)*A
   15 CONTINUE
      MM=0
      GO TO 21
C     ..............................................................
C        MAIN DO LOOP FOR ORTHONORMALIZED ROSENBROCK SEARCHES
C     ..............................................................
  508 DO 509 J=1,NN
      IF(G(J).NE.1.0) GO TO 510
      DO 511 I=1,NN
  511 X(I)=X(I)+U(J)*E(J,I)
      G(J)=0.0
      GO TO 512
  510 DO 513 I=1,NN
  513 X(I)=X(I)+U(J)*E(J,I)
  512 CALL SIMUL(X(1),X(2),X(3),X(4),X(5))
      WRITE(6,121)(X(LL),LL=1,NN),Y1,Y2,HRGAIN
      IF(Y2-Y1)515,514,514
C        TREATMENT OF FAILURES
C.....................................................................
  514 Y1=Y1
      G(J)=0.0
      L(J)=L(J)+1
      MM=MM+1
      DO 516 I=1,NN
  516 X(I)=X(I)-U(J)*E(J,I)
C   ONLY EXIT FROM THIS LOOP IS AT LEAST 1 FAILURE PER DIRECTION
C.....................................................................
      IF(MM.EQ.NN) K=0
      IF(MM.EQ.NN) GO TO 120
      IF(L(1).GE.1.AND.L(2).GE.1.AND.L(3).GE.1.AND.L(4).GE.1.AND.L(5).
     1GE.1) GO TO 517 -
      U(J)=BB*U(J)
      GO TO 509
C        TREATMENT OF SUCCESSES
C.....................................................................
  515 Y1=Y2
      MM=0
      U(J)=U(J)*A
  509 CONTINUE
      GO TO 508
C     ..............................................................
C        GENERAL PRINT OUT AFTER EACH STAGE  -  AND STEP LENGTH REDUCT.
C     ..............................................................
  517 CONTINUE
   71 WRITE(6,74)(X(I),I=1,NN)
   74 FORMAT(1H ,23H THE NEXT BASE POINT IS/1H ,6F15.6)
C        C ADJUSTMENT FOR FINER SEARCH IN LATER STAGES
      C=C*0.95
      WRITE(6,79) C
   79 FORMAT(1H ,3H C=,F10.6)
C        IF HAVE DESIRED ACCURACY - STOP - OTHERWISE CONTINUE WITH
C        MORE STAGES
C.....................................................................
      IF(ABS(Y2-Y1).LT..000001) LLL=LLL+1
      IF(LLL.EQ.NN) GO TO 43
  600 CONTINUE
      MM=0
C     ..............................................................
C        GRAM - SCHIMDT ORTHONORMALIZATION PROCEDURE
C     ..............................................................
      K=1
```

```
      DO 61 J=1,NN
      DO 61 I=1,NN
      AA(J,I)=X(I)-R(I)
   61 CONTINUE
      I=1
      DO 62 J=2,NN
      AA(J,I)=0.0
      I=I+1
      IF(I.EQ.NN) GO TO 63
      DO 62 KK=1,NN
      AA(J+1,KK)=AA(J,KK)
   62 CONTINUE
   63 CONTINUE
      SUMSQS=0.0
      DO 64 I=1,NN
   64 SUMSQS=AA(1,I)**2+SUMSQS
      DO 65 I=1,NN
   65 E(1,I)=AA(1,I)/SQRT(SUMSQS)
      J=2
   76 SUM=0.0
      DO 66 I=1,NN
      PROD=AA(J,I)*E(J-1,I)
   66 SUM=PROD+SUM
      DO 67 I=1,NN
   67 PRODA(J,I)=SUM*E(J-1,I)
      DO 68 I=1,NN
   68 AB(J,I)=AA(J,I)-PRODA(J,I)
      SUMT=0.0
      DO 69 I=1,NN
   69 SUMT=AB(J,I)**2+SUMT
      DO 500 I=1,NN
  500 E(J,I)=AB(J,I)/SQRT(SUMT)
      IF(J.EQ.NN) GO TO 501
      J=J+1
      GO TO 76
  501 CONTINUE
      WRITE(6,700)
  700 FORMAT(1H0,18H END OF THIS STAGE/1H0)
      GO TO 120
C......................................................................
C   PROGRAMME EXIT IF HAVE DESIRED ACCURACY
C......................................................................
   43 NM=NM-1
  601 WRITE(6,122) NM,Y1,Y2
  122 FORMAT(1H ,3H N=,I10,4H Y1=,F12.7,4H Y2=,F12.7)
      WRITE(6,121)(X(LL),LL=1,NN),Y1,Y2,HRGAIN
      STOP
      END
C
C
C
C
$IBFTC SIMUL
      SUBROUTINE SIMUL(RAT1,RAT2,TSTEAM,Z1LAST,Z2LAST)
      DIMENSION W(5),B(5),V(5),H1(16),H2(16),AAA(16),BBB(16),CCC(16),
     1C1(16),C2(16),C3(16),WTMOL(16),AMTCMD(16),AMTSEC(16),RKK(6,5),
     2Q(6,5),XX(6,5),AMTLBM(16),ALL(16),O(6)
      DIMENSION AA(10,10),E(10,10),PRODA(10,10),AB(10,10)
      DIMENSION X(10),F(10),G(10),L(10),R(10),U(10)
      COMMON ALL,AMTCMD,AMTLBM,WTMOL,AMTSEC,W,B,V,H1,H2,AAA,BBB,CCC,C1,
     1C2,C3,O,DIAM,CATWT,ZLAST,Z,EO,DP,Y2,NRR,K,HRGAIN,NN,U,E,NM,X
C   TIMTST STOPS PROGRAMME IF WITHIN 20 SECONDS FROM PERMITTED JOB TIME
C......................................................................
      CALL TIMTST(IU)
      IF(IU.LT.0)STOP
      Z11=Z1LAST
      Z22=Z2LAST
      DREW1=RAT1
      DREW2=RAT2
C   HIGH RESPONSE FOR CASE WHERE X(I) EXCEEDS ITS CONSTRAINT
C......................................................................
      NRN=0
      IF(X(1).LT.0.0) NRN=1
      IF(X(2).LT.0.0) NRN=1
      IF(X(3).LT.1000..OR.X(3).GT.1050.0) NRN=1
      IF(Z1LAST.LT.0.0.OR.Z1LAST.GT.558.33) NRN=1
      IF(Z2LAST.LT.0.0.OR.Z2LAST.GT.558.33) NRN=1
      IF(NRN.EQ.1) Y2=1000.
      IF(NRN.EQ.1) GO TO 800
C   MIRROR IMAGE CONSTRAINT TREATMENT FOR STEAM RATE
C   IE. (X(1)+X(2)).LT.18000. LB/HR
C......................................................................
      IF((X(1)+X(2)).LT.1800.) GO TO 300
      RAT11=X(1)-(X(1)+X(2)-1800.)
      RAT22=X(2)-(X(1)+X(2)-1800.)
      IF(RAT11.LT.0.0) RAT11=100.
      IF(RAT22.LT.0.0) RAT22=100.
      RAT1=RAT11
      RAT2=RAT22
  300 CONTINUE
C   REMOVE SCALING FACTORS ON VARIABLES
C......................................................................
      AMTCMD(11)=RAT1*10.
