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KINETIC AND REACTOR MODELS FOR THE ETHYLBENZENE DEHYDROGENATION REACTION

by

Charles Mark Sheppard

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June 25, 1982
(date)

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Abstract

Five kinetic models, which included three from the literature, were tested by using them to correlate 21 sets of catalyst manufacturers' isothermal tubular reactor data for Shell 105 catalyst. The best model contained an inhibition term dominated by the partial pressure of styrene squared and predicted the manufacturers' styrene conversion within an average of 5%. This model was used to predict the conversion in an industrial fixed-bed reactor. The measured and predicted styrene conversions were within an average of 10% and their ratio was between 1.1 and 0.75 with 85% of the conversion ratios below 1.0 (probably due to catalyst deactivation with age). The importance of diffusion, along with a quantitative model, is briefly discussed. An optimization of reactor conditions for a single-stage and a two-stage reactor confirmed the merits of high-selectivity catalysts such as Shell 015. A general plug flow reactor model which can simulate either an isothermal or adiabatic reactor and can correlate the kinetics from isothermal data was developed and is included.

Introduction

Thesis Objective

The purpose of this work is the development, evolution, and application of a computer model simulating an industrial ethylbenzene dehydrogenation reactor. The reactor modeled is an adiabatic fixed-bed reactor packed with Shell 105 catalyst. The model developed includes differential component, energy, and momentum balances used to predict the conversion, temperature, and pressure profiles.

Since no kinetic experiments were performed, the form of the kinetic equations was limited to the few available in the literature. The parameters were adjusted to fit the bench-scale data provided by the catalyst manufacturers.

The model was then compared to available plant data and was used to determine the optimum operating conditions for an existing reactor and a proposed two-stage reactor with interstage heating.

Overview of the Process

The dehydrogenation of ethylbenzene is an endothermic reaction usually run over an iron oxide catalyst. The reactor feed is usually preheated using the reactor effluent and then taken up to temperature (∿630°C) by injecting superheated steam. The steam provides additional heat capacity to the mixture as well as reducing the coking of the catalyst. Since the reaction is improved by low pressure, a shallow reactor is used to minimize the pressure drop.

As previously mentioned, the reactor effluent is cooled in the feed preheat heat exchanger and also other heat exchangers. The effluent is then condensed. It separates into three phases: the gas phase contains hydrogen, carbon dioxide, methane, and other by-products; the aqueous phase is primarily water; and the organic phase contains styrene, ethylbenzene, toluene, benzene, and other hydrocarbons.

The organic phase is decanted off and sent to a distillation column where the ethylbenzene, toluene, and benzene go overhead and are recycled. The bottoms, which is impure styrene, is sent to the finishing section. In this part of the plant, the styrene is purified. Low-pressure distillation columns with an inhibitor added to the crude styrene are used so that the styrene does not polymerize. A schematic representation of the process is given in Figure 1.

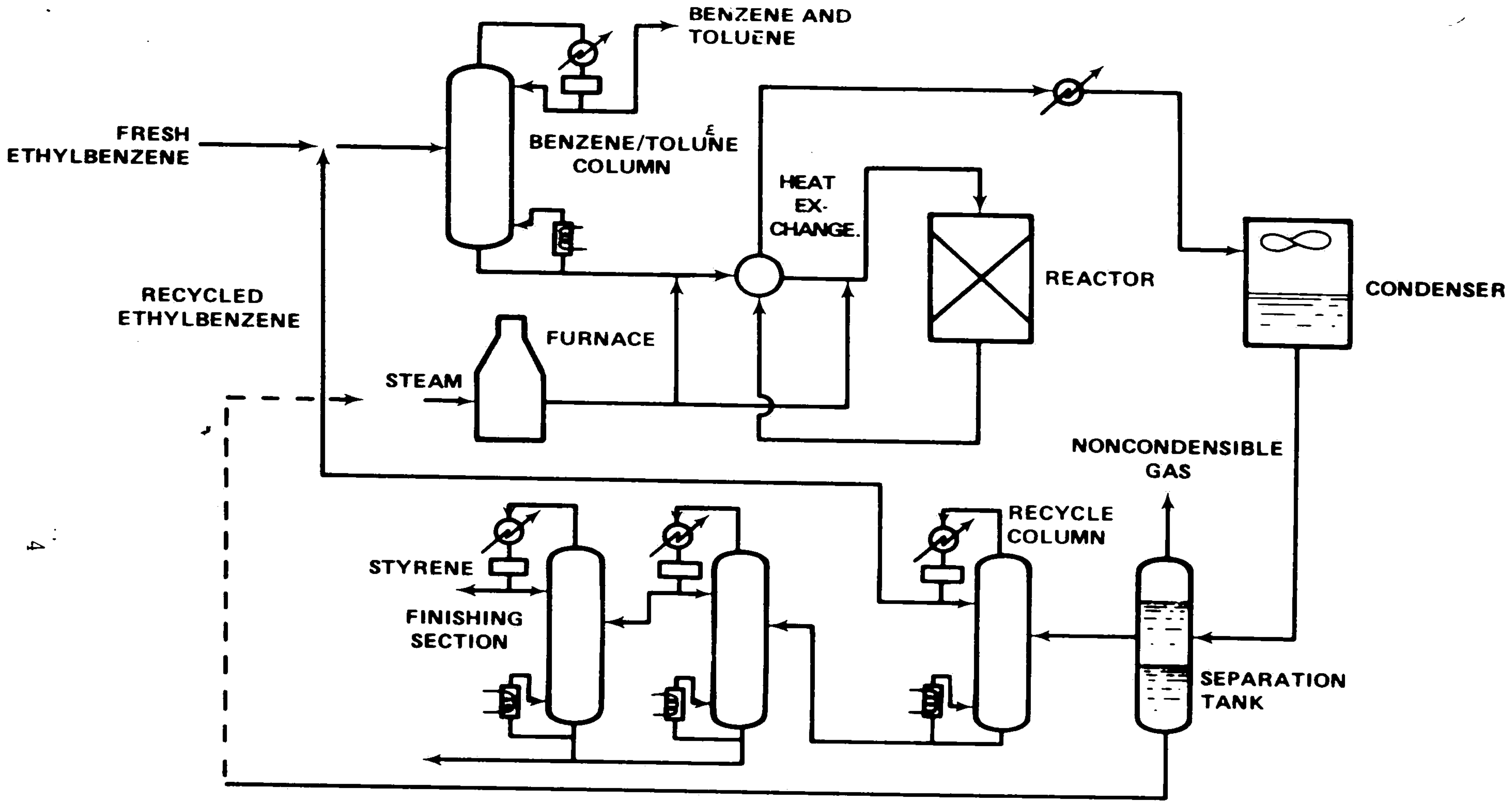

Figure 1 A SCHEMATIC REPRESENTATION OF THE ETHYLBENZENE DEHYDROGENATION PROCESS

Literature Review

Reaction Kinetics

The three important reactions in an ethylbenzene dehydrogenation reactor are:

$$\phi\text{-}CH_2\text{-}CH_3 \rightleftharpoons \phi\text{-}CH{=}CH_2 + H_2 \qquad (1)$$

$$EB \rightleftharpoons STY + H_2$$

$$\phi\text{-}CH_2\text{-}CH_3 + H_2 \longrightarrow \phi\text{-}CH_3 + CH_4 \qquad (2)$$

$$EB + H_2 \longrightarrow TOL + CH_4$$

$$\phi\text{-}CH_2\text{-}CH_3 \longrightarrow \phi\text{-}H + CH_2{=}CH_2 \qquad (3)$$

$$EB \longrightarrow BEN + C_2H_4$$

Under reactor conditions, the main reaction is reversible and the two side reactions are essentially irreversible. The main reaction is favored by high temperatures and low pressures because it is endothermic and produces two moles of gas for every one consumed. Note also that as equilibrium is approached, the rate of the main reaction approaches zero whereas the side reactions continue.

Other organics in the reactor feed may also be dealkylated. If the reactor feed is obtained by distilling the eight-member aromatic stream in a refinery, xylenes may be present in the feed due to imperfect separation. Thus, the fourth reaction in this model is

$$CH_3\text{-}\phi\text{-}CH_3 \quad + \quad H_2 \longrightarrow \phi\text{-}CH_3 \quad + \quad CH_4 \qquad (4)$$

$$\text{XYL} \quad + \quad H_2 \longrightarrow \text{TOL} \quad + \quad CH_4$$

Gas phase oxidation and water shift reactions also occur. They adequately complete the picture of what happens in the reactor:

$$CH_4 \quad + \quad H_2O \rightleftharpoons CO \quad + \quad 3H_2 \qquad (5)$$

$$\tfrac{1}{2}C_2H_4 \quad + \quad H_2O \longrightarrow CO \quad + \quad 2H_2 \qquad (6)$$

$$CO \quad + \quad H_2O \rightleftharpoons CO_2 \quad + \quad H_2 \qquad (7)$$

One of the inherent limitations of this reaction model is that it assumes none of the aromatic rings are broken. Another limitation is that other organic species may be present in the feed or generated in the reactor in small concentrations. Those species are not considered.

Kinetics are available for Reactions 5 and 7 in the literature (1-3)*, and a kinetic expression similar to that of Reaction 5 was used for Reaction 6 (see Appendix A). Kinetics were also available from several sources for Reactions 1 through 3 on iron oxide catalysts. A summary of the data available is given in Appendix B, and a discussion of these literature kinetics follows. Reaction 4 only occurs to a small extent so the kinetics were approximated.

Wenner and Dybdal (4) were among the first (1948) to investigate the catalytic dehydrogenation of ethylbenzene.

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* See References.

One of the catalysts they used was self-regenerating in the presence of steam; presumably this was either Shell 105 or an earlier-generation catalyst. Their experiment involved preheating an ethylbenzene/water mixture and then reacting the mixture in a 3/4-inch ID (1.91 cm) by 4-foot (1.22 m) long tube packed with whole catalyst pellets. The reactor was a non-isothermal heated reactor with temperature around 600°C.

Their simple kinetic model [which was used in an optimization study by Sheel (5) and a control study by Clough (6) with modified kinetic constants] is given below.

$$r_1 = k_1 \left[P_{EB} - \frac{1}{K_{eq}} P_{STY} P_{H_2} \right] \qquad (8)$$

$$r_2 = k_2 P_{EB} P_{H_2} \qquad (9)$$

$$r_3 = k_3 P_{EB} \qquad (10)$$

where

r_j = rate of reaction j, kg mol/kg catalyst

k_j = rate constant of reaction j, kgmol/kg catalyst hr atm^n (n = the total power of the pressure term, 1 or 2)

P_i = partial pressure of component i, atm

K_{eq} = equilibrium constant, atm

The reported kinetic constants are given in Appendix B.

In 1965, Carrá and Forni (7) proposed a kinetic model that agreed with their experimental data for crushed Shell

105 catalyst. Their article states the composition of the Shell 105 catalyst as 93% Fe_2O_3, 5% Cr_2O_3, and 2% KOH, which is different than the composition Shell states (see Table II, "Catalyst Information" section). Perhaps the compositions were determined using different techniques. By crushing the catalyst to between 10 and 30 mesh (0.55 and 1.68 mm) they sought to remove the diffusional effects and obtain intrinsic kinetics. They also investigated and accounted for the chemisorption of styrene and ethylbenzene on the catalyst surface. By varying the amount of styrene feed with the ethylbenzene and using a linearized form of the rate expression, a relative adsorption coefficient of styrene to ethylbenzene was determined. The catalyst was held in a small stainless-steel basket, and their reactors operated isothermally within at least ±3°C. The temperature range of investigation was 495 to 630°C.

Their model, which will be known as Model 2, is

$$r_1 = k_1 \frac{\left[P_{EB} - \frac{1}{K_{eq}} P_{STY} P_{H_2} \right]}{P_{EB} + z P_{STY}} \tag{11}$$

$$r_{2+3} = \frac{k_{2+3} P_{EB}}{P_{EB} + z P_{STY}} \tag{12}$$

where z = the relative styrene adsorption coefficient

This model agrees with Carrá's observation that the initial rate of styrene formation is independent of the partial pressure of ethylbenzene but very dependent on that of styrene (see Figures 2 and 3). In deriving this model, they assumed that hydrogen did not adsorb to a significant extent and that the reaction was unimolecular on the catalyst surface. In addition, they assumed the reaction was rate controlling and most of the active catalyst sites were occupied. This model differs from the first model not only by the inclusion of an inhibition term (the denominator) but the toluene generation reaction rate is proportional to the partial pressure of ethylbenzene not ethylbenzene and hydrogen (see Equations 12 and 9). The Langmuir-Hinshelwood mechanism is included in Appendix C.

A third model was proposed in 1977 by Lebedev, et al. (8). Again, crushed catalyst was used so that the reaction would be kinetics controlled. This time, iron-chromium catalyst (KMS-1) was ground to about 2-2.5 mm. The experimentation was carried out in an isothermal (±2°C) tubular reactor at three temperatures between 552 and 607°C. Using a linearized form of the rate expression, the rate constant for the main reaction and the adsorption coefficient was fit at each temperature. Then the rate constant and the adsorption coefficient were correlated with an Arrhenius type relationship.

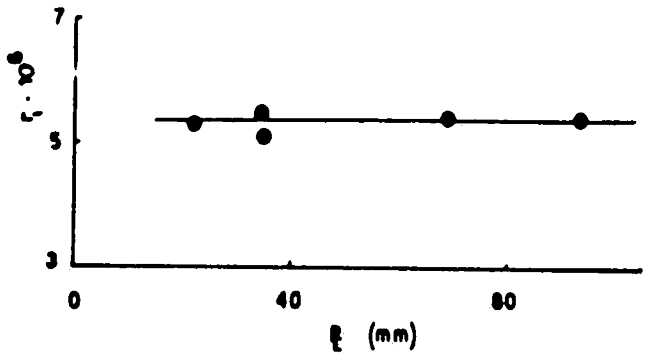

FIG. 2. Effect of ethylbenzene partial pressure on reaction rate. (Ref. 7)
Temp., 495°C

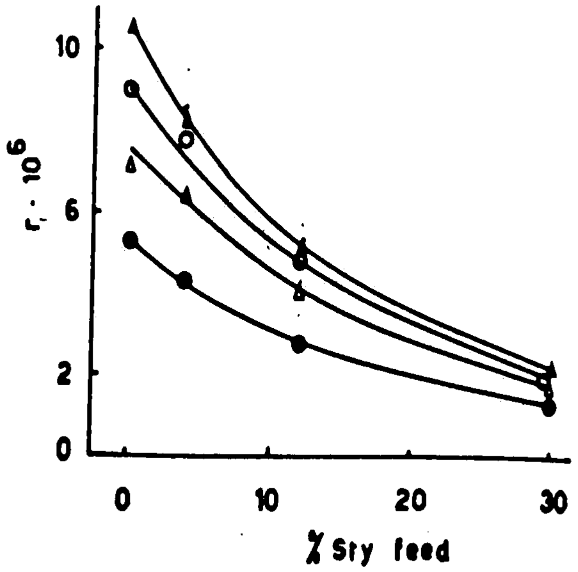

FIG. 3. Effect of styrene percentage in feed mixture on reaction rate. (Ref. 7)

● 495°C △ 505°C ○ 510°C ▲ 515°C

Model 3 is given below

$$r_1 = k_1 \frac{P_{EB} - \frac{1}{K_{eq}} P_{STY} P_{H_2}}{\left(1 + b P_{STY}\right)^2} \qquad (13)$$

$$r_2 = \frac{k_2 P_{EB} P_{H_2}}{\left(1 + b P_{STY}\right)^2} \qquad (14)$$

$$r_3 = \frac{k_3 P_{EB}}{\left(1 + b P_{STY}\right)^2} \qquad (15)$$

$$b = b_o \exp(\lambda/T) \qquad (16)$$

where b = the styrene adsorption coefficient

In deriving this model, it was assumed that the reaction is bimolecular on the catalyst surface and the reaction is rate-controlling. The inhibitors of both models contain a styrene partial pressure term; however, this inhibitor is squared rather than to the first power. This inhibitor also differs from the one used in Model 2 in that there is no partial pressure of ethylbenzene term in the denominator. The two-term adsorption coefficient is probably not justified. The kinetic constants are again given in Appendix B, and the Langmuir-Hinshelwood mechanism is given in Appendix D.

Thus, the literature contains three different forms for the ethylbenzene dehydrogenation and side-reaction kinetics.

These are summarized in Table I. Of the three, only for Carrá's kinetics is it certain that Shell 105 catalyst was used. The second and third models were derived for crushed catalyst so, strictly speaking, if diffusion is important, an effectiveness factor should be included in the form of the kinetics.

Catalyst Information

A catalyst is used both to accelerate the desired reaction and inhibit the undesirable side reactions. Lee (9) states, "Alkali-promoted iron oxide is uniquely better than any other catalyst known for ethylbenzene dehydrogenation in the presence of steam." In the reactor, the iron oxide (Fe_2O_3) is reduced in the presence of steam to black Fe_3O_4. In this form, there are "thermally excited electronic energy levels in the catalyst which probably relate to the high catalytic activity" and selectivity (9). Shell 105 catalyst was the workhorse of the industry but now other high-selectivity catalysts are also being used. The composition of six typical dehydrogenation catalysts is given in Table II. The composition of the more recently developed high-selectivity catalysts is a closely guarded secret.

Lee (9) demonstrated that the presence of potassium can promote the catalyst activity tenfold (see Figure 4). It is interesting to note that there is an optimum potassium

Table I

Summary of Three Literature Kinetic Models

Model	Inhibitor	Driving Force for the Reaction Generation			
		Styrene	Toluene	Benzene	Ref.
1 (Wenner)	None	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	$P_{EB} P_{H_2}$	P_{EB}	4-6
2 (Carrá)	$P_{EB} + z\ P_{STY}$	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	P_{EB}	P_{EB}	7
3 (Lebedev)	$(1 + b\ P_{STY})^2$	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	$P_{EB} P_{H_2}$	P_{EB}	8

$$r_j = k_j \frac{\text{(Driving Force)}}{\text{(Inhibitor)}}$$

where

r_j = rate of reaction j

k_j = rate constant of reaction i

z = the relative absorption coefficient between styrene and ethylbenzene

b = the absorption coefficient of styrene

$= b_o \exp(\lambda/T)$

(See Appendix B for a summary of the kinetic constants.)

Table II

Compositions of Typical Dehydrogenation Catalysts (Ref. 10 & 11)

	Catalyst					
	Shell		United Catalyst			
	105	005	G64A	G64C	G64D	C97-1-01
Weight Percent						
Fe_2O_3	88.6	84.4	60.	58.	76.	74.6
K^+*	7.47	10.46	14.71	13.01	11.32	11.32
Cr_2O_3	2.4	2.4	2.5	<0.10	4.0	2.0
H_2O	--	--	<2.5	<2.5	--	--
CeO_3	--	--	--	5.1	--	--
CoO	--	1.6	--	--	--	--
MoO_3	--	--	--	2.5	--	--
Ni	--	--	<0.05	<0.05	--	--
Cl	--	--	--	--	<0.001	<0.001
S	--	--	--	--	<0.30	<0.30
V_2O_5	--	3.0	--	--	<0.10	3.5
Zr	--	--	--	--	<0.10	<0.10

* Shell adds the potassium as K_2O and United adds it as K_2CO_3.

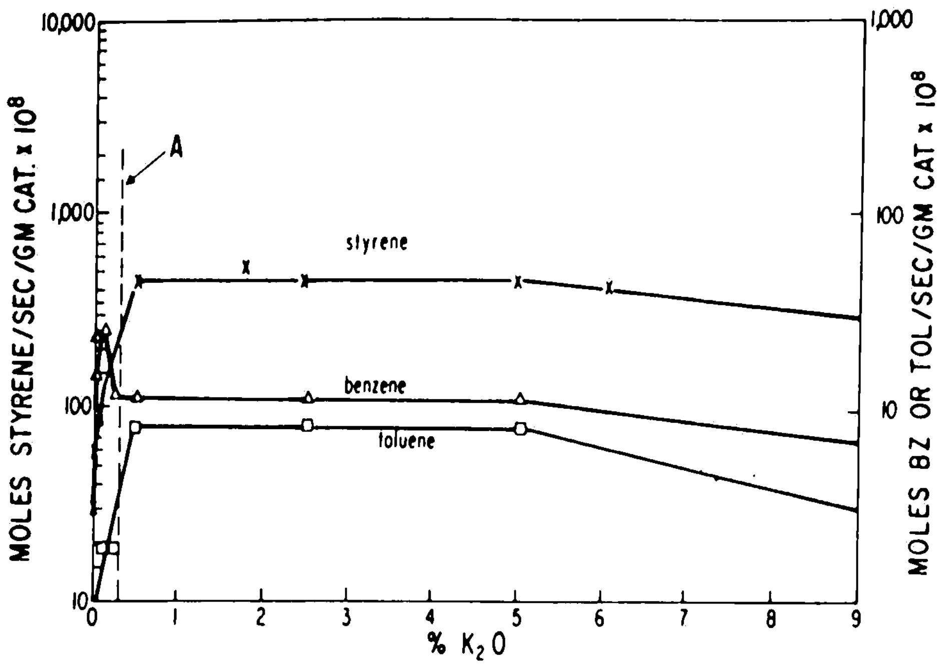

FIG. 4. Catalytic activity of iron oxide with increasing amounts of K_2O promoter.

Dotted line A is the amount of K_2O to give an equivalent monolayer of K^+ on the catalyst surface. (Ref. 9)

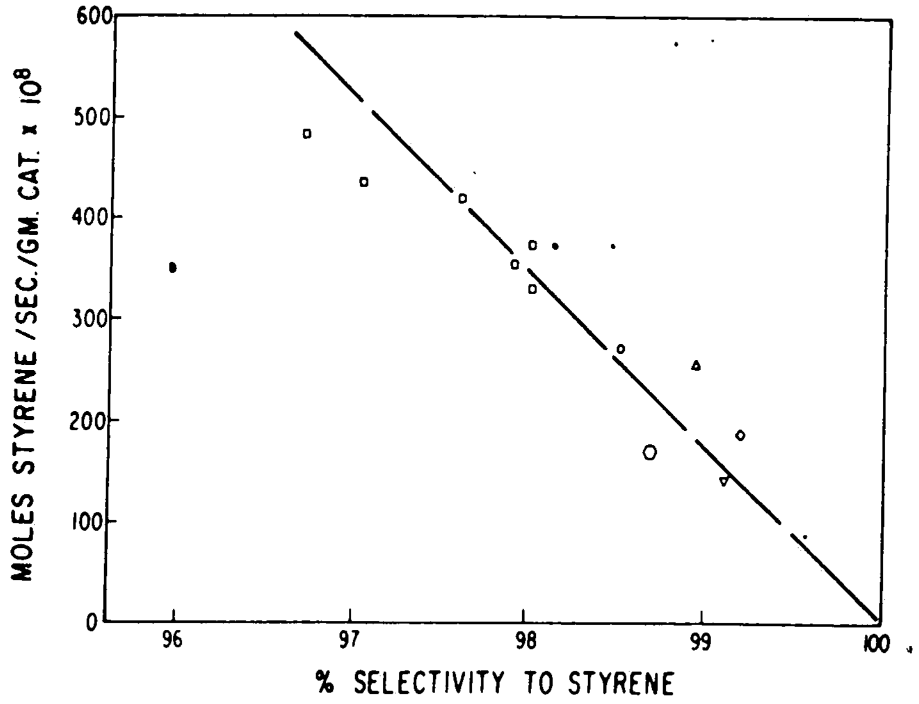

FIG. 5. Apparent relation between activity and selectivity for iron oxide catalysts with various promoters. (Ref. 9)

concentration range. Other promoters can be added to improve selectivity, but usually there is a loss in catalyst activity (9). In Figure 5 from Lee (9), the apparent relationship between activity and selectivity for a family of iron oxide catalysts (having small amounts of V_2O_5, KF, KCl, $K_4P_2O_7$, and others) is given. An idea of the promoters used industrially can be obtained by consulting Table II.

Chromium oxide is added to the catalyst for stability. Figure 6 shows the activity of two different catalysts versus time. The one containing 5% Cr_2O_3 was and remained more active than the catalyst without chromium oxide. Lee theorizes that the loss of activity is due to loss of surface area by sintering of the catalyst (9).

Another effect of catalyst aging is that potassium migrates to the colder areas of the reactor. This is caused by the slight shift in vapor pressure with temperature. Since the reaction is endothermic, this means that potassium migrates toward the catalyst particle centers and the reactor exit. Evidence of this can be seen in Figures 7 and 8. From Figures 4 and 7, we see "that the active region of this aged catalyst is in a rather narrow band between the periphery and center." The potassium content also dropped from 4.2% to 2.8% during the 20,000 hours of operation. This loss of potassium would account for the gain in pore volume (see Figure 8); and when the loss is coupled with

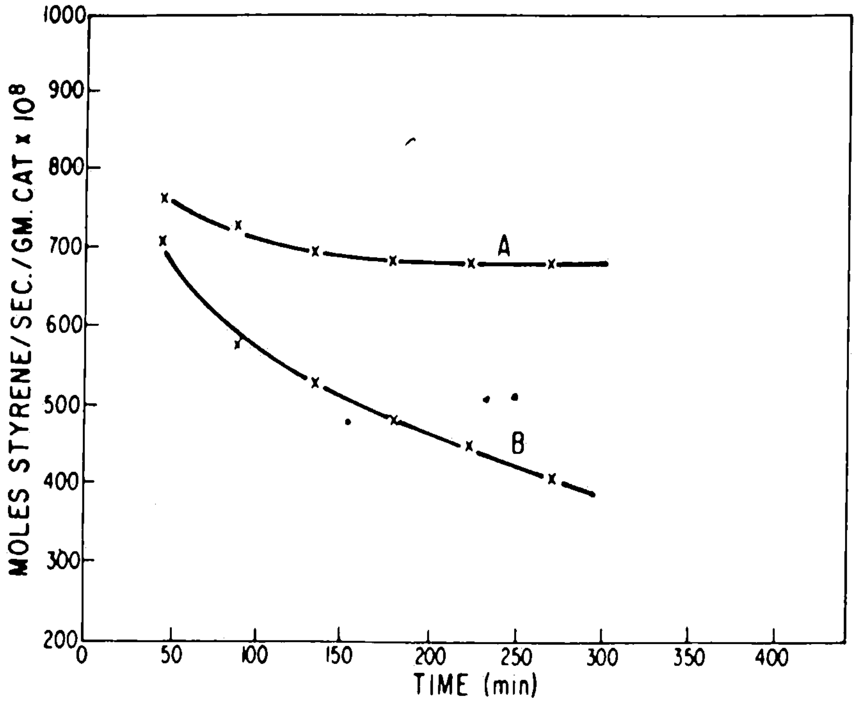

FIG. 6. Effect of chromium on the stability of an alkali-promoted iron oxide catalyst. Catalyst A had 5% Cr_2O_3 and Catalyst B had none. (Ref. 9)

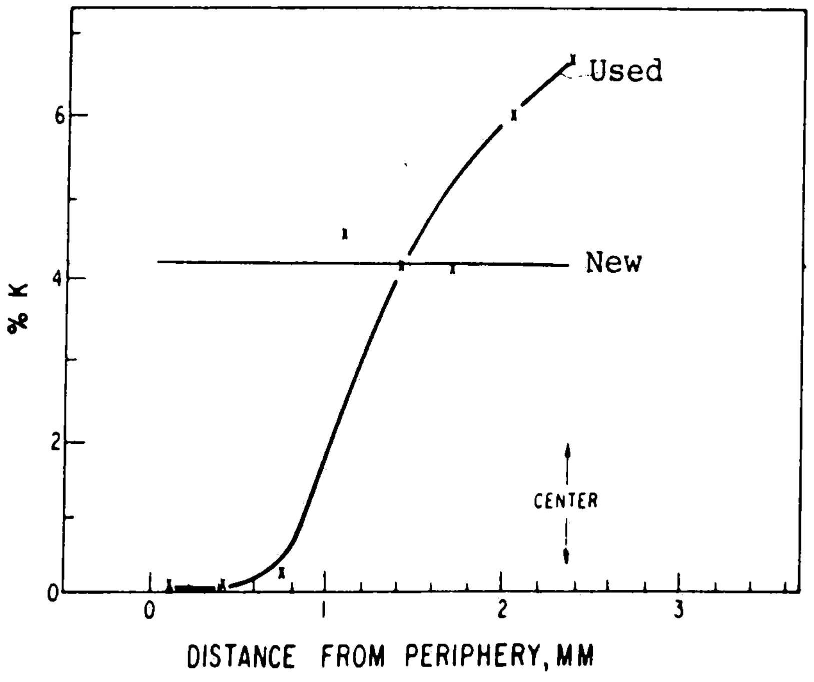

FIG. 7. Radial concentrations of potassium in a 5-mm catalyst pellet aged 20,000 hr as determined by x-ray microprobe analyzer. (Ref. 9)

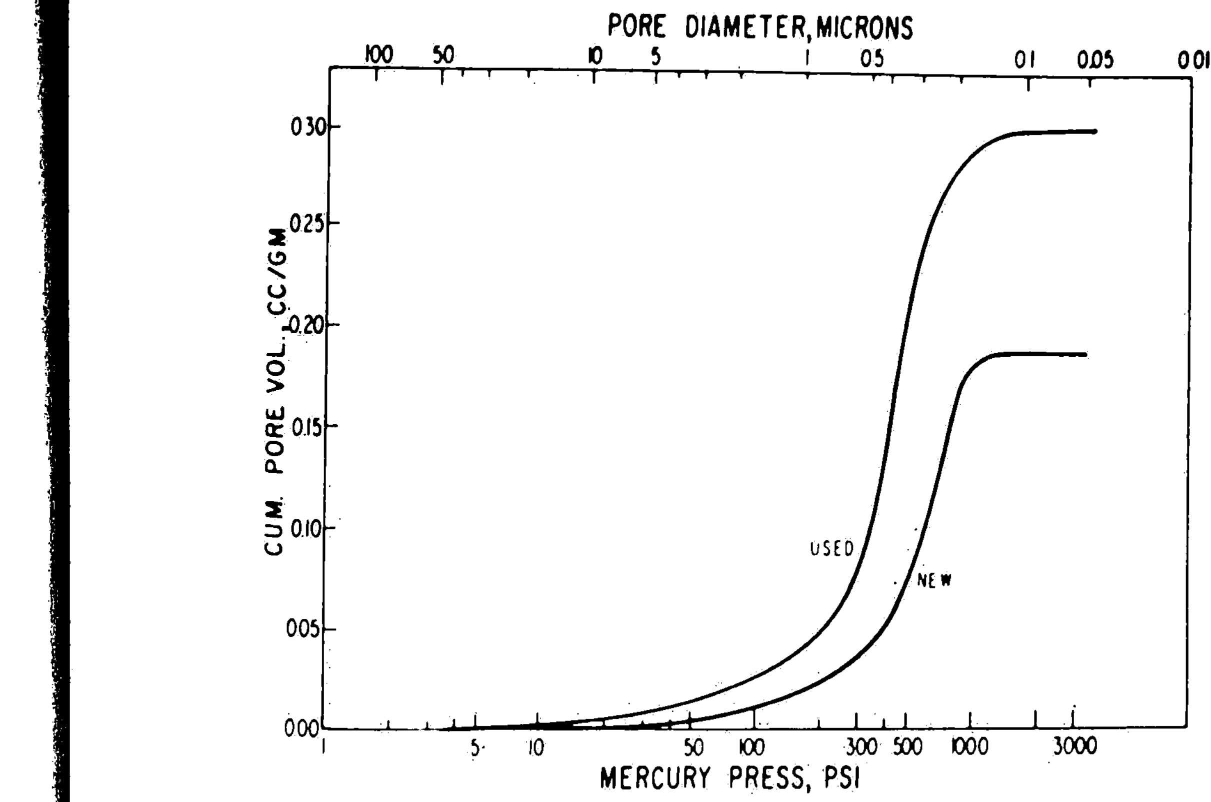

FIG. 8. Cumulative pore volume by mercury injection for a new commercial iron oxide catalyst and one largely depleted of potassium. (Ref. 9)

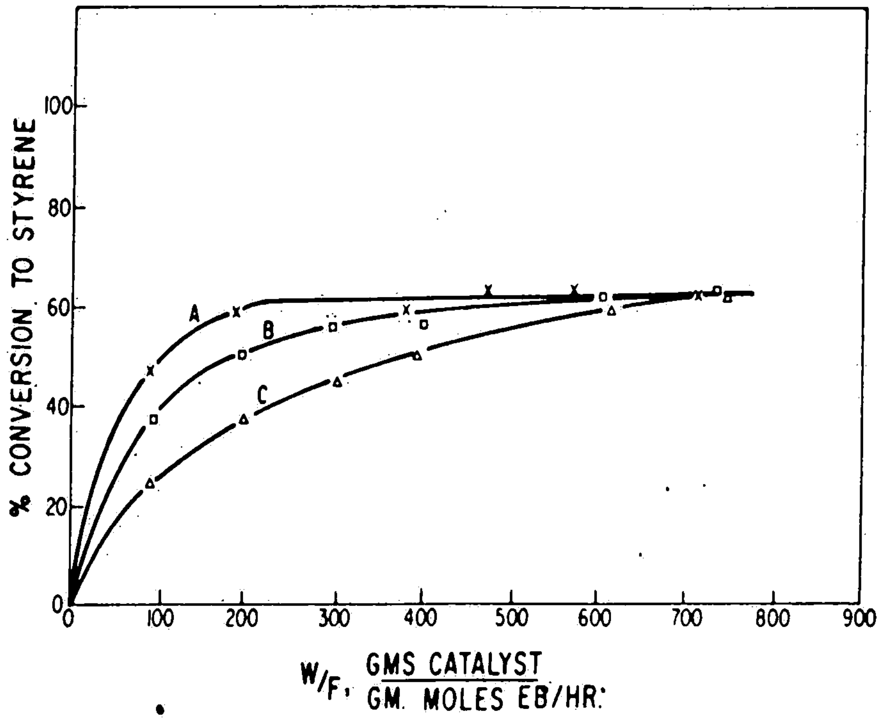

FIG. 9. Conversion to styrene by aged catalysts in a laboratory reactor with sample taps. Catalysts A, B, and C had 1,100, 12,000, and 20,000 hr of prior use in plant reactors. (Ref. 9)

the different potassium distribution in the older catalyst, the loss of activity (see Figure 9) is understandable (9).

Besides losing surface area or promoter, the catalyst can be poisoned by halides (9 & 12). It is interesting to note that a small amount of chlorine improves the catalyst selectivity (e.g., United Catalyst G64-D), but large amounts greatly decrease the catalyst activity (see Figure 10). This effect is especially detrimental for those plants that produce the ethylbenzene feed over an aluminum chloride catalyst.

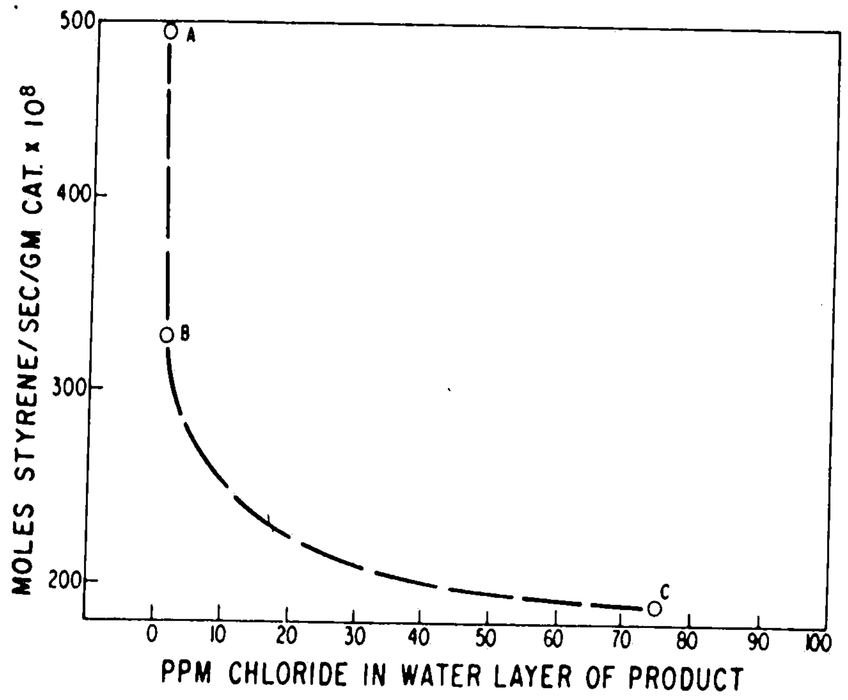

FIG. 10. Effect of chlorides in the ethylbenzene feed on the activity of an alkali-promoted iron oxide catalyst. Feed A contained no measurable chlorides and none was detectable in the product water layer. Feed B had 2 to 3 ppm organic chlorides in the feed and gave 0.5 ppm chlorides in the product water layer. Feed C had an unknown level of chlorides in the feed and gave 75 ppm chlorides in the product water layer. (Ref. 9)

Coking of the catalyst is a fourth way catalyst activity is lost with age. A carbonaceous residue can form that covers some of the active catalyst surface. Injecting steam with the ethylbenzene feed reduces this problem. There is a minimum steam-to-hydrocarbon ratio for the feed for each catalyst above which catalyst coking is not a problem. Since one of the biggest energy losses is the condensing of the cooled effluent, it is desirable to minimize steam-to-hydrocarbon ratio. United Catalyst's 64-E catalyst has one of the lowest minimums available: in a bench-scale reactor it has been operated with a molar ratio of 3. The manufacturer states it could operate in a plant reactor at this ratio for at least a year (13). As discussed below, one sacrifice for lowering the steam-to-hydrocarbon ratio is a lower equilibrium conversion.

There are two reasons unrelated to the catalyst that make it desirable to run this reaction in the presence of steam. The first is that the steam dilutes the gas and thus shifts the equilibrium toward the production of styrene. The second reason is that superheated steam is a convenient way to introduce part of the heat required for this endothermic reaction. (Typically, reactors operate with inlet temperatures around 630°C, and direct heating of ethylbenzene to these temperatures would cause extensive dealkylation.)

Commercially, 1/8" diameter by 3/16" long cylindrical catalyst pellets are used in fixed-bed reactors (14). This catalyst is replaced after one to two years of use, depending upon the capacity and operating conditions of the plant (9). Some of the loss in catalyst activity with use can be compensated for by raising the reactor inlet temperature (15).

Mass Transfer Considerations

Mass transfer limitations, as discussed in the literature, appear to play an important role in the reaction. There are two possible types of mass transfer: external and internal. External mass transfer limitations are only possible with internal mass transfer limitations (16). Two indications of internal mass transfer limitations or diffusion control are that the reaction rate increases as catalyst particle size is decreased and that the apparent activation energy is approximately half the intrinsic activation energy (17).

Lee (9), in his paper, shows that the reaction rate decreases with increasing pellet size (see Figure 11). He also calculated an effectiveness factor (discussed later) of 1 for the 25 x 30 mesh particles. The apparent activation energy for the 3/16" particle, although not cut by a factor of 2, is lower than for the 25 x 30 mesh (15 kcal/mol compared to 23 kcal/mol).

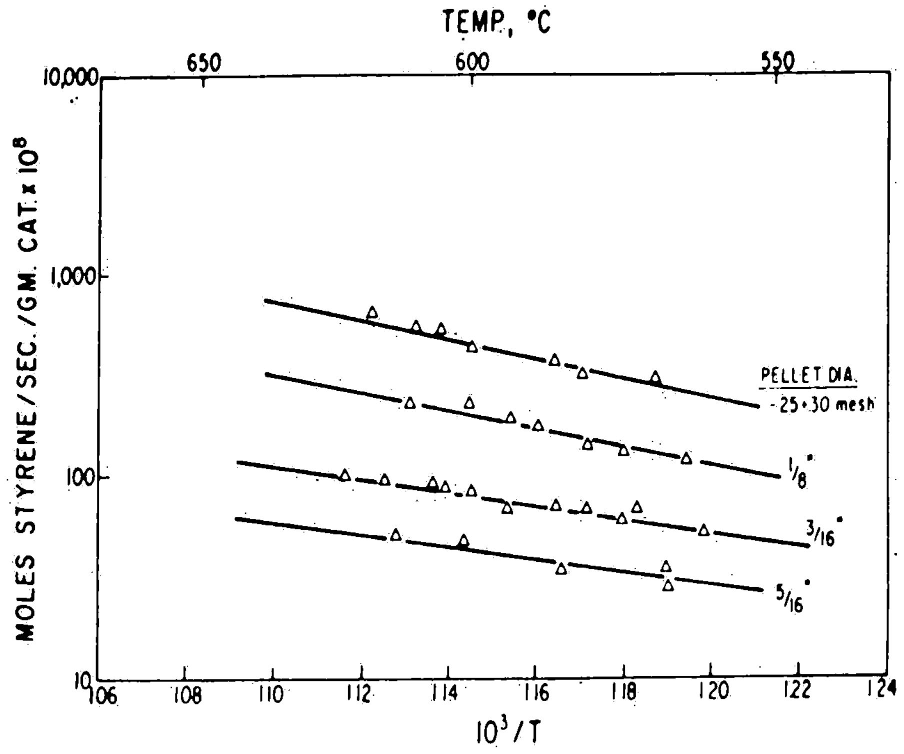

FIG. 11. Effect of catalyst pellet size on activity of potassium-promoted iron oxide. (Ref. 9)

Development of Reactor Model

Computer Reactor Model Capabilities

The program is a one dimensional, steady state, plug flow reactor model. It can be used to simulate an isothermal or an adiabatic reactor.

Isothermal isoboric reactors are approximated by the experimental reactors used in kinetic studies and can be simulated with this model. Thus, the literature kinetics and the catalyst manufacturers' conditions can be used to simulate the manufacturers' reactors and compare the conversions. The program may also be used to extract the apparent kinetic constants from isothermal conversion data. The program is given the reactor conditions, the measured conversions to styrene, toluene, and benzene, the form of the kinetic equations, and an approximate set of kinetic constants, the program then adjusts the kinetic constants for the three main reactions until the conversions agree. This is done using the Internation Mathematical and Statistical Library subroutine (18) which employs a modified Leverberg-Marquart algorithm to minimize the sum of the squares of the difference between the predicted and measured conversions (the styrene conversion is weighted by a factor of 2). With isothermal data over a range of temperatures and conditions, one can use the apparent kinetic constants to fit the Arrhenius equation. With this procedure, the kinetic constants for the main reactions can be extracted for each proposed mechanism with its corresponding reaction rate expressions.

The program can calculate an effectiveness factor, which is a quantitative measure of diffusion importances (see "Description of Diffusion Model" section). This calculation will either be performed at the reactor inlet and the results printed out, or it will be done throughout the reactor and the results used in the kinetic expression.

Adiabatic one or two stage reactors are used industrially and can be simulated with this model. When simulating a two stage reactor, either the inlet temperature and amount of steam (if any) injected into the second stage may be specified or the steam temperature and amount of steam injected into the second stage may be specified. In addition to simulating plant reactor operation, the program can be used to compare the predicted and measured conversions. As discussed in the "Comparison of the Model With Plant Data" section, deactivation can be correlated with catalyst age. Plant operating conditions can be optimized by simulating the reactor's behavior under different conditions and having the program calculate the objective function, profit (see "Approximate Plant Economics" section for definition).

The differential component, energy, and momentum balances were integrated down the reactor height using

EPISODE (19), a published integration program. The program was written to be general, handling up to 15 components and 15 reactions; later a library was added containing component names, molecular weights, and heat capacities.

The component balance has the form

$$\frac{dF_i}{dZ} = \rho_{bulk} \, XA \sum_{j=1}^{M} \alpha_{ij} r_j \qquad (17)$$

with the reactions represented by

$$\sum_{i=1}^{N} \alpha_{ij} C_i = 0 \qquad j = 1, 2 \ . \ . \ . \ M \qquad (18)$$

where

F_i = the molar flow rate of component i, kgmol/hr

Z = the vertical distance from the top of the reactor, m

ρ_{bulk} = the bulk density of the catalyst, kg/m³

XA = the reactor cross-sectional area, m²

α_{ij} = the stoichiometric coefficient of component i in reaction j (<0 for reactants)

r_j = the rate of reaction j, kgmol/kgcat-hr

C_i = component i

M = the number of reactions

N = the number of components

For generality, the model uses irreversible mechanistic reactions,

i.e., $r_j = k_j \prod_i C_i^{-\alpha_{ij}} \quad \alpha_{ij} < 0$ (19)

where the rate constant is represented by the Arrhenius relation

$$\text{i.e.,} \quad k_j = \exp\left(A_j - Ea_j/R_G T\right) \tag{20}$$

where

k_j = the rate constant of reaction j, kgmol/kgcat-hr

A_j = the frequency factor of reaction j

Ea_j = the activation energy of reaction j, kcal/mol

Thus, to simulate a reversible reaction, one uses two opposite irreversible reactions with the ratio of the rate constants being in equilibrium constant. Similar manipulation can be made to get the desired rate expressions. For example, the toluene formation reaction can be represented as

$$\phi\text{-}CH_2\text{-}CH_3 \longrightarrow \phi\text{-}CH_3 + CH_2 \qquad r_3 = k_3 P_{EB} \tag{21}$$

$$CH_2 + H_2 \longrightarrow CH_4 \qquad \text{fast} \tag{22}$$

+

$$\phi\text{-}CH_2\text{-}CH_3 + H_2 \longrightarrow \phi\text{-}CH_3 + CH_4 \qquad r_3 = k_3 P_{EB} \tag{23}$$

An inhibition term can also be included in the reaction rate expression for the aromatic reactions. The program can include one of the four different inhibitors discussed in the "Calibration of the Model" section.

The energy balance has the form

$$\frac{dT}{dZ} = \rho_{bulk}\, XA \sum_j \left[r_j \left(-\Delta H_{rxnj} \right) \right] / \sum_i \left(F_i\, C_{pi} \right) \tag{24}$$

where T = the absolute temperature, °K

ΔH_{rxnj} = the heat of reaction j, cal/kgmol

C_{pi} = the heat capacity of component i, cal/kgmol °K

The heat of reaction data used are from American Petroleum Institute Project 44 (20), and the ideal gas heat capacities are from The Properties of Gases and Liquids (21) (see Appendix E).

The momentum balance uses the Ergun (22) pressure drop equation and has the form

$$\frac{dP_p}{dZ} = 150. \; \frac{(1 - \varepsilon)^2}{\varepsilon^3} \; \frac{v\mu}{D_p{}^2} \qquad (25)$$

$$+ \; 1.75 \; \frac{(1 - \varepsilon)}{\varepsilon^3} \; \frac{\rho_{gas} \; v^2}{D}$$

where

P_p = the pressure at this point in the reactor, Pa

ε = the catalyst void fraction

v = the superficial gas velocity, m/sec

μ = the gas viscosity, kg/m-sec

D_p = the catalyst pellet diameter, m

ρ_{gas} = the gas density, kg/m³

The void fraction used is discussed in the "Comparison of the Model With Plant Data" section. For more details about the program, see Appendix L where the documented program is listed along with sample input data sets.

Evaluation of Available Data

There are three different types of data available: catalyst manufacturer's bench-scale data, literature data, and plant data. The procedure for obtaining these data and some of the inherent limitations are discussed below. Also, the merits of the literature kinetics are discussed in light of the manufacturer's data.

From Shell (10) and United Catalyst (11), isothermal bench-scale reactor data are available for whole Shell 105 and other catalyst pellets under various conditions. Both manufacturers used tubular reactors with catalyst volumes of around 100 cm³ that were heated electrically and operated isothermally within a few centigrade degrees (i.e., the top, middle, and bottom temperatures were all within about ±2°C) (23). The reactors were operated at fixed liquid hourly space velocities (LHSV) which were reported, along with the reactor temperature, inlet pressure, and exit ethylbenzene conversions.

The Shell data are presented in the form of graphs without any points shown. Some of the conversion correlations are straight lines (presumably drawn through scattered data). The points selected from the graphs are presented in Table III. Also, the variable pressure data are reported

Table III

Manufacturers' Performance Test Data for Shell 105 (Ref. 10 & 11)

No.	Data Set	Temperature, °C	Pressure, atm	Molar Steam-to-Oil Ratio	Conversion, % Styrene*	Conversion, % Toluene	Conversion, % Benzene	Styrene Selectivity, %
1	1**	550	1.0	12.5	40.0	1.87	1.52	92.0
2		560	1.0	12.5	45.2	2.45	1.78	91.3
3		570	1.0	12.5	50.2	3.16	2.11	90.5
4		580	1.0	12.5	55.4	4.17	2.44	89.3
5		593	1.0	12.5	60.9	5.90	3.15	87.0
6	2**	580	0.34	12.5	63.4	4.20	2.38	90.6
7		586	0.68	12.5	62.4	5.04	2.73	89.1
8		600	1.36	12.5	59.3	7.0	3.64	84.7
9		606	1.70	12.5	57.4	8.4	4.2	82.0
10	3†	566	1.27	8.85	40.9	1.75	0.95	93.8
11		573	1.27	8.85	52.9	3.73	1.57	91.0
12		621	1.27	8.85	60.7	7.51	2.78	85.5
13	4†	566	1.27	8.85	43.1	2.15	0.99	93.2
14		593	1.27	8.85	55.6	4.92	1.39	89.8
15		621	1.27	8.85	61.9	8.86	3.46	83.4
16	5	566	1.27	14.7	33.9	--	--	96.3
17		593	1.27	14.7	51.9	--	--	93.3
18		621	1.27	14.7	64.7	--	--	89.0
19	6	566	0.68	8.85	37.6	--	--	97.9
20		593	0.68	8.85	56.1	--	--	95.4
21		621	0.68	8.85	68.3	--	--	92.3

* Calculated from total conversion and styrene selectivity.

** Selected points from graphs.

† Toluene and benzene conversions calculated from benzene/toluene (B/T) ratio.

only at total conversions of 70%; to obtain 70% conversion requires severe conditions and using a low-selectivity catalyst (such as Shell 105), so, the side reactions occur to a significant extent. Therefore, it is difficult to evaluate the accuracy of their data.

United Catalyst, unlike Shell, gives tabulated data. Presumably, these are actual laboratory data. Four different sets at three different conditions are reported. Two of the four different condition sets are incomplete, only giving total conversion and styrene selectivity. The two complete United Catalyst sets are at the same conditions (i.e., pressure, temperature, LHSV, and steam-to-oil ratio) but were run in different test units. These two complete sets (see Table IV) do not agree exactly, giving some idea of the variability of the data. This disagreement between different test units reinforces their statement that the data are only relative and have been presented to show the relative merits of one catalyst over another (24).

The literature kinetics, along with the experimental procedures and the data's limitations, are briefly summarized in the "Reaction Kinetics" section. Some of the limitations are highlighted here. Also, the merits of the literature kinetics, evaluated in light of the manufacturers' data, are discussed below.

Table IV

Comparison of Two Sets of United Catalyst (Ref. 11) Data

Conditions: Pressure = 4.0 psig
Liquid Hourly Space Velocity (LHSV) = 1.0 hr^{-1}
Steam-to-Oil Ratio = 1.5 by weight
= 8.85 by mole

	Set 3			Set 4		
	566°C	593°C	621°C	566°C	593°C	621°C
Total Conversion, %	43.6	58.2	71	46.2	61.9	74.2
Styrene Selectivity, %	93	91.0	85.5	93.2	89.8	83.4
Benzene-to-Toluene Ratio	0.54	0.42	0.37	0.46	0.39	0.39
Toluene Selectivity,[1] %	4.0	6.3	10.6	4.7	7.8	12.8
Benzene Selectivity,[1] %	2.2	2.7	3.9	2.1	2.4	3.8
Test Unit No.:		126-31			126-50	

1) Calculated from the above data.

The Wenner model has several drawbacks. One is that the analysis of non-isothermal heated reactor data required several approximations, especially since there were no computers available to the author in 1948. Sheel empirically fit the rate constants with fixed activation energies for his four different sets of plant data. The limitations of this approach are demonstrated by the fact that the main reaction's rate constants for two different sets vary by 30%. Clough also empirically fit the constants to agree with the performance of his abiabatic pilot plant reactor. However, the biggest drawback to this model is that the form cannot fit variable pressure data as discussed in the next section.

The kinetics proposed by Carrá's and Forni appeared the most promising, for a thorough investigation was conducted using the catalyst of interest. Also, by using crushed catalyst, diffusion effects could be accounted for theoretically (see "Description of Diffusion Model" section). However, when their kinetics were used to model a reactor at manufacturers' conditions, the predicted conversions were below the manufacturers' actual conversions (see Table V). One would expect the predicted conversions to be equal to (or greater than, if diffusion was important) the manufacturers' conversions. Therefore, Carrá's kinetic constants are deemed unreliable.

Table V

Carré's Kinetics Used to Simulate Catalyst Manufacturers' Performance Test Data Conversions

No.	Data Set	Tempera-ture, °C	Pressure, atm	Molar Steam-to-Oil Ratio	Styrene Conversion, % Model	Styrene Conversion, % Manufacturer
1	1	550	1.0	12.5	26.3	40.0
2		560	1.0	12.5	31.3	45.2
3		570	1.0	12.5	36.4	50.2
4		580	1.0	12.5	41.6	55.4
5		543	1.0	12.5	48.1	60.9
6	2	580	0.34	12.5	43.8	63.4
7		586	0.68	12.5	46.4	62.4
8		600	1.36	12.5	49.4	59.3
9		606	1.70	12.5	50.0	57.4
10	3	566	1.27	8.85	27.4	40.9
11		573	1.27	8.85	40.2	52.9
12		621	1.27	8.85	52.0	60.7
13	4	566	1.27	8.85	27.4	43.6
14		593	1.27	8.85	40.2	55.6
15		621	1.27	8.85	52.0	61.9
16	5	566	1.27	14.7	19.0	33.9
17		593	1.27	14.7	30.8	51.9
18		621	1.27	14.7	44.7	64.7
19	6	566	0.68	8.85	19.0	37.6
20		593	0.68	8.85	31.0	56.1
21		621	0.68	8.85	45.1	68.3

The kinetics prepared by Lebedev showed the same drawbacks as those proposed by Carrá. The catalyst was crushed so the investigation yielded intrinsic kinetics which should be equal to or faster than the apparent kinetics, but a reactor simulated with these kinetics predicted lower conversions than the manufacturers' actual conversions (see Table VI).

In summary, using the catalyst manufacturers' performance data as criteria, none of the literature kinetics is reliable. However, the form of the kinetics (i.e., the different driving forces and the inhibitor, including the adsorption coefficient values) may be useful and that is discussed in the next section.

By the end of the research, operating and conversion data for a plant reactor were available from two sources, the USS Chemicals reactor and the Masters Thesis by Sheel (25). These data were used in a comparison with the final kinetic model's predictions. However, there are three reasons why they were not used in the evaluation of the literature kinetics or the calibration of the kinetic models. The first reason is that plant data are typically less reliable, since in operating a plant, one is more concerned with detecting changes than measuring precise numbers. The second reason is that plant data in most cases (this one included) are only available over a limited range

Table VI

Lebedev's Kinetics Used to Simulate Catalyst Manufacturers' Performance Test Data Conversions

No.	Data Set	Temperature, °C	Pressure, atm	Molar Steam-to-Oil Ratio	Styrene Conversion, % Model	Styrene Conversion, % Manufacturer
1	1	550	1.0	12.5	29.7	40.0
2		560	1.0	12.5	35.5	45.2
3		570	1.0	12.5	41.8	50.2
4		580	1.0	12.5	48.7	55.4
5		593	1.0	12.5	58.1	60.9
6	2	580	0.34	12.5	50.7	63.4
7		586	0.68	12.5	56.0	62.4
8		600	1.36	12.5	59.8	59.3
9		606	1.70	12.5	61.6	57.4
10	3	566	1.27	8.85	31.2	40.9
11		573	1.27	8.85	47.2	52.9
12		621	1.27	8.85	65.8	60.7
13	4	566	1.27	8.85	31.2	43.6
14		593	1.27	8.85	47.2	55.6
15		621	1.27	8.85	65.8	61.9
16	5	566	1.27	14.7	25.2	33.9
17		593	1.27	14.7	40.2	51.9
18		621	1.27	14.7	59.5	64.7
19	6	566	0.68	8.85	25.3	37.6
20		593	0.68	8.85	40.7	56.1
21		621	0.68	8.85	60.6	68.3

operating conditions. The third is that if the reactor's residence time is large, the actual kinetics are not as crucial as the equilibrium conversion and energy balance. This is seen in Figure 8 where catalysts with three different ages have markedly different kinetics (i.e., the rate of conversion, or the slope, differs at the beginning of the reactor), yet each reaches about the same conversion. The data available consisted of inlet and outlet temperatures, pressures, flow rates, and compositions. There are thermocouples inside the reactor bed, but their readings are of questionable value. The age of the catalyst at the time of the test was also available for the plant.

Calibration of the Model

To test each of the literature kinetic forms, the computer program is run in a mode which allows a search to evaluate the apparent reaction rate constants for the three ethylbenzene reactions (Equations 1-3). This is done for each set of conditions independently. A linear least-squares routine is then used to correlate the apparent reaction rate constants for each of the three major reactions, using the Arrhenius relationship. The best model should form the best linear fit of Arrhenius's equation (see "Computer Reactor Model Capabilities" section for details).

The accuracy of kinetic constants obtained by curve-fitting manufacturers' data depends heavily on the accuracy of the data. How close to isothermal the reactors were operated and whether the experiments reached steady state is not known. The accuracy of Shell's data are more suspect than United Catalysts' because no data points are given.

The Arrhenius equation is

$$k_j = \exp\left(A_j - \frac{E_{a_j}}{R_G T}\right) \qquad (26)$$

where

k_j = rate constant of reaction j, kgmol/kg catalyst hr atm^n (n = the total power of the pressure term, 1 or 2)

A_j = frequency factor of reaction j

E_{a_j} = activation energy of reaction j, kcal/mol

R_G = ideal gas constant, 1.987 cal/mol °K

T = absolute temperature, °K

The activation energy (E_a) is always positive. For the main reaction (Equation 1), which is reversible, the equilibrium constant equals the forward reaction rate constant divided by the reverse reaction rate constant,

$$K_{eq} = \frac{k_1}{k_{-1}} \qquad (27)$$

From Rossini's (26) Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds in the region of interest (see Appendix B):

$$\ln K_{eq} \cong 15.202 - \frac{29.008 \text{ kcal/mol}}{R_G T} \qquad (28)$$

Combining Equations 27 and 28, and 29

$$\frac{15.202 - 29.008 \text{ kcal/mol}}{R_G T} = A_1 - A_{-1} - \frac{E_{a_1} - E_{a_1}}{R_G T} \qquad (29)$$

Therefore

$$E_{a_1} - E_{a_1} = 29.0 \text{ kcal/mol} \qquad (30)$$

And since $E_{a_{-1}} > 0$

$$E_{a_1} > 29.0 \text{ kcal/mol} \qquad (31)$$

This criteria, along with the correlation coefficients and the average absolute deviation between predicted and manufacturers' conversion, are used to evaluate the different models.

Model 1

An Arrhenius plot for the styrene generation reaction of Wenner's model is shown in Figure 12*. Examining this figure shows two reasons why Model 1 should be rejected. First, there is an unacceptable amount of scatter in the apparent reaction rate constants (see Table VII for the correlation coefficient) and, second, the apparent activation energy from the least-squares fit (24.1 kcal/mol) is less than the acceptable minimum (29.0 kcal/mol). Earlier investigation had shown that this model could adequately fit a constant pressure data.

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* Note that all figures and tables referenced in this section are found at the end of the section.

Model 2

Looking next at a model based on the driving forces and inhibitor (including the relative adsorption coefficient value) proposed by Carrá, the following observations can be made. Rate constants for the main reaction (see Figure 13) under each set of conditions fall approximately on in a straight line with the negative slope. Shell's 70% conversion variable pressure data still have a slope that corresponds to an activation energy less than the acceptable minimum. The kinetic data presented by Carrá and Forni (3) are in the same range as the apparent kinetics from the catalyst data. Two lines were fit, using a linear least-squares routine, through the points. One has the best slope and intercept; the other used the activation energy from Carrá's (3) paper and calculated the best intercept. The correlation coefficients for the fits are given in Table VII. Table VIII shows the average absolute deviation between the styrene conversions based on catalyst manufacturers' data and the conversions predicted by the models.

Arrhenius plots of the toluene and benzene formation reactions are given in Figures 14 and 15. Figures 27 through 32 show comparisons of catalyst manufacturers' data with the predictions of Model 2. The kinetics used in Model 2 for this comparison were calibrated using this same manufacturer's data.

Model 3

The kinetic form (i.e., driving forces, inhibitor, and adsorption coefficient) proposed by Lebedev fits the data about as well as Model 2. See Tables VII and VIII for a comparison of the fits. The reaction rate constants under each set of conditions do not form lines as straight as in Model 2 (compare Figures 14 and 17). This is the first model where Shell's 70% conversion data form a line with an activation energy above the minimum. The rate expressions for the toluene formation reaction of Models 2 and 3 are different. Comparing Figures 14 and 17, the expression of Model 2 allows for a better fit of the data, so a modified Model 3 was tested using Model 2's rate expression for the toluene reaction. This can also be seen in Tables VII and VIII by the higher correlation coefficient and the lower average absolute deviation for the conversion of the toluene reaction for the modified Model 3. Comparing the Arrhenius plots of the two different toluene formation reactions (Figures 17 and 18) shows that the rate expression based solely on ethylbenzene partial pressure is superior to the one which includes hydrogen. Another flaw in Model 3 is that the adsorption coefficient in the inhibitor having two parameters (Equation 16) is probably unjustified.

Figure 19 shows an Arrhenius plot of the apparent reaction rate constants for the benzene formation reaction.

Figure 27 through 32 again allow the comparison of manufacturers' data and the various models calibrated using these same data.

Model 4

A fourth model was investigated which is very similar to that proposed by Lebedev. The relevant equations are listed below.

$$r_1 = \frac{\left[P_{EB} - \frac{1}{K_{eq}} P_{STY} \; H_2 \right]}{\left(P_{EB} + z \, P_{STY} \right)^2} \qquad (32)$$

$$r_2 = \frac{k_2 \, P_{EB}}{\left(P_{EB} + z \, P_{STY} \right)^2} \qquad (33)$$

$$r_3 = \frac{k_3 \, P_{EB}}{\left(P_{EB} + z \, P_{STY} \right)^2} \qquad (34)$$

The relative adsorption coefficient, unlike the adsorption coefficient of Model 3, is independent of temperature. The value of the relative adsorption coefficient that is chosen will determine whether the partial pressure of ethylbenzene makes a contribution. Notice, however, that the inhibitor (see Table I for definition) must contain a term in addition to the styrene term; otherwise, the reaction rate expressions would be undefined when styrene is not present (e.g., at the beginning of a reactor).

Two values of the relative adsorption coefficient were investigated: 10 and 280. In the latter case, once the main reaction has proceeded to a small extent, the styrene term begins to dominate the inhibitor, so that ethylbenzene partial pressure either does not contribute to the rate of reaction. Figures 20 and 21 show the apparent reaction rate constants for Model 4 with the two different relative adsorption coefficients. One can see very little difference in the goodness of fit. By consulting Tables VII and VIII, one sees that when the styrene term dominates (i.e., z = 280), the correlation coefficient is closer to one and the average absolute deviation is a little lower. Figures 22 and 23 show the Arrhenius plots for the toluene and benzene formation reactions for a relative adsorption coefficient of 280.

Model 5

A third Langmuir-Hinshelwood mechanism was proposed in order to reconcile Carrà's observation that the initial reaction rate was independent of the partial pressure of ethylbenzene and Lebedev's observation that the inhibitor was approximately proportional to the partial pressure of styrene squared (see Appendix F). Once again, it was assumed that the reaction step was rate-controlling and that most of the surface sites were occupied. The relevant equations follow:

$$r_1 = \frac{P_{EB} - \frac{1}{K_{eq}} P_{STY} P_{H_2}}{P_{EB} + \left(y\, P_{STY} \right)^2} \qquad (37)$$

$$r_2 = \frac{k_2 P_{EB}}{P_{EB} + \left(y P_{STY}\right)^2} \tag{37}$$

$$r_3 = \frac{k_3 P_{EB}}{P_{EB} + \left(y P_{STY}\right)^2} \tag{38}$$

where

y = a combined adsorption coefficient, atm$^{-\frac{1}{2}}$

It was necessary to make an approximation between the region where the ethylbenzene and styrene partial pressures dominated the inhibitor.

For large combined adsorption coefficients, the fit this model gives is the same as Model 4. In fact, to use the activation energies and frequency factors from Model 4, one would use a combined adsorption coefficient (y) equal to the relative adsorption coefficient (z).

The model was run with a combined adsorption coefficient of 100, which fits the data as well as Model 4 does. This value was arbitrarily chosen. Tables VII and VIII should again be consulted, along with Figures 24-26. Figures 27 through 32 can be consulted to compare the model's predicted conversion and the manufacturers' data it was calibrated with.

One note of caution regarding Table VII. In the latter stages of my research, the mode in which the program searched for the apparent reaction-rate constants was not working properly. The program did not converge within the specified error criterion on the apparent reaction rate constants. The reason for this is unknown. However, this problem makes the high correlation coefficient for the last three models in Table VI questionable. The low average absolute deviations between the model and experimental data vindicate the calibration of the data.

Table VII

Correlation Coefficient for the Arrhenius Equations of Various Models

Model	Correlation Coefficient for the Reaction Generating		
	Styrene	Toluene	Benzene
1[1]	0.53	0.50	0.68
2	0.90	0.98	0.93
2[2]	0.85	0.96	0.90
3	0.95	0.58	0.86
3[3]	0.90	0.99	0.91
4[4]	0.909	0.961	0.959
4[5]	0.975	0.997	0.984
5	0.994	0.998	0.985
6[6]	0.995	0.998	0.993

1) United Catalyst Set 4 not included in the fit.

2) Carrá's activation energy used for main reaction.

3) Modified Model 3 - toluene formation reaction's driving force = P_{EB}.

4) With a relative adsorption coefficient of 10.

5) With a relative adsorption coefficient of 280.

6) Calibrated for Shell 015 catalyst.

Table VIII

Comparison of Predicted and Experimental Conversions for Various Models

	Average Absolute Deviation Between the Model and Manufacturers' Data for		
Model	Styrene Conversion, %	Toluene Conversion, %	Benzene Conversion, %
1[1]	9.62	2.43	0.57
2	4.00	0.84	0.57
2[2]	3.60	1.97	0.59
3	3.08	1.31	0.53
3[3]	2.67	0.76	0.56
4[4]	3.26	0.83	0.59
4[5]	2.29	0.89	0.58
5	2.28	0.86	0.58
6[6]	1.97	0.56	0.75

1) United Catalyst Set 4 not included in the fit.

2) Carra's activation energy used for main reaction.

3) Modified Model 3 - toluene formation reaction's driving force = P_{EB}.

4) With a relative adsorption coefficient of 10.

5) With a relative adsorption coefficient of 280.

6) Calibrated for Shell 015 Catalyst.

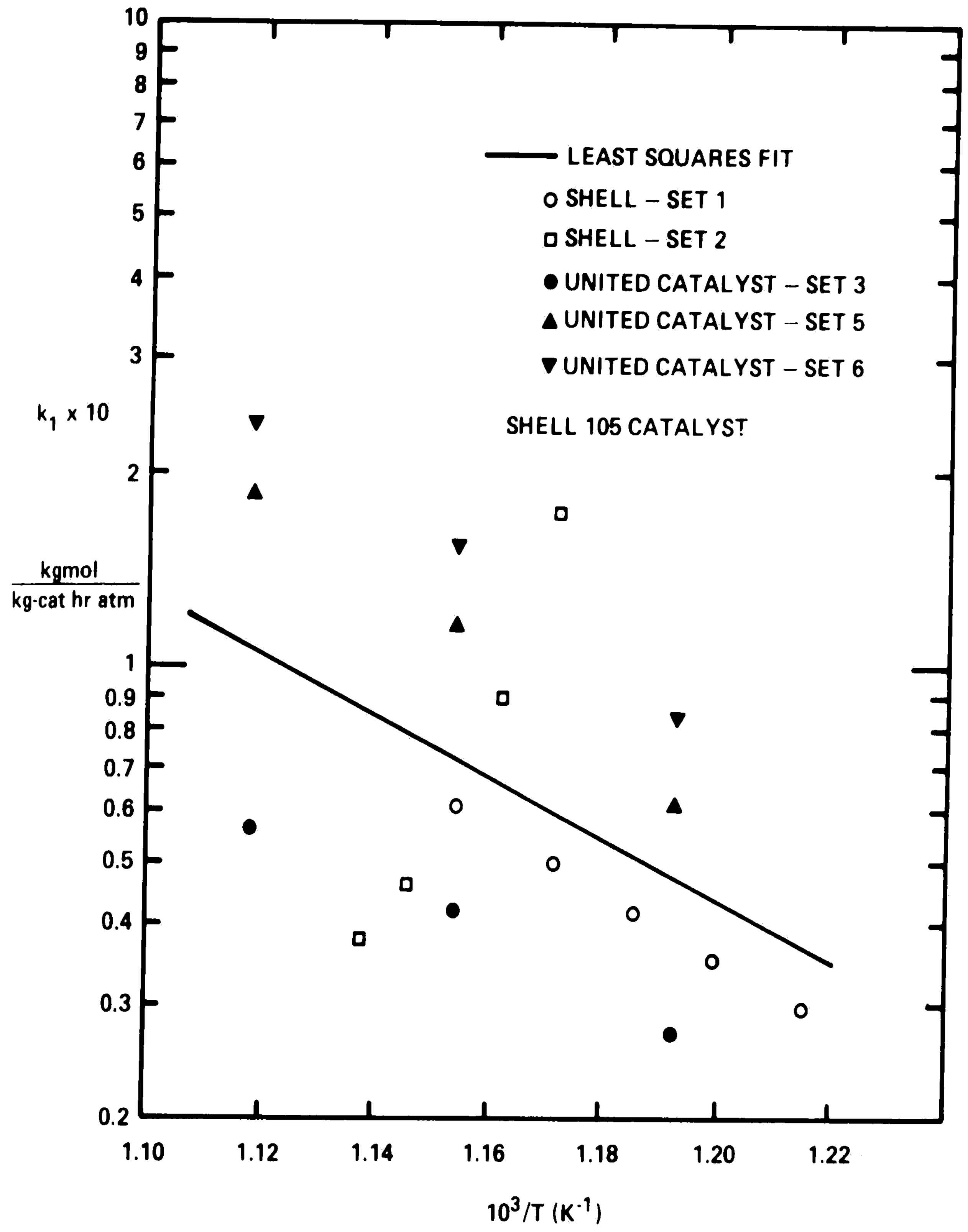

Figure 12 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 1

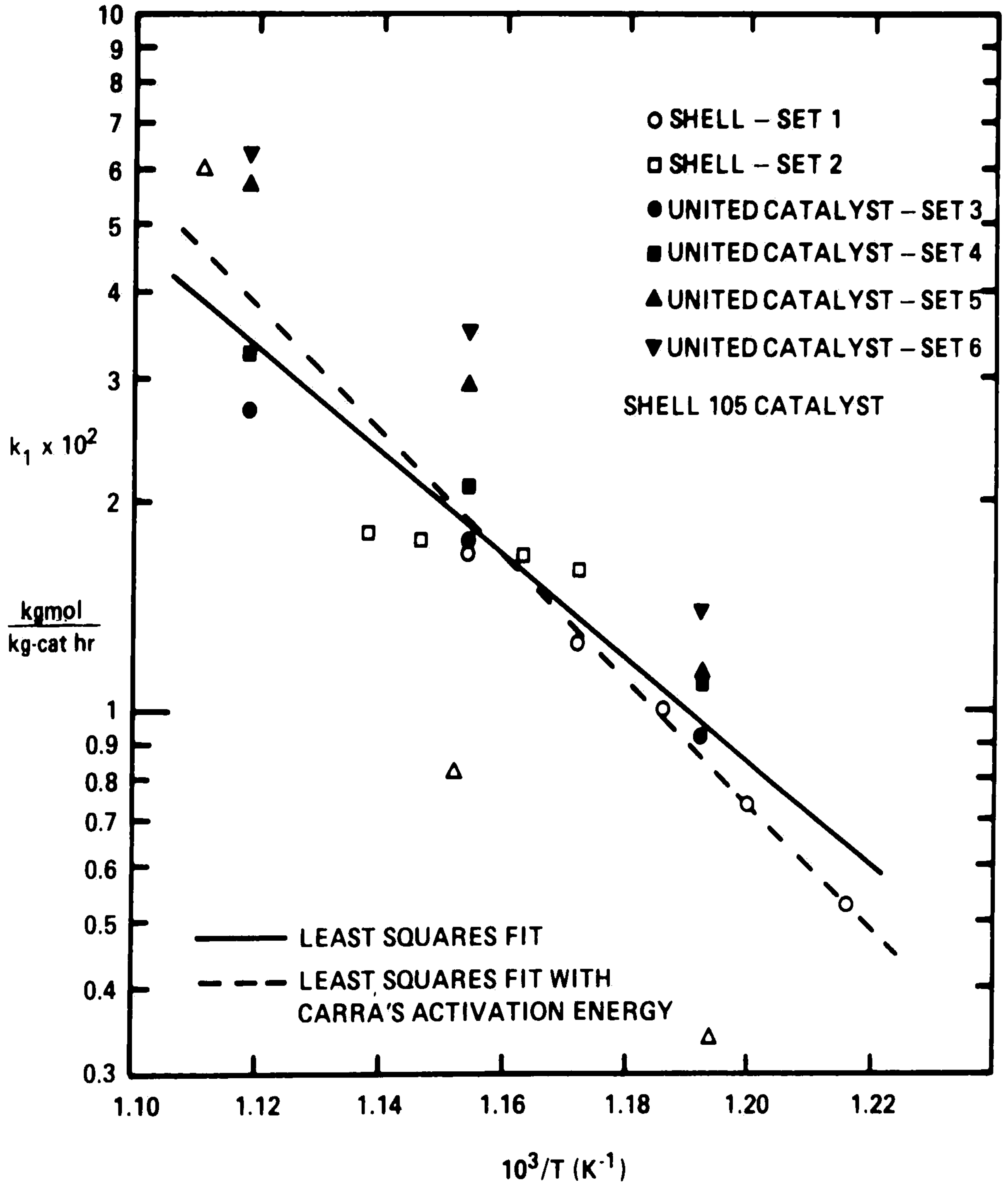

Figure 13 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 2

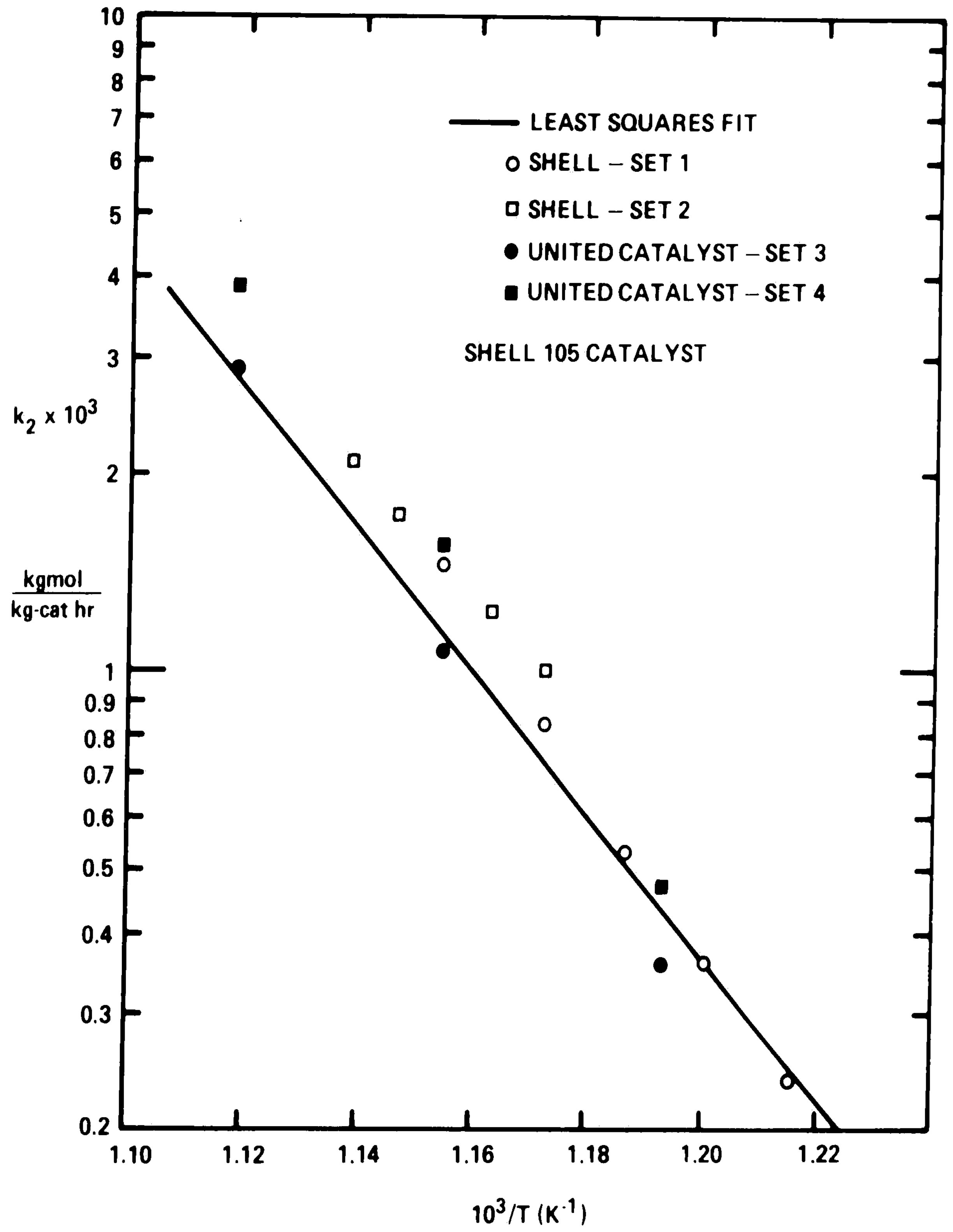

Figure 14 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE TOLUENE FORMATION REACTION OF MODEL 2