      Z1LAST=Z1LAST/100.
      Z2LAST=Z2LAST/100.
C   MIRROR IMAGE CONSTRAINT TREATMENT FOR BED DEPTHS
C   IE. (Z1+Z2).LT.5.5833 FEET
C......................................................................
      IF((Z1LAST+Z2LAST).LT.5.5833) GO TO 301
      Z1LA=Z1LAST-(Z1LAST+Z2LAST-5.5833)
      Z2LA=Z2LAST-(Z1LAST+Z2LAST-5.5833)
      IF(Z1LA.LT.0.0) Z1LA=0.5
      IF(Z2LA.LT.0.0) Z2LA=0.5
      Z1LAST=Z1LA
      Z2LAST=Z2LA
  301 CONTINUE
      ALL(11)=AMTCMD(11)
      AMTSEC(11)=ALL(11)/(3600.*WTMOL(11))
C   COUNTER NRR  IS USED SO THAT THIS IS SET ONLY ONCE
C......................................................................
      IF(NRR.GT.1) GO TO 717
      NRCT=6
      N=14
      AREA=3.1416*(DIAM/2.)**2
      VISC=0.03*6.72*1.0E-04
      ARM=0.05937/3600.
```

```
      EFF=AREA*CATWT
      EEL=EO*EO*EO
      OFE=144.*14.7*32.2
      FEBO=AMTSEC(1)
      FSTYO=AMTSEC(2)
      FH2O=AMTSEC(3)
      FC2H4O=AMTSEC(4)
      FBZO=AMTSEC(5)
      FTOLO=AMTSEC(6)
      FCH4O=AMTSEC(7)
      FC2H6O=AMTSEC(8)
      FC2H2O=AMTSEC(9)
      FRC2HO=AMTSEC(10)
      FCOO=AMTSEC(12)
      FCO2O=AMTSEC(13)
      FCO=AMTSEC(14)
  717 CONTINUE
      DO 33 M=1,NRCT
      XX(M,1)=0.0
      Q(M,1)=0.0
   33 RKK(M,1)=0.0
      NBED=1
      FH2OO=AMTSEC(11)
      SUMMLS=0.0
      DO 22 M=1,N
   22 SUMMLS=SUMMLS+AMTSEC(M)
      SUMIN=SUMMLS-FEBO
      IF(NBED.NE.1) GO TO 821
      TIN=0.0
      PIN=2.37
C   TMIX CALCULATES MIXED FEED TEMPERATURE
C......................................................................
      CALL TMIX(TIN,TSTEAM,RAT1,RAT2,NBED)
C   CORRECT INTEGRATION STEP SIZE DETERMINATION
C......................................................................
      NSTEP=75
      IF(TIN.LT.985.) NSTEP=50
      IF(TIN.LT.960.) NSTEP=25
      IF(TIN.LT.960..AND.AMTCMD(11).GT.22000.) NSTEP=NSTEP*2
      IF(X(1).LT.1200.) NSTEP=NSTEP*2
      AOR=Z1LAST/2.79165
      ANIT=FLOAT(NSTEP)*AOR
      NSTEP=IFIX(ANIT)
      H=Z1LAST/FLOAT(NSTEP)
  821 CONTINUE
      IF(NBED.NE.2) GO TO 820
      TIN=TIN
      PIN=PIN
C   TMIX CALCULATES MIXED FEED TEMPERATURE
C......................................................................
      CALL TMIX(TIN,TSTEAM,RAT1,RAT2,NBED)
C   CORRECT INTEGRATION STEP SIZE DETERMINATION
C......................................................................
      NSTEP=75
      IF(TIN.LT.985.) NSTEP=50
      IF(TIN.LT.960.) NSTEP=25
      IF(TIN.LT.960..AND.AMTCMD(11).GT.22000.) NSTEP=NSTEP*2
      IF((X(1)+X(2)).LT.1200.) NSTEP=NSTEP*2
      AOR=Z2LAST/2.79165
      ANIT=FLOAT(NSTEP)*AOR
      NSTEP=IFIX(ANIT)
      H=Z2LAST/FLOAT(NSTEP)
      FH2OO=FH2OO+RAT2*10./(3600.*WTMOL(11))
      AMTSEC(11)=AMTSEC(11)+RAT2*10./(3600.*WTMOL(11))
      SUMMLS=0.0
      DO 37 M=1,N
   37 SUMMLS=SUMMLS+AMTSEC(M)
      SUMIN=SUMMLS-FEBO
  820 CONTINUE
      AVMLWT=0.0
      DO 24 M=1,N
   24 AVMLWT=AVMLWT+WTMOL(M)*AMTSEC(M)/SUMMLS
      DENGAS=PIN*AVMLWT/(1.314*TIN)
      VO=SUMMLS*(TIN*359./(273.*PIN))/AREA
      IF(NBED.EQ.2) GO TO 837
      WRITE(6,44)
   44 FORMAT(1H ,3X,7H LENGTH,8X,6H TEMP ,8X,6H PRES ,8X,6H  X1  ,8X,
     16H  X2  ,8X,6H  X3  ,8X,6H  X4  ,8X,6H  X5  ,8X,6H  X6  )
  837 CONTINUE
      WRITE(6,454) Z,TIN,PIN,(XX(LO,1),LO=1,NRCT)
  454 FORMAT(1H ,9E14.5)
C**********************************************************************
C   PLEASE REFER TO SECTION 5 IN APPENDIX FOR DETAIL OF INTEGRATION
C**********************************************************************
      DO 7 NSEC=1,NSTEP
      RST=(AAA(1)/TIN+BBB(1)+CCC(1)*TIN)*1000./1.987
      SST=EXP(-RST)
      FACEB=EFF/FEBO
      FACST=EFF/FH2OO
      EX1=EXP(-10925./TIN+O(1))
      EX2=EXP(-25000./TIN+O(2))
      EX3=EXP(-11000./TIN+O(3))
      EX4=EXP(-12500./TIN+O(4))
      EX5=EXP(-7900.0/TIN+O(5))
      EX6=EXP(-8850.0/TIN+O(6))
      EX66=PIN/(TIN*TIN*TIN)
      DO 100 M=2,5
      M1=M-1
      PEB=FEBO*(1.-XX(1,M1)-XX(2,M1)-XX(3,M1))
      PSTY=FEBO*XX(1,M1)+FSTYO
      PCO=FH2OO*(XX(4,M1)+XX(5,M1)-XX(6,M1))+FCOO
      PCO2=FH2OO*XX(6,M1)+FCO2O
      PH2O=FH2OO*(1.-XX(4,M1)-XX(5,M1)-XX(6,M1))
      PCH4=FEBO*XX(3,M1)+FCH4O-FH2OO*XX(5,M1)
      PC2H4=FEBO*XX(2,M1)+FC2H4O-FH2OO*0.5*XX(4,M1)
      PH2=FEBO*(XX(1,M1)-XX(3,M1))+FH2O+FH2OO*(3.*XX(5,M1)+XX(6,M1)+
     12.0*XX(4,M1))
      PTOTAL=FEBO*(1.+XX(1,M1)+XX(2,M1))+SUMIN+FH2OO*(2.*XX(5,M1)+
     11.5*XX(4,M1))
      POST=PIN/PTOTAL
      RKK(1,M)=FACEB*EX1*POST*(PEB-PSTY*PH2*POST/SST)/3600.
      RKK(2,M)=FACEB*EX2*PEB*POST
      RKK(3,M)=FACEB*EX3*PEB*PH2*POST*POST
      RKK(4,M)=FACST*EX4*PH2O*SQRT(PC2H4*POST)*POST
      RKK(5,M)=FACST*EX5*PCH4*POST
      RKK(6,M)=EX66*FACST*EX6*PH2O*PCO*POST*POST
```

```
      DO 92 IS=1,NRCT
      XX(IS,M)=XX(IS,M1)+H*(W(M)*(RKK(IS,M)-B(M)*Q(IS,M1)))
   92 Q(IS,M)=Q(IS,M1)+3.0*(W(M)*(RKK(IS,M)-B(M)*Q(IS,M1)))-V(M)*RKK(IS,
     1M)
  100 CONTINUE
      HEATIN=0.0
      DO 56 M=1,N
   56 HEATIN=HEATIN+1.8*AMTSEC(M)*(C1(M)+C2(M)*TIN+C3(M)*TIN*TIN)
      AMTSEC(1)=FEBO*(1.0-XX(1,5)-XX(2,5)-XX(3,5))
      AMTSEC(2)=FEBO*XX(1,5)+FSTYO
      AMTSEC(3)=FEBO*(XX(1,5)-XX(3,5))+FH2O+FH2OO*(3.*XX(5,5)+XX(6,5)+
     12.0*XX(4,5))
      AMTSEC(4)=FEBO*XX(2,5)+FC2H4O-FH2OO*0.5*XX(4,5)
      AMTSEC(5)=FEBO*XX(2,5)+FBZO
      AMTSEC(6)=FEBO*XX(3,5)+FTOLO
      AMTSEC(7)=FEBO*XX(3,5)+FCH4O-FH2OO*XX(5,5)
      AMTSEC(11)=FH2OO*(1.-XX(4,5)-XX(5,5)-XX(6,5))
      AMTSEC(12)=FH2OO*(XX(5,5)-XX(6,5)+XX(4,5))+FCOO
      AMTSEC(13)=FH2OO*XX(6,5)+FCO2O
      SUMMLS=0.0
      DO 50 M=1,N
   50 SUMMLS=SUMMLS+AMTSEC(M)
      HEATRX=0.0
      DO 57 M=1,3
   57 HEATRX=HEATRX+1.8*(XX(M,5)-XX(M,1))*FEBO*(H1(M)+H2(M)*TIN)
      DO 691 M=1,3
  691 HEATRX=HEATRX+1.8*(XX(M+3,5)-XX(M+3,1))*FH2OO*(H1(M+3)+H2(M+3)*TIN
     1)
      TIN=TIN-HEATRX/HEATIN
      DPT=VO*(1.-EO)/(EEL*DP)*(150.*VISC*(1.-EO)/DP+1.75*VO*DENGAS)
     1/OFE*H
      PIN=PIN-DPT
      AVMLWT=0.0
      DO 34 M=1,N
   34 AVMLWT=AVMLWT+WTMOL(M)*AMTSEC(M)/SUMMLS
      DENGAS=PIN*AVMLWT/(1.314*TIN)
      VO=SUMMLS*(TIN*359./(273.*PIN))/AREA
      DO 97 M=1,NRCT
      XX(M,1)=XX(M,5)
   97 Q(M,1)=Q(M,5)
      Z=FLOAT(NSEC)*H
    7 CONTINUE
      WRITE(6,454) Z,TIN,PIN,(XX(LO,1),LO=1,NRCT)
C   ADJUST FOR STEAM ADDITION BETWEEN BEDS
C.......................................................................
      IF(NBED.NE.1) GO TO 678
      NBED=2
      Z=0.0
      DO 822 M=1,NRCT
      RKK(M,1)=0.0
  822 Q(M,1)=0.0
      STRRAT=RAT1/(RAT1+RAT2)
      DO 823 M=4,6
  823 XX(M,1)=XX(M,5)*STRRAT
      GO TO 821
  678 CONTINUE
      DO 66 M=1,N
      AMTLBM(M)=AMTSEC(M)*3600.
   66 AMTCMD(M)=AMTLBM(M)*WTMOL(M)
C.......................................................................
C      FOLLOWING IS THE COST FUNCTION
C.......................................................................
      DOLLAR=0.0440*WTMOL(2)*(AMTSEC(2)-FSTYO)-0.0447*WTMOL(5)*(AMTSEC(5
     1)-FBZO)-0.0508*WTMOL(6)*(AMTSEC(6)-FTOLO)-FH2OO/100.*WTMOL(11)*
     2(.11819875E-01+.64625E-04*TSTEAM)+WTMOL(3)*AMTSEC(3)*0.0300+WTMOL
     3(7)*AMTSEC(7)*0.0120+WTMOL(4)*AMTSEC(4)*0.0110+WTMOL(8)*AMTSEC(8)
     4*0.0110+ARM*(2.*2.79165-(Z1LAST+Z2LAST))
      HRGAIN=DOLLAR*3600.
      Y2=1.0/HRGAIN
      WRITE(6,457) HRGAIN,Y2
  457 FORMAT(1H /21X,13H DOLLARS/HR =,F10.2,3X,5H Y2 =,F10.7)
      WRITE(6,451)(AMTCMD(LN),LN=1,14)
  451 FORMAT(1H ,20X,7F15.3)
      DO 112 M=1,N
      AMTSEC(M)=ALL(M)/(3600.*WTMOL(M))
  112 AMTCMD(M)=ALL(M)
      Z=0.0
      Z1LAST=Z11
      Z2LAST=Z22
      RAT1=DREW1
      RAT2=DREW2
  800 CONTINUE
      RETURN
      END
C
C
C
C
$IBFTC TMIX
      SUBROUTINE TMIX(TIN,TSTEAM,RAT1,RAT2,NBED)
C.......................................................................
C   PROGRAMME GIVES TEMP OF MIXED STREAM FROM UP TO
C   5 STREAMS , 14 COMPONENTS EACH
C   ENTER TSTRM IN DEG K....C1,C2,AND C3 ARE COEFFS OF
C   A+BT+CT**2...(T= DEG K)  AND UNITS ARE BTU/LBMOL*DEG F
C   ENTER ALL 14 COMPS/STREAM(1) IN ROW AND FOLLOW WITH 14
C   COMPS OF STREAM(2)...ETC
C.......................................................................
      DIMENSION STRCMD(140),TSTRM(5),STRMOL(140),HEAT(5),TOCOMO(14)
     1,AMTCMD(16),WTMOL(16),C1(16),C2(16),C3(16),STOR(140)
     2,ALL(16),AMTLBM(16),AMTSEC(16),O(6),W(5),B(5),V(5),H1(16),H2(16),
     3AAA(16),BBB(16),CCC(16)
      DIMENSION AA(10,10),E(10,10),PRODA(10,10),AB(10,10)
      DIMENSION X(10),F(10),G(10),L(10),R(10),U(10)
      COMMON ALL,AMTCMD,AMTLBM,WTMOL,AMTSEC,W,B,V,H1,H2,AAA,BBB,CCC,C1,
     1C2,C3,O,DIAM,CATWT,ZLAST,Z,EO,DP,Y2,NRR,K,HRGAIN,NN,U,E,NM,X
      NSTRM=2
      NCOMP=14
      NR=NSTRM*NCOMP
      TSTRM(1)=TSTEAM
      IF(NRR.GT.0) GO TO 688
      READ(5,650)(STRCMD(NI),NI=1,NR)
  650 FORMAT(7F10.2)
      DO 683 NI=1,NR
  683 STOR(NI)=STRCMD(NI)
  688 CONTINUE
      NRR=NRR+1
      IF(NBED.NE.1) GO TO 675
      TSTRM(2)=807.0
      DO 684 NI=1,NR
  684 STRCMD(NI)=STOR(NI)
C   STEAM RATE TO FIRST BED LESS 2000.LB/HR ALREADY MIXED
C   WITH HYDROCARBON FEED
C.......................................................................