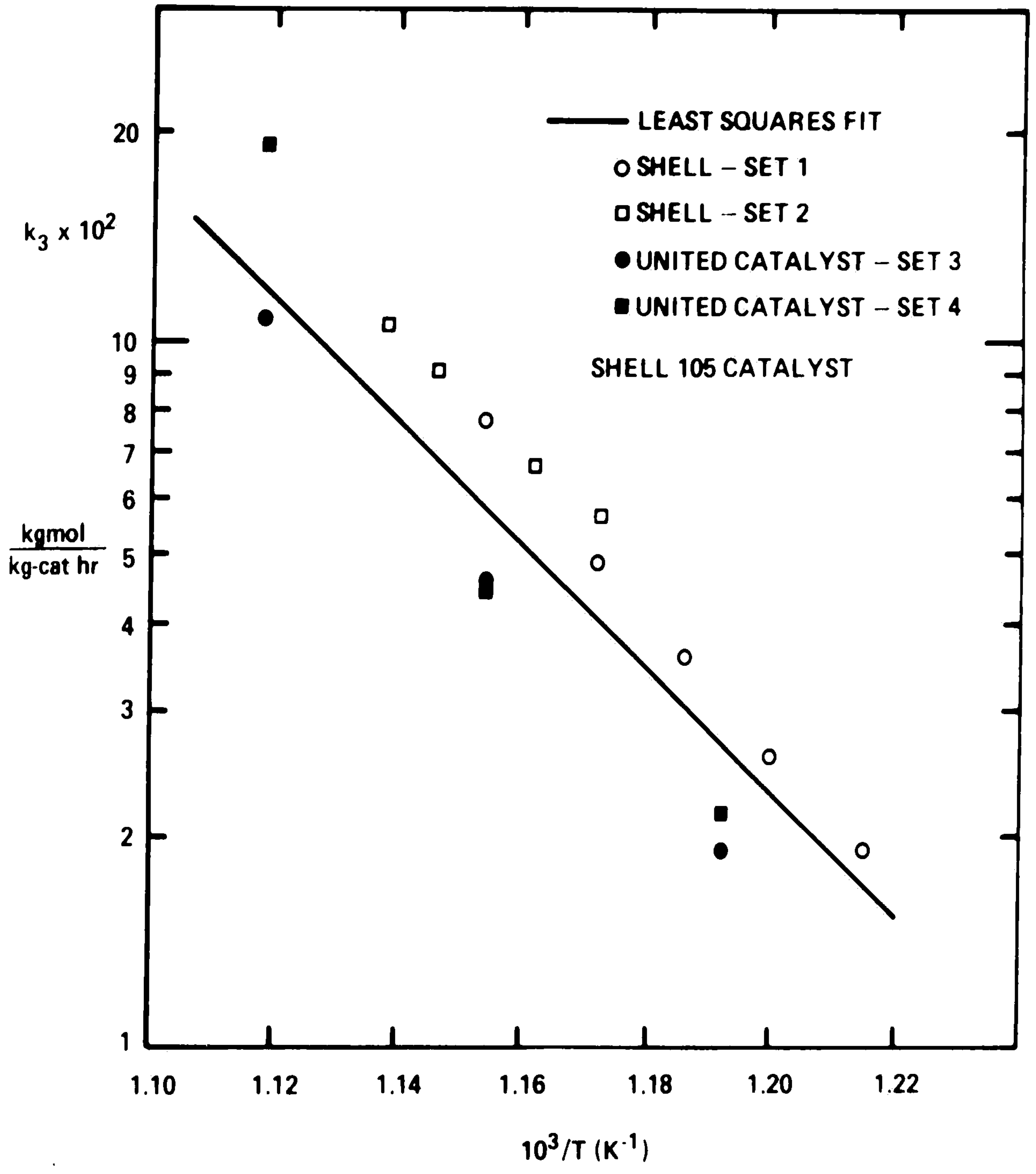

Figure 15 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE BENZENE FORMATION OF MODEL 2

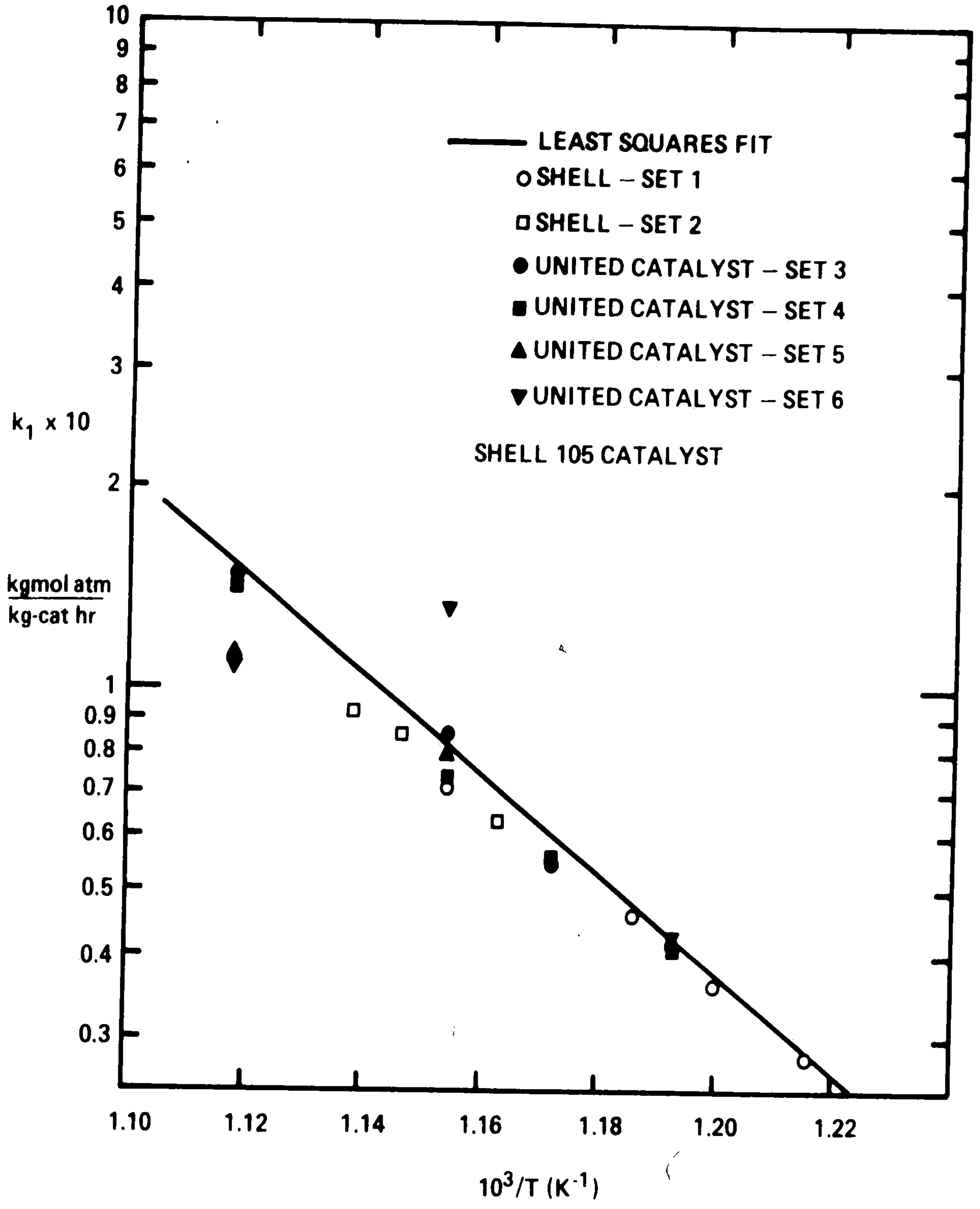

Figure 16 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 3

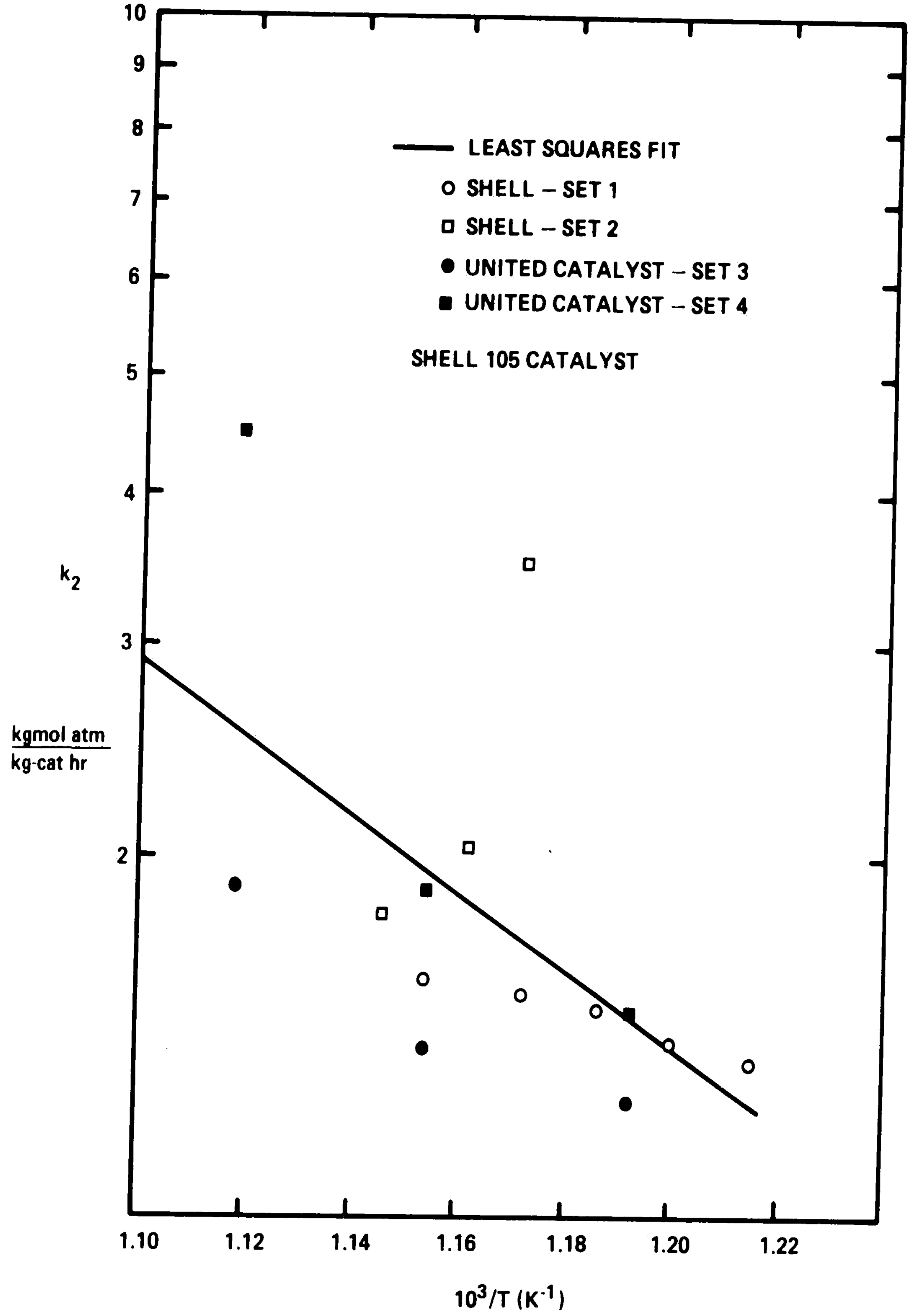

Figure 17 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANT FOR THE TOLUENE FORMATION REACTION OF MODEL 3

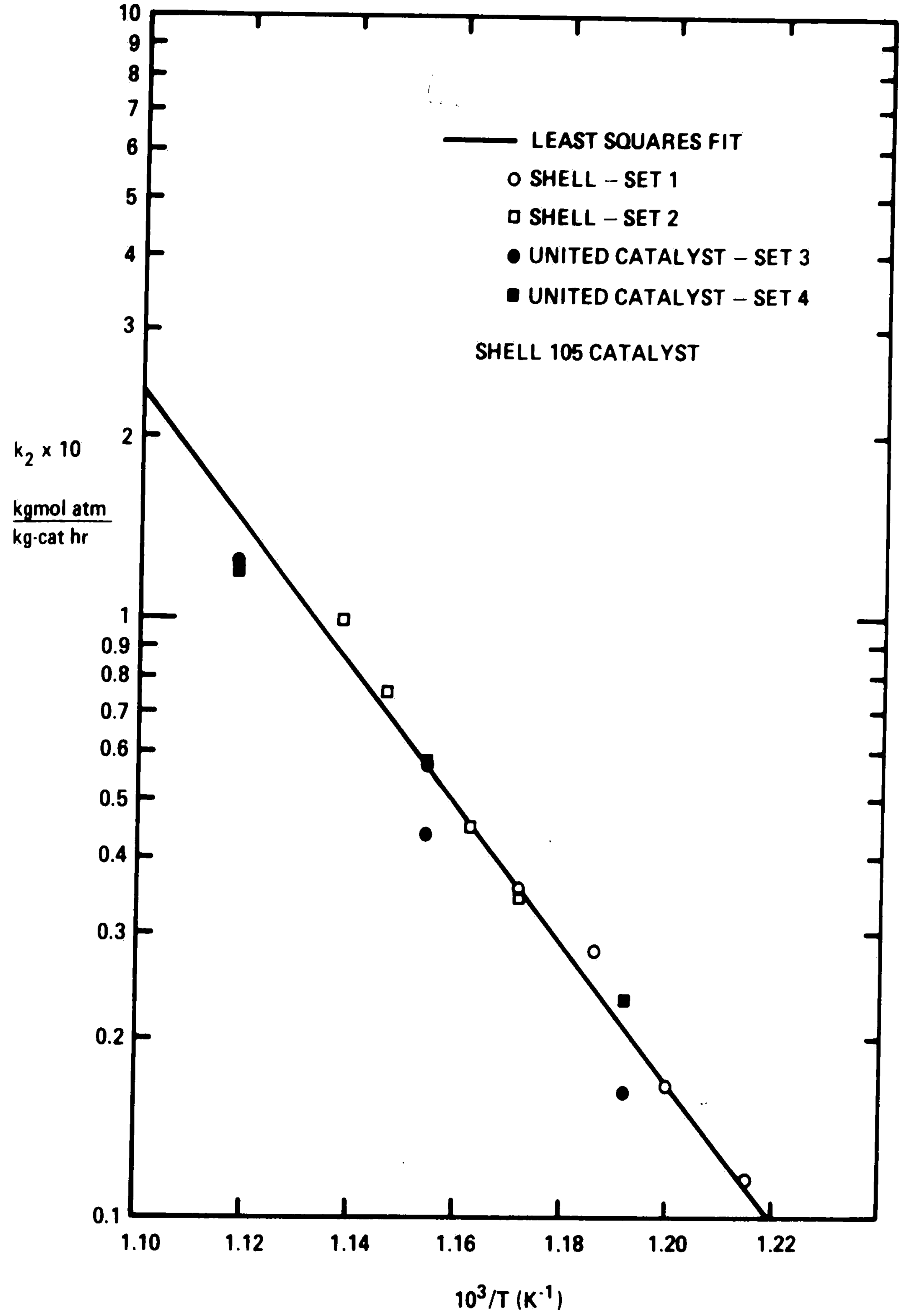

Figure 18 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MODIFIED TOLUENE FORMATION REACTION OF MODEL 3

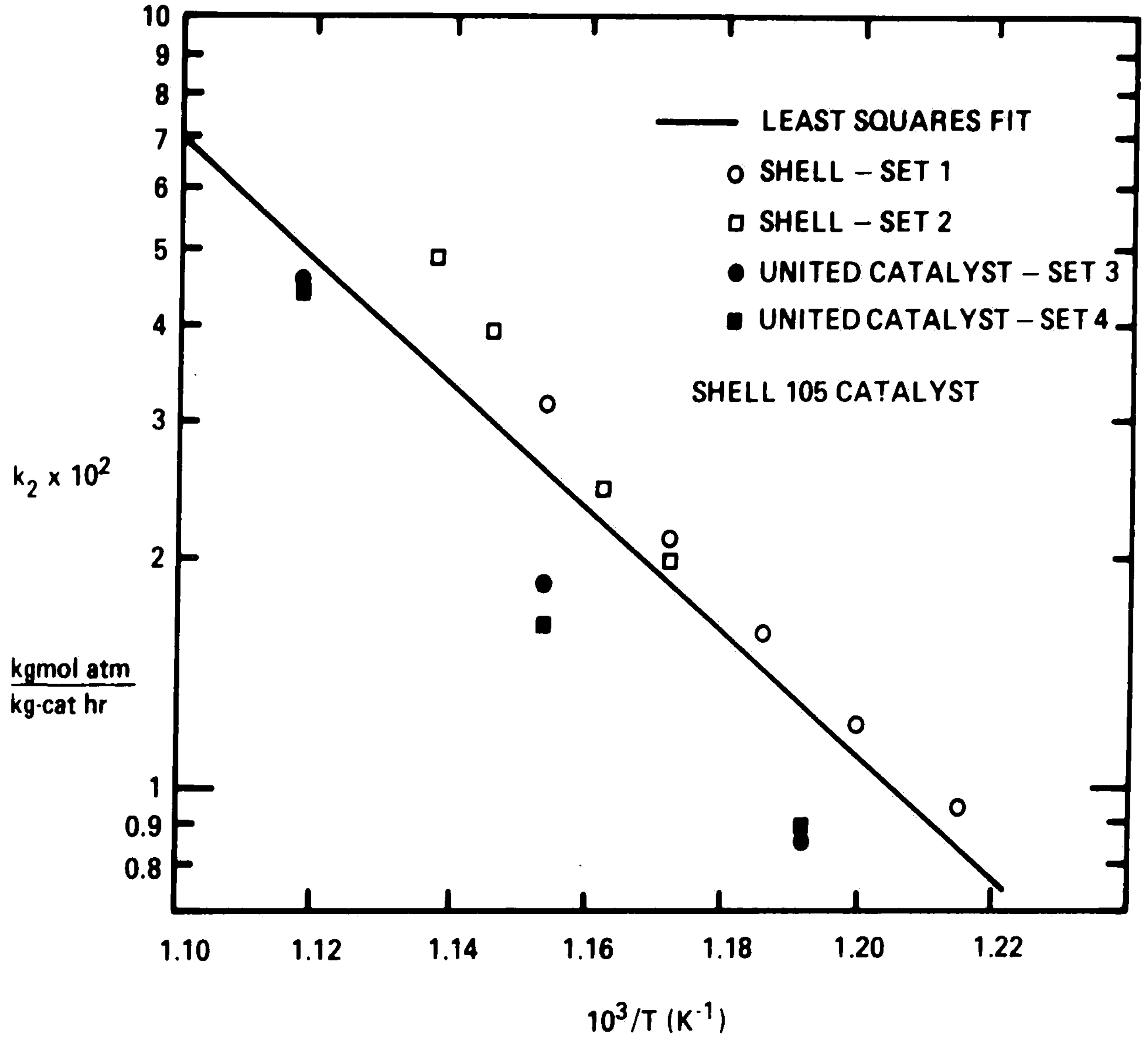

Figure 19 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE BENZENE FORMATION REACTION OF MODEL 3

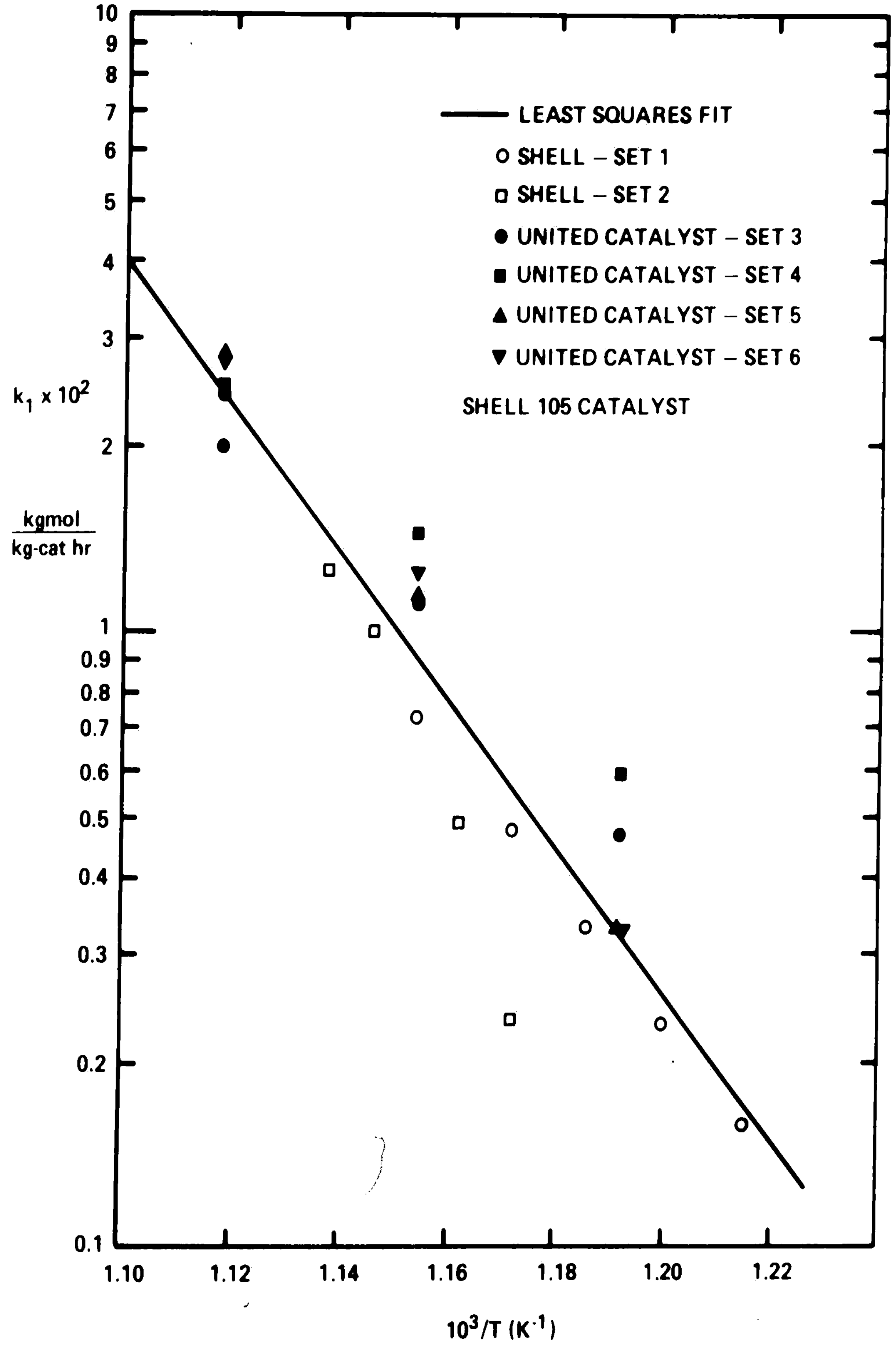

Figure 20 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 4 WITH A RELATIVE ADSORPTION CONSTANT OF 10

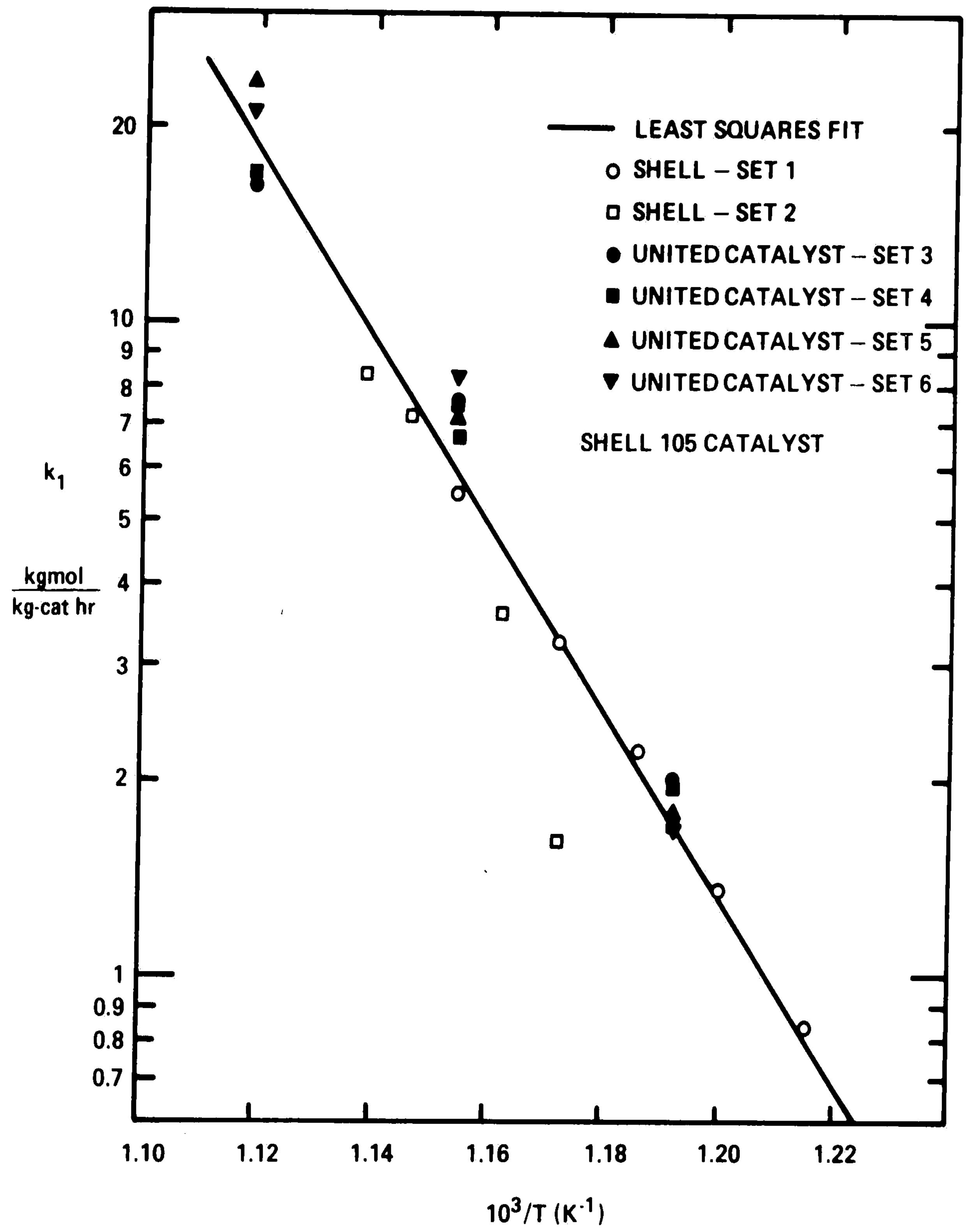

Figure 21 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 4 WITH A RELATIVE ADSORPTION CONSTANT OF 280

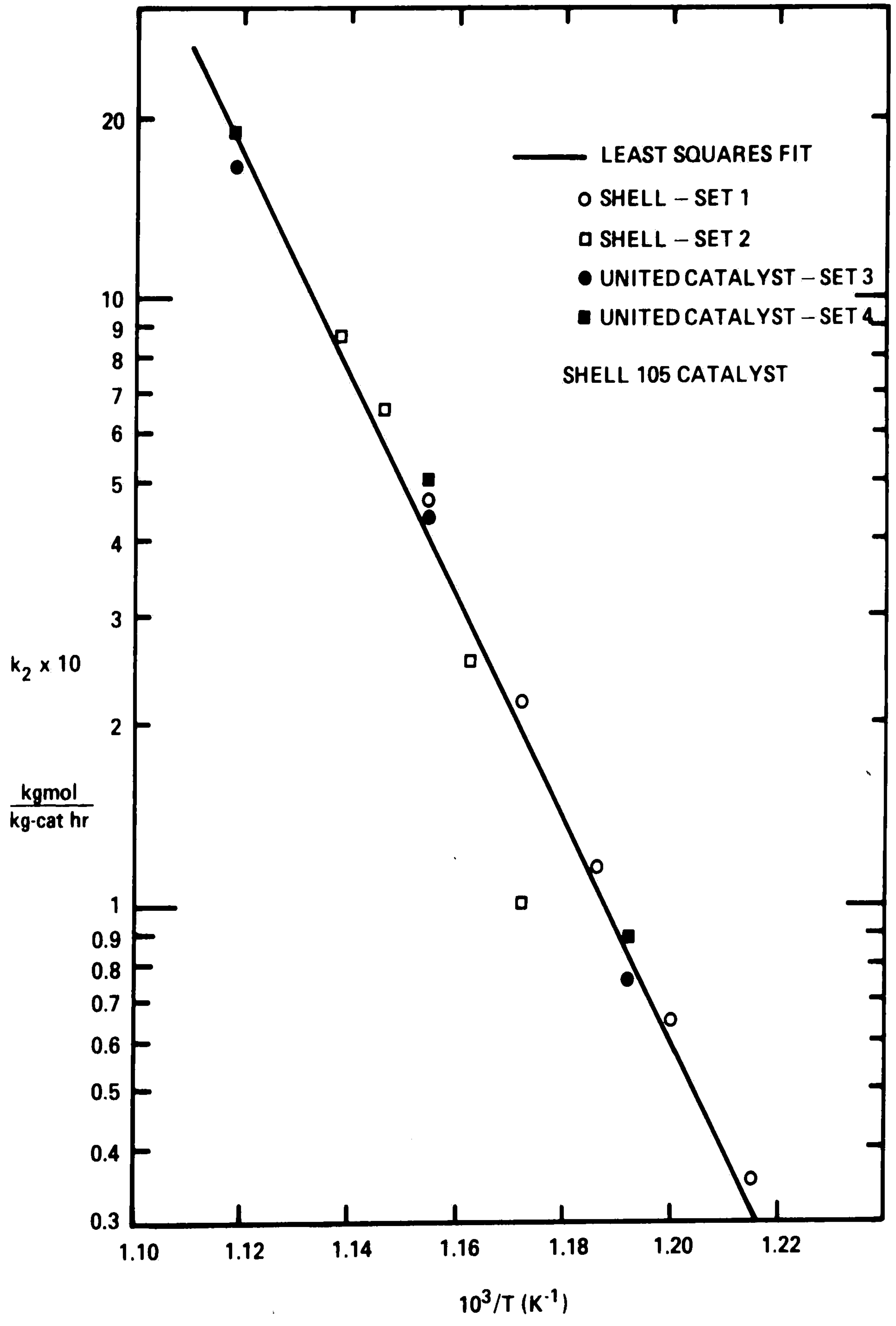

Figure 22 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE TOLUENE FORMATION REACTION WITH A RELATIVE ADSORPTION CONSTANT OF 280

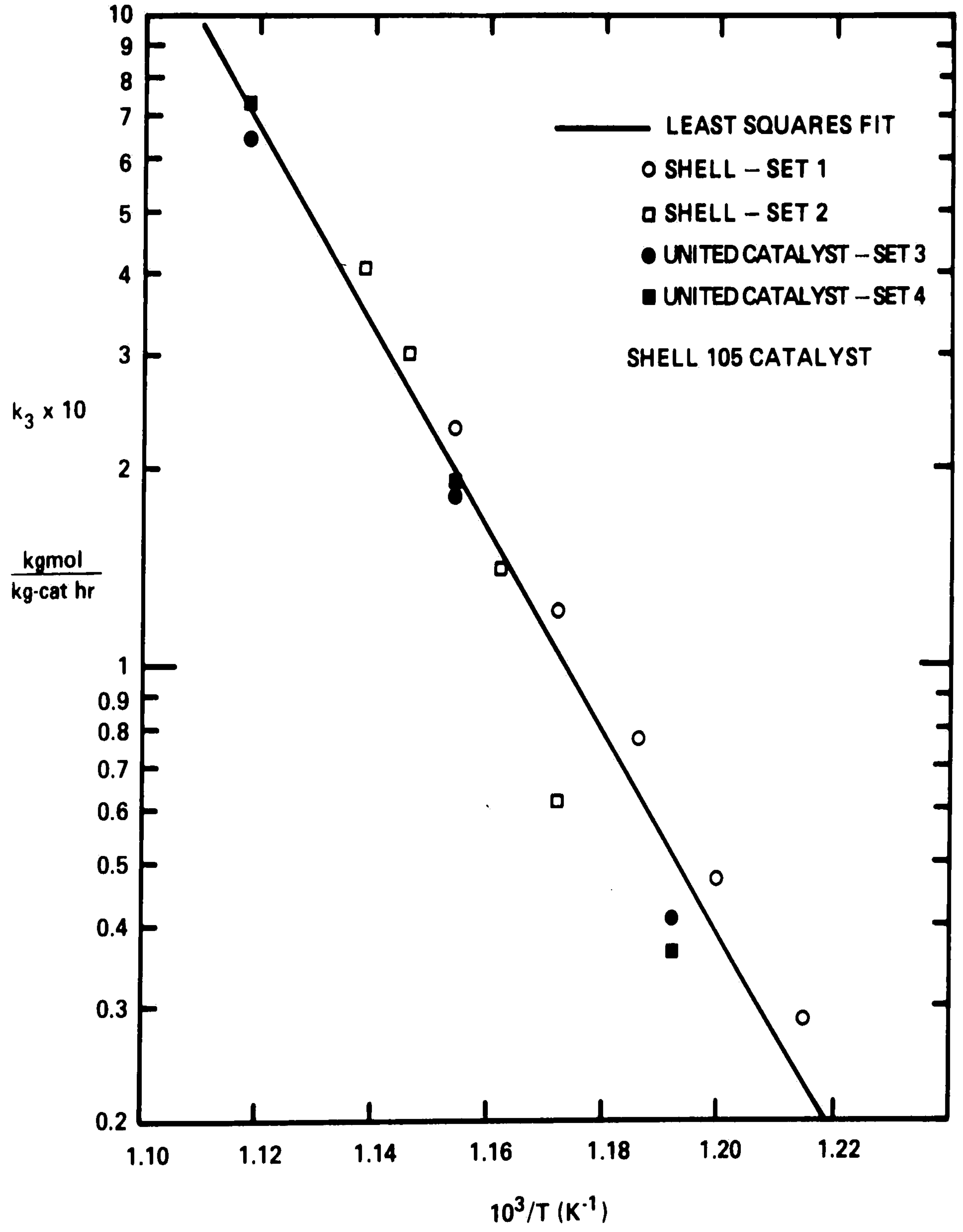

Figure 23 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE BENZENE FORMATION REACTION OF MODEL 4 WITH A RELATIVE ADSORPTION CONSTANT OF 280

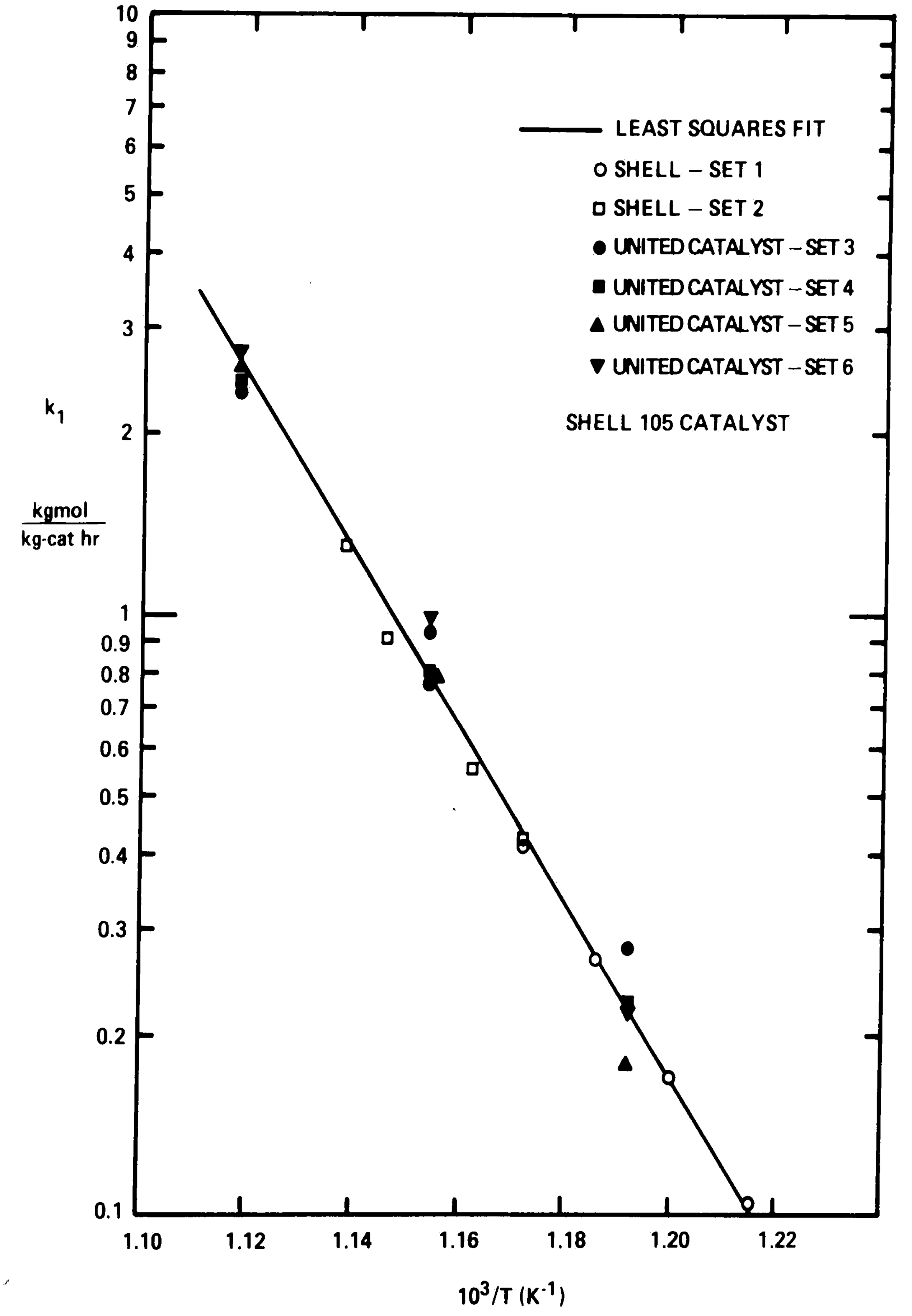

Figure 24 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 5

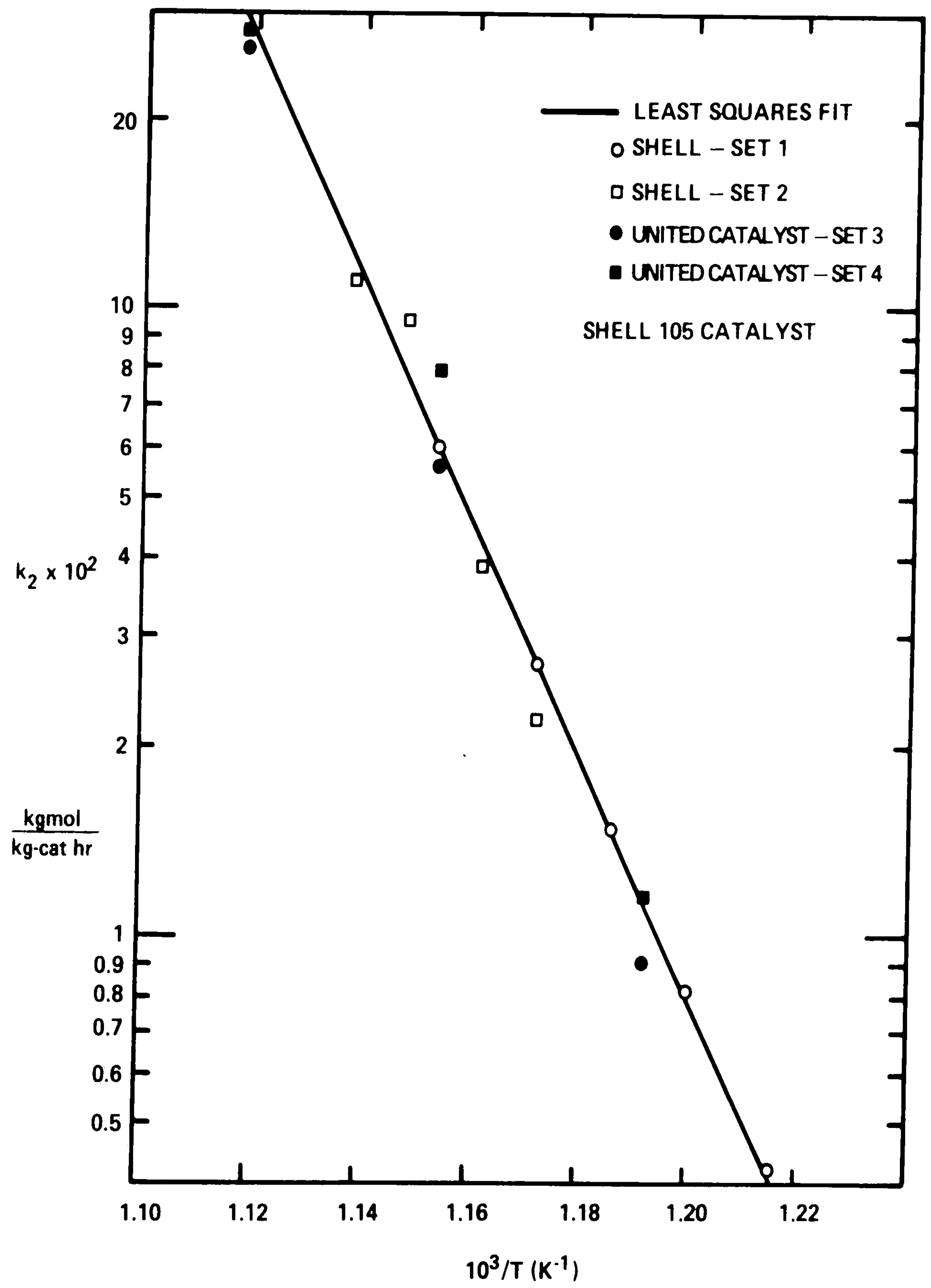

Figure 25 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE TOLUENE FORMATION REACTION FOR MODEL 5