      STRCMD(11)=RAT1*10.-2000.
  675 CONTINUE
      IF(NBED.NE.2) GO TO 685
      TSTRM(2)=TIN
      DO 682 NI=1,NCOMP
      AMTCMD(NI)=AMTSEC(NI)*WTMOL(NI)*3600.
      STRCMD(NI)=STOR(NI)
      NJ=NI+14
  682 STRCMD(NJ)=AMTCMD(NI)
C   STEAM RATE TO SECOND BED
C.......................................................................
      STRCMD(11)=RAT2*10.
  685 CONTINUE
      NK=0
  654 DO 653 NA=1,NCOMP
      NO=NA+NK
  653 STRMOL(NO)=STRCMD(NO)/WTMOL(NA)
      NK=NK+NCOMP
      IF(NK.EQ.NR) GO TO 681
      GO TO 654
  681 NC=0
  655 DO 656 NI=1,NSTRM
      HEAT(NI)=0.0
      DO 657 NB=1,NCOMP
      NS=NB+NC
  657 HEAT(NI)=HEAT(NI)+STRMOL(NS)*(C1(NB)+C2(NB)*TSTRM(NI)+C3(NB)*
     1TSTRM(NI)*TSTRM(NI))*(1.8*(TSTRM(NI)-273.1)+32.)
      NC=NC+NCOMP
      IF(NC.EQ.NR) GO TO 658
  656 CONTINUE
C   TO HERE HAVE ENTHALPIES OF EACH STREAM
C.......................................................................
  658 HTTOT=0.0
      DO 659 NI=1,NSTRM
  659 HTTOT=HTTOT+HEAT(NI)
C   NOW NEED TOTAL MOLES EACH COMP IN MIXED STREAM
C.......................................................................
      DO 661 NI=1,NCOMP
  661 TOCOMO(NI)=0.0
      ND=0
  664 DO 662 NI=1,NCOMP
      NZ=NI+ND
  662 TOCOMO(NI)=TOCOMO(NI)+STRMOL(NZ)
      ND=ND+NCOMP
      IF(ND.EQ.NR) GO TO 663
      GO TO 664
  663 CONTINUE
C   TO HERE HAVE ALL MOLES COMP I FROM ALL STREAMS IN TOCOMO(I)
C   NEWTON-RAPHSON METHOD FOR SOLVING FOR TOUT OR TEMP OF MIXED FEED
C   CHOOSE FIRST TOUT AS TMAX OF INCOMING STREAMS
C.......................................................................
      TOUT=TSTRM(1)
  667 HTNWRN=0.0
      DO 665 NI=1,NCOMP
  665 HTNWRN=HTNWRN+TOCOMO(NI)*(C1(NI)+C2(NI)*TOUT+C3(NI)*TOUT*TOUT)*
     1(1.8*(TOUT-273.1)+32.)
      DELT=TOUT+.001
      DELHT=0.0
      DO 666 NI=1,NCOMP
  666 DELHT=DELHT+TOCOMO(NI)*(C1(NI)+C2(NI)*DELT+C3(NI)*DELT*DELT)*
     1(1.8*(DELT-273.1)+32.)
C   USE SIMILAR TRIANGLES RULE TO GET TOUT NEXT
C.......................................................................
      TNEXT=TOUT-(DELT-TOUT)*(HTNWRN-HTTOT)/(DELHT-HTNWRN)
      IF((TNEXT-TOUT).LT.0.25.AND.ABS(HTNWRN-HTTOT).LT.100.) GO TO 668
      TOUT=TNEXT
      GO TO 667
  668 CONTINUE
      TIN=TOUT
      RETURN
      END
C
C
$ENTRY
    903.80   1552.80   1124.72    174.00    384.10
   8630.73    153.45      0.00      0.00     18.54    178.74      0.00
      0.00      0.00      0.00      0.00      0.00      0.00      0.00
    6.3875    5.5833     134.0       0.0     0.445  0.015306
                  .0                  .0                  .0
              .50000             2.00000              .50000
              .29289             1.00000              .29289
             1.70711             1.00000             1.70711
              .16667             2.00000              .50000
 .288430E 05 .109000E 01
 .259920E 05-.190000E 01
-.127020E 05-.315000E 01
 .196020E 05 .211000E 01
 .500460E 05 .396000E 01
-.108020E 05 .250000E 01
 .000000E 00 .000000E 00
 .000000E 00 .000000E 00
 .000000E 00 .000000E 00
 .000000E 00 .000000E 00
0.29310942E 02-0.30157089E-01-0.52385439E-06
 .223000E 01 .110000E 00-.367000E-04
 .407000E 01 .097700E 00-.331000E-04
 .694700E 01-.200000E-03 .481000E-06
 .283000E 01 .286010E-01-.872600E-05
-.409000E 01 .776210E-01-.264260E-04
 .576000E 00 .934930E-01-.312270E-04
 .338100E 01 .180440E-01-.430000E-05
 .224700E 01 .382010E-01-.110490E-04
 .733100E 01 .126220E-01-.388900E-05
 .347000E 01 .919000E-01-.314000E-04
 .725600E 01 .229800E-02 .283000E-06
 .642000E 01 .166500E-02-.196000E-06
 .621400E 01 .103960E-01-.354500E-05
 .410000E 01 .102000E-02    0.0
```

```
   106.16    104.14      2.02     28.05     78.11     92.13     16.04
    30.07     26.00    102.00     18.00     28.01     44.01     12.00
     0.00      0.00      0.00      0.00      0.00      0.00      0.00
     0.00      0.00      0.00      0.00      0.00      0.00      0.00
  8630.73    153.45      0.00      0.00     18.54    178.74      0.00
     0.00      0.00      0.00   2000.00      0.00      0.00      0.00
$IBSYS

                               CD TOT   0704
```

APPENDIX 12

ROSENBROCK SEARCHES

Legend: T = Steam temperature...........°K
S.R.= Steam flow rate............Lb./Hr.
Z = Bed depth..................Ft.
P = Inlet pressure.............Atmos.
S.R.1 = Steam flow rate to bed 1....Lb./Hr.
S.R.2 = Steam flow rate to bed 2....Lb./Hr.
Z1 = Depth of bed 1..............Ft.
Z2 = Depth of bed 2..............Ft.

REF.#	REFERENCES TO ROSENBROCK SEARCHES
A	The standard April case is included in the other cases for comparison with extrapolated model results.
B	Only Z was varied here.
C	The failure of the cost function becomes apparent here. There is a saddle point somewhere between the two gains or the cost function is inadequate (see 6.2).