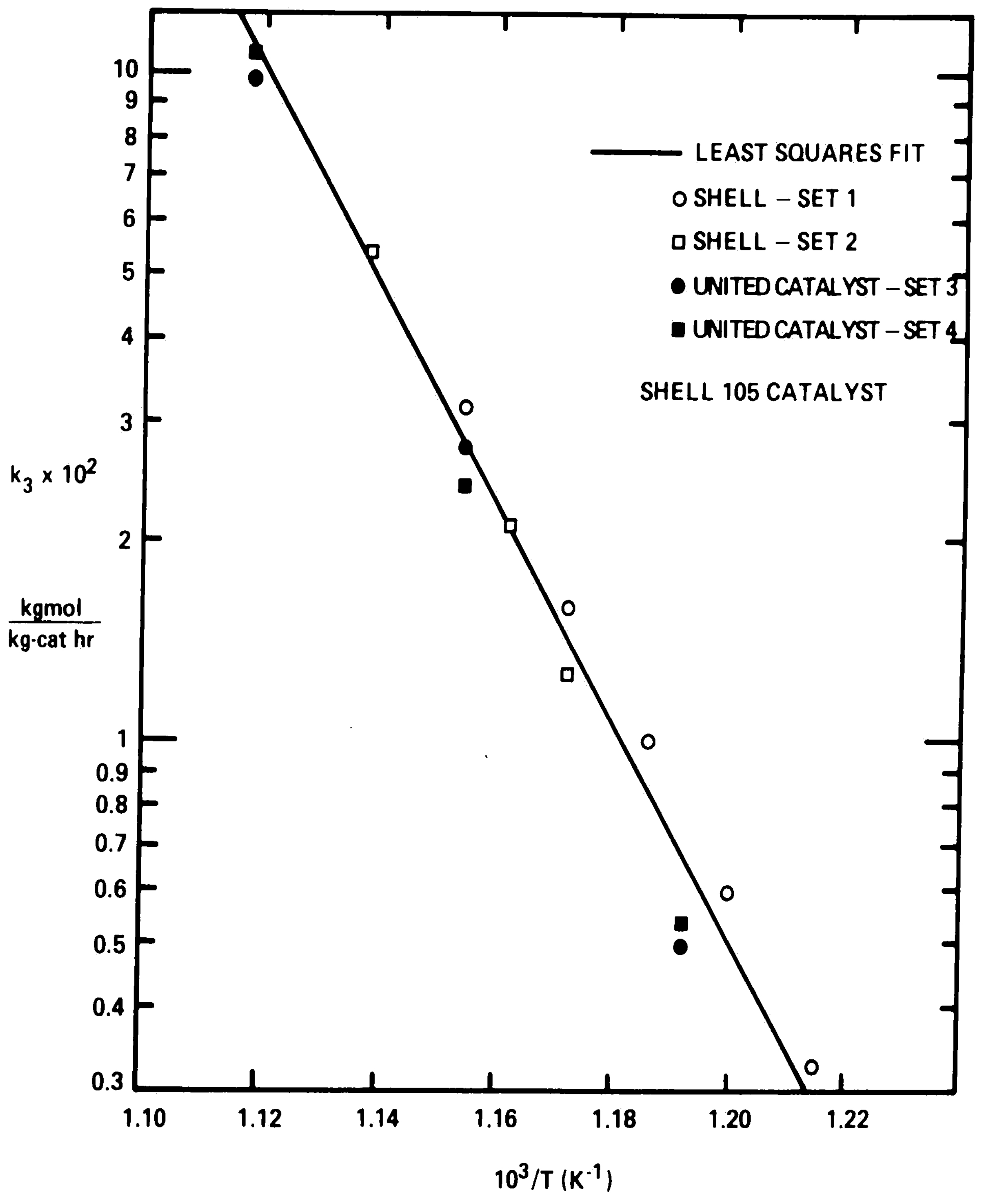

Figure 26 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE BENZENE FORMATION REACTION OF MODEL 5

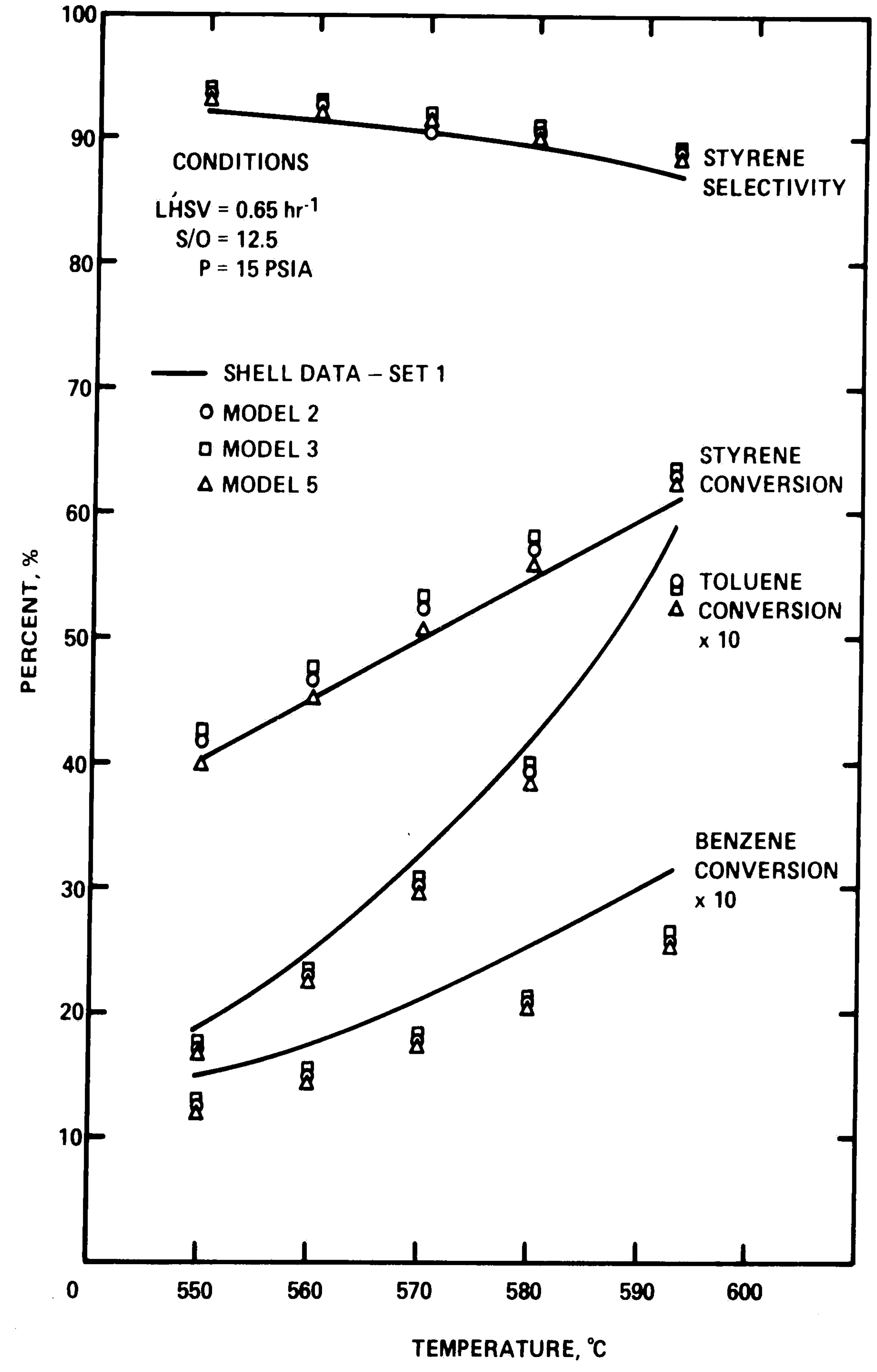

Figure 27 COMPARISON OF MODELS 2, 3 & 5 AND SHELL CONVERSION DATA FOR SHELL 105 CATALYST

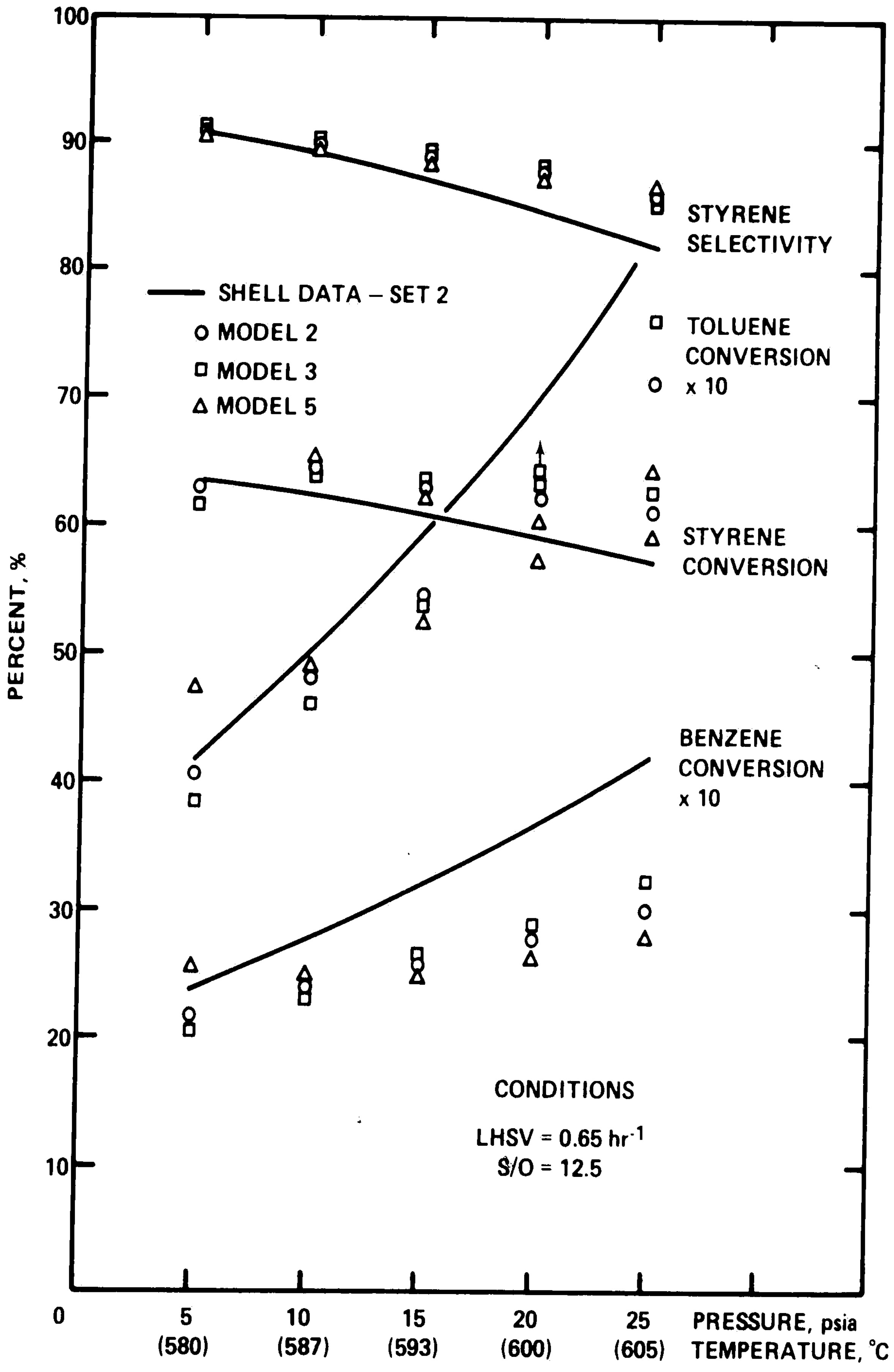

Figure 28 COMPARISON OF MODELS 2, 3 & 5 AND SHELL VARIABLE PRESSURE CONVERSION DATA FOR SHELL 105 CATALYST

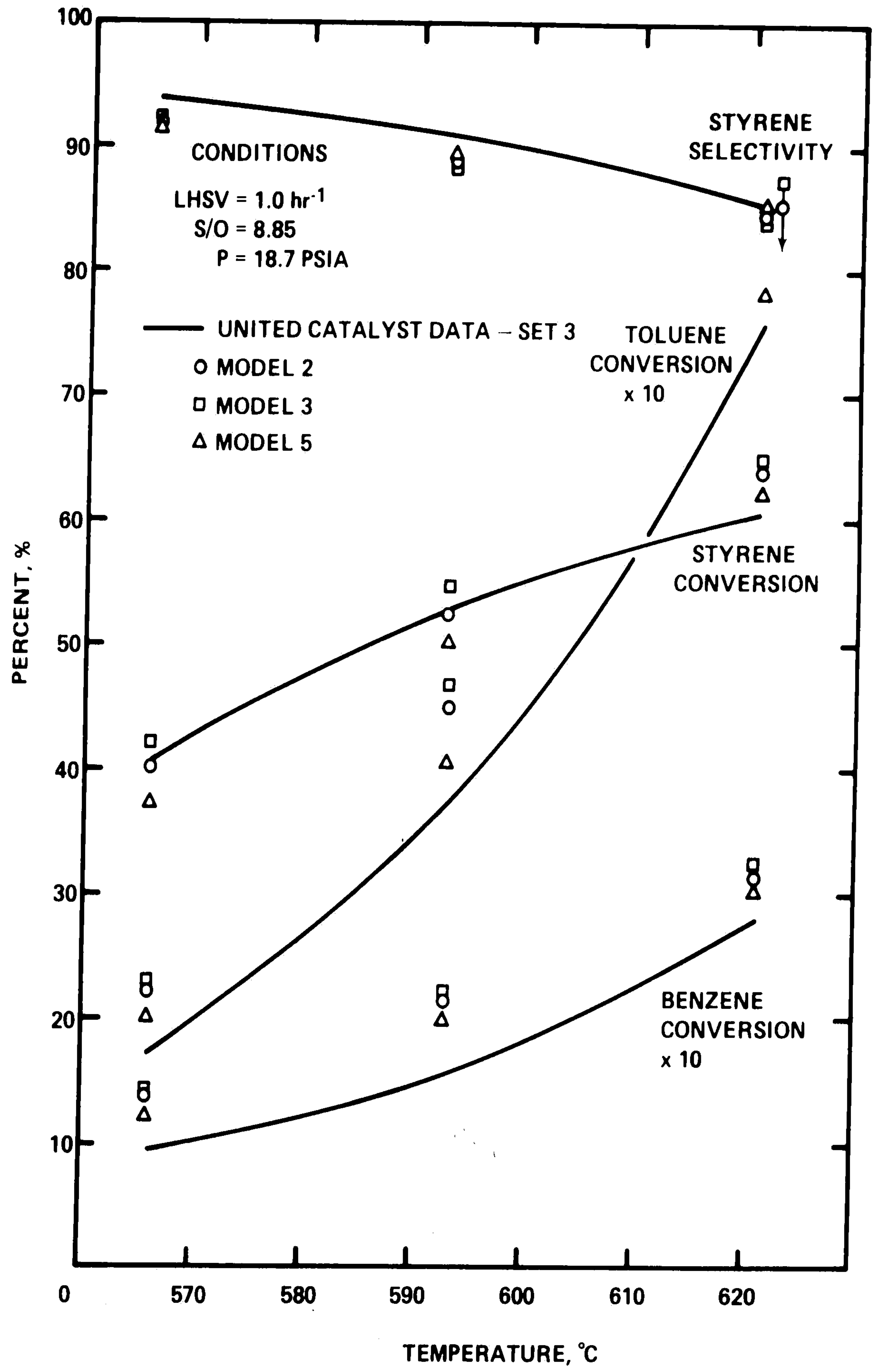

Figure 29 COMPARISON OF MODELS 2, 3 & 5 AND UNITED CATALYST CONVERSION DATA FOR SHELL 105 CATALYST

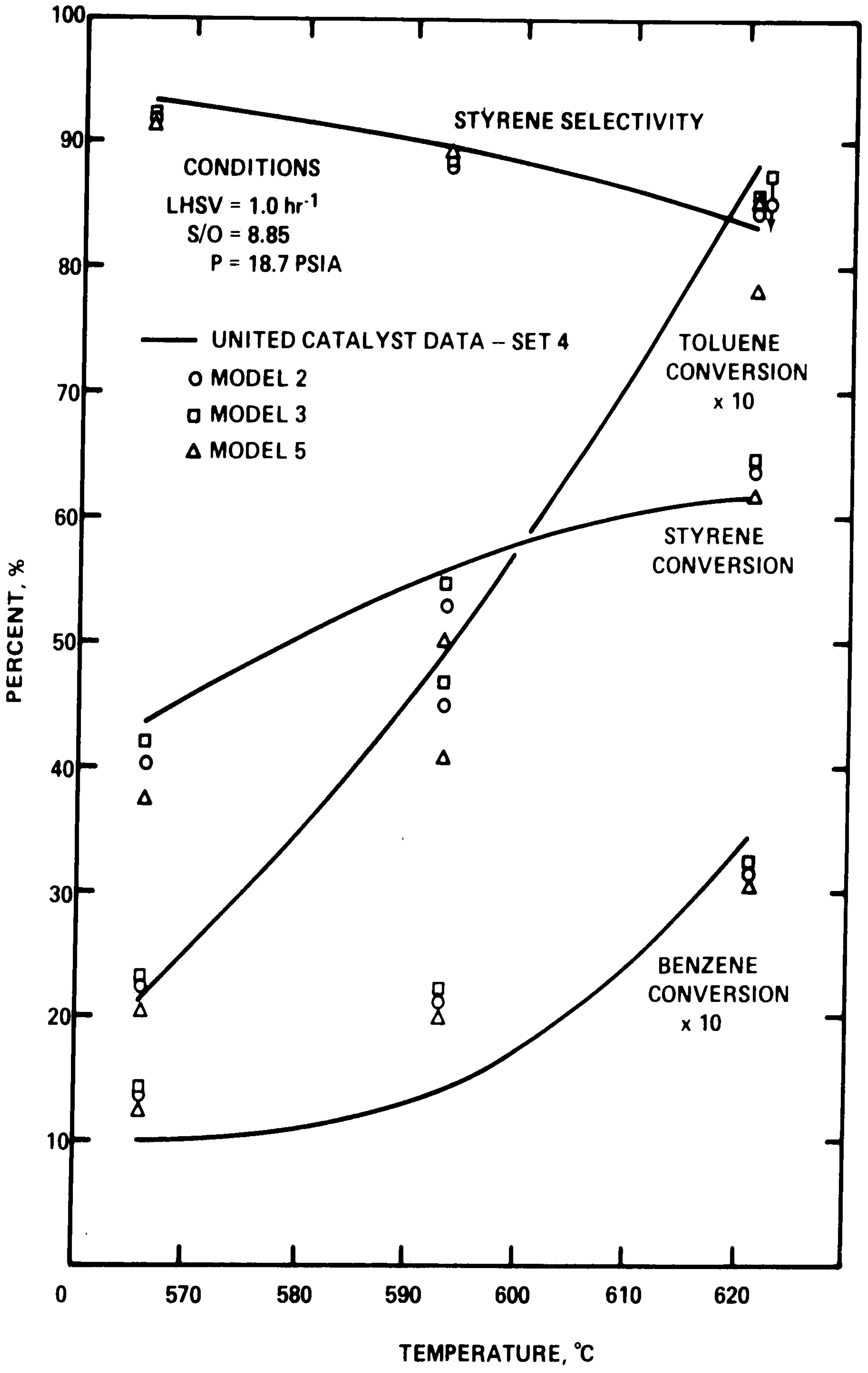

Figure 30 COMPARISON OF MODELS 2, 3 & 5 AND UNITED CATALYST CONVERSION DATA FOR SHELL 105 CATALYST

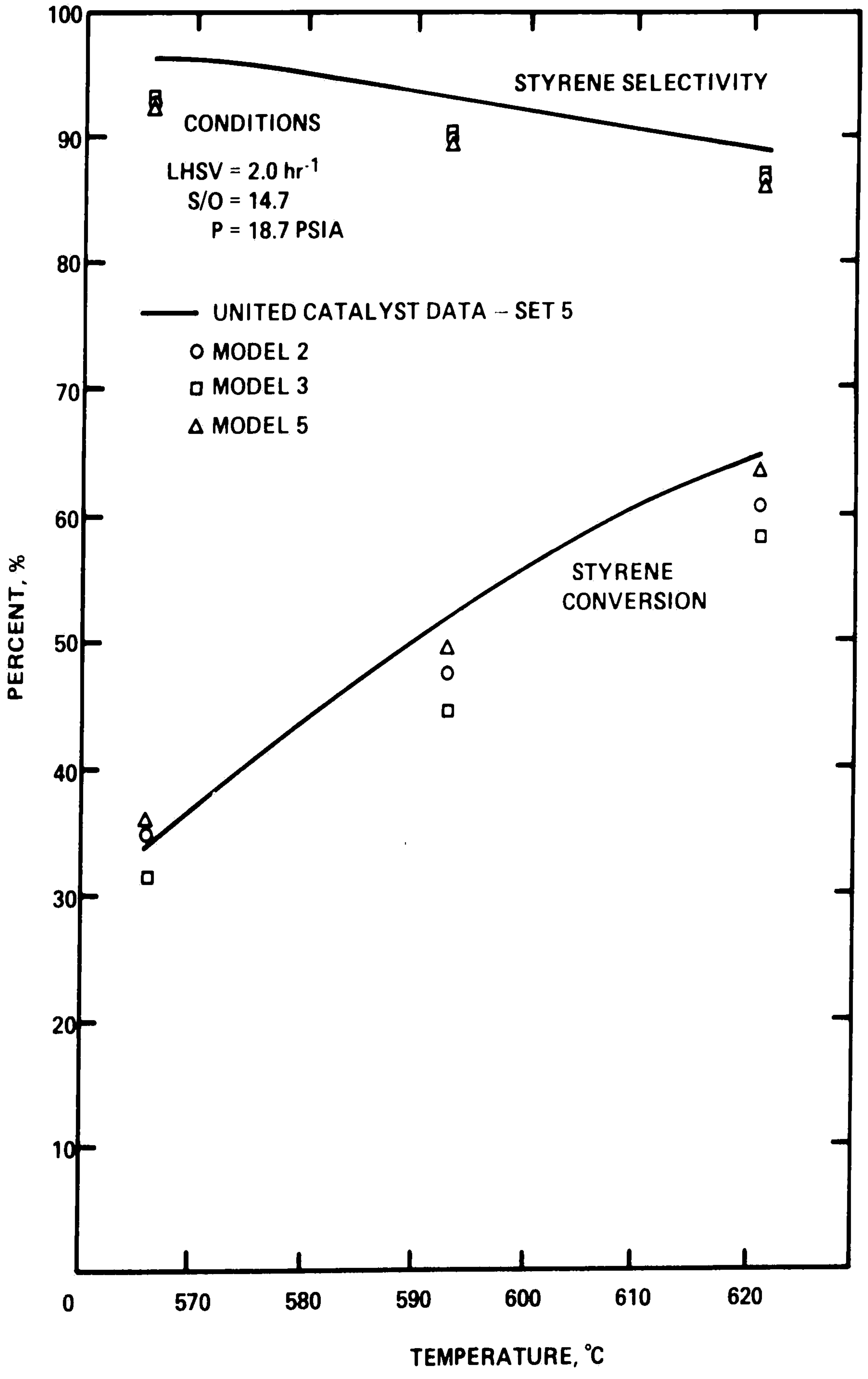

Figure 31 COMPARISON OF MODELS 2, 3 & 5 AND UNITED CATALYST CONVERSION DATA FOR SHELL 105 CATALYST

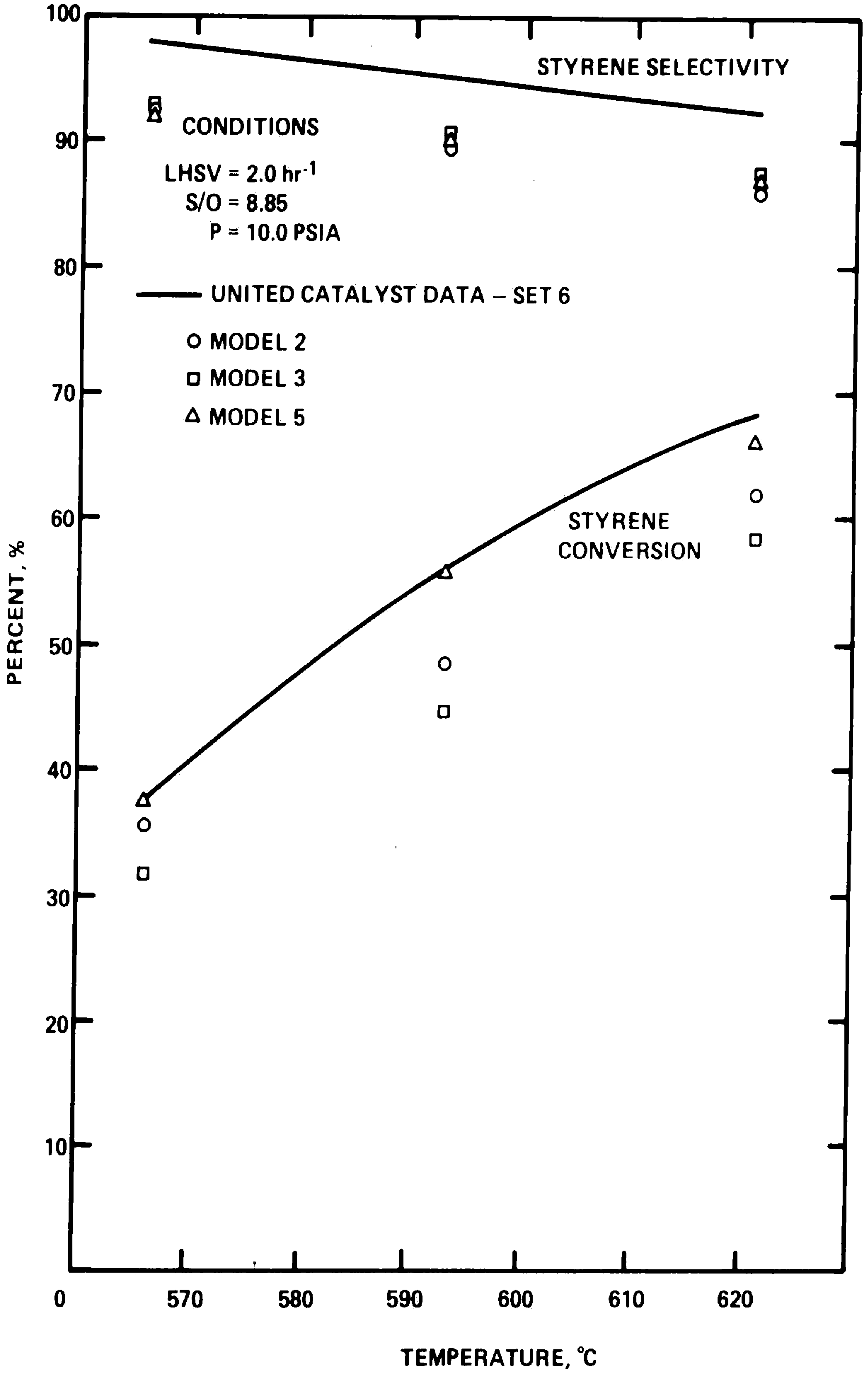

Figure 32 COMPARISON OF MODELS 2, 3 & 5 AND UNITED CATALYST CONVERSION DATA FOR SHELL 105 CATALYST

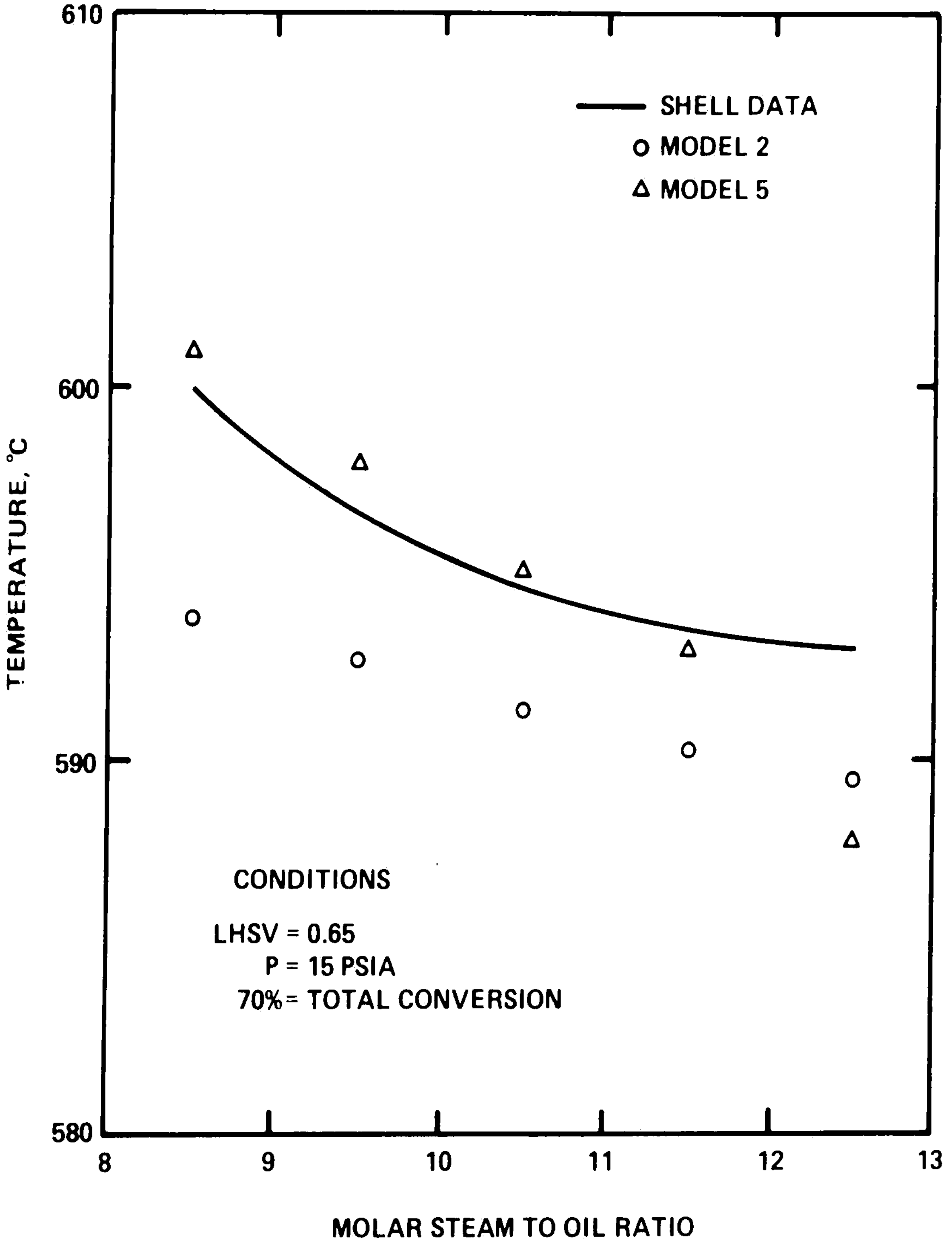

Figure 33 COMPARISON OF MODELS 2 & 5 WITH SHELL VARIABLE STEAM TO OIL RATIO DATA FOR SHELL 105 CATALYST

Final Version of the Model

Tables IX and X summarize the kinetic expressions investigated and the best calibrated kinetics for each of these models. Model 5 is the best model for Shell 105 catalyst investigated to date. It predicts the manufacturer's styrene conversion data within an average of 2.3 percentage points (±5% relative). It does a better job of correlating the data than Carrá's or Lebedev's models. It is less complicated than Lebedev's. Also, its theoretical basis (i.e., Langmuir-Hinshelwood mechanism) agrees at low styrene concentrations with Carrá's observation that the initial rate is independent of the partial pressure of ethylbenzene and with Lebedev's observation that the inhibitor is approximately proportional to the partial pressure of styrene squared.

Model 5 is also compared to manufacturers' data unused in its calibration. Figure 33 shows Shell's 70% total conversion data at different steam-to-oil ratios. Results of Model 2 are also included. Notice that although the shape of Model 2's curve is better than Model 5's, Model 5 does a better job in an absolute sense of predicting the data.

Since the form of Model 5 was suitable for predicting Shell 105 catalyst behavior, it was used for calibrating a kinetic model for Shell 015 catalyst. This is Model 6. Nineteen sets of catalyst manufacturers' performance test data were available, see Table XI. The styrene conversion was calibrated within 2% absolute (4% relative), see Table VII. The correlation coefficient (whose value is in question as discussed) is given in Table VI. See Figures 34 through 36 for the Arrhenius plots and Figures 37 through 42 for a comparison of the model and manufacturers' data.

Table IX

Summary of Five Kinetic Models Investigated

		Driving Force for the Reaction Generation			
Model	Inhibitor	Styrene	Toluene	Benzene	Ref.
1 (Wenner)	None	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	$P_{EB} P_{H_2}$	P_{EB}	4-6
2 (Carrá)	$P_{EB} + z P_{STY}$	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	P_{EB}	P_{EB}	7
3 (Lebedev)	$(1 + b P_{STY})^2$	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	$P_{EB} P_{H_2}$	P_{EB}	8
4	$(P_{EB} + z P_{STY})^2$	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	P_{EB}	P_{EB}	
5	$P_{EB} + (yP_{STY})^2$	$P_{EB} - \frac{P_{STY} P_{H_2}}{K_{eq}}$	P_{EB}	P_{EB}	

$$r_j = k_j \frac{\text{Driving Force}}{\text{Inhibitor}}$$

where

r_j = rate of reaction j

k_j = rate constant of reaction j

z = the relative absorption coefficient between styrene and ethylbenzene

b = the absorption coefficient of styrene
= $b_o \exp(\lambda/T)$

y = the combined adsorption coefficient

Table X

Kinetic Constants for the Calibrated Models

The form of the kinetic constants is

$$k_j = \exp\ (A_j - Ea_j/R_G T)$$

where

k_j = kinetic constant, kgmol/kgcat-hr
A_j = frequency factor
Ea_j = activation energy, kcal/mol
R_G = ideal gas constant, 1.987 cal/mol °K
T = absolute temperature, °K

The form of the inhibitors all listed in Table IX.

Model	Styrene		Toluene		Benzene		Notes
	A	Ea	A	Ea	A	Ea	
1[1]	11.48	24.08	16.58	31.25	13.19	33.21	
2	18.31	38.21	20.62	46.77	18.87	45.16	z = 8.03
2[2]	22.75	45.8	25.75	54.92	16.54	41.10	z = 8.02
3	17.50	30.61	9.05	14.42	16.02	34.05	$b_o = 0.0218\ atm^{-1}$ $\lambda = 6995$°K
3[3]	17.2	30.18	26.93	51.41	18.28	37.80	$b_o = 0.0218\ atm^{-1}$ $\lambda = 6995$°K
4	27.02	54.59	35.42	73.60	26.97	60.34	z = 10.0
4	39.43	64.82	48.80	85.44	39.73	71.11	z = 280
5	38.05	65.93	47.93	87.40	39.94	74.91	y = 100
6[4]	42.33	74.52	61.4	115.51	61.6	114.35	y = 100

1) United Catalyst Set 4 not included in the fit.
2) Carrá's activation energy used for main reaction.
3) Modified Model 3 - toluene-formation reaction's driving force = P_{EB}.
4) Calibrated for Shell 015.

Table XI

Manufacturers' Performance Test Data for Shell 015 (Ref. 10 & 11)

No.	Data Set	Temperature, °C	Pressure, atm	Molar Steam-to-Oil Ratio	Conversion, % Styrene*	Conversion, % Toluene	Conversion, % Benzene	Styrene Selectivity, %
1	7**	570	1.0	12.5	44.86	1.06	0.32	97.0
2		580	1.0	12.5	50.71	1.34	0.39	96.6
3		590	1.0	12.5	56.46	1.67	0.44	96.1
4		600	1.0	12.5	62.11	2.11	0.54	95.6
5		610	1.0	12.5	67.54	2.64	0.93	94.8
6	8**	594	0.34	12.5	67.90	1.40	0.70	97.0
7		601	0.68	12.5	67.41	1.96	0.80	96.3
8		608	1.00	12.5	66.64	2.52	0.90	95.2
9		615	1.36	12.5	65.73	3.22	1.03	93.9
10		622	1.70	12.5	64.75	4.06	1.19	92.5
11	9†	566	1.27	8.85	27.83	0.14	0.03	99.4
12		573	1.27	8.85	46.60	0.91	0.19	97.7
13		621	1.27	8.85	61.06	2.18	0.57	95.7
14	10	566	1.27	14.7	25.30	0.00	0.00	99.9
15		593	1.27	14.7	42.10	--	--	99.3
16		621	1.27	14.7	58.73	--	--	97.7
17	11	566	0.68	8.85	24.60	0.00	0.00	99.9
18		593	0.68	8.85	41.19	--	--	99.5
19		621	0.68	8.85	55.89	--	--	98.4

* Calculated from total conversion and styrene selectivity.

** Selected points from graphs.

† Toluene and benzene conversions calculated from benzene/toluene (B/T) ratio.