D	The search was conducted along S.R.1 + S.R.2 constraint, i.e. S.R.1 was varied and S.R.2 was set equal to (18000 - S.R.1). Hence this is a search in one less variable.
E	The search was concluded early so that it may be used for comparison with other runs of the same situation.
F	The (S.R.1 + S.R.2 $\leq$ total steam flow) constraint was handled by the mirror image method. I.e. both S.R.1 and S.R.2 were variables.
G	The search was terminated after 20 minutes due to very slow progress or because it is at a false optimum.
H	These cases are reruns of 3ii-1, 2, 3 but with a smaller step size in the integration.

SITUATION NUMBER	CASE NUMBER	SEARCH BEGAN			SEARCH ENDED			GAIN $/HR.	REFERENCE
			T	S.R.	T	S.R.			
1i	1		1045	5000	1049.98	17999		120.45	
	2		1025	16000	1049.54	17985		120.39	
1ii	1		1040	12000	1061.55	22470		123.09	
	2		1150	24000	1059.20	22354		123.10	
	3		1175	28000	1064.34	21864		123.04	
	4		1100	5000	1063.24	21970		123.07	
		T	S.R.	Z	T	S.R.	Z		
2i	1	1010	10000	7.5	1049.85	17997	8.19	124.66	
	2	1025	16000	4.0	1049.28	17999	8.12	124.66	
	3	1045	5000	3.0	1049.29	17999	8.12	124.66	
2ii	1	1150	6000	5.5833	1048.96	20013	7.605	125.80	
	2	1050	12000	5.5833	1046.21	19570	7.658	125.87	
	3	1175	20000	7.5	1044.18	19874	7.449	125.95	
	4	1025	28000	8.0	996.05	29999	9.999	130.98	C
7i	1	1027.7	18000	5.5833	1027.7	18000	8.27	122.80	B
Standard April Case		1027.7	18000	5.5833	1027.7	18000	5.5833	117.31	A
		T	S.R.1	S.R.2	T	S.R.1	S.R.2		
3i	1	1020	13000	5000	1049.98	12824	5176	123.28	D
	2	1040	5000	13000	1049.91	12835	5165	123.26	D
	3	1049.99	17999.9	0.1	1049.99	14353	3647	123.03	D,E
	1A	1020	9000	7000	1049.97	10446	7560	122.59	F,G
	1B	1040	13000	4000	1049.97	12643	5357	123.27	F
3ii	1	1020	9000	7000	1131.45	11166	13703	140.17	
	2	1080	3000	16000	1131.46	11255	13805	140.16	
	3	1150	20000	5000	1131.76	11157	13719	140.17	
	1A	1020	9000	7000	1131	11051	13914	140.08	H
	2A	1080	3000	16000	1125.42	11312	14039	140.04	H
	3A	1150	20000	5000	1131.7	11048	13710	140.08	H
3iii	1	1150	10000	8000	1161.55	8729	9271	134.97	D
	2	1050	4000	14000	1162.42	8635	9365	134.97	D
	1A	1150	9000	7000	1163.6	8408	9590	134.95	F
	1B	1050	4000	14000	1165.0	4000	14000	123.46	F,G

		T	S.R.1	S.R.2	Z1	Z2	T	S.R.1	S.R.2	Z1	Z2		
4i	1	1040	12000	6000	3	6	1049.96	9900	8100	1.892	6.180	133.44	D
	2	1025	6000	12000	3	6	1049.56	9543	8457	2.268	7.367	132.95	D,G
	1A	1040	9000	7000	3	3	1049.93	10322	7678	1.814	6.551	133.30	F
	2A	1010	13000	4000	6	6	1048.8	13312	4704	5.394	5,169	123.70	F,G
4ii	1	1150	9000	7000	2.7916	2.7916	1054.66	12809	17752	2.717	9.92	159.91	
	2	1050	5000	13000	4	2	1052.5	10530	19470	2.627	9.99	161.11	
	3	1150	9000	7000	2.7916	2.7916	1051.57	11463	18315	2.798	9.92	160.80	

		T	S.R.1	S.R.2	Z1	Z2	P	T	S.R.1	S.R.2	Z1	Z2	P		
5i	1	1020	8000	10000	6	2	2.4	1050.00	10209	7791	2.236	9.724	2.00	143.98	D
	2	1040	14000	4000	3	5	2.1	1049.88	11389	6611	2.845	9.57	2.00	143.06	D
	1A	1040	10000	4000	4	4	2.25	1049.97	13850	4152	3.798	8.289	2.00	140.04	F,G
	2A	1025	7000	5000	4	3	2.40	1049.56	11589	6270	1.894	7.699	2.01	140.49	F
5ii	1	1150	9000	7000	2.7916	2.7916	2.25	1081	11370	17810	3.73	9.99	2.01	169.85	C
	2	1100	5000	13000	6	2	2.10	1076.48	11897	18105	4.06	10.00	2.00	170.49	C

		T	S.R.1	S.R.2	Z1	Z2	T	S.R.1	S.R.2	Z1	Z2		
6i	1	1025	10000	4000	1.5	1.5	1050	11214	6778	2.341	3.242	124.99	
6ii	1	1020	14000	3000	2	2	1027.67	14538	3456	3.168	2.414	117.89	G
	2	1025	11000	6600	2.34	3.24	1027.64	11292	6703	2.324	3.259	119.87	
6iii	1	1025	11000	6600	2.34	3.24	1153.48	8955	8890	1.739	3.848	139.44	
	2	1100	5000	5000	1.75	3.00	1155.44	8167	9831	1.796	3.792	140.19	
6iv	1	1020	14000	3000	2	2	1049.83	16002	11437	3.133	2.452	129.03	G
	2	1045	8000	8000	1.75	3	1049.96	11998	15082	2.115	3.469	133.40	
6v	1	1137	11000	6000	1.60	3.80	1124.72	9038	15528	1.740	3.841	144.53	
	2	1060	5000	20000	2	2	1130.76	9757	14368	2.04	3.544	144.14	
6vi	1	1025	11000	6600	2.34	3.24	1027.7	13769	13218	2.331	3.252	126.39	
	2	1025	10000	10000	1.75	2.00	1027.7	16530	9500	2.971	2.613	124.19	G
	3	1025	8000	12000	2	3	1027.65	12797	13934	2.032	3.553	127.25	

APPENDIX 13

SELECTED CASES - COMPLETE OPTIMUM OPERATING CONDITIONS

Conditions at Entrance to Bed 1
Conditions at Exit of Bed 1
Conditions at Entrance to Bed 2 } For Single Bed Cases This is Naturally Missing
Conditions at Exit of Bed 2

SITUATION NUMBER	CASE NUMBER	BED DEPTH FT.	MIXED FEED TEMP. $^{\circ}$K	PRESSURE ATMOS.	X1	X2	X3	X14	X15	X16	
		LB./HR. INDICATED PRODUCTS			ETHYLBENZENE ETHANE	STYRENE ACETYLENE	HYDROGEN $C_6H_5C_2H$	ETHYLENE STEAM	BENZENE CO	TOLUENE CO_2	METHANE CARBON
1i	1	0	934.76	2.37	0.0	0.0	0.0	0.0	0.0	0.0	
	*	5.5833	857.27	2.29	.42537 E 00	.47539 E-01	.37083 E-01	.58996 E-02	.11492 E-02	.69774 E-02	
					4229.12	3754.86	108.62	25.75	320.42	454.98	29.82
					0.0	0.0	0.0	17748.65	1.99	304.65	0.0
	* Began Search at 1049.98, 17983						$/Hr.	$120.43			
1ii	4	0	956.09	2.638	0.0	0	0	0	0	0	
		5.5833	877.65	2.545	.46560 E 00	.69078 E-01	.47167 E-01	.76669 E-02	.13050 E-02	.89089 E-02	
					3608.98	4095.46	138.14	26.28	457.20	532.03	35.96
					0	0	0	21577.19	2.16	478.56	0.0
2i	3	0	934.79	2.37	0	0	0	0	0	0	
		8.128	851.67	2.25	.45054 E 00	.47896 E-01	.50813 E-01	.66211 E-02	.19400 E-02	.84948 E-02	
					3890.27	3967.98	121.29	16.40	322.70	559.33	35.16
					0.0	0.0	0.0	17687.05	1.86	373.73	0.0
2ii	3	0	938.22	2.50	0	0	0	0	0	0	
		7.450	839.00	2.38	.45711 E 00	.50198 E-01	.48688 E-01	.63371 E-02	.16279 E-02	.79074 E-02	
					3832.10	4023.55	123.87	16.34	337.31	543.42	34.66
					0.0	0.0	0.0	19559.00	1.78	384.25	0.0
7i	1	0	922.59	2.37	0.0	0	0	0	0	0	
		8.27	843.64	2.25	.43416 E 00	.41189 E-01	.44378 E-01	.56726 E-02	.16189 E-02	.72332 E-02	
					4145.09	3829.28	111.35	14.37	280.11	511.13	30.90
					0.0	0.0	0.0	17738.56	1.63	318.33	0.0
3i	1	0	911.17	2.37	0	0	0	0	0	0	
		2.79165	846.79	2.34	.3096 E 00	.2426 E-01	.2081 E-01	.3153 E-02	.5921 E-03	.3675 E-02	
		0	881.95	2.34	.3096 E 00	.2426 E-01	.2081 E-01	.2246 E-02	.4219 E-03	.2618 E-02	
		2.79165	860.17	2.30	.4245 E 00	.3360 E-01	.3810 E-01	.4088 E-02	.1249 E-02	.5270 E-02	
					4347.93	3747.66	98.19	19.30	231.93	464.13	29.65
					0.0	0.0	0.0	17809.07	1.86	231.95	0.0

3i	1B	0	910.16	2.37	0	0	0	0	0	0	
		2.79165	845.66	2.34	.3082 E 00	.2373 E-01	.2089 E-01	.3123 E-02	.6035 E-03	.3657 E-02	
		0	882.25	2.34	.3082 E 00	.2373 E-01	.2089 E-01	.2195 E-02	.4239 E-03	.2568 E-02	
		2.79165	860.28	2.30	.4243 E 00	.3317 E-01	.3818 E-01	.4031 E-02	.1254 E-02	.5219 E-02	
					4353.04	3745.67	97.83	19.10	229.14	464.74	29.67
					0.0	0.0	0.0	17810.60	1.86	229.67	0.0
3ii	1	0	934.74	2.37	0	0	0	0	0	0	
		2.79165	854.54	2.34	.3502 E 00	.3638 E-01	.3468 E-01	.5433 E-02	.1371 E-02	.6692 E-02	
		0	958.89	2.34	.3502 E 00	.3638 E-01	.3468 E-01	.2439 E-02	.6157 E-03	.3005 E-02	
		2.79165	923.90	2.29	.5413 E 00	.8094 E-01	.6078 E-01	.7354 E-02	.1833 E-02	.9073 E-02	
					2735.59	4736.48	160.63	42.08	532.55	634.02	38.64
					0.0	0.0	0.0	24414.91	4.41	551.70	0.0
3ii	1A	0	933.58	2.37	0.0	0.0	0	0	0	0	
		2.79165	852.20	2.34	.3522 E 00	.3699 E-01	.3507 E-01	.5583 E-02	.1411 E-02	.6884 E-02	
		0	958.62	2.34	.3522 E 00	.3699 E-01	.3507 E-01	.2471 E-02	.6245 E-03	.3047 E-02	
		2.79165	923.98	2.28	.5416 E 00	.8112 E-01	.6100 E-01	.7355 E-02	.1837 E-02	.9078 E-02	
					2729.79	4738.87	161.01	41.92	533.64	635.66	38.69
					0.0	0.0	0.0	24509.74	4.41	554.12	0.0
3iii	2	0	921.24	2.37	0.0	0.0	0.0	0.0	0.0	0.0	
		2.79165	837.59	2.35	.3281 E 00	.2853 E-01	.3997 E-01	.5308 E-02	.2148 E-02	.7334 E-02	
		0	940.88	2.35	.3281 E 00	.2853 E-01	.3997 E-01	.2546 E-02	.1030 E-02	.3518 E-02	
		2.79165	900.39	2.30	.5136 E 00	.6273 E-01	.73979 E-01	.7622 E-02	.3167 E-02	.1067 E-01	
					3018.39	4501.59	143.74	36.14	416.87	732.85	45.64
					0.0	0.0	0.0	17613.73	3.43	469.51	0.0
4i	1	0	892.97	2.37	0	0	0	0	0	0	
		1.892	837.41	2.35	.2409 E 00	.1416 E-01	.1431 E-01	.1959 E-02	.4059 E-03	.2301 E-02	
		0	894.73	2.35	.4642 E 00	.1416 E-01	.1431 E-01	.1078 E-02	.2232 E-03	.1266 E-02	
		6.180	851.87	2.26	.4642 E 00	.3421 E-01	.5047 E-01	.4658 E-02	.2022 E-02	.6620 E-02	
					3893.35	4083.69	112.39	12.69	235.80	556.79	33.39
					0.0	0.0	0.0	17760.60	1.70	291.34	0.0
4i	1A	0	895.87	2.37	0.0	0	0	0	0	0	
		1.814	841.70	2.35	.2390 E 00	.1488 E-01	.1348 E-01	.1950 E-02	.3542 E-03	.2241 E-02	
		0	894.93	2.35	.2390 E 00	.1488 E-01	.1348 E-01	.1118 E-02	.2031 E-03	.1285 E-02	
		6.551	851.15	2.25	.4659 E 00	.3555 E-01	.5163 E-01	.4898 E-02	.2091 E-02	.6931 E-02	
					3857.01	4098.16	114.51	12.38	244.32	565.48	33.78
					0.0	0.0	0.0	17749.29	1.70	305.01	0.0
4ii	3	0	903.90	2.37	0.0	0.0	0.0	0.0	0.0	0.0	
		2.799	838.65	2.34	.2989 E 00	.2034 E-01	.2145 E-01	.2921 E-02	.6894 E-03	.3542 E-02	
		0	932.19	2.34	.2989 E 00	.2034 E-01	.2145 E-01	.1124 E-02	.2654 E-03	.1363 E-02	
		9.925	887.32	2.10	.5935 E 00	.6660 E-01	.6013 E-01	.6204 E-02	.1860 E-02	.8016 E-02	
					2414.71	5178.28	174.48	7.938	441.44	629.11	29.07
					0.0	0.0	0.0	29298.26	2.18	583.61	0.0