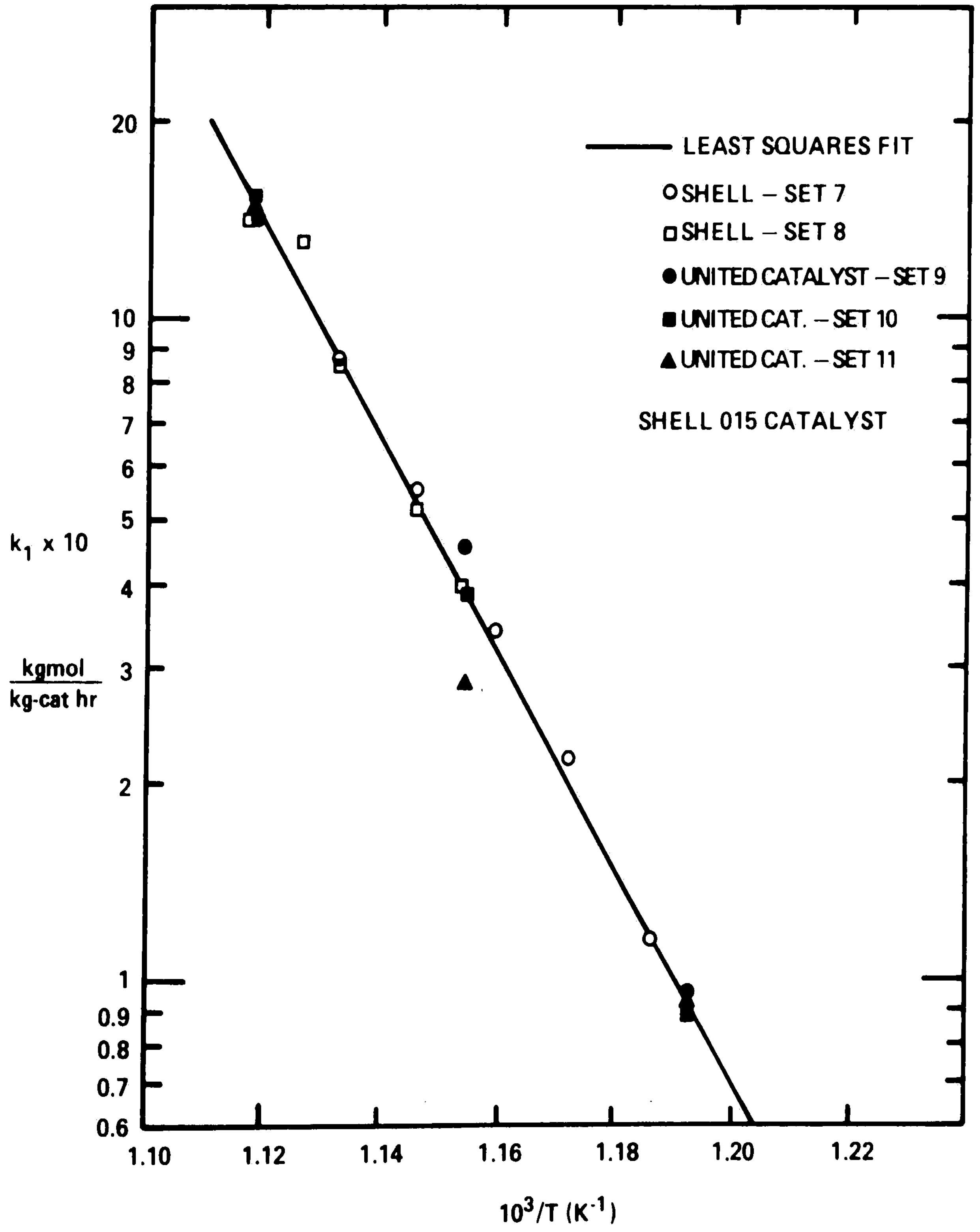

Figure 34 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE MAIN REACTION OF MODEL 6

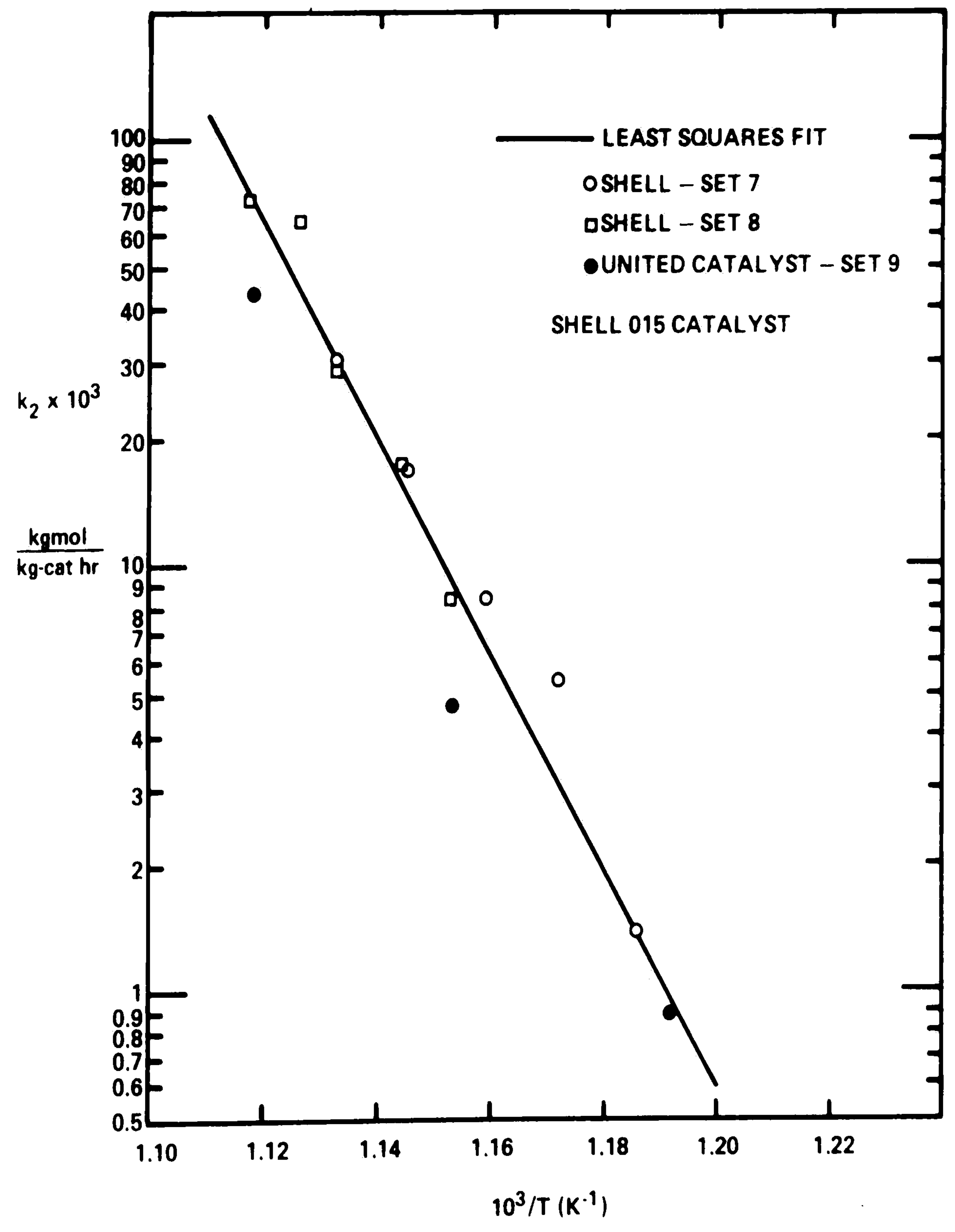

Figure 35 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE TOLUENE FORMATION REACTION OF MODEL 6

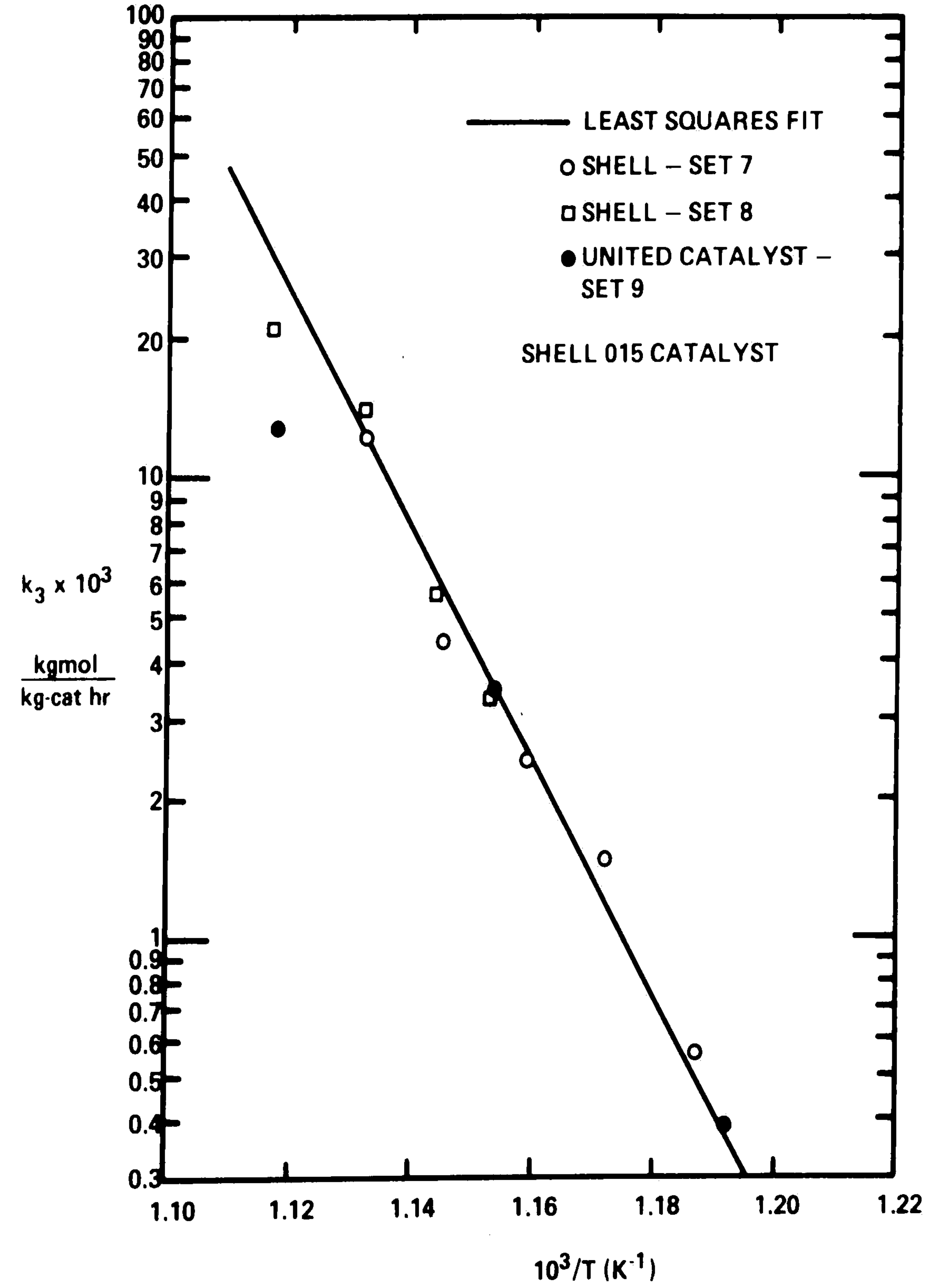

Figure 36 ARRHENIUS PLOT OF THE APPARENT REACTION RATE CONSTANTS FOR THE BENZENE FORMATION REACTION OF MODEL 6

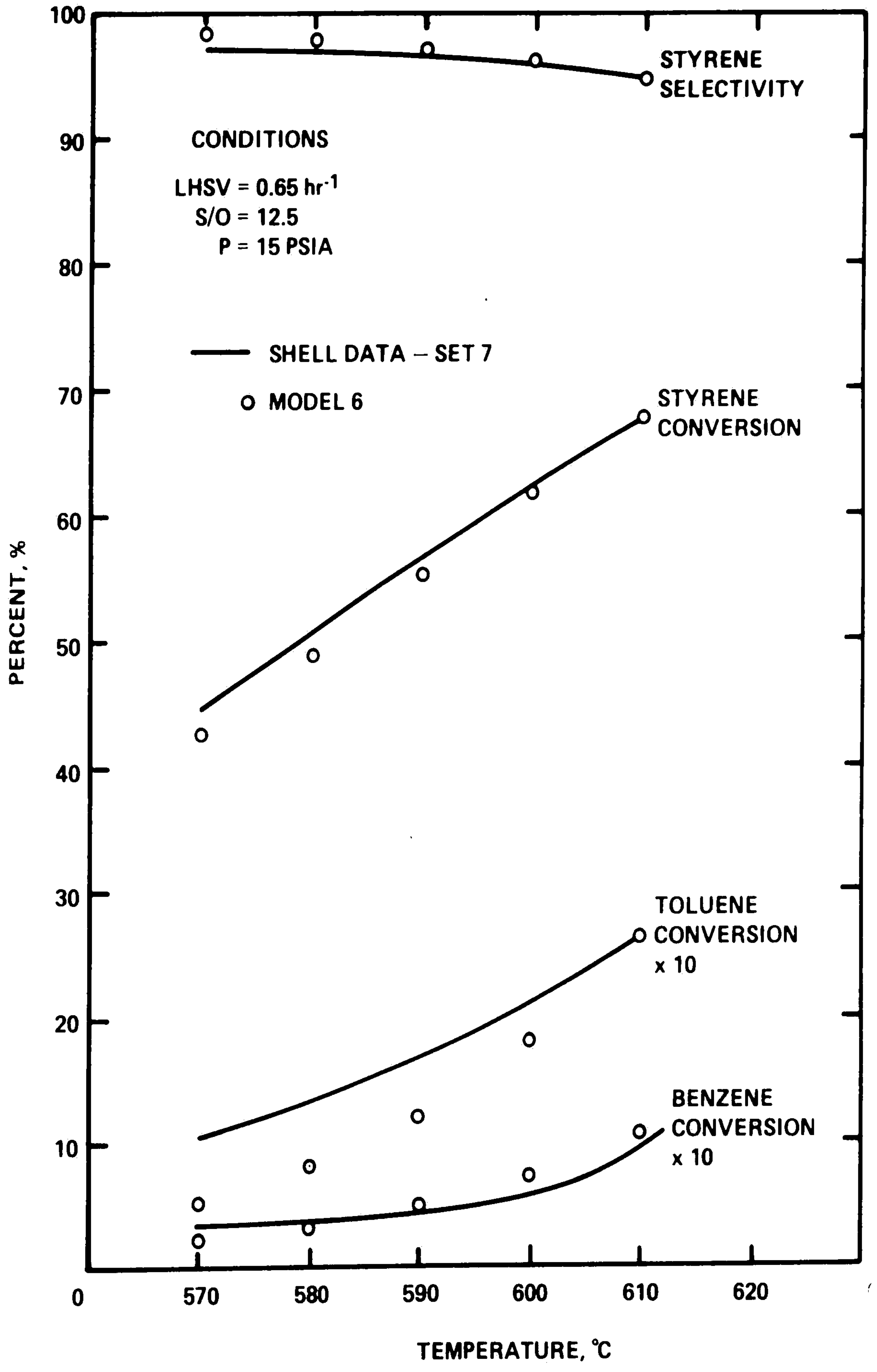

Figure 37 COMPARISON OF MODEL 6 AND SHELL CONVERSION DATA FOR SHELL 015 CATALYST

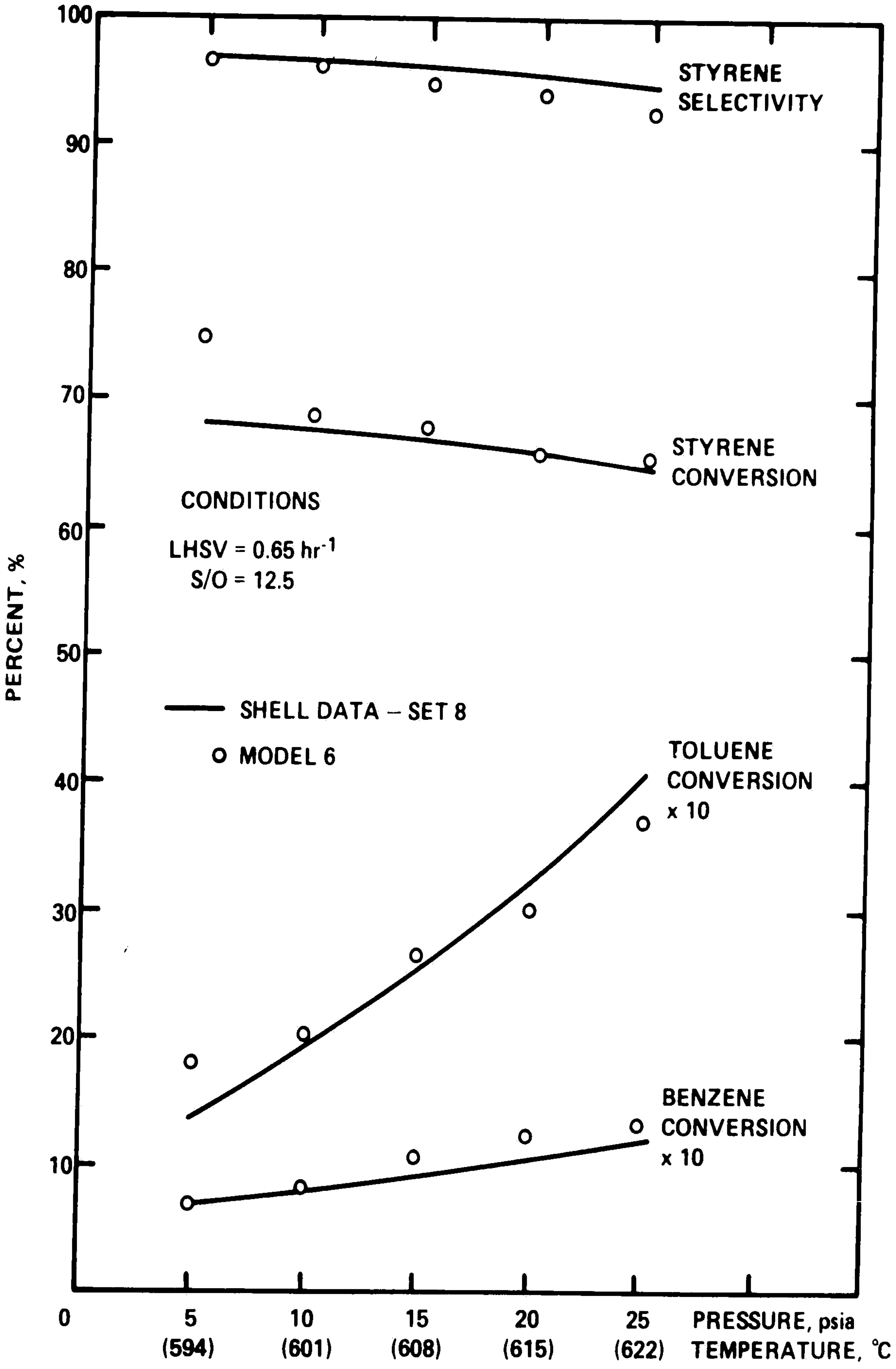

Figure 38 COMPARISON OF MODEL 6 AND SHELL CONVERSION DATA FOR SHELL 015 CATALYST VARIABLE PRESSURE

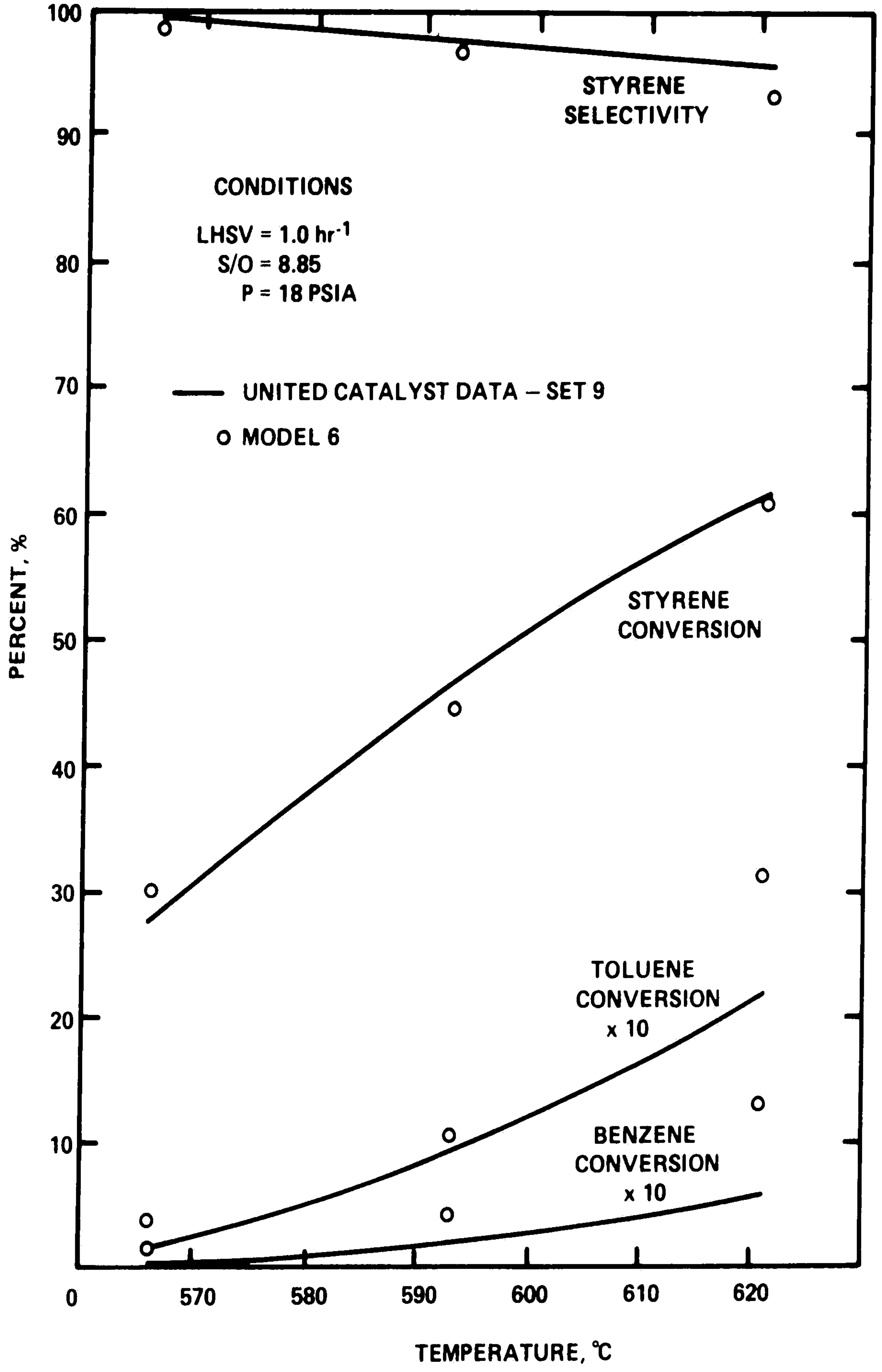

Figure 39 COMPARISON OF MODEL 6 AND SHELL CONVERSION DATA FOR SHELL 015 CATALYST

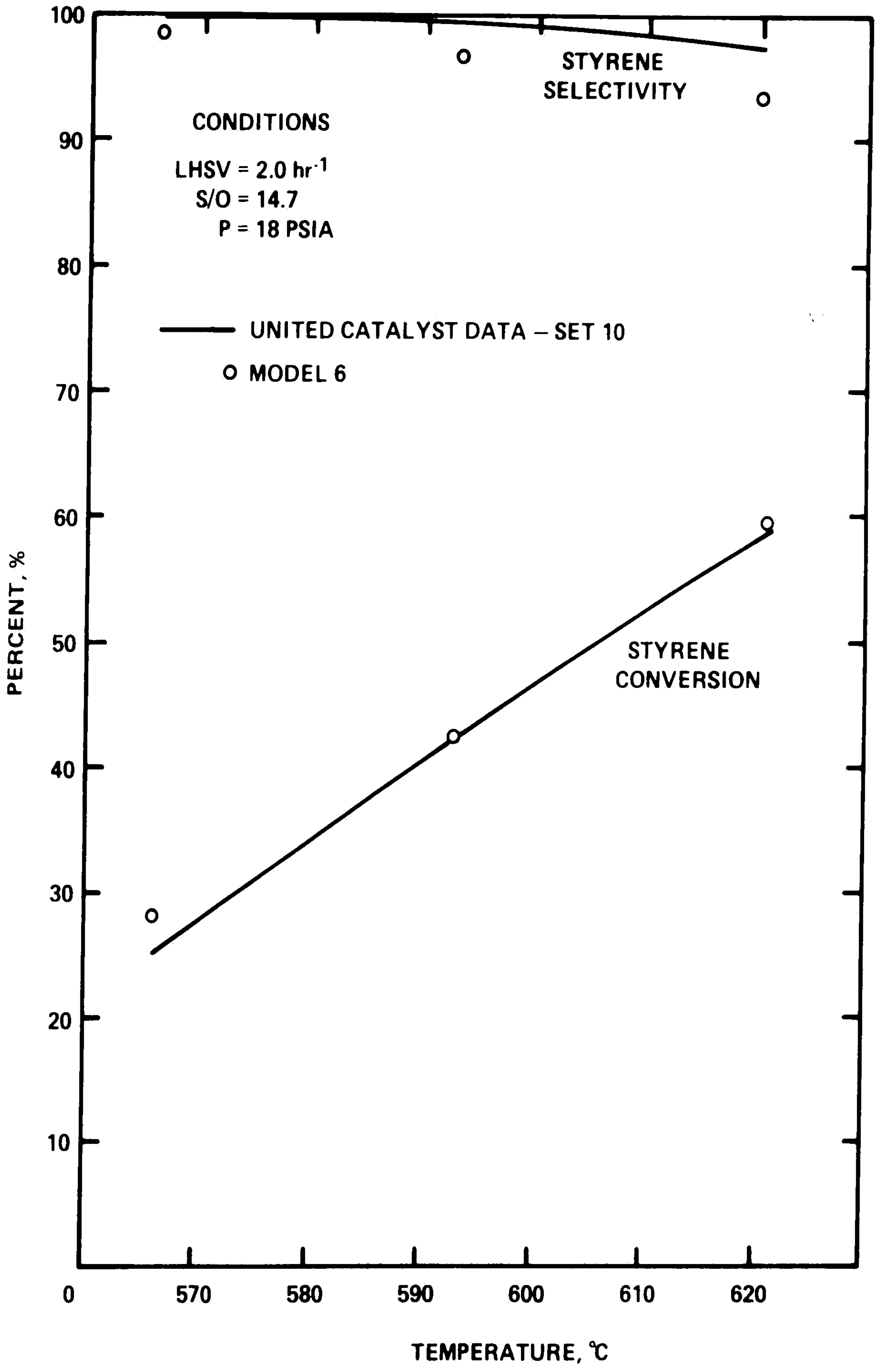

Figure 40 COMPARISON OF MODEL 6 AND UNITED CATALYST CONVERSION DATA FOR SHELL 015 CATALYST

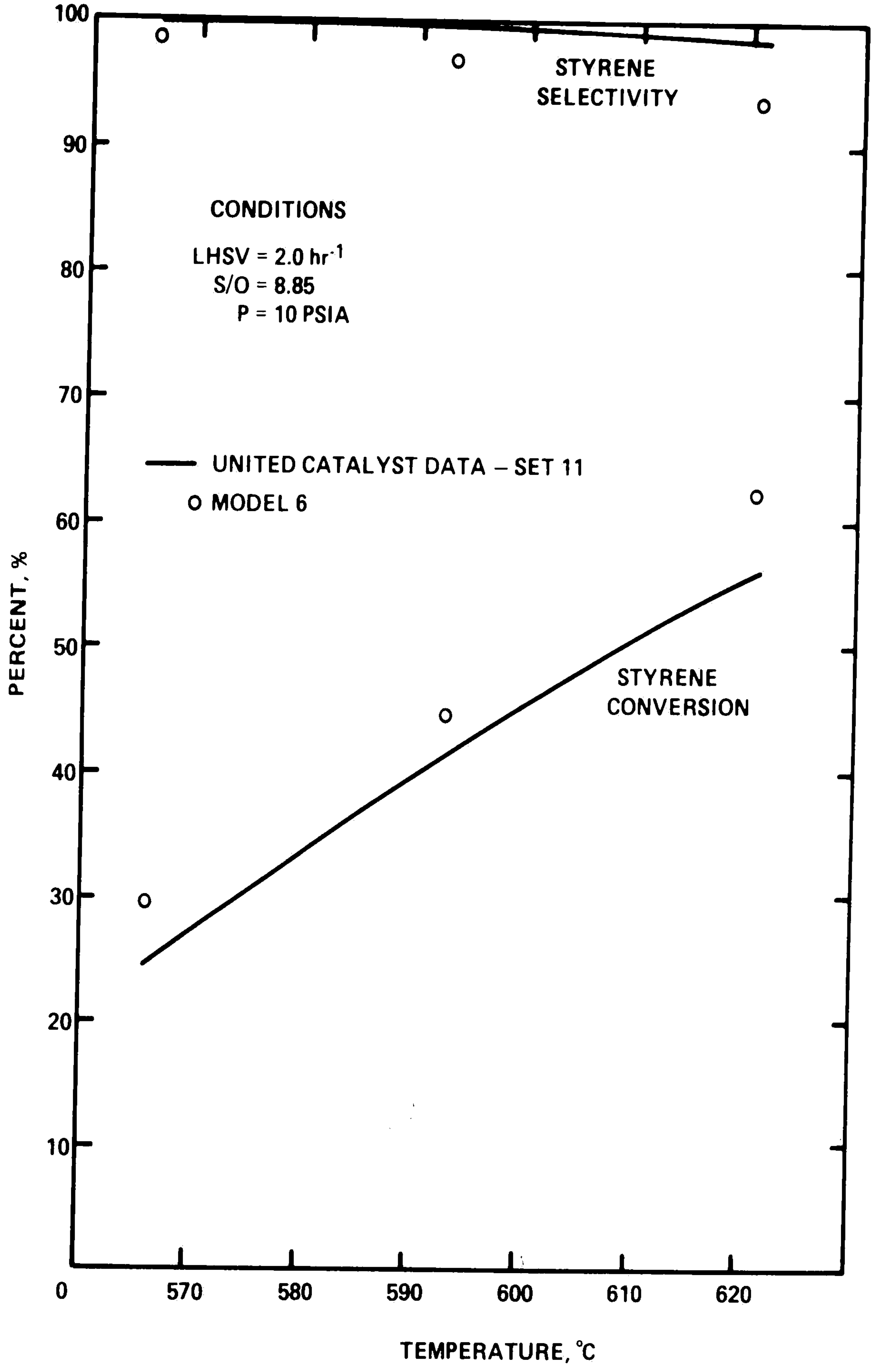

Figure 41 COMPARISON OF MODEL 6 AND UNITED CATALYST DATA FOR SHELL 015 CATALYST

Description of Diffusion Model

Previous reports indicate that the reaction may be subject to considerable diffusion limitations. An effort is presented here to evaluate the effectiveness factor (η) for the catalyst particles at reactor conditions. A critical element for these calculations is the value of the effective diffusivity, and details of its calculation are given in Appendix J.

The general form of the main reaction rate expression is

$$r_{EB} = \frac{k_1 \left[P_{EB} - P_{STY} P_{H_2}/K_{eq} \right]}{\text{Inhibitor}} \qquad (31)$$

where Table IX can be consulted for the various inhibitors. The steady state conservation equations for ethylbenzene, styrene, and hydrogen are

$$r_{EB} = \frac{-D_{EB}}{R_G T} \frac{d^2 P_{EB}}{dZ^2} \qquad (32)$$

$$r_{EB} = \frac{D_{STY}}{R_G T} \frac{d^2 P_{STY}}{dZ^2} \qquad (33)$$

$$r_{EB} = \frac{D_{H_2}}{R_G T} \frac{d^2 P_{H_2}}{dZ^2} \qquad (34)$$

The boundary conditions for these equations are

$$P_i/_{\text{Surface}} = P_i^s \qquad i = \text{EB, STY, } H_2 \tag{35}$$

$$\left.\frac{dP_i}{dZ}\right|_{\substack{\text{Particle}\\ \text{Center}}} = 0 \tag{36}$$

It is convenient to define the pore conversion (x_p)

$$X_p\ (Z) = 1 - \frac{P_{EB}/_Z}{P_{EB}/_{\text{Surface}}} \tag{37}$$

Thus $$P_{EB}/_Z = (1 - X_p)\ P_{EB}/_{\text{Surface}} \tag{38}$$

Using the boundary conditions and equating Equations 32-34, the partial pressure of styrene and hydrogen can be written as a function of pore conversion. It is possible to reduce the problem to a single second order differential equation in terms of the pore conversion. This may be solved using the same boundary conditions. Details of this entire derivation are given in Appendix G. One obtains:

$$\eta = \frac{\sqrt{2\int_o^{X_o} H(X_p)dX_p}}{\phi\ H(X_p)\big|_{X_p = 0}} \tag{39}$$

for

$$\phi^2 = \frac{k_1' \; L^2 \; R_G T}{D_{EB} \; P_{EB}/\text{Surface}} \qquad (40)$$

where

η = the effectiveness factor

X_p = the pore conversion

X_o = the pore conversion at the catalyst particle's center
It will approach the equilibrium conversion (X_{eq}) under diffusion control conditions.

$H(X_p)$ = the RHS of Equation 31 in terms of X_p, "the effective driving force"

ϕ = the Thiele modulus

k_1 = the main reaction rate constant, kgmol/m^3cat-hr

L = the equivalent particle radius, m

K_G = the ideal gas constant, 82.057 x 10^{-3} m^3atm/kgmol °K

T = absolute temperature, °K

D_{EB} = diffusivity of ethylbenzene, m^2/hr

$P_{EB}/_{Surface}$ = the surface ethylbenzene partial pressure, atm

Thus, the effectiveness factor depends both on the Thiele modulus and the form of driving force divided by the inhibitor. The actual forms, along with a more complete derivation for Carrá's model and Model 5, are given in Appendix G. Table XII shows the Thiele modulus, center or equilibrium conversion, and the effectiveness factor for the catalyst manufacturer's test conditions, using a tortuosity factor

Table XII

Effectiveness Factor for Catalyst Manufacturers' Performance Test Reactor Inlet Conditions

No.	Data Set	Temperature, °C	Pressure, atm	Molar Steam-to-Oil Ratio	Thiele* Modulus	Equilibrium Conversion, %	Effectiveness Factor
1	1	550	1.0	12.5	0.63	89.4	0.97
2		560	1.0	12.5	0.75	91.2	0.82
3		570	1.0	12.5	0.89	92.6	0.71
4		580	1.0	12.5	1.04	93.8	0.60
5		543	1.0	12.5	1.28	95.1	0.49
6	2	580	0.34	12.5	1.65	97.7	0.38
7		586	0.68	12.5	1.36	96.2	0.46
8		606	1.36	12.5	1.26	94.1	0.49
9		606	1.70	12.5	1.28	93.5	0.49
10	3	566	1.27	8.85	0.65	87.4	0.94
11		573	1.27	8.85	1.00	91.9	0.62
12		621	1.27	8.85	1.53	94.9	0.41
13	4	566	1.27	8.85	0.65	87.4	0.94
14		593	1.27	8.85	1.00	91.9	0.62
15		621	1.27	8.85	1.53	94.9	0.41
16	5	566	1.27	14.7	0.82	91.3	0.76
17		593	1.27	14.7	1.26	94.6	0.50
18		621	1.27	14.7	1.92	96.7	0.33
19	6	566	0.68	8.85	0.83	92.6	0.75
20		593	0.68	8.85	1.28	95.4	0.49
21		621	0.68	8.85	1.96	97.2	0.32

* A tortuosity factor of 20 and Carrá's kinetic were used.

of 20. Figure 42 shows the effectiveness factor as a function of steam-to-oil ratio at 621°C for two different tortuosity factors. The decrease in the effectiveness factor with increasing steam-to-oil ratio is probably due to the corresponding increase in the Thiele modulus.

The effectiveness factor was calculated at various points down an isothermal reactor simulated with the kinetics proposed by Carrá. By consulting Equation 39, one sees that the effectiveness factor is made up of three components. Table XIII gives the values of the effectiveness factor and these components at various reactor depths. Going down the reactor, the Thiele modulus increased due to a decrease in the partial pressure of ethylbenzene. The integral of the driving force divided by the inhibitor decreased due to a lower particle center or equilibrium conversion. And the driving force divided by the inhibitor evaluated at the pore mouth decreased due to equilibrium being approached. This last term dominated, as can be seen in Figure 43, for the effectiveness factor approaching unity as one goes down the reactor (i.e., as conversion increases).

The single-pore diffusion model derived in this thesis behaves as expected. In order to make full use of it, one would need to obtain trustworthy experimental results for the intrinsic kinetics. A large tortuosity factor (i.e., 20) was used which emphasized the effect of diffusion. The role of diffusion in this reaction is still in question. Lee (5) gives strong evidence of diffusion's importance (see Figure 11). However, the slope of the line for the industrial size (1/8") catalyst pellets is approximately the same as that for the crushed (25-30 mesh) catalyst, and he also states that in commercial operation, due to catalyst deactivation, the evidence of intraparticle diffusion limitation becomes less pronounced.

Table XIII

The Effectiveness Factor at Various Depths

Reactor Depth, m	Effectiveness Factor	Thiele** Modulus	$\sqrt{2\int H(X_p)dX_p}$	$H(X_p)\big\|_{X_p = 0}$
0.0	0.41	1.53	0.62	1.0
0.04	0.62	1.66	0.49	0.48
0.08	0.73	1.77	0.43	0.33
0.12	0.80	1.86	0.38	0.25
0.16	0.86	1.94	0.34	0.21
0.20	0.90	2.02	0.31	0.17
0.24	0.94	2.10	0.28	0.14
0.28	0.96	2.17	0.26	0.13
0.32	0.98	2.23	0.24	0.11
0.36	1.0	2.28	0.22	0.10
0.40	1.0	2.30	0.22	0.09
0.60	1.0	2.65	0.13	0.05
0.80	1.0	2.82	0.10	0.03
1.0	1.0	2.98	0.07	0.02

* For reactor conditions, see Table XI, No. 12.

** Tortuosity factor of 20 and Carrá's kinetics were used.

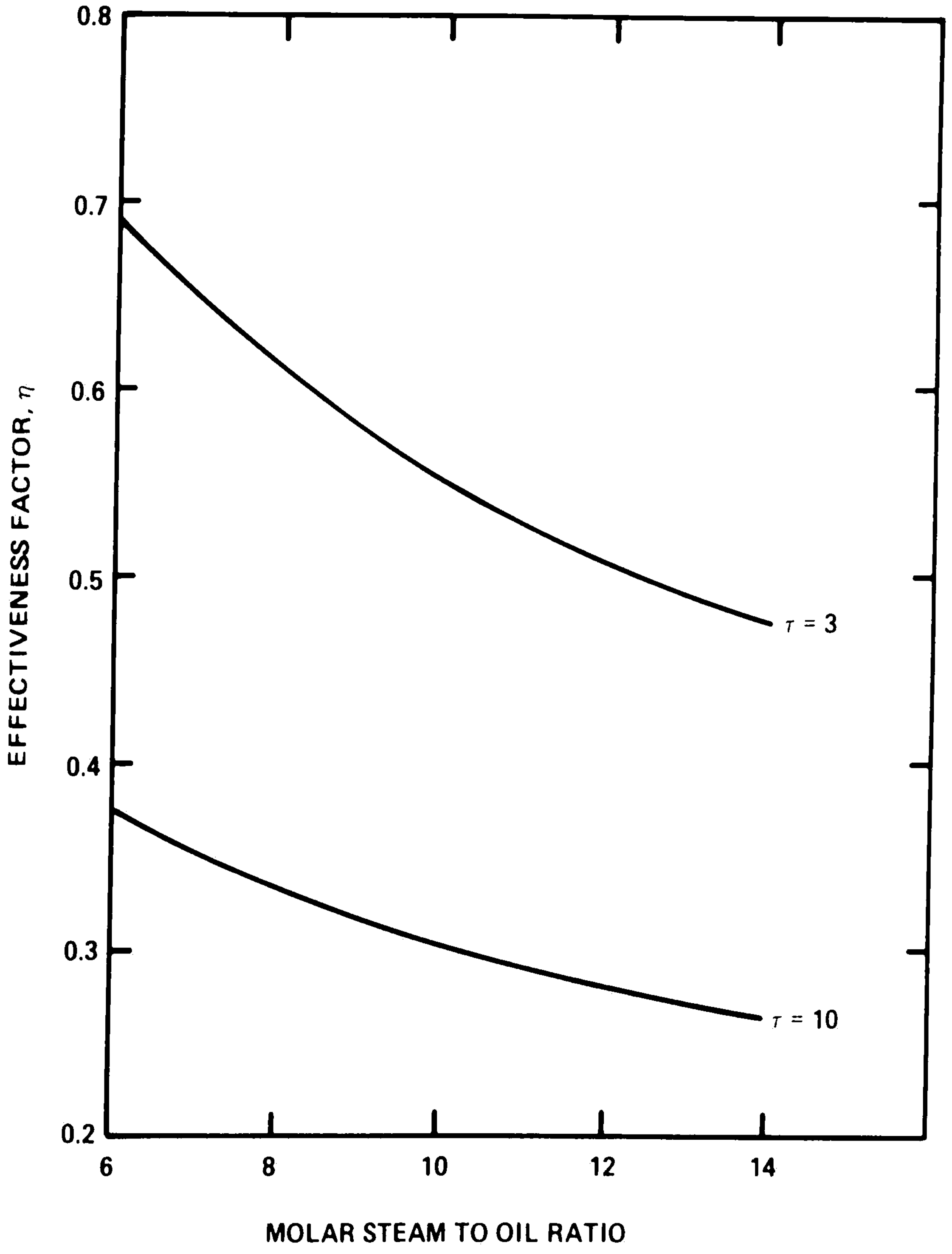

Figure 42 EFFECTIVENESS FACTOR VERSUS STEAM TO OIL RATIO FOR TWO DIFFERENT TORTUOSITY FACTORS

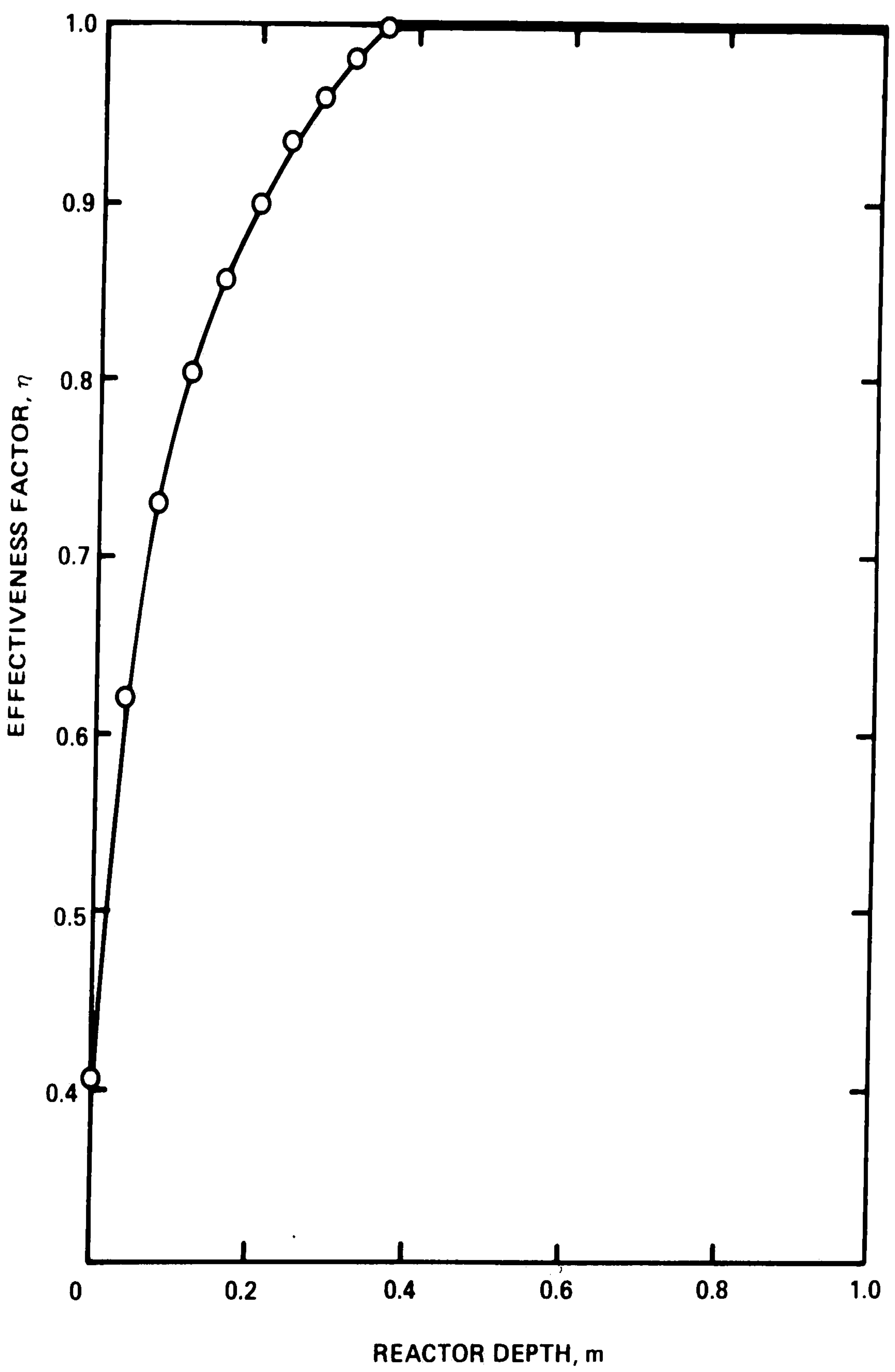

Figure 43 EFFECTIVENESS FACTOR VERSUS REACTOR DEPTH FOR TYPICAL REACTOR CONDITION

Application of the Model

Comparison of the Model With Plant Data

Model 5 was further tested by comparing the conversion of the model predicted under plant conditions with the actual plant conversions. These data are from the USS Chemicals reactor located in Houston and the Polymers Corporation reactor located in Ontario [as referenced by Sheel (25)]. The USS Chemicals data consisted of five points selected from production sheets and test results. The Polymers Corporation data consisted of four points; three are the mean operating conditions for periods of one to five days in April, May, and June of 1966; the fourth is the mean value of a factorial design run with 29 steady-state simulations known as "POLY 29". Table XIV contains reactor feed and effluent composition data for these nine pieces of plant data. Tables XV and XVI compare the conversions predicted by the model and those measured in the plant for the USS Chemicals and Polymer Corporation conditions, respectively, given in Table XIV. Inlet and outlet temperatures and pressures are also compared. The good agreement between the predicted and measured conversions confirms the ability of this model to predict the behavior of an industrial reactor.

The disagreement between the predicted and measured conversions may be due to reactor non-idealities. Three of

Table XIV

Reactor Feed and Effluent Ratios

Date	Run No.		Hydro-carbons, kgmol/hr	Molar Steam-to-Oil Ratio	Composition, mole %					
					Ethyl-benzene	Styrene	Toluene	Benzene	Xylene	Others*
				USS Chemicals** Data						
1/1/78	1	Feed	128.6	13.4	79.74	0.44	2.16	0.0	16.04	1.62
		Effluent			42.67	34.40	5.05	1.21	15.46	1.17
12/1/78	2	Feed	190.2	12.4	80.22	2.69	1.14	0.00	15.03	0.92
		Effluent			44.80	33.01	3.68	1.15	13.97	0.69
3/6/79	3	Feed	118.11	11.9	82.27	0.78	0.66	0.00	15.28	1.01
		Effluent			47.89	33.01	2.41	1.01	14.44	0.92
6/8/82	4	Feed	115.3	12.3	73.87	0.65	0.37	0.00	20.84	4.28
		Effluent			40.05	32.02	2.23	0.99	20.17	4.32
7/2/81	5	Feed	118.0	13.3	75.94	0.49	1.63	0.0	15.36	6.58
		Effluent			36.54	36.84	4.63	1.42	14.77	5.81
				Polymer Corporation† Data						
4/66	1	Feed	38.54	11.8	95.86	1.67	2.04	0.22	0.0	0.22
		Effluent			51.8	39.8	4.8	3.1	0.0	0.4
5/66	2	Feed	38.70	11.7	95.32	1.32	2.62	0.68	0.0	0.05
		Effluent			50.5	40.1	5.6	3.5	0.0	0.2
6/66	3	Feed	39.06	11.7	94.93	1.93	2.80	0.15	0.0	0.19
		Effluent			53.6	38.3	5.1	2.5	0.0	0.4

(Continued)

Table XIV (Continued)

	Run No.		Hydro-carbons, kgmol/hr	Molar Steam-to-Oil Ratio	Composition, mole %					
					Ethyl-benzene	Styrene	Toluene	Benzene	Xylene	Others*
"POLY 29"	4	Feed	36.94	10.9	94.50	1.26	4.04	0.21	0.0	0.0
		Effluent			48.5	[illegible]	[illegible]	[illegible]	0.0	0.0

* For the USS Chemicals reactor, these were identified as mainly normal octanes, nonanes, and decanes; since Sheel did not identify the "others" present in the Polymer Corporation reactor, the same components were assumed.

** The catalyst-bed dimensions are 16' in diameter and 4' in depth.

\+ The catalyst-bed dimensions are 6' 4-1/4" in diameter and [illegible] in depth.

Table XV

Comparison of Model 5 and USS Chemicals Plant Data

	Run No.	Temperature In, °C	Temperature Out, °C	Pressure In, Atm	Pressure* Out, Atm	Percent Conversion Styrene	Percent Conversion Benzene	Percent Conversion Toluene	Styrene Selectivity, %
Model	1	617.78	555.44	1.952	1.766	43.66	1.77	3.96	88.39
Data	1	617.78	558.33	1.952	1.755	42.59	1.52	3.62	89.23
Model	2	632.22	568.33	2.429	2.231	41.08	1.81	4.48	86.72
Data	2	632.22	571.11	2.429	2.170	41.16	1.43	3.17	89.15
Model	3	623.33	555.37	1.884	1.734	42.61	1.78	4.03	87.99
Data	3	623.33	560.00	1.884	1.721	39.18	1.23	2.13	92.11
Model	4	628.89	559.38	1.680	1.476	49.07	2.16	5.38	86.68
Data	4	628.89	565.56	1.680	1.572	43.17	1.34	2.52	91.67
Model	5	628.89	561.20	1.816	1.621	48.99	2.16	5.70	86.94
Data	5	628.89	562.22	1.816	1.707	47.87	1.87	3.95	89.16

Average Difference Between Experimental and Predicted Conversions

Generation Reaction	Absolute, %	Relative, %
Styrene	2.3	5.5
Toluene	1.5	57
Benzene	0.5	33

* Using a void fraction of 0.325 in the Ergun Pressure Drop Equation.

Table XVI

Comparison of Model 5 and Polymer Corporation Plant Data

	Run No.	Temperature In, °C	Temperature Out, °C	Pressure In, Atm	Pressure* Out, Atm	Percent Conversion			Styrene Selectivity, %
						Styrene	Benzene	Toluene	
Model	1	649.44	570.43	2.37	1.953	40.63	1.91	4.65	86.11
Data	1	649.44	593.33	2.37	2.29	39.80	2.99	2.29	87.09
Model	2	648.85	570.10	2.37	1.953	40.71	1.90	4.62	86.18
Data	2	648.85	597.83	2.37	--	40.72	2.99	3.17	86.86
Model	3	647.18	569.83	2.31	1.955	40.30	1.87	4.50	86.35
Data	3	647.18	592.62	2.37	--	38.35	2.53	2.40	88.60
Model	4	649.44	568.0	2.71	1.795	40.60	1.89	4.58	86.25
Data	4	649.44	--	2.71	--	43.22	2.67	2.79	88.78

Average Difference Between Experimental and Predicted Conversions

Generation Reaction	Absolute, %	Relative, %
Styrene	1.4	3.4
Toluene	1.7	75
Benzene	0.9	32

* Using a void fraction of 0.325 in the Ergun Pressure Drop Equation.

the more likely differences between the reactor model and the plant reactor are: heat losses to the surroundings (this is the least likely), deactivation of the catalyst with age, and reactor dead spots due to uneven flow distribution and channeling.

In order to look at the possibility of reactor nonidealities, it was necessary to obtain more data. Data were available from 1969 to 1981 from tests that are conducted about every month for the designed purpose of assessing catalyst activity. These test data consist of absolute flow rates of steam and organic into the reactor, organic phase composition of the feed and effluent, and inlet and outlet temperatures and pressures.

Heat Losses: The plant reactor's catalyst bed is 16 feet in diameter and 4 feet deep. With the large volume to surface area ratio and the reactor being insulated, it should behave as an adiabatic reactor. To test this, exit temperatures were calculated from energy balances and compared to measured exit temperatures; the difference for the plant data described above had a mean of 3.6°C and a standard deviation of 5.0°C. The energy balance used heat of formation data, ideal heat capacity data, measured inlet temperatures, and measured inlet and exit compositions. So, judging from the results of the energy balances, the reactor is described well by an adiabatic reactor model.

Catalyst Deactivation: To investigate catalyst deactivation, the program was run for plant conditions, and the plant conversions were compared with the predicted conversions. Catalyst activity for our purposes is defined as the styrene conversion measured in the plant divided by that predicted by the model. The model was calibrated with data from fresh catalyst. Therefore, one would expect the activity to start at unity and decrease with age. Figure 44 shows a graph of catalyst activity versus age (i.e., pounds of styrene produced per pound of catalyst) for all the available data. This definition of age is used rather than production hours, since the reactor throughput was not constant.

The data are very scattered. Some of the points are suspect, particularly when the catalyst activity increases with time. The suspect data sets (December 1969 through February 1972 and 1972 to April 1975) were deleted (see Figure 45). The line fit through the data in Figure 45 was generated by assuming that the catalyst initially behaved as the catalyst manufacturer's performance test data predicted, and then the catalyst activity dropped off exponentially to a fixed value. The coordinates were chosen to linearize the plot.

The equation of the line is

$$(\text{activity}) = \alpha + (1 - \alpha) \exp(- \text{age}/\beta)$$

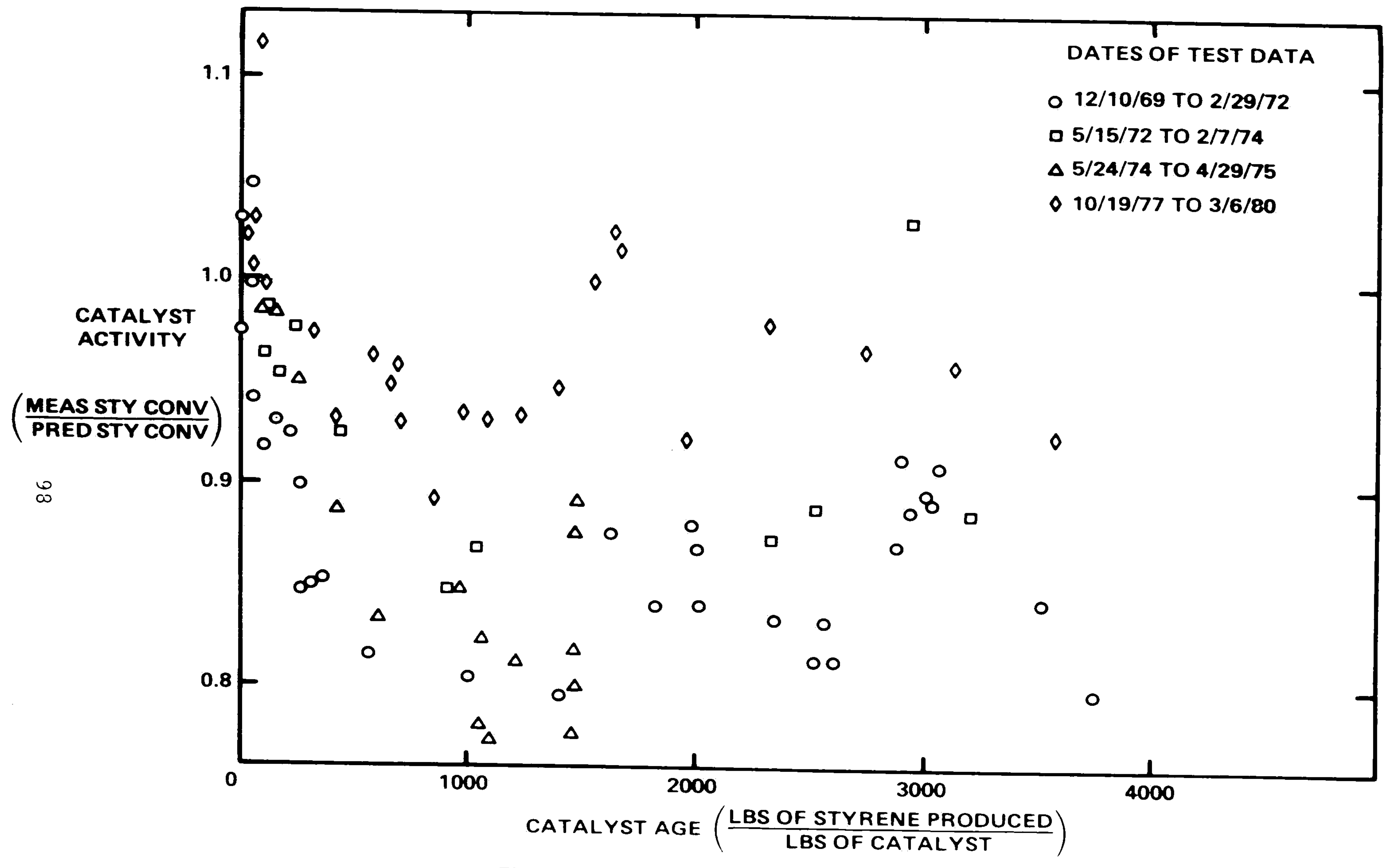

Figure 44 CATALYST ACTIVITY VERSUS CATALYST AGE

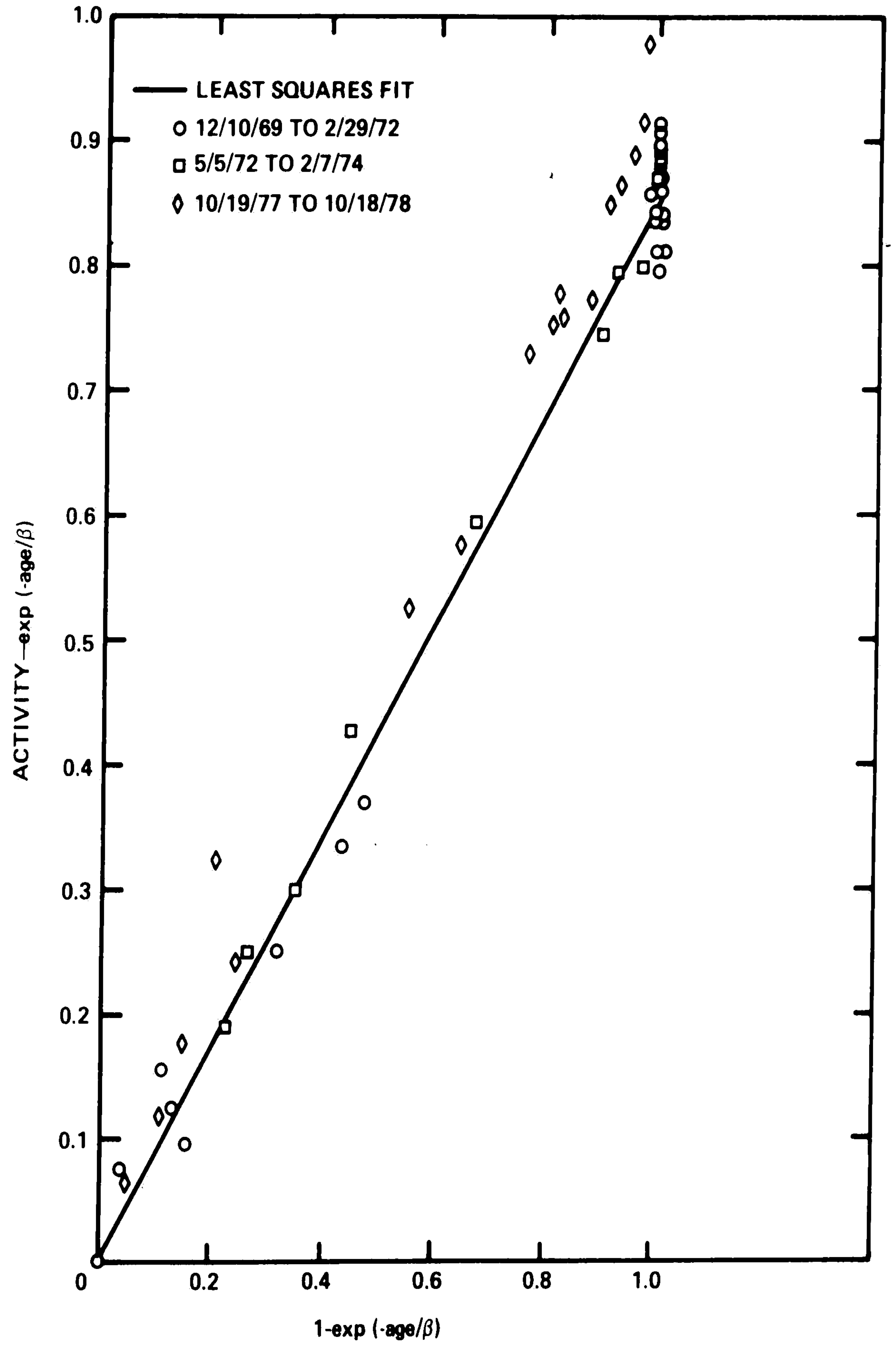

Figure 45 A LINEARIZED PLOT OF CATALYST ACTIVITY VERSUS CATALYST AGE FOR SELECTED DATA

where

activity = catalyst activity, $\frac{\%\ \text{plant styrene conversion}}{\%\ \text{model styrene conversion}}$

α = "infinite time activity"

= 0.885

age = catalyst age, lb styrene produced/lb catalyst

β = deactivation rate, lb styrene produced/lb catalyst

= 400 lb styrene produced/lb catalyst

The linear least-squares fit of the catalyst activity had a correlation coefficient of 0.7. This is a fairly good fit considering the variability of the data. This deactivation model assumes the catalyst activity levels off at a value of 89%. In practice, the catalyst is replaced approximately every two years (15) because of the belief that the catalyst is continuously deactivating. More accurate data would be necessary for a conclusive investigation.

<u>Flow Maldistribution</u>: There is still the third possible reactor non-ideality, areas within the reactor where no reaction occurs (i.e., dead spots) due to poor flow distribution or channeling. Polymer Corporation's reactor is 6½ feet in diameter compared to U. S. Steel's 16 foot diameter reactor. The better agreement between the model and the data collected by Sheel may be due to the smaller reactor having better flow distribution, or the reactor may have contained relatively fresh catalyst. One way to detect

the flow distribution problem is to measure the temperature distribution in the reactor. At a given depth in the reactor, the conversion and thus the temperature should be a constant. However, if there is a dead spot, the temperature would be higher in this area due to the reaction having not proceeded as far. Unfortunately, there are only four thermocouples in the plant reactor, one of which does not work and another which is of questionable value due to unreasonable temperature readings.

Temperature Profile: For three of the five points of USS Chemical data, the temperature profile predicted by the model and that measured in the plant (inlet and outlet temperatures and the two thermocouples) are compared in Figure 46.

Pressure Drop: The reactor bed void fraction used in the Ergun pressure drop equation was found to have a value of 0.325 by calibrating plant pressure drop data (see Figure 47). This is within the range of 0.3 to 0.5 expected for a packed bed (29).

Gas Reactions: The reactions which do not involve the aromatics are known as the gas reactions because the reactants and products are gases at room temperature. The kinetics used for these reactions do not predict plant data well. The plant data show a volume of non-condensable gas produced of two and one-half times as much as the model

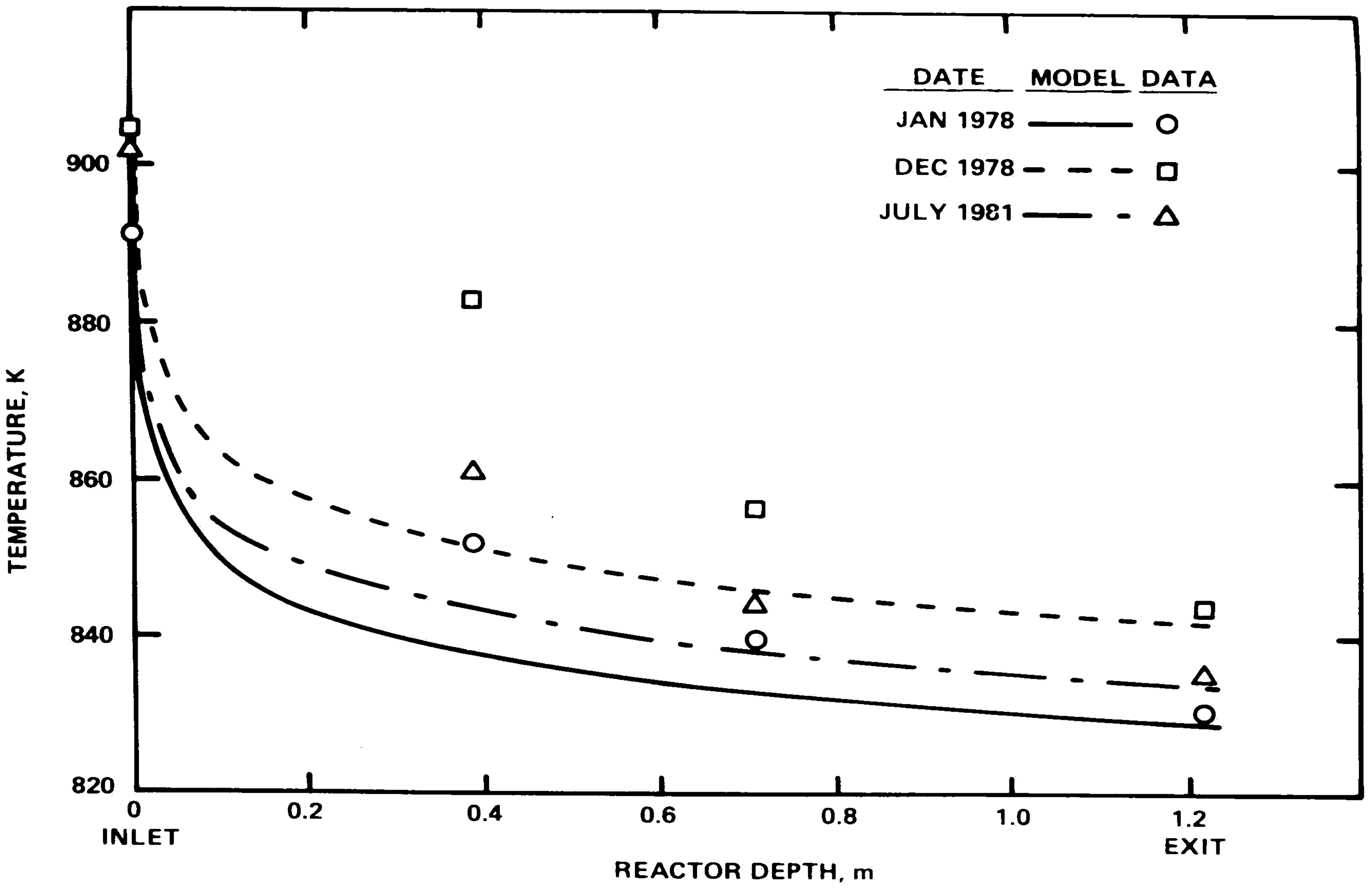

Figure 46 TEMPERATURE PROFILE COMPARISON BETWEEN MEASURED AND PREDICTED VALUES

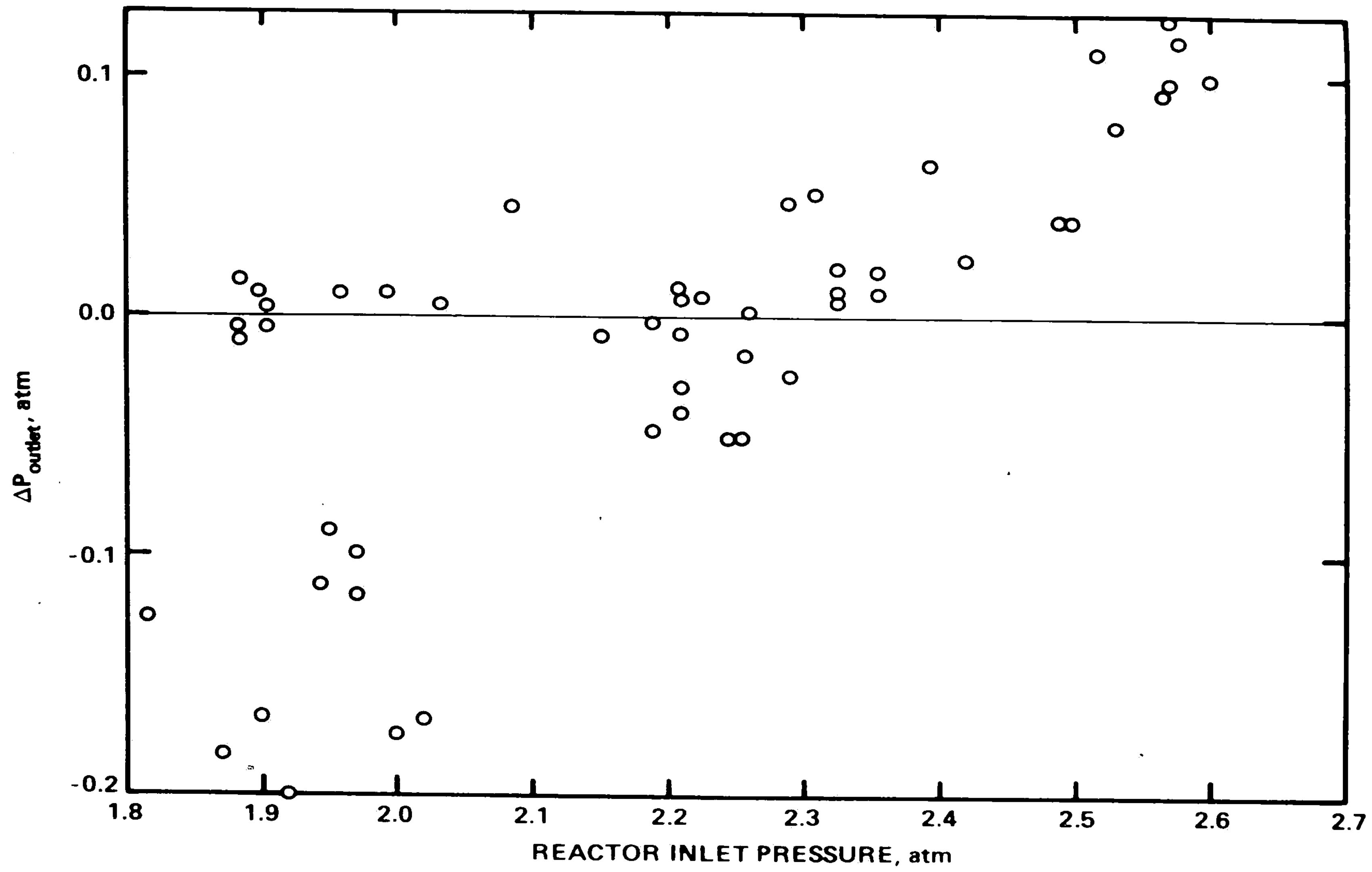

Figure 47 THE DEVIATION BETWEEN MEASURED AND PREDICTED REACTOR OUTLET PRESSURES VERSUS INLET PRESSURE (A VOID FRACTION OF 0.325 WAS USED IN THE PREDICTION)

predicts. This may be due in part to neglecting any dealkylation of the paraffins and naphthalenes present in the plant feed that may occur. Table XVII shows a comparison of the typical composition of measured and predicted non-condensable gas. Predicting the amount and composition of the non-condensable gas is not crucial, and no effort was made to obtain the correct kinetics. However, since the model was calibrated while including these gas reactions, the kinetics presented are maintained for consistency.

Xylene Reaction: One of the unique features of U. S. Chemical's Houston reactor is that xylenes are present in the reactor feed. This is due to imperfect separation in the distillation column separating eight member aromatics. It has been found that the xylenes are dealkylated in the reactor to a small extent. This prevents the xylene concentration from continuously building into the recycle stream. A reaction was included and calibrated to account for the small change in xylene concentration in the reactor.

Approximate Plant Economics

Choosing the optimal reactor operating conditions requires a definition of the objective function. This research is concerned mainly with the reactor section of the plant. In this case, the objective is to maximize the profit defined as:

Profit = [Selling Price (¢/lb) - Cost (¢/lb)] [Production Rate (lb/hr)]

Table XVII

Non-Condensable Gas Composition

Component	Typical Plant Data, mole %	Typical Computer Run*, mole %
Hydrogen	81.83	89.1
Oxygen	0.09	--
Nitrogen	0.14	--
Carbon Monoxide	0.10	6.9
Carbon Dioxide	8.57	4.0
Methane	8.01	0.04
Ethane	0.44	--
Ethylene	0.56	0.0
Propane	0.07	--
Propylene	0.19	--

* Simulation of December 10, 1969, conditions.

This is to be maximized by proper choice of inlet temperature, pressure, and steam to oil ratio.

The cost to produce a pound of styrene is made up in this simplified model of three components: fixed costs, raw-materials costs, and energy costs. Within a range of feed rates, the fixed costs are estimated to be around $190 per hour.

The largest raw-material cost is that of ethylbenzene. It is estimated that ethylbenzene, purified in-house or purchased, costs about 15.7¢/lb (see Table XVIII). The amount of ethylbenzene needed to make up the feed is calculated by subtracting the predicted recycle rate from the fixed feed rate. The plant does not get a credit for the toluene and benzene produced. It does get a credit for the vent gas produced. Since the model's prediction of the amount of vent gas is low, it is multiplied by 2.5. By adding up these costs and dividing by the pounds of styrene produced, one obtains the raw-materials cost per pound of styrene.

The major energy requirements in the plant are those to preheat the feed and those to supply heat to the recycle, benzene-toluene, and finishing column reboilers (see Appendix K for the details of this analysis). The energy required to preheat the reactor feed by steam injection can be broken down into two components: that to generate the steam

Table XVIII

Cost Data

Fixed Costs	\$190/hr
Raw-Material Costs	
Ethylbenzene	15.7¢/lb
Toluene	(0¢/lb)
Benzene	(0¢/lb)
Vent Gas	(0.131¢/std ft^3)
Energy Costs	\$4.16/10^6 Btu

and that to superheat the steam. The first component is the largest energy consumer in the plant. It can be estimated as the energy lost in the condenser when the reactor effluent is cooled from a vapor at 300°F to a liquid at its condensate temperature. The energy required to superheat the steam can be calculated from the specified steam, rate, the enthalpy of steam at 700°F, and the final steam temperature. (It is assumed that the heat exchange equipment is adequate for the heat recovered by cooling the effluent to 300°F to be transferred to heat the steam to 700°F.) To calculate the final steam temperature, an energy balance is done knowing the specified feed inlet temperature and flow rate, an estimated hydrocarbon temperature out of the effluent heat exchanger, and its flow rate and the steam flow rate.

The duty for the recycle column was calculated by assuming it is proportional to the recycle flow rate within the range of interest. The design case was used to calculate the heat duty required per pound of recycle (30).

The benzene-toluene column reboiler duty is small, and both fresh feed and the recycle stream are distilled in it. A constant heat duty per pound of styrene (that of the design case) is assumed because its contribution to the total energy cost does not justify a more rigorous analysis.

The finishing columns are used to purify the crude styrene taken off the bottom of the recycle column. Their combined reboiler duty is roughly constant per pound of styrene processed and the design value is used (30).

By adding the fixed costs, raw-material costs, and energy cost per pound of styrene, one calculates the cost to produce a pound of styrene. Each set of operating conditions has associated with it not only a styrene production cost but also a styrene production rate. To just look at the styrene production cost would be deceptive. Which conditions are optimum also depend on the selling price of styrene, for this affects the cost margin and thus the profit at a given production rate (see Table XIX).

Optimization of the Plant Operating Conditions

Using the objective function, profit, as defined in the previous section, different possible operating conditions for the existing plant (which uses Shell 105 catalyst) were investigated. The reactor inlet temperature, pressure, steam-to-oil ratio, and feed rate and composition were set at typical plant values (see Table XX). Then the inlet temperature was varied between 593 and 700°C. Since the largest energy loss in the plant is from the condensing of the reactor effluent, the steam-to-oil ratio was also varied. The plant operates at a molar steam to oil ratio of 14.1; values of 10 and 6 were also tested. To calculate the

Table XIX

Calculation of the Objective Function, Profit

Calculating Styrene Cost:

Fixed

1. Total Fixed Cost = $190.00/hr
2. Record Production Rate = lb/hr
3. Fixed Cost per Pound (divide 1 by 2) = $/lb
   = ¢/lb

Raw Materials

4. Record Ethylbenzene Cost per Pound = ¢/lb
5. Record Vent Gas Credit per Pound = (¢/lb)
6. Raw Materials Cost per Pound (subtract 5 from 4) = ¢/lb

Energy

7. Energy Cost for Finishing Section and Benzene-Toluene Column = 0.458¢/lb
8. Record Furnace Energy Cost = ¢/lb
9. Record Interstage Heating Cost for Two-Stage Reactor = ¢/lb
10. Record Recycle Distillation Column Energy Cost = ¢/lb
11. Total Energy Cost per Pound (add 7 through 10) = ¢/lb
12. Styrene Production Cost (add 3, 6, & 11) = ¢/lb

Profit:

13. Select a Styrene Selling Price = ¢/lb
14. Calculate the Cost Margin (subtract 12 from 13) = ¢/lb
15. Total Profit (multiply 2 by 14) = $ /hr

Table XX

Reactor Conditions Used in the Optimization Studies

	Single-Stage Optimization	Two-Stage Optimization
Feed Rate, kgmol/hr	110.7	190.0
Feed Composition, mole % of		
Ethylbenzene	82.40	88.09
Styrene	0.54	1.88
Toluene	0.75	0.77
Benzene	0.00	0.00
Xylene	16.30	6.55
Paraffins	0.00	2.71
Catalyst Bed Diameter (m)	4.85	4.85 (for both)
Catalyst Bed Depth (m)	1.22	1.0 (for both)
Liquid Hourly Space Velocity (LHSV), hr^{-1}	0.60	0.63

reactor inlet pressure at these different flow rates, it was assumed that the non-condensable gas compressor inlet pressure is about 0.20 atm and that the pressure drop in the piping between this point and the reactor outlet is proportional to the total flow rate squared. Thus using plant data for a given flow rate, the reactor outlet pressure can be approximated and an estimated reactor pressure drop can be added to this number to give a representative reactor inlet pressure. Then the study was repeated for a reactor packed with Shell 015 catalyst. Table XXI gives the reactor conditions and conversion information, and Table XXII gives the production and cost information for the study with Shell 105 catalyst. Tables XXIII and XXIV give the corresponding information for the Shell 015 study. Profit as a function of inlet temperature is presented in Figure 48 for a styrene selling price of 25 cents per pound. The optimum conditions have a steam to oil ratio around 10.0. The greatest gains in profit for the present plant would be realized by changing to Shell 015 or a similar high-selectivity catalyst. To facilitate this, it would be necessary to remove the xylenes from the recycle by another means.

The equilibrium conversion is defined as the conversion of ethylbenzene to styrene that would result if, from this point only, the main reaction occurs and it proceeds to equilibrium. At high temperatures, the reactions are very fast and the irreversible side reactions may produce hydrogen fast enough that the styrene conversion is greater than the calculated equilibrium conversion (i.e., the equilibrium is shifted so that styrene is converted back into ethylbenzene). This is why the styrene selectivity versus styrene conversion in Figure 49 bends backwards, and demonstrates the inherent advantage of a high-selectivity catalyst. That is that less by-products produced means less hydrogen and a greater equilibrium conversion. High-selectivity catalysts usually have the disadvantage of being less active (i.e., requiring higher reactor temperatures for the same conversion).

A graph was also constructed of profit versus reactor inlet pressure from the results for Shell 105 catalyst presented in Table XXI; it is shown in Figure 50. As expected, the lower the reactor pressure, the more profitable the operation due to higher styrene conversion.