5i	1	0	895.12	2.00	0	0	0	0	0	0	
		2.236	839.42	1.977	.24460 E 00	.14730 E-01	.11792 E-01	.18489 E-02	.32166 E-03	.20891 E-02	
		0	894.06	1.977	.24460 E 00	.14730 E-01	.11792 E-01	.10486 E-02	.18243 E-03	.11849 E-02	
		9.724	846.48	1.813	.49183 E 00	.36288 E-01	.48122 E-01	.50248 E-02	.21177 E-02	.70628 E-02	
					3657.35	4317.54	120.27	12.28	248.98	539.18	28.79
					0.0	0.0	0.0	17744.30	2.23	310.83	
5ii	2	0	917.10	2.00	0	0	0	0	0	0	
		4.062	840.89	1.95	.34961 E 00	.28023 E-01	.25351 E-01	.39830 E-02	.94925 E-03	.48273 E-02	
		0	943.13	1.95	.34961 E 00	.28023 E-01	.25351 E-01	.15794 E-02	.36741 E-03	.19142 E-02	
		9.999	900.41	1.67	.62389 E 00	.77734 E-01	.55213 E-01	.69615 E-02	.17551 E-02	.86297 E-02	
					2098.71	5435.58	187.04	14.55	512.17	592.29	25.08
					0.0	0.0	0.0	29478.02	4.06	632.96	0.0
6i	1	0	901.71	2.37	0	0	0	0	0	0	
		2.341	841.24	2.35	.27546 E 00	.18401 E-01	.17626 E-01	.25024 E-02	.50995 E-03	.29456 E-02	
		0	888.46	2.35	.27546 E 00	.18401 E-01	.17626 E-01	.15597 E-02	.31784 E-03	.18360 E-02	
		3.242	860.19	2.30	.42700 E 00	.30850 E-01	.37926 E-01	.37341 E-02	.12589 E-02	.49285 E-02	
					4351.84	3768.63	96.55	18.01	214.45	462.81	29.27
					0.0	0.0	0.0	17813.01	1.81	216.80	0.0
6ii	2	0	893.13	2.37	0	0	0	0	0	0	
		2.324	837.18	2.35	.25756 E 00	.15130 E-01	.14889 E-01	.20265 E-02	.40006 E-03	.23690 E-02	
		0	879.61	2.35	.25756 E 00	.15130 E-01	.14889 E-01	.12716 E-02	.25105 E-03	.14866 E-02	
		3.259	853.03	2.30	.40372 E 00	.25325 E-01	.32487 E-01	.30379 E-02	.10184 E-02	.40006 E-02	
					4647.34	3571.58	87.49	15.16	179.36	422.07	26.03
					0.0	0.0	0.0	17850.32	1.559	176.02	0.0
6iii	2	0	913.36	2.37	0	0	0	0	0	0	
		1.791	842.04	2.36	.27996 E 00	.21854 E-01	.24818 E-01	.35384 E-02	.10371 E-02	.44682 E-02	
		0	946.27	2.36	.27996 E 00	.21854 E-01	.24818 E-01	.16055 E-02	.47057 E-03	.20274 E-02	
		3.787	893.67	2.30	.52434 E 00	.67247 E-01	.68663 E-01	.84689 E-02	.28961 E-02	.11251 E-01	
					2926.33	4598.63	149.43	34.59	445.58	693.03	43.09
					0.0	0.0	0.0	17590.79	3.19	495.10	0.0
6iv	2	0	906.46	2.37	0.0	0.0	0	0	0	0	
		2.115	849.27	2.35	.26850 E 00	.19780 E-01	.15455 E-01	.24281 E-02	.38626 E-03	.27473 E-02	
		0	926.79	2.35	.26850 E 00	.19780 E-01	.15455 E-01	.10758 E-02	.17114 E-03	.12172 E-02	
		3.469	895.99	2.27	.47598 E 00	.47999 E-01	.33754 E-01	.39293 E-02	.75934 E-03	.46207 E-02	
					3817.06	4183.37	117.47	26.55	323.35	431.56	25.69
					0.0	0.0	0.0	26827.94	2.87	305.94	0.0
6v	1	0	912.55	2.37	0.0	0	0	0	0	0	
		1.740	846.25	2.35	.27198 E 00	.21331 E-01	.20747 E-01	.31221 E-02	.72563 E-03	.37533 E-02	
		0	965.60	2.35	.27198 E 00	.21331 E-01	.20747 E-01	.11487 E-02	.26697 E-03	.13809 E-02	
		3.841	915.89	2.28	.54934 E 00	.84935 E-01	.55412 E-01	.79988 E-02	.16590 E-02	.95519 E-02	
					2678.23	4804.44	165.27	40.59	557.90	593.78	35.94
					0.0	0.0	0.0	24093.73	4.05	573.71	0.0

6vi	1	0 2.331 0 3.252	905.84 851.84 911.39 886.35	2.37 2.34 2.34 2.27	0 .27179 E 00 .27179 E 00 .44534 E 00 4200.24 0.0	0 .20446 E-01 .20446 E-01 .39507 E-01 3921.65 0.0	0 .14023 E-01 .14023 E-01 .28494 E-01 104.73 0.0	0 .22972 E-02 .11721 E-02 .32268 E-02 22.25 26775.22	0 .30379 E-03 .15495 E-03 .59697 E-03 269.13 2.43	0 .25403 E-02 .12961 E-02 .37659 E-02 391.97 248.06	22.79 0.0
6vi	3	0 2.031 0 3.552	901.14 849.87 913.69 885.22	2.37 2.35 2.35 2.27	0 .24974 E 00 .24974 E 00 .44668 E 00 4192.60 0.0	0 .17580 E-01 .17580 E-01 .39344 E-01 3935.28 0.0	0 .12288 E-01 .12288 E-01 .28198 E-01 104.89 0.0	0 .19890 E-02 .95218 E-03 .32428 E-02 22.18 26527.02	0 .26100 E-03 .12494 E-03 .59652 E-03 268.39 2.40	0 .21910 E-02 .10489 E-02 .37817 E-02 389.95 247.16	22.56 0.0
Standard April Case		0 5.5833	922.59 850.76	2.37 2.29	0 .40397 E 00 4550.58 0.0	0 .37634 E-01 3573.64 0.0	0 .31145 E-01 96.41 0.0	0 .46211 E-02 21.01 17802.21	0 .90337 E-03 257.53 1.70	0 .54637 E-02 412.02 240.46	26.13 0.0

APPENDIX 14

ERROR IN C_p OF BENZENE

The value of (a) for benzene should have been -.409. This error was made in all programmes run but it is almost unnoticeable. The April case was run with this correction and the results below may be compared to the April case in Appendix 13.

	INITIAL	FINAL
Bed Depth (Ft.)	0	5.5833
Temperature (^{O}K)	922.59	850.79
Pressure (Atmosphere)	2.37	2.29
X_1	0	.40411 E 00
X_2	0	.37643 E-01
X_3	0	.31153 E-01
X_{14}	0	.46222 E-02
X_{15}	0	.90368 E-03
X_{16}	0	.54652 E-02

PRODUCT DISTRIBUTION

COMPOUND	AMT. IN PRODUCT LB/HR.	COMPOUND	AMT. IN PRODUCT LB/HR.