TABLE XXI- CONDITION AND CONVERSION INFORMATION FOR A SINGLE STAGE REACTOR PACKED WITH SHELL 105 CATALYST

Run No.	Molar Steam to Oil Ratio	Temperature in (C)	Pressure in (ATM)	Conversion %				Styrene Selectivity %
				Styrene	Equilibrium	Toluene	Benzene	
1	14.1	593.00	1.816	38.59	53.11	2.50	1.34	90.94
2		628.33	1.816	48.21	57.23	4.97	2.09	87.22
3		650.00	1.816	53.07	58.72	7.28	2.67	84.22
4		675.00	1.816	56.93	59.27	11.03	3.46	79.71
5		700.00	1.816	57.92	58.12	16.50	4.44	73.44
6		725.00	1.816	54.82	53.95	24.85	5.77	64.17
7	14.1	628.33	1.400	52.56	68.08	5.14	2.18	87.78
8		628.33	1.600	49.93	60.86	5.03	2.13	87.46
9		628.33	1.800	48.31	57.46	4.97	2.10	87.24
10		628.33	2.000	47.01	55.09	4.92	2.07	87.06
11		628.33	2.200	45.96	53.30	4.88	2.05	86.89
12	10.0	593.00	1.502	36.14	50.82	2.66	1.25	91.51
13		628.33	1.502	45.80	55.13	5.34	1.99	88.02
14		650.00	1.502	51.03	56.90	7.95	2.57	85.19
15		675.00	1.502	55.48	57.82	12.34	3.40	80.89
16	6.0	593.00	1.228	31.58	45.58	2.22	1.07	91.74
17		628.33	1.228	40.18	49.95	4.42	1.70	88.46
18		650.00	1.228	45.02	52.00	6.51	2.18	85.85
19		675.00	1.228	49.66	53.43	9.97	2.86	82.03

TABLE XXII - PRODUCTION AND COST[1] INFORMATION FOR A SINGLE STAGE REACTOR PACKED WITH SHELL 105 CATALYST

Run No.	Styrene Produced (Lbs/Hr)	Styrene Product Cost	Fixed Costs	Material Costs		Finishing	Energy Costs		Recycle
				Ethylbenzene	Vent Gas		Furnace	Condenser	
1	8066.	26.33	2.356	17.48	(.7908)	.4580	.8174	3.929	2.071
2	10076.	24.99	1.886	18.17	(.8862)	.4580	.7605	3.137	1.464
3	11093.	24.80	1.713	18.76	(.9678)	.4580	.7512	2.843	1.241
4	11900.	25.17	1.597	19.72	(1.100)	.4580	.7657	2.641	1.091
5	12107.	26.40	1.569	21.23	(1.309)	.4580	.8174	2.584	1.056
6	11459.	29.16	1.658	23.92	(1.691)	.4580	.9339	2.712	1.170
7	10986.	24.23	1.729	18.06	(.8776)	.4580	.7059	2.877	1.262
8	10437.	24.67	1.820	18.12	(.8776)	.4580	.7378	3.028	1.380
9	10099.	24.97	1.881	18.17	(.8856)	.4580	.7590	3.130	1.459
10	9827.	25.22	1.933	18.20	(.8919)	.4580	.7775	3.217	1.526
11	9606.	25.44	1.978	18.24	(.8976)	.4580	.7931	3.291	1.584
12	7553.63	25.76	2.515	17.49	(.8012)	.4580	.7704	3.047	2.278
13	9573.58	24.41	1.985	18.18	(.9029)	.4580	.6996	2.395	1.592
14	10667.32	24.18	1.781	18.79	(.9916)	.4580	.6783	2.143	1.329
15	11597.60	24.52	1.638	19.79	(1.139)	.4580	.6758	1.961	1.145
16	6600.30	25.78	2.879	17.44	(.7873)	.4580	.7958	2.238	2.747
17	8399.79	24.34	2.262	18.09	(.8797)	.4580	.7059	1.751	1.951
18	9411.72	24.03	2.019	18.64	(.9577)	.4580	.6749	1.556	1.636
19	10380.20	24.17	1.830	19.51	(1.080)	.4580	.6583	1.403	1.393

[1] All costs presented in ¢/Lb of styrene produced

TABLE XXIII - CONDITION AND CONVERSION INFORMATION FOR A SINGLE STAGE REACTOR PACKED WITH SHELL 015 CATALYST

Run No.	Molar Steam to Oil Ratio	Temperature in (C)	Pressure in (ATM)	Conversion % Styrene	Conversion % Equilibrium	Conversion % Toluene	Conversion % Benzene	Styrene Selectivity %
1	14.1	593.00	1.816	35.16	60.83	.48	.19	98.14
2		628.33	1.816	47.27	66.42	1.42	.57	95.97
3		650.00	1.816	54.10	68.45	2.58	1.05	93.71
4		675.00	1.816	60.22	68.94	4.88	2.03	89.70
5		700.00	1.816	62.83	66.83	8.80	3.73	83:37
6	14.1	628.33	1.400	51.20	76.96	1.45	.58	96.17
7		628.33	1.600	48.85	70.17	1.43	.57	96.05
8		628.33	1.800	47.37	66.64	1.42	.57	95.97
9		628.33	2.000	46.23	64.28	1.41	.57	95.91
10		628.33	2.200	45.29	62.44	1.40	.56	95.85
11	10.0	593.00	1.816	32.52	58.13	.45	[illegible]	98.16
12		628.33	1.816	44.11	63.92	1.33	.53	96.00
13		650.00	1.816	50.80	66.09	2.42	.99	93.77
14		675.00	1.816	57.03	66.85	4.57	1.90	89.88
15		700.00	1.816	60.25	65.20	8.15	3.46	83.93
16	6.0	593.00	1.816	28.48	52.65	.37	.14	98.25
17		628.33	1.816	38.57	58.41	1.10	.44	96.22
18		650.00	1.816	44.52	60.81	1.99	.81	94.14
19		675.00	1.816	50.33	62.10	3.74	1.56	90.54
20		700.00	1.816	53.98	61.31	6.67	2.83	85.11

TABLE XXIV - PRODUCTION AND COST[1] INFORMATION FOR A SINGLE STAGE REACTOR PACKED WITH SHELL 015 CATALYST

Run No.	Styrene Produced (Lbs/Hr)	Styrene Product Cost	Fixed Costs	Material Costs			Energy Costs		
				Ethylbenzene	Vent Gas	Finishing	Furnace	Condenser	Recycle
1	7350.	26.32	2.585	16.30	(.5876)	.4580	.8743	4.326	2.368
2	9880.	23.89	1.923	16.67	(.6415)	.4580	.7577	3.215	1.513
3	11309.	23.23	1.680	17.07	(.6996)	.4580	.7213	2.804	1.199
4	12588.	23.18	1.509	17.83	(.8086)	.4580	.7106	2.512	.9781
5	13132.	24.11	1.447	19.17	(1.000)	.4580	.7427	2.396	.8973
6	10701.	23.23	1.775	16.63	(.6350)	.4580	.7067	2.968	1.322
7	10210.	23.61	1.861	16.65	(.6389)	.4580	.7362	3.111	1.432
8	9901.	23.87	1.919	16.67	(.6413)	.4580	.7563	3.208	1.507
9	9663.	24.09	1.966	16.68	(.6432)	.4580	.7727	3.287	1.568
10	9467.	24.27	2.007	16.69	(.6449)	.4580	.7866	3.355	1.621
11	6796.73	25.84	2.795	16.30	(.5870)	.4580	.8313	3.401	2.640
12	9221.02	25.45	2.061	16.67	(.6400)	.4580	.7095	2.503	1.690
13	10618.94	22.80	1.789	17.07	(.6965)	.4580	.6704	2.169	1.340
14	11920.51	22.72	1.594	17.81	(.8007)	.4580	.6552	1.926	1.087
15	12595.04	23.52	1.509	19.07	(.9774)	.4580	.6771	1.812	.9771
16	5953.89	25.85	3.191	16.29	(.5837)	.4580	.8520	2.495	3.151
17	8061.59	23.44	2.357	16.63	(.6322)	.4580	.7145	1.839	2.073
18	9305.07	22.74	2.042	17.00	(.6836)	.4580	.6674	1.590	1.666
19	10520.64	22.57	1.806	17.68	(.7772)	.4580	.6425	1.400	1.361
20	11284.04	23.16	1.684	18.80	(.9326)	.4580	.6507	1.296	1.204

[1] All costs presented in ¢/Lb of styrene produced

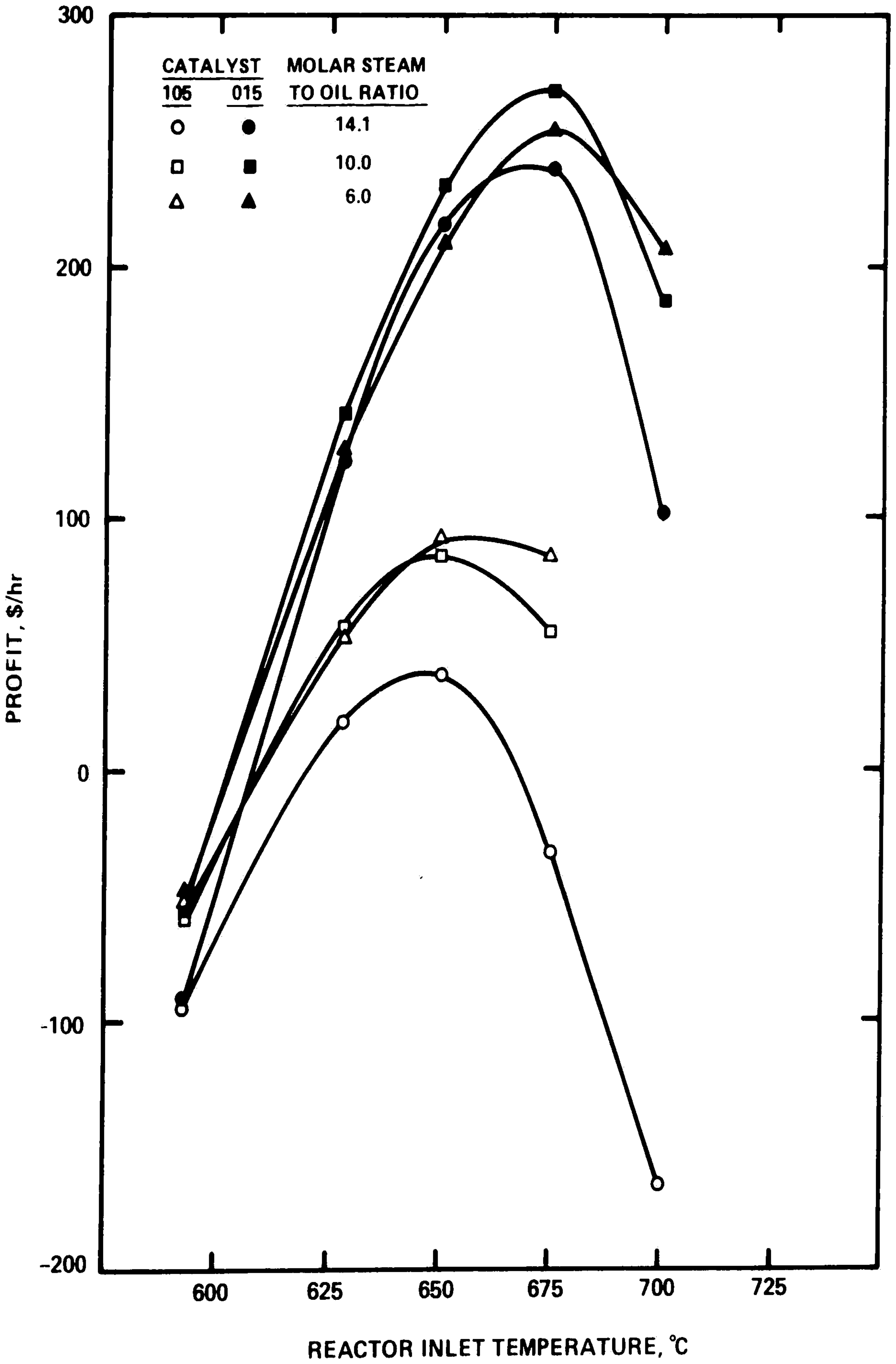

Figure 48 PROFIT VERSUS REACTOR INLET TEMPERATURE FOR A SINGLE STAGE REACTOR PACKED WITH EITHER SHELL 105 OR 015 CATALYST

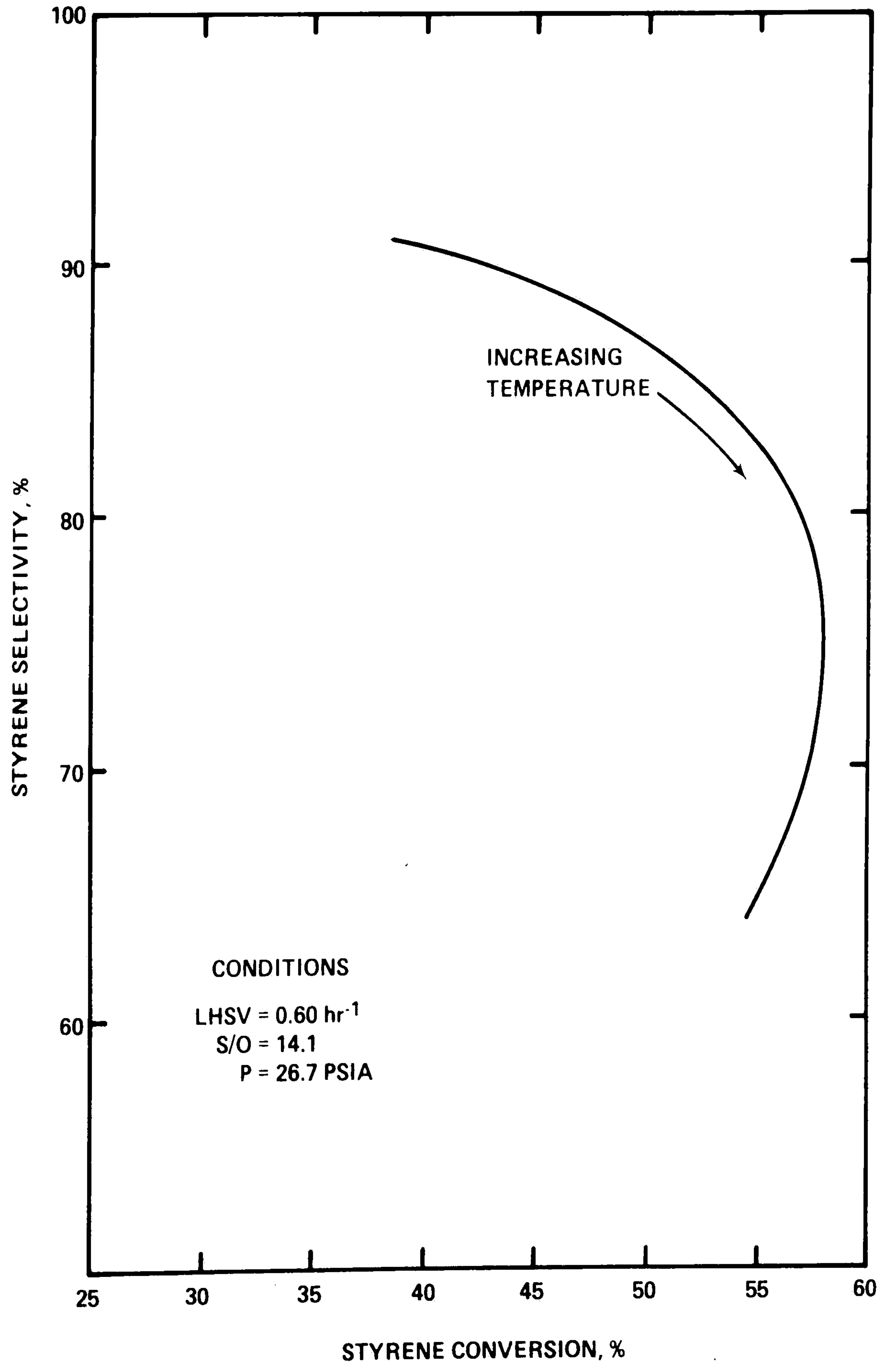

Figure 49 STYRENE SELECTIVITY VERSUS STYRENE CONVERSION FOR SHELL 105 CATALYST

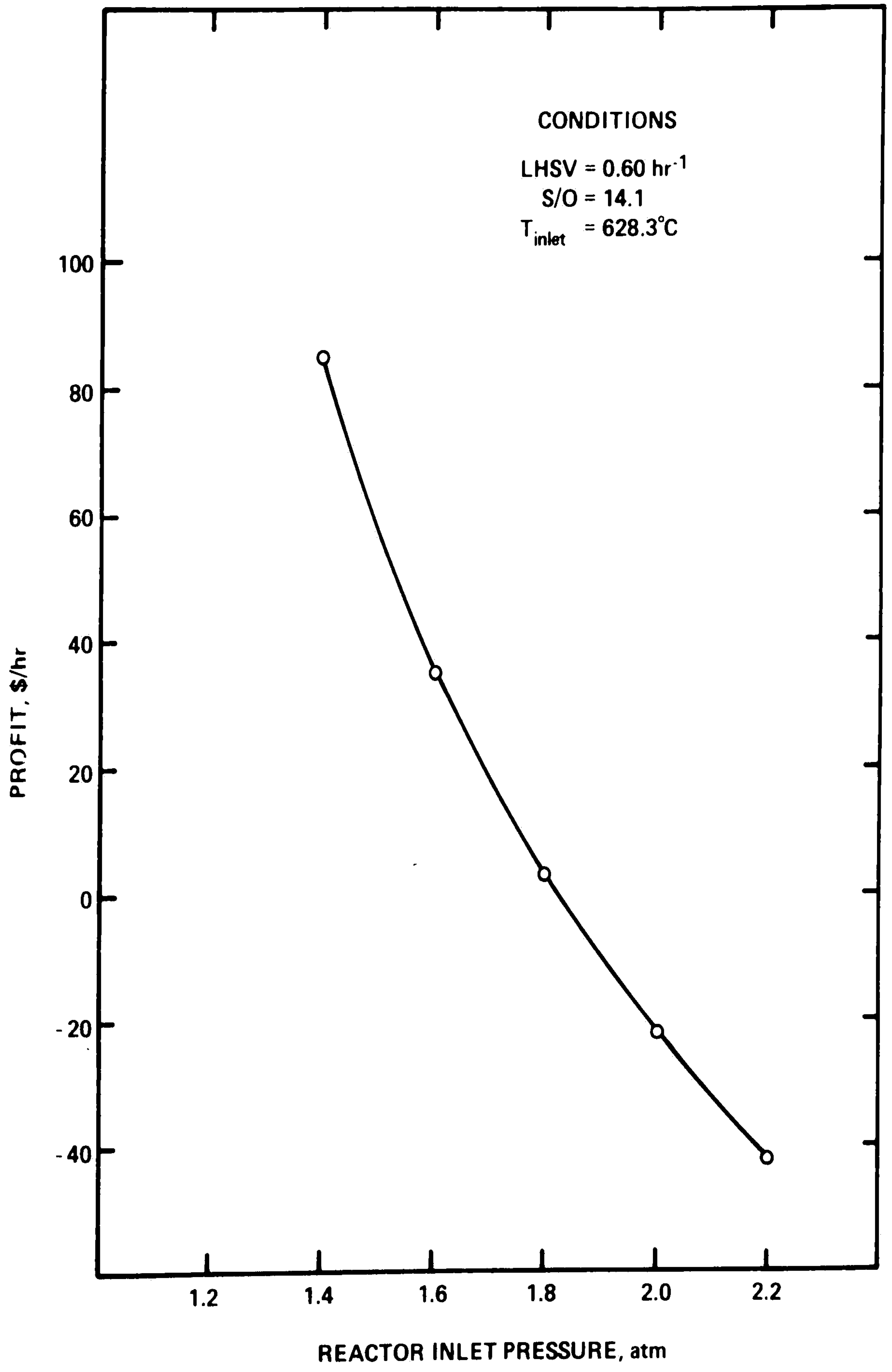

Figure 50 PROFIT VERSUS REACTOR INLET PRESSURE FOR A STYRENE SELLING PRICE OF 25¢/LB

Optimization of a Two-Stage Reactor Operation

Optimizations similar to the previous ones were done for a two-stage reactor with three different packing arrangements: Shell 105 catalyst in both stages, Shell 105 and Shell 015 catalyst in the first and second stages, and Shell 015 catalyst in both stages. The reactor conditions are given in Table XX. The second stage inlet temperature was set to the first stage inlet temperature, which was varied between 593 and 675°C. Interstage heating can be accomplished by heat exchange or steam injection. The three interstage heating/steam to oil ratio configurations investigated for each packing arrangement are shown in Figure 51.

Tables XXV through XXX give the results of the study, and the profit as a function of inlet temperature is presented in Figures 52 through 54 for a styrene selling price of 25 cents per pound. The most profitable operation involves an inlet temperature of 650°C, a high steam to oil ratio (11.8) in both beds with interstage heating by heat exchanger, and the use of a high-selectivity catalyst. Interstage heating by heat exchanger would require a higher capital investment than heating by steam injection.

TABLE XXV - CONDITIONS AND CONVERSION INFORMATION FOR A TWO STAGE REACTOR WITH BOTH STAGES PACKED WITH SHELL 105 CATALYST

Run No.	Molar Steam to Oil Ratio Bed 1	Molar Steam to Oil Ratio Bed 2	Temperature in (C)	Pressure in (ATM)	Conversion % Styrene	Conversion % Equilibrium	Conversion % Toluene	Conversion % Benzene	Styrene Selectivity
1	8.0	8.0	593.00	2.000	38.04	53.05	2.60	1.42	90.43
2			628.33	2.000	49.46	58.19	5.55	2.38	86.19
3			650.00	2.000	55.09	59.98	8.44	3.15	82.62
4			675.00	2.000	58.74	60.34	13.40	4.27	76.88
5	8.0	11.8	593.00	2.000	41.82	59.80	2.84	1.55	90.50
6			628.33	2.000	54.19	64.54	6.03	2.57	86.31
7			650.00	2.000	60.11	65.92	9.17	3.38	82.73
8			675.00	2.000	63.36	65.50	14.55	4.55	76.84
9	11.8	11.8	593.00	2.000	45.13	63.80	3.10	1.67	90.43
10			628.33	2.000	58.30	68.79	6.62	2.79	86.10
11			650.00	2.000	64.18	70.08	10.13	3.68	82.29
12			675.00	2.000	66.41	69.12	16.38	5.00	75.64

TABLE XXVI - PRODUCTION AND COST[1] INFORMATION FOR A TWO STAGE REACTOR WITH BOTH STAGES PACKED WITH SHELL 105 CATALYST

Run No.	Styrene Produced (Lbs/Hr)	Styrene Product Cost	Fixed Cost	Materials Cost		Energy Costs				
				Ethylbenzene	Vent Gas	Finishing	Furnace	Interstage	Condenser	Recycle
1	14596.	23.34	1.302	17.65	(.7958)	.4580	.5550	.1610	2.212	1.799
2	18978.	22.55	1.001	18.49	(.9033)	.4580	.4858	.1700	1.692	1.159
3	21138.	22.71	.8988	19.25	(1.001)	.4580	.4691	.1800	1.512	.9414
4	22538.	23.65	.8430	20.62	(1.176)	.4580	.4748	.1999	1.407	.8225
5	16044.	23.69	1.184	17.63	(.7978)	.4580	.5061	.2995	2.859	1.549
6	20791.	22.83	.9138	18.46	(.9045)	.4580	.4442	.2928	2.197	.9732
7	23064.	22.98	.8238	19.22	(1.003)	.4580	.4300	.2999	1.973	.7815
8	24311.	23.98	.7815	20.61	(1.183)	.4580	.4390	.3254	1.861	.6916
9	17317.	23.14	1.097	17.65	(.7972)	.4580	.5634	.1603	2.648	1.364
10	22367.	22.45	.8494	18.50	(.9069)	.4580	.5024	.1703	2.041	.8362
11	24625.	22.71	.7716	19.30	(1.011)	.4580	.4926	.1824	1.846	.6704
12	25480.	23.98	.7457	20.88	(1.215)	.4580	.5148	.2083	1.772	.6153

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[1] All costs presented in ¢/Lb styrene produced

TABLE XXVII – CONDITIONS AND CONVERSION INFORMATION FOR A TWO STAGE REACTOR WITH THE FIRST STAGE PACKED WITH SHELL 105 AND THE SECOND WITH SHELL 015 CATALYST

Run No.	Molar Steam to Oil Ratio		Temperature in (C)	Pressure in (ATM)	Conversion %				
	Bed 1	Bed 2			Styrene	Equilibrium	Toluene	Benzene	Styrene Selectivity
1	8.0	8.0	593.00	2.000	35.30	57.92	1.68	.92	93.13
2			628.33	2.000	48.77	63.70	3.73	1.65	89.99
3			650.00	2.000	55.51	65.63	5.90	2.36	87.05
4			675.00	2.000	61.10	65.88	9.76	3.58	82.08
5	8.0	11.8	593.00	2.000	38.42	64.89	1.73	.94	93.49
6			628.33	2.000	52.77	70.25	3.89	1.72	90.39
7			650.00	2.000	60.45	71.67	6.19	2.48	87.45
8			675.00	2.000	65.99	71.10	10.33	3.38	82.34
9	11.8	11.8	593.00	2.000	41.76	68.54	2.02	1.09	93.07
10			628.33	2.000	56.97	74.02	4.49	1.96	89.83
11			650.00	2.000	64.76	75.37	7.10	2.80	86.73
12			675.00	2.000	69.51	74.22	11.84	4.29	81.16

TABLE XXVIII - PRODUCTION AND COST[1)] INFORMATION FOR A SINGLE STAGE REACTOR PACKED WITH SHELL 105 CATALYST

Run No.	Styrene Produced (Lbs/Hr)	Styrene Product Cost	Fixed Cost	Material Cost			Energy Costs			
				Ethylbenzene	Vent Gas	Finishing	Furnace	Interstage	Condenser	Recycle
1	13543.	23.46	1.403	17.16	(.7211)	.4580	.5817	.1735	2.389	2.014
2	18560.	22.03	1.024	17.75	(.7963)	.4580	.4845	.1738	1.736	1.207
3	21299.	21.88	.8920	18.34	(.8725)	.4580	.4554	.1786	1.507	.9269
4	23443.	22.44	.8105	19.44	(1.016)	.4580	.4485	.1922	1.360	.7532
5	14740.	23.88	1.289	17.09	(.7142)	.4580	.5358	.3260	3.118	1.772
6	20248.	22.31	.9383	17.67	(.7891)	.4580	.4449	.3006	2.263	1.025
7	23194.	22.13	.8192	18.26	(.8662)	.4580	.4185	.2982	1.970	.7718
8	25320.	22.72	.7504	19.38	(1.014)	.4580	.4148	.3124	1.795	.6253
9	16024.	23.27	1.186	17.17	(.7246)	.4580	.5953	.1732	2.867	1.552
10	21858.	21.95	.8692	17.78	(.8029)	.4580	.5041	.1743	2.095	.8783
11	24847.	21.89	.7647	18.40	(.8842)	.4580	.4805	.1807	1.837	.6557
12	26669.	22.70	.7124	19.65	(1.047)	.4580	.4862	.1990	1.701	.5446

[1)] All cost presented are in ¢/Lb of styrene produced

TABLE XXIX - CONDITION AND CONVERSION INFORMATION FOR A TWO STAGE REACTOR WITH BOTH STAGES PACKED WITH SHELL 015 CATALYST

Run No.	Molar Steam to Oil Ratio		Temperature in (C)	Pressure in (ATM)	Conversion %				
	Bed 1	Bed 2			Styrene	Equilibrium	Toluene	Benzene	Styrene Selectivity
1	8.0	8.0	593.00	2.000	33.92	59.27	.52	.21	97.89
2			628.33	2.000	48.17	66.19	1.68	.69	95.30
3			650.00	2.000	56.28	68.73	3.19	1.33	92.57
4			675.00	2.000	63.09	69.37	6.28	2.65	87.60
5	8.0	11.8	593.00	2.000	37.17	66.32	.57	.23	97.89
6			628.33	2.000	52.67	72.86	1.84	.76	95.29
7			650.00	2.000	61.35	74.90	3.49	1.45	92.54
8			675.00	2.000	68.22	74.72	6.86	2.90	87.49
9	11.8	11.8	593.00	2.000	40.22	70.40	.63	.25	97.86
10			628.33	2.000	56.91	77.09	2.03	.83	95.21
11			650.00	2.000	66.02	79.14	3.85	1.60	92.36
12			675.00	2.000	72.54	78.68	7.63	3.22	86.98

TABLE XXX - PRODUCTION AND COST[1] INFORMATION FOR A SINGLE STAGE REACTOR WITH BOTH STAGES PACKED WITH SHELL 015 CATALYST

Run No.	Styrene Produced (Lbs/Hr)	Styrene Product Cost	Fixed Cost	Material Cost			Energy Costs			
				Ethylbenzene	Vent Gas	Finishing	Furnace	Interstage	Condenser	Recycle
1	13014.	23.06	1.460	16.35	(.5917)	.4580	.6090	.1439	2.494	2.135
2	18480.	21.23	1.028	16.79	(.6537)	.4580	.4886	.1466	1.752	1.216
3	21592.	20.90	.8798	17.29	(.7224)	.4580	.4508	.1522	1.495	.9008
4	24208.	21.28	.7848	18.27	(.8569)	.4580	.4360	.1656	1.325	.6985
5	14259.	23.50	1.332	16.35	(.5927)	.4580	.5567	.3035	3.231	1.864
6	20208.	21.56	.9402	16.79	(.6559)	.4580	.4474	.2757	2.276	1.029
7	23537.	21.21	.8071	17.29	(.7260)	.4580	.4137	.2719	1.949	.7461
8	26173.	21.61	.7258	18.29	(.8648)	.4580	.4027	.2833	1.744	.5731
9	15430.	22.85	1.231	16.35	(.5928)	.4580	.6216	.1432	2.986	1.649
10	21836.	21.12	.8702	16.81	(.6569)	.4580	.5069	.1466	2.106	.8803
11	25329.	20.86	.7500	17.33	(.7291)	.4580	.4732	.1533	1.810	.6246
12	27831.	21.42	.6826	18.40	(.8767)	.4580	.4680	.1702	1.638	.4811

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[1] All costs presented in ¢/Lb of styrene produced

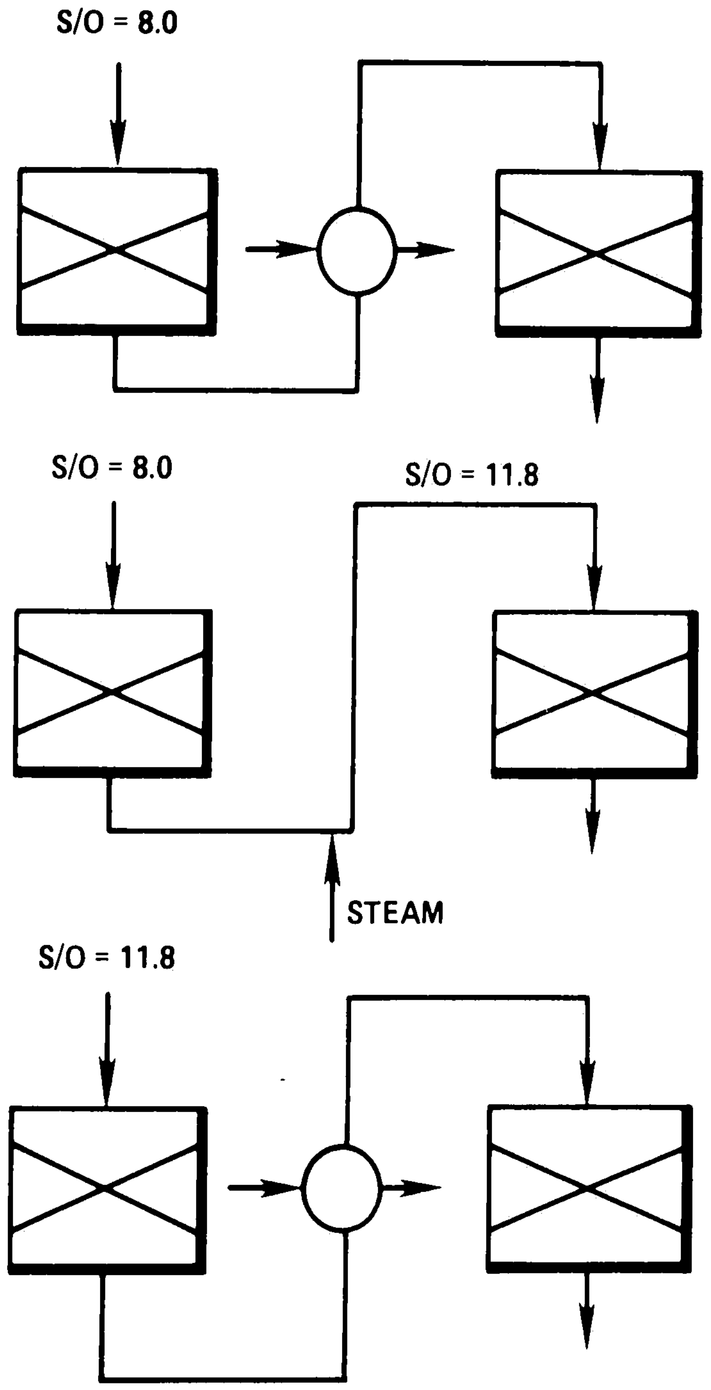

Figure 51 THE THREE INTERSTAGE HEATING CONFIGURATIONS INVESTIGATED

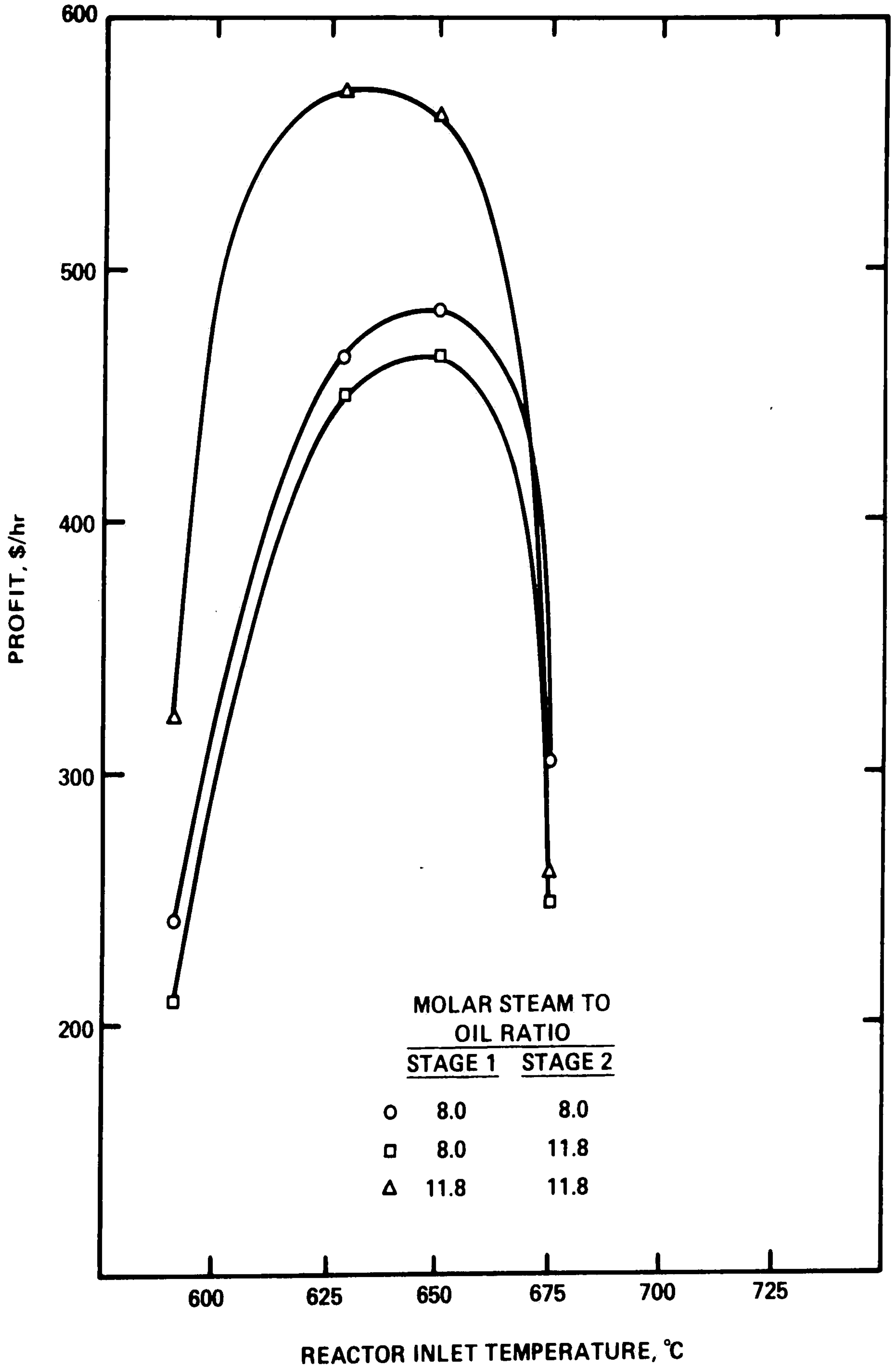

Figure 52 PROFIT VERSUS REACTOR INLET TEMPERATURE FOR A TWO STAGE REACTOR PACKED WITH SHELL 105 CATALYST

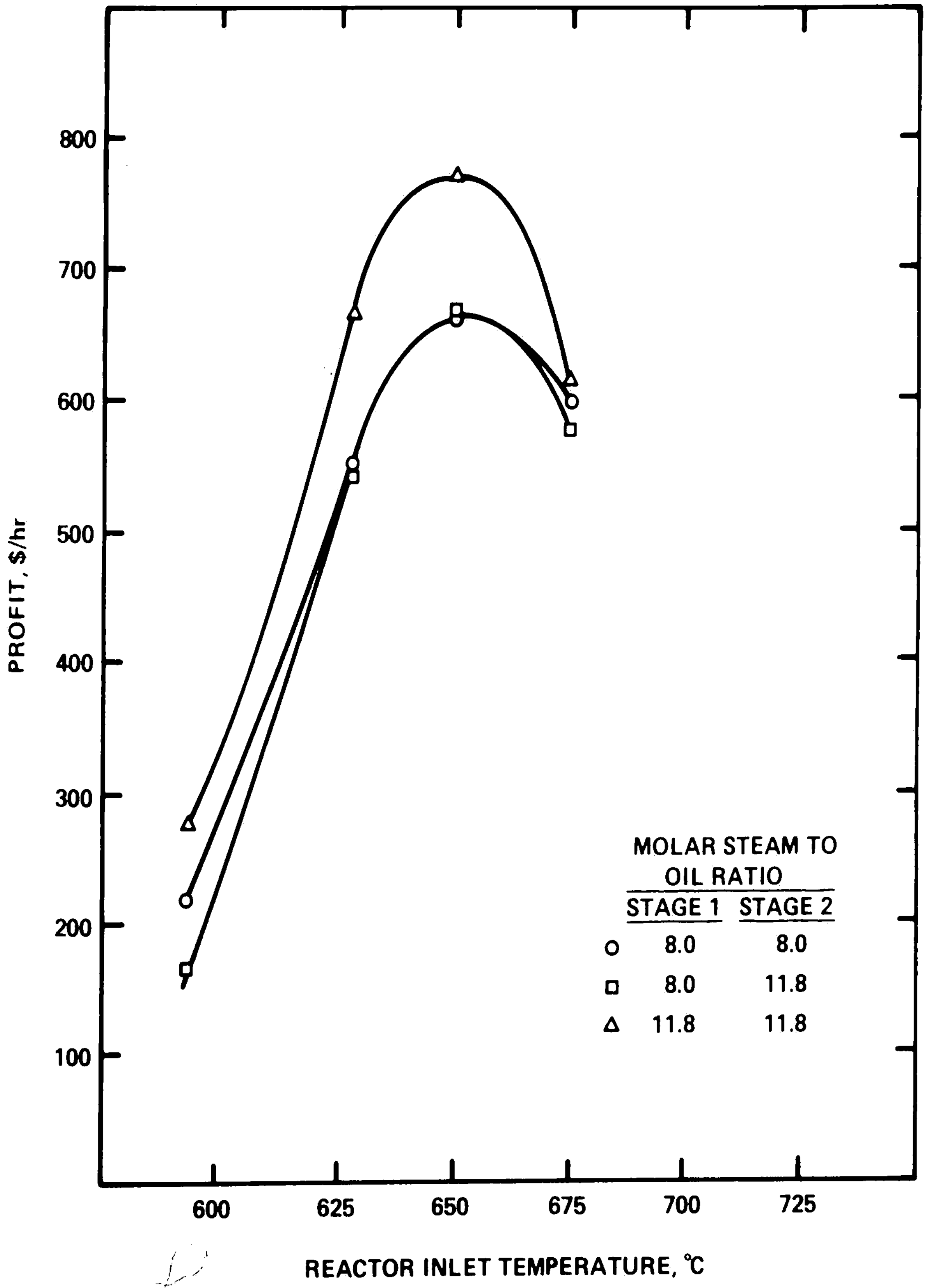

Figure 53 PROFIT VERSUS REACTOR INLET TEMPERATURE FOR A TWO STAGE REACTOR WITH THE FIRST STAGE PACKED WITH SHELL 105 CATALYST AND THE SECOND STAGE PACKED WITH SHELL 015 CATALYST

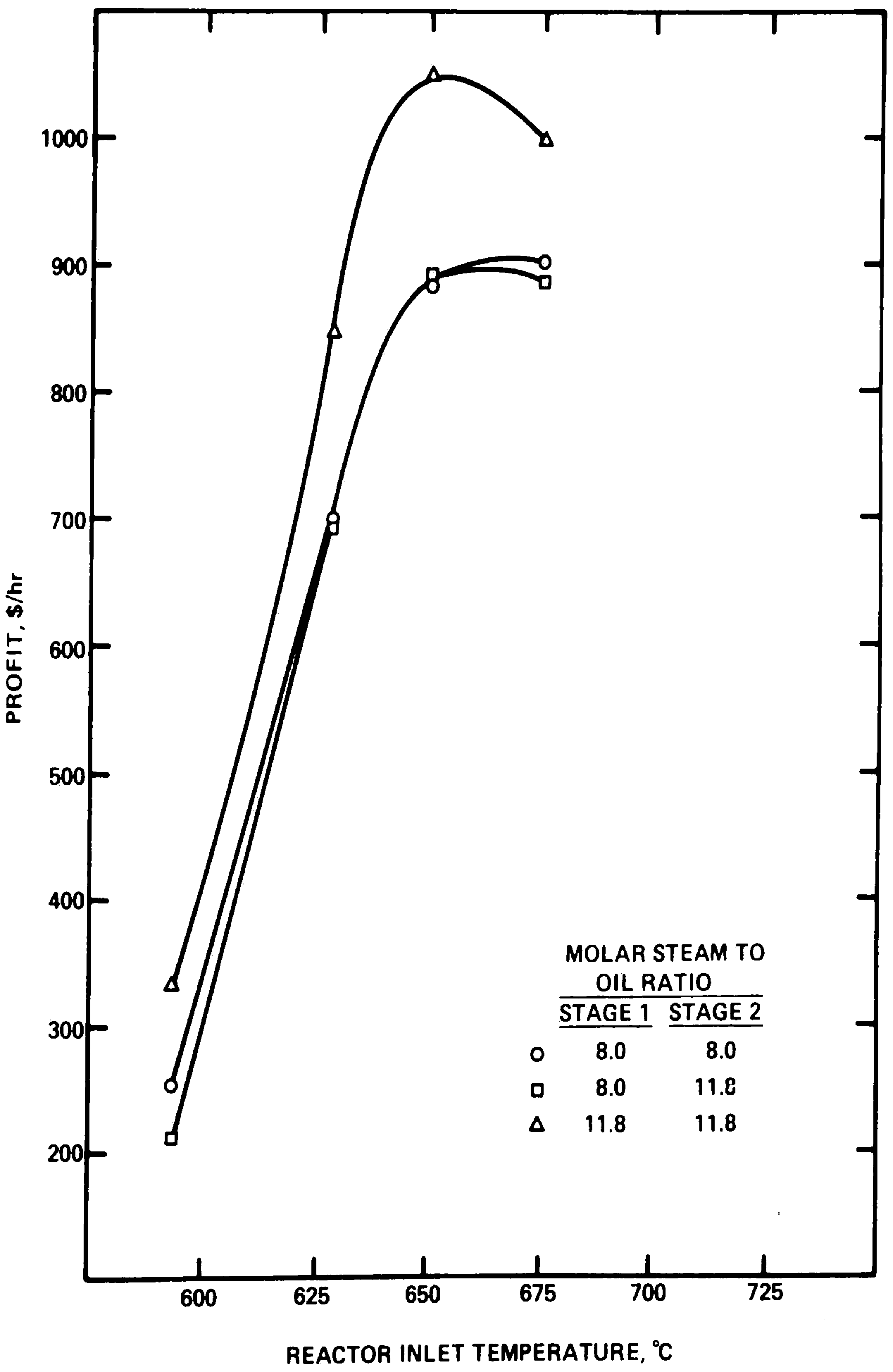

Figure 54 PROFIT VERSUS REACTOR INLET TEMPERATURE FOR A TWO STAGE REACTOR PACKED WITH SHELL 015 CATALYST

Conclusions and Recommendations

The literature kinetics and manufacturers' performance test data do not agree. The conversions reported by the manufacturers are higher than those predicted by the literature kinetics. The models predict styrene conversions which agree within an average of 5% of the manufacturers' data for both Shell 105 and 015 catalysts and within an average 10% for plant data.

The calibration of the gas reaction kinetics would be made possible by the reporting of gas production as well as ethylbenzene conversion for isothermal tests. Also, the dealkylation of paraffins present would have to be considered. Presently, the non-aromatic reaction kinetics under-predict the amount of non-condensable gas formed. The lower gas production has little or no effect on the mass or energy balances but could be corrected if it were deemed feasible.

Diffusion appears to be important. Reliable intrinsic kinetic data are needed to confirm this conclusion. The form of the kinetic model presented represents that data well over the entire range of testing, with the effect of the diffusion built into the expression. This type of approach does not allow the extension of the model to other particle sizes or structures.

In order to detect reactor non-idealities and study catalyst deactivation, more precise plant data, including a complete reactor temperature profile, would be needed. The reactor does appear to be adiabatic, with the difference between the calculated (by an energy balance) and measured exit temperatures having a mean of 3.6°C and a standard deviation of 5°C. The present correlation of catalyst activity with catalyst age is at best inaccurate and at worst very questionable due to the variability of plant data. It is possible that the catalyst deactivation is accelerated by temperature, which might reconcile the predicted and measured temperature profiles. The profiles agree at the reactor exit but not inside the bed.

Regarding the optimization study, the use of a high-selectivity catalyst requires a higher inlet temperature, which may not be feasible due to constraints on the boiler. Also, there are other catalysts, such as G64I, available which are high-selectivity catalysts and which are reported to be more active than Shell 015.

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Appendix A

Gas Reaction Kinetics

The gas reactions are

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{A-1}$$

$$1/2C_2H_4 + H_2O \rightarrow CO + 2H_2 \qquad \text{A-2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \text{A-3}$$

Although all the reactions occur in the gas phase these are called the gas reactions because both their reactants and products are gases at room temperature.

The kinetics for the first reaction over a reduced nickel catalyst are available from Akers (1) 1955 article. He investigated the reaction rate at temperature between 336 and 638°C, and proposed that the rate determining step was

$$CH_4 \rightarrow CH_2 + H_2$$

and his results were

$$r = kP_{CH_4} \qquad \text{A-4}$$

$$k = \exp\,[4.84 - (15.8\ \text{kcal/mol})/R_GT] \qquad \text{A-5}$$

However I used the rate expression used by Sheel (25)

i.e. $$r = k\,P_{CH_4}\,P_{H_2O} \qquad \text{A-6}$$

which assumes the reaction mechanism is the overall reaction.

Since no information was found in the literature for the second reaction kinetics, the same kinetic as reaction one could be used,

i.e. $$r = k\,P_{C_2H_4} \qquad \text{A-7}$$

However, I again assumed like Sheel (25) that the mechanism was the overall reaction,

i.e. $$r = k\,P_{C_2H_4}^{1/2}\,P_{H_2} \qquad \text{A-8}$$

Kinetics for the third reaction were available for an iron oxide catalyst containing chromium oxide from Moe (2). He fit National Bureau of Standards equilibrium data:

$$K_{eq} = \exp\,[-4.33 + (29.47\ \text{kcal/mol})/R_G T] \qquad \text{A-9}$$

$$K_{eq} = \frac{P_{CO_2}\,P_{H_2}}{P_{CO}\,P_{H_2O}} \qquad \text{A-10}$$

where

K_{eq} = the equilibrium constant

R_G = ideal gas content, 1.987 ca/mol °K

T = absolute temperature, °K

P_i = partial pressure of component i

Using this expression, his experimental analysis yielded

$$k = \exp\,[16.0 - (31.54 \text{ kcal/mol})/R_G T] \qquad \text{A-11}$$

for

$$r = k\left[P_{CO}\ P_{H_2}\ \frac{1}{K_{eq}}\ P_{CO_2}\ P_{H_2O}\right] \qquad \text{A-12}$$

There is a more recent article that came to my attention toward the end of my research by Singh and Saraf (3). They reviewed the available data and proposed a rate expression which is valid over a large range of conditions.

As discussed in the text, the gas reaction kinetics are not crucial. As long as the gas reactions give reasonable results and the aromatic reaction rates are calibrated with a model including the gas reactions, the model should predict the conversions of interest. The table that follows summarizes the kinetic expressions and constants used.

Reaction	Rate Expression	Frequency Factor (A)	Activation Energy (E_a, kcal/mol)
$CH_4+H_2O \rightarrow CO+3H_2$	$k\ P_{CH_4}\ P_{H_2O}$	4.84	15.8
$1/2C_2H_4+H_2O \rightarrow CO+2H_2$	$k\ P_{C_2H_4}^{1/2}\ P_{H_2O}$	4.84	15.8
$CO+H_2O \rightarrow CO_2+H_2$	$k\ P_{CO}\ P_{H_2O}$	16.0	31.54
$CO_2+H_2 \rightarrow CO+H_2O$	$k\ P_{CO_2}\ P_{H_2}$	20.33	61.01

where

k = reaction rate constant, kg mol/kg catalyst hr

= $\exp(A - E_a/R_GT)$

A = frequency factor

E_a = activation energy, kcal/mol

R_G = ideal gas constant, 1.987 cal/mol °K

T = absolute temperature, °K

Appendix B

Aromatic Reaction Rate Constants and Equilibrium Data

The three main reactions are:

$$\phi\text{-CH}_2\text{-CH}_3 \rightleftharpoons \phi\text{-CH=CH}_2 + \text{H}_2 \qquad \text{B-1}$$

$$\phi\text{-CH}_2\text{-CH}_3 + \text{H}_2 \rightarrow \phi\text{-CH}_3 + \text{CH}_4 \qquad \text{B-2}$$

$$\phi\text{-CH}_2\text{-CH}_3 \rightarrow \phi\text{-H} + \text{C}_2\text{H}_4 \qquad \text{B-3}$$

Of the three only the first one is reversible as demonstrated by the following calculations:

From Rossini (26) at 900°K

$$K_{eq_1} = 0.375 \text{ atm} \qquad \text{B-4}$$

$$K_{eq_2} = 3.57 \times 10^6 \qquad \text{B-5}$$

$$K_{eq_3} = 1.07 \times 10^9 \text{ atm} \qquad \text{B-6}$$

Assuming that 1% of the ethylbenzene is converted to toluene and 1% to benzene. Then the partial pressures of EB, SYY and H_2 assuming the first reaction goes to equilibrium can be calculated. Next the mass action expressions for the second and third reactions can be calculated and compared to their equilibrium constants.

Basis:

1 atm pressure

1 mole EB

12.5 moles H_2O

900°K temperature

Species i	Initial moles of i	Final moles of i	Partial Pressure of i (atm)
EB	1	0.142	0.00986
H_2O	12.5	12.5	0.8616
STY	0	0.838	0.5776
H_2	0	0.828	0.5707
Tol or CH_4	0	0.01	0.0069
BEN or C_2H_4	0	0.01	0.0069
Total moles =	13.5	14.508	

From the table on above

$$J_{A,2} = \frac{(0.0069 \text{ atm})\ (0.0069 \text{ atm})}{(0.00986 \text{ atm})\ (0.5776 \text{ atm})} \qquad \text{B-7}$$

$$= 8.84 \times 10^{-4}$$

$$<< 10^{6}$$

So the reaction is essentially irreversible.

Similarly

$$J_{A3} = 4.8 \times 10^{-3} \text{ atm} \qquad \text{B-8}$$
$$<< 10^9 \text{ atm}$$

Thus only the main reaction is reversible. Rossni's equilibrium data between 300°K and 1000°K was fit weighting the 800, 900, and 1000°K points. This yielded the following equation

$$\ln K_{eq_1} = 15.202 - (29.0 \text{ kcal/mol})/R_G T \qquad \text{B-9}$$

where

K_{eq} = reaction 1's equilibrium constants, atm

R_G = ideal gas content, 1.987 cal/mol °K

T = absolute temperature °K

Literature Kinetics

The kinetics available in the literature for these three reactions is summarized in the table that follows:

Source	Styrene		Toluene		Benzene		Notes	References
	A	E_a (kcal/mol)	A	E_a (kcal/mol)	A	E_a (kcal/mol)		
Wenner & Dybdal	9.233	21.775	-	-	-	-	-	4
Sheet								
April	8.1030	21.708	8.4848	21.851	21.4279	49.675	-	5
May	8.1614	21.708	8.5962	21.857	21.4541	49.675	-	25
June	8.0272	21.708	8.3106	21.857	21.2604	49.675	-	25
Poly-29	8.2907	21.708	8.4628	21.85	21.4181	49.675	-	6
Clough	7.189		18.52	-	-	-	-	6
Carrá	22.00	45.8	14.78	45.8 1)	5.91	45.8 1)	Z = 8.03	7
Lebedev	25.91 2)	46.1	- 3)	- 3)	- 3)	- 3)	$b_o = 0.0218$ atm^{-1} $\lambda = 6995$°K	8

$$k = \exp\,(A - E_a/R_GT)\ \text{kg mol/kg catalyst-hr}$$

See Table I for the form of the literature kinetics

1) The combined reaction rate constant for the dealkylation reaction to benzene and toluene was given at 630°C. The numbers in this table were calculated using the main reaction activation energy and assuming a benzene to toluene (B/T) ratio of 0.4.

2) A missprint was discovered in the article. The k_{10} was reported as 2.18×10^{14} rather than 1.78×10^{14} mol/kg catalyst atm hr obtained from a least squares fit of the three points in the article.

3) The article can be consulted for these kinetics. They are not reported here since the analysis of the data is not straight forward.

Appendix C

Langmuir-Hinshelwood Mechanism for Carrás (7) Kinetics

The main reaction is

$$EB \rightleftharpoons STY + H_2 \quad \text{and} \quad K_{eq} = \frac{P_{STY} P_{H_2}}{P_{EB}} \qquad \text{C-1}$$

The proposed reaction scheme is

Step

1 $$EB_{(g)} + S \rightleftharpoons (EB \cdot S) \quad K_{EB} = \frac{(EB \cdot S)}{P_{EB}\, S} \qquad \text{C-2}$$

2 $$(EB \cdot S) \rightleftharpoons (STY \cdot S) + H_{2(g)}$$

$$K'_{eq} = \frac{(STY \cdot S)\, P_{H_2}}{(EB \cdot S)} \qquad \text{C-3}$$

3 $$(STY \cdot S) \rightleftharpoons STY_{(g)} + S$$

$$K_{STY} = \frac{(STY \cdot S)}{P_{STY}\, S} \qquad \text{C-4}$$

where

S = an unoccupied active catalyst site

EB = an ethylbenzene molecule

STY = a styrene molecule

(N•S) = a molecule of N adsorbed on an active site

H_2 = a hydrogen gas molecule

K_{EB} K_{STY} = the equilibrium adsorption coefficient for ethylbenzene

K_{eq} = the equilibrium constant in terms of partial pressure

K'_{eq} = the equilibrium constant in terms of adsorbed species

P_N = the partial pressure of component N

Combining equations 1-4,

$$K_{eq} = \frac{K'_{eq}\ K_{EB}}{K_{STY}} \qquad \text{C-5}$$

Assuming that the reaction (Step 2) is rate controlling,

$$r_{EB} = k_1\ \left[(EB\cdot S) - \frac{1}{K'_{eq}}\ (STY\cdot S)\ P_{H_2}\right] \qquad \text{C-6}$$

where

r_{EB} = the rate of disappearance of EB

k_1 = the reaction rate constant

If Step 2 is rate controlling, the other two steps will be in equilibrium. Substituting equations 2 and 4 into equation 6:

$$r_{EB} = k_1\ \left[K_{EB}\ P_{EB}\ S - \frac{1}{K'_{EB}}\ K_{STY}\ P_{STY}\ P_{H_2}\ S\right] \qquad \text{C-7}$$

The total number of surface sites (S_{TOTAL}) equals:

$$S_{TOTAL} = S + (EB \cdot S) + (STY \cdot S) \qquad \text{C-8}$$

Again, using equations 2 and 4:

$$S_{TOTAL} = S + K_{EB}\ P_{EB}\ S + K_{STY}\ P_{STY}\ S \qquad \text{C-9}$$

or

$$S = \frac{TOTAL}{(1 + K_{EB}\ P_{EB} + K_{STY}\ P_{STY})} \qquad \text{C-10}$$

Using this result in equation 7 and equation 5,

$$r_{EB} = k_1\ K_{EB}(S_{TOTAL})\ \frac{[P_{EB} - \frac{1}{K_{eq}}\ P_{STY}\ P_{H_2}]}{(1 + K_{EB}\ P_{EB} + K_{STY}\ P_{STY})} \qquad \text{C-11}$$

Carrá and Forni found the one in the denominator to be small compared with the other two terms. This is equivalent to saying the number of unoccupied sites is small compared to the occupied sites (see equation 8). Neglecting this term and dividing the numerator and denominator of equation 11 by K_{EB}, it becomes:

$$r_{EB} = k'_1\ \frac{P_{EB} - \frac{1}{K_{eq}}\ P_{STY}\ P_{H_2}}{P_{EB} + z\ P_{STY}} \qquad \text{C-12}$$

where

$k'_1 = k_1 S_{TOTAL}$

$z = K_{STY}/K_{EB}$

This is the kinetic expression Carrá and Forni (7) used.

Appendix D

Langmuir-Hinshelwood Mechanism for Lebedev's (8) Kinetics

The main reaction is

$$EB \rightleftharpoons STY + H_2 \quad \text{and} \quad K_{eq} = \frac{P_{STY} P_{H_2}}{P_{EB}} \qquad \text{D-1}$$

The proposed reaction scheme is

Step

1 $EB_{(g)} + 2S \rightleftharpoons (EB \cdot S_2)$

$$K_{EB} = \frac{(EB \cdot S_2)}{P_{EB} S^2} \qquad \text{D-2}$$

2 $(EB \cdot S_2) \rightleftharpoons (STY \cdot S_2) + H_{2(g)}$

$$K'_{eq} = \frac{(STY \cdot S_2) P_{H_2}}{(EB \cdot S_2)} \qquad \text{D-3}$$

3 $(STY \cdot S_2) \rightleftharpoons STY_{(g)} + 2S$

$$K_{STY} = \frac{(STY \cdot S_2)}{P_{STY} S^2} \qquad \text{D-4}$$

where

S = an unoccupied active catalyst site

EB = an ethylbenzene molecule

STY = a styrene molecule

$(N \cdot S_n)$ = a molecule of N adsorbed on n active sites

H_2 = a hydrogen gas molecule

K_{EB} K_{STY} = the equilibrium adsorption coefficient for ethylbenzene

K_{eq} = the equilibrium constant in terms of partial pressure

K'_{eq} = the equilibrium constant in terms of adsorbed species

P_N = the partial pressure of component N

Combining equations 1-4

$$K_{eq} = \frac{K'_{eq} K_{EB}}{K_{STY}} \qquad \text{D-5}$$

Assuming that the reaction (Step 2) is rate controlling,

$$r_{EB} = k_1 \left[(EB \cdot S_2) - \frac{1}{K'_{eq}} (STY \cdot S_2) P_{H_2} \right] \qquad \text{D-6}$$

where

r_{EB} = the rate of disappearance of EB

k_1 = the reaction rate constant

If Step 2 is rate controlling, the other two steps will be in equilibrium. Substituting equations 2 and 4 into equation 6:

$$r_{EB} = k_1 \left[K_{EB} P_{EB} S^2 - \frac{1}{K'_{eq}} K_{STY} P_{STY} P_{H_2} S^2 \right] \qquad \text{D-7}$$

The total number of surface sites (S_{TOTAL}) equals:

$$S_{TOTAL} = S + 2(EB \cdot S_2) + 2(STY \cdot S_2) \qquad \text{D-8}$$

Again, using equations 2 and 4:

$$S_{TOTAL} = S + 2K_{EB}\, P_{EB}\, S + 2K_{STY}\, P_{STY}\, S \qquad \text{D-9}$$

or

$$S = \frac{S_{TOTAL}}{(1 + 2K_{EB}\, P_{EB} + 2K_{STY}\, P_{STY})} \qquad \text{D-10}$$

Using this result in equation 7 and equation 5,

$$r_{EB} = k_1\, K_{EB}(S_{TOTAL})^2 \frac{[P_{EB} - \frac{1}{K_{eq}} P_{STY}\, P_{H_2}]}{(1 + 2K_{EB}\, P_{EB} + K_{STY}\, P_{STY})^2} \qquad \text{D-11}$$

Lebedev assumed that styrene was adsorbed much more strongly than ethylbenzene. Thus,

$$r_{EB} = k_1\, K_{EB}(S_{TOTAL})^2 \frac{[P_{EB} - \frac{1}{K_{eq}} P_{STY}\, P_{H_2}]}{(1 + 2K_{STY}\, P_{STY})^2} \qquad \text{D-12}$$

Letting

$$k'_1 = k_1\, K_{EB}(S_{TOTAL})^2 \qquad \text{D-13}$$

and

$$b = 2K_{STY} \qquad \text{D-14}$$

where

$$b = b_o \exp \lambda/T \qquad \text{D-15}$$

equation 12 becomes

$$r_{EB} = k'_1 \frac{[P_{EB} - \frac{1}{K_{eq}} P_{STY} P_{H_2}]}{(1 + b\, P_{STY})^2} \qquad \text{D-16}$$

This is the rate expression Lebedev (8) et al. used.

Appendix E

Heat of Reaction and Heat Capacity Data

Heat of Reaction Data

Sheel fit API 44 heat of reaction (ΔH_{rxn}) data with a first order temperature dependence equation (25).

i.e. $$\Delta H_{rxni} = HOj + H1{*}T_i \text{ cal/kgmol} \qquad \text{E-1}$$

where

ΔH_{rxnj} = the heat of reaction j, cal/kgmol

H_{Oj} = the tempeature independent heat of reaction term, cal/kgmol

H_{1j} = the temperature dependent heat of reaction term, cal/kgmol °K

T = absolute temperature, °K

Most of the data in the table below is from his thesis.

Reaction No.	Reaction	HO x 10^{-6} cal/kg mol	Hτ x 10^{-3} cal/kg mol °K
1	$EB \rightleftharpoons STY + H_2$	28.84	1.090
2	$EB + H_2 \rightarrow Tol + CH_4$	25.99	-1.90
3	$EB \rightarrow BEN + C_2H_4$	-12.70	-3.15
4	$CH_4+H_2O \rightarrow CO+3H_2$	19.60	2.11
5	$1/2C_2H_4+H_2O \rightarrow CO+2H_2$	50.46	3.96
6	$CO + H_2O \rightleftharpoons CO_2 + H_2$	10.80	2.50
7	$XYL + H_2 \rightarrow Tol + CH_4$	-9.853 1)	-2.425 1)

1) These numbers were obtained by a linear fit of API 44 (20) data between 600 and 1100°K by the author.

Heat Capacity Data

The heat capacities were taken from the appendix of The Properties of Liquids and Gases (21).

$$C_p = C_p0 + C_p1(T) + C_p2(T)^2 + C_p3(T)^3$$

where

C_p = heat capacity, cal/kgmol °K

T = absolute temperature °K

Component	$C_p0 \times 10^{-3}$	Cp1	$Cp2 \times 10^3$	$Cp3 \times 10^6$
Ethylbenzene	-10.92	168.9	-114.9	31.07
Styrene	-6.747	147.1	-96.09	23.73
Toluene	-5.817	122.4	-66.05	11.73
Benzene	-8.101	113.3	-72.06	17.03
Xylene	6.495	147.4	85.04	18.27
Water	7.701	0.4595	25.21	-0.859
Hydrogen	6.483	2.215	-32.98	1.826
Carbon Monoxide	7.373	-3.070	6.662	-3.037
Carbon Dioxide	4.728	17.54	-13.38	18.27
Methane	4.598	12.45	2.860	-2.703
Ethylene	0.909	37.40	-19.94	4.192
Parafins 1)	-1.456	184.2	-100.2	21.15

1) The reactor feed contains parafins which were identified by chromatography as octanes. These heat capacity constants are those of n-octane.

Appendix F

Langmuir-Hinshelwood Equations for Model 5 Kinetics

The main reaction is

$$EB \rightleftharpoons STY + H_2 \text{ and } K_{eq} = \frac{P_{STY}\,P_{H_2}}{P_{EB}} \qquad \text{F-1}$$

The proposed reaction scheme is

Step

1 $EB_{(g)} + 2S \rightleftharpoons (EB\cdot S_2)$

$$K_{EB} = \frac{(EB\cdot S_2)}{P_{EB}\,S^2} \qquad \text{F-2}$$

2 $(EB\cdot S_2) \rightleftharpoons (STY\cdot S) + H_2 + S$

$$K'_{eq} = \frac{(STY\cdot S)\,P_{H_2}\,S}{(EB\cdot S_2)} \qquad \text{F-3}$$

3 $(STY\cdot S) \rightleftharpoons STY + S$

$$K_{STY} = \frac{(STY\cdot S)}{P_{STY}\,S} \qquad \text{F-4}$$

where

S = an unoccupied active catalyst site

EB = an ethylbenzene molecule

STY = a styrene molecule

$(N \cdot S_n)$ = a molecule of N adsorbed on n active site(s)

H_2 = a hydrogen gas molecule

K_{EB} K_{STY} = the equilibrium adsorption coefficient for ethylbenzene

K_{eq} = the equilibrium constant in terms of partial pressure

K'_{eq} = the equilibrium constant in terms of adsorbed species

P_N = the partial pressure of component N

Combining equations 1-4,

$$K_{eq} = K'_{eq} \frac{K_{EB}}{K_{STY}} \qquad \text{F-5}$$

Assuming that the reaction (Step 2) is rate controlling,

$$r_{EB} = k_1 \left[(EB \cdot S_2) - \frac{1}{K'_{eq}} S\ (STY \cdot S)\ P_{H_2} \right] \qquad \text{F-6}$$

where

r_{EB} = the rate of disappearance of EB

k_1 = the reaction rate constant

If Step 2 is rate controlling, the other two steps will be in equilibrium. Substituting equations 2 and 4 into equation 6:

$$r_{EB} = k_1 \left[K_{EB} P_{EB} S^2 - \frac{1}{K'_{eq}} S \, (STY \cdot S) \, P_{H_2} \right] \qquad \text{F-7}$$

The total number of surface sites (S_{TOTAL}) equals:

$$S_{TOTAL} = S + 2(EB \cdot S_2) + (STY \cdot S) \qquad \text{F-8}$$

Again, using equations 2 and 4:

$$S_{TOTAL} = S + 2K_{EB} P_{EB} S^2 + K_{STY} P_{STY} S \qquad \text{F-9}$$

$$\therefore 2K_{EB} P_{EB} S^2 + (1 + K_{STY} P_{STY}) S - S_{TOTAL} = 0.0 \qquad \text{F-10}$$

$$\frac{2K_{EB} P_{EB}}{(1 + K_{STY} P_{STY})} S^2 + S - \frac{S_{TOTAL}}{(1 + K_{STY} P_{STY})} = 0 \qquad \text{F-11}$$

Using the quadratic formula

$$S = \frac{(1 + K_{STY} P_{EB})}{-4 K_{EB} P_{EB}} \left[1 \pm \sqrt{1 + \frac{8 S_{TOTAL} K_{EB} P_{EB}}{(1 + K_{STY} P_{STY})^2}} \right] \qquad \text{F-12}$$

The functional surface coverage (S, i.e. the fraction of uncovered active surface sites) is usually small. To evaluate the radical in equation 12 we will look at two extremes.

Case I

$$\text{When } 1 \ll \frac{8\, S_{TOTAL}\, K_{EB}\, P_{EB}}{(1 + K_{STY}\, P_{STY})^2} \qquad \text{F-13}$$

$$\sqrt{1 + \frac{8\, S_{TOTAL}\, K_{EB}\, P_{EB}}{(1 + K_{STY}\, P_{STY})^2}} \cong \sqrt{\frac{8\, S_{TOTAL}\, K_{EB}\, P_{EB}}{(1 + K_{STY}\, P_{STY})}}$$

Taking the positive root

$$S_I = \sqrt{\frac{2\, S_{TOTAL}}{K_{EB}\, P_{EB}}} - \frac{(1 + K_{STY}\, P_{STY})}{4\, K_{EB}\, P_{EB}} \qquad \text{F-14}$$

$$S_I \cong \sqrt{\frac{2\, S_{TOTAL}}{K_{EB}\, P_{EB}}} \qquad \text{F-15}$$

Case II

$$\text{When } 1 \gg \frac{8\, S_{TOTAL}\, K_{EB}\, P_{EB}}{(1 + K_{STY}\, P_{STY})^2}$$

(i.e., $K_{STY}\, P_{STY}$ is large)

$$\sqrt{1 + \frac{8\, S_{TOTAL}\, K_{EB}\, P_{EB}}{(1 + K_{STY}\, P_{STY})^2}} \cong 1 + \frac{4\, S_{TOTAL}\, K_{EB}\, P_{EB}}{(1 + K_{STY}\, P_{STY})^2} \qquad \text{F-16}$$

Therefore the positive root of S is

$$S_{II} = \frac{S_{TOTAL}}{(1 + K_{STY}\ P_{STY})} \qquad \text{F-17}$$

$$\cong \frac{S_{TOTAL}}{K_{STY}\ P_{STY}} \qquad \text{F-18}$$

Cases I and II need to be combined to cover the transition region. Since S appears to the second power in equation 7 the following approximation is used:

$$\frac{1}{S^2} \cong \frac{1}{S_I^2} + \frac{1}{S_{II}^2} \qquad \text{F-19}$$

$$\cong \frac{K_{EB}\ P_{EB}}{2\ S_{TOTAL}} + \frac{(K_{STY}\ P_{STY})^2}{S_{TOTAL}^2} \qquad \text{F-20}$$

$$\cong \frac{(1/2\ K_{EB}\ S_{TOTAL})\ P_{EB} + (K_{STY}\ P_{STY})^2}{S_{TOTAL}^2} \qquad \text{F-21}$$

Substituting equation 20 into equation 7 and using equation 5

$$r_{EB} = \frac{k_1\ K_{EB}\ S_{TOTAL}^2\ [P_{EB} - 1/K_{eq}\ P_{STY}\ P_{H_2}]}{(1/2\ K_{EB}\ S_{TOTAL})\ P_{EB} + (K_{STY}\ P_{STY})^2}$$

F-22

let

$$k'_1 = 2k_1 S_{TOTAL} \qquad \text{F-23}$$

$$y = K_{STY} \sqrt{\frac{2}{K_{EB} S_{TOTAL}}} \qquad \text{F-24}$$

Then

$$r_{EB} = k'_1 \frac{[P_{EB} - 1/K_{eq} P_{STY} P_{H_2}]}{P_{EB} + (y P_{STY})^2} \qquad \text{F-25}$$

The initial reaction rate when

$$P_{STY} \sim 0$$

$$r_{EB\ initial} \cong k'_1 \qquad \text{F-26}$$

This agrees with Carra's experimental results. Once the reaction has proceeded,

$$(y P_{STY})^2 >> P_{EB}$$

$$r_{EB} \cong \frac{k'_1 [P_{EB} - 1/K_{eq} P_{STY} P_{H_2}]}{(y P_{STY})^2} \qquad \text{F-27}$$

This agrees with Lebedev's results.

Appendix G

Effectiveness Factor Derivation

The kinetic expression for the ethylbenzene dehydrogenation reaction is:

$$r_{EB} = k'_1 \frac{P_{EB} - P_{STY} \, P_{H_2}/K_{eq}}{\text{inhibitor}} \qquad \text{G-1}$$

In the catalyst pore, since the reaction is unimolar in all species, the rate of reaction also equals the rate of diffusion of the species, i.e.,

$$r_{EB} = \frac{-D_{EB}}{R_G T} \frac{d^2 P_{EB}}{dZ^2} \qquad \text{G-2}$$

$$r_{EB} = \frac{+D_{STY}}{R_G T} \frac{d^2 P_{STY}}{dZ^2} \qquad \text{G-3}$$

$$r_{EB} = \frac{+D_{H_2}}{R_G T} \frac{d^2 P_{H_2}}{dZ^2} \qquad \text{G-4}$$

Combining equations 2 and 3 and 2 and 4

$$D_{EB} \frac{d^2 P_{EB}}{dZ^2} + D_{STY} \frac{d^2 P_{STY}}{dZ^2} = 0 \qquad \text{G-5}$$

$$D_{EB} \frac{d^2 P_{EB}}{dZ^2} + D_{H_2} \frac{d^2 P_{H_2}}{dZ} = 0 \qquad \text{G-6}$$

The following boundary conditions apply

BC1 $$\left.\frac{dP_N}{dZ}\right|_{Z=0} = 0$$ Symmetry about particles center line

BC2 $P_{EB}\ (Z=L) = P_{EB,S}$ Know conditions

$P_{STY}\ (Z=L) = P_{STY,S}$ at catalyst

$P_{H_2}\ (Z=L) = P_{H_2,S}$ surface

Integrating equations 5 and 6 once using BC1

$$D_{EB} \frac{d\,P_{EB}}{dZ} + D_{STY} \frac{d\,P_{STY}}{dZ} = 0 \qquad \text{G-7}$$

$$D_{EB} \frac{d\,P_{EB}}{dZ} + D_{H_2} \frac{d\,P_{H_2}}{dZ} = 0 \qquad \text{G-8}$$

Integrating a second time using BC2

$$D_{EB}\ (P_{EB} - P_{EB,S}) + D_{STY}\ (P_{STY} - P_{STY,S}) = 0 \qquad \text{G-9}$$

$$D_{EB}\ (P_{EB} - P_{EB,S}) + D_{H_2}\ (P_{H_2} - P_{H_2,S}) = 0 \qquad \text{G-10}$$

Defining the following variables

$$X_P = \frac{P_{EB,S} - P_{EB}}{P_{EB,S}} \qquad \text{G-11}$$

(Note, this is the conversion that takes place in the pore, not the reactor conversion.)

$$\alpha_S = \frac{P_{STY,S}}{P_{EB,S}} \qquad \text{G-12}$$

$$\beta_S = \frac{P_{H_{2,S}}}{P_{EB,S}} \qquad \text{G-13}$$

$$\delta = \frac{D_{EB}}{D_{STY}} \qquad \text{G-14}$$

$$\zeta = \frac{D_{EB}}{D_{H_2}} \qquad \text{G-15}$$

Rearranging equations 9 and 10

$$P_{STY} = \left[\frac{P_{STY,S}}{P_{EB,S}} + \frac{D_{EB}}{D_{STY}} \frac{(P_{EB,S} - P_{EB})}{P_{EB,S}} \right] P_{EB,S} \qquad \text{G-16}$$

$$P_{H_2} = \left[\frac{P_{H_{2,S}}}{P_{EB,S}} = \frac{D_{EB}}{D_{H_2}} \frac{(P_{EB,S} - P_{EB})}{P_{EB,S}} \right] P_{EB,S} \qquad \text{G-17}$$

Using the variables defined in equations 11-15

$$P_{STY} = P_{EB,s}\,(\alpha_S + \delta X_p) \qquad \text{G-18}$$

$$P_{H_2} = P_{EB,S}\,(\beta_S + \zeta X_p) \qquad \text{G-19}$$

And from the definition of X_p

$$P_{EB} = P_{EB,S}\,(1-X_p) \qquad \text{G-20}$$

Substituting equations 18-20 into equation 1

$$r_{EB} = k'_1\,\frac{(1-X_p) - P_{EB,S}/K_{eq}\,(\alpha_S + \delta X_p)\,(\beta_S + \zeta X_p)}{\text{inhibitor}\,(X_p)} \qquad \text{G-21}$$

Let

$$H(X_p) = \frac{(1-X_p) - \gamma\,(\alpha_S + \delta X_p)\,(\beta_S + \zeta X_p)}{\text{inhibitor}\,(X_p)} \qquad \text{G-22}$$

where

$$\gamma = \frac{P_{EB,S}}{K_{eq}} \qquad \text{G-23}$$

Then

$$r_{EB} = k'_1\,H(X_p) \qquad \text{G-24}$$

Equating equations 2 and 24

$$\frac{D_{EB}}{RT}\,\frac{d^2\,P_{EB}}{dZ^2} = k'_1\,H(X_p) \qquad \text{G-25}$$

Using the definition of X_p (equation 20)

$$\frac{-D_{EB}\ P_{EB}}{RT}\ \frac{d^2\ X_p}{dZ^2} = k'_1\ H(X_p) \qquad \text{G-26}$$

Let

$$z = \frac{Z}{L} \qquad \text{G-27}$$

$$\phi^2 = \frac{k'_1 L^2\ RT}{D_{EB}\ P_{EB,S}} \qquad \text{G-28}$$

where

Z = the dimensionless position

ϕ = the Theile modulus

Then

$$\frac{d^2\ X_p}{dz^2} = -\phi^2\ H(X_p) \qquad \text{G-29}$$

$$2\ \frac{dX_p}{dz}\ \frac{d}{dz}\left(\frac{dX_p}{dz}\right) = -2\phi^2\ H(X_p)\ \frac{dX_p}{dz} \qquad \text{G-30}$$

$$\int 2\ \frac{dX_p}{dz}\ d\left(\frac{dX_p}{dz}\right) = \int -2\phi^2\ H(X_p)\ dX_p \qquad \text{G-31}$$

At the surface

BC3 $X_p = 0$ at $z = 1$

let $X_p = X_o$ at $z = 0$

BC4 $$\left.\frac{dX_p}{dz}\right|_{z\,=\,0} = 0$$

Using BC4

$$\int_{o}^{\frac{dX_p}{dz}} 2\,\frac{dX_p}{dz}\, d\,\frac{dX_p}{dz} = \int_{X_p}^{X_o} -2\phi^2\, H(X_p)\, dX_p \qquad \text{G-32}$$

$$\left(\frac{dX_p}{dz}\right)^2 \Bigg|_{o}^{\frac{dX}{dz}} = 2\phi^2 \int_{X_p}^{X_o} H(X_p)\, dX_p \qquad \text{G-33}$$

$$\frac{dX_p}{dz} = \sqrt{2\phi^2 \int_{o}^{X_o} H(X_p)\, dX_p} \qquad \text{G-34}$$

Using BC3 $$\left.\frac{dX_p}{dz}\right|_{z\,=\,1} = \phi\,\sqrt{2\int_{o}^{X_o} H(X_p)\, dX_p} \qquad \text{G-35}$$

The effectiveness factor (η) is defined as

$$\eta = \frac{\text{rate of reaction with pore diffusion resistance}}{\text{rate of reaction at surface conditions}} \qquad \text{G-36}$$

$$= \frac{\int k'_1\, H(X_p)\, dV}{\int k'_1\, H(X_p|_S)\, dV} \qquad \text{G-37}$$

$$= \frac{\int_o^1 k'_1\, H(X_p)\, dz}{k'_1\, H(0)} \qquad \text{G-38}$$

Substituting equation 29 into the numerator

$$\eta = \frac{+1}{H(0)\ \phi^2} \int_0^1 \frac{d^2\ X_p}{dz^2}\, dz \qquad \text{G-39}$$

$$= \frac{-1}{H(0)\ \phi^2} \int_0^{z=1} d \left(\frac{d^2\ X_p}{dz^2} \right) \qquad \text{G-40}$$

$$\eta = \frac{+1}{\phi^2} \frac{dX_p}{dz} \Bigg|_{z\ =\ 1} \qquad \text{G-41}$$

From equation 35

$$\eta = \frac{1}{\phi\ H(0)} \sqrt{2 \int_0^{X_o} H(X_p)\ dX_p} \qquad \text{G-42}$$

It is likely that if diffusion is an important consideration that

$$X_o \cong X_{eq} \qquad \text{G-43}$$

This can be checked by using a rearranged form of equation 34

$$\int_0^{X_o} \frac{dX_p}{\{2\phi^2 \int_0^{X_o} H(X_p)\ dX_p\}^{1/2}} = \int_0^1 dz = 1 \qquad \text{G-44}$$

Let

$$\phi^2 = \frac{\phi^2 H(X_p = 0)^2}{2 \int_o^{X_{eq}} H(X_p)\, dX_p} \qquad \text{G-45}$$

Then

$$\eta = 1/\Phi \qquad \text{G-46}$$

Integration of $\int_o^{X_{eq}} H(X_p)\, dX_p$:

Up to this point nothing has been said about the form of the inhibitor which is included in $H(X_p)$. The integration will be carried out for two different inhibitors: Carrá