Ethylbenzene	4550.03	Ethane	0.0
Styrene	3574.04	Acetylene	0.0
Hydrogen	96.42	Ethynylbenzene	0.0
Ethylene	21.02	Steam	17302.16
Benzene	257.58	Carbon Monoxide	1.70
Toluene	412.08	Carbon Dioxide	240.52
Methane	26.13	Carbon	0.0

It is concluded that there is no need for worry.

APPENDIX 15

VALIDITY OF dP/dZ TREATMENT

The pressure drop of the reactor had been found by the following "wrong" equation (Equation 1):

$$\frac{dP}{dZ} = \frac{V_o(1-\epsilon)}{D_p\,\epsilon^3}\cdot\left(\frac{150\,\mu\,(1-\epsilon)}{D_p} + 1.75\,\rho_g\right)\cdot\frac{1}{144 \times gc \times 14.7}$$

where a choice of $\epsilon = 0.35$ gave the reported plant pressure drop of about 1 psi. This equation is linear with respect to V_o.

The correct Ergun Equation, not used in any of the runs, is (Equation 2)

$$\frac{dP}{dZ} = \frac{V_o(1-\epsilon)}{D_p\,\epsilon^3}\cdot\left(\frac{150\,\mu\,(1-\epsilon)}{D_p} + 1.75\,V_o\rho_g\right)\cdot\frac{1}{144 \times gc \times 14.7}\;\frac{\text{atmos.}}{\text{ft.}}$$

The second term on the right hand side accounts for pressure drop due to turbulent flow, i. e. V_o^2. By choosing an appropriate ϵ ($\epsilon = 0.445$) for Equation 2 it was possible to establish a pressure profile almost as that given by Equation 1. Both values are reasonable choices for the catalyst bed in question and over the range of V_o values met (about 2.0 ft./sec. to 7.0 ft./sec.), the equations are equivalent. Hand calculations of pressure drop for the existing bed (length = 5.5833 ft.) and several comparisons of programmes run with each equation are offered as proof.

(i) Hand Calculations

dP/dZ BY EQUATION NUMBER	BED VOID-AGE ϵ	V_o FT./SEC.	APPROX.* dP FOR 5.5833 FT. (ATMOS.)	dP psi
1	0.35	2.0	0.0335	.492
1	0.35	7.0	0.117	1.72
2	0.445	2.0	0.018	.264
2	0.445	7.0	0.156	2.29

* For the calculations leading to these results the following terms were considered to be constant throughout :

ρ_g = 0.045 Lb./Ft.^{3}

D_p = 0.0153 Ft.

μ = 0.03 x 6.72 x 10^{-4} Lb./Ft. Sec.

Since the reactor normally runs around 4 to 5 ft./sec. (superficial velocity), equations 1 and 2 give almost the same pressure drops.

(ii) Various Cases Run With Both dP/dZ Equations

(1) April Case

dP/dZ BY EQUATION	1	2	2	2
ϵ	0.35	0.35	0.44	0.45
Inlet pressure (Atmos.)	2.37	2.37	2.37	2.37
Outlet pressure (Atmos.)	2.287	2.156	2.282	2.290
Inlet temperature ($^{\circ}$K)	922.59	922.59	922.59	922.59
Outlet temperature ($^{\circ}$K)	850.76	851.12	850.78	850.76
PRODUCT FLOW RATES (LB./HR.)				
Ethylbenzene	4550.58	4578.78	4551.51	4549.93
Styrene	3573.64	3563.01	3573.32	3573.86
Hydrogen	96.41	95.31	96.37	96.43
Ethylene	21.01	21.96	21.04	20.99
Benzene	257.53	255.68	257.47	257.57
Toluene	412.02	399.13	411.57	412.34
Methane	26.02	24.81	26.08	26.16
Ethane	0.0	0.0	0.0	0.0
Acetylene	0.0	0.0	0.0	0.0
Ethynylbenzene	0.0	0.0	0.0	0.0
Steam	17802.21	17808.54	17802.43	17802.06
Carbon Monoxide	1.70	1.87	1.71	1.70
Carbon Dioxide	240.46	232.59	240.19	240.65
Carbon	0.0	0.0	0.0	0.0

(2) Situation 6v (defined in section 8.1.2)

dP/dZ by Equation	1	2	2
ϵ	0.35	0.35	0.445
Bed 1 Depth (Ft.)	1.74	1.74	1.74
Bed 2 Depth (Ft.)	3.841	3.841	3.841
Steam Rate To Bed1(Lb./Hr.)	9038	9038	9038
Steam Rate to Bed 2 (Lb./Hr.)	15528	15528	15528
Steam Temperature (°K)	1124.72	1124.72	1124.72
Inlet Pressure Bed 1, (Atmos.)	2.37	2.37	2.37
Exit Pressure Bed 1, (Atmos.)	2.35	2.34	2.36
Inlet Pressure Bed 2, (Atmos.)	2.35	2.34	2.36
Exit Pressure Bed 2, (Atmos.)	2.28	2.09	2.26
Inlet Temperature, Bed 1, (°K)	912.55	912.55	912.55
Exit Temperature, Bed 1, (°K)	846.25	846.29	846.22
Inlet Temperature, Bed 2, (°K)	965.60	965.62	965.58
Exit Temperature, Bed 2, (°K)	915.89	916.60	915.92
PRODUCT FLOW RATES (LB./HR.)			
Ethylbenzene	2678.23	2727.58	2680.32
Styrene	4804.44	4786.33	4803.77
Hydrogen	165.27	162.07	165.11
Ethylene	40.59	43.73	40.74
Benzene	557.90	551.80	557.43
Toluene	593.78	574.17	593.11
Methane	35.94	34.37	35.86
Ethane	0.0	0.0	0.0
Acetylene	0.0	0.0	0.0
Ethynylbenzene	0.0	0.0	0.0
Steam	24093.73	24112.38	24095.06
Carbon Monoxide	4.05	4.75	4.10
Carbon Dioxide	573.71	550.82	572.51
Carbon	0.0	0.0	0.0
GAIN ($/HR.)	144.53	144.92	144.55

(3) Extreme Extrapolation of Model-(Single bed)Like April Case with Bed Deoth = 10 Ft., Steam Rate = 30000 Lb./Hr.

dP/dZ BY EQUATION	1	2
ϵ	0.35	0.445
Inlet Temperature (^{O}K)	922.59	922.59
Exit Temperature (^{O}K)	859.38	859.35
Inlet Pressure (Atmos.)	3.183	3.183
Exit Pressure (Atmos.)	2.989	2.936
PRODUCT FLOW RATES (LB./HR.)		
Ethylbenzene (Lb./Hr.)	3630.20	3632.53
Styrene	4254.69	4258.25
Hydrogen	131.38	131.30
Ethylene	3.84	3.97
Benzene	315.01	315.42
Toluene	540.47	534.80
Methane	32.24	31.81
Ethane	0.0	0.0
Acetylene	0.0	0.0
Ethynylbenzene	0.0	0.0
Steam	29668.15	29669.36
Carbon Monoxide	0.85	0.88
Carbon Dioxide	405.02	403.51
Carbon	0.0	0.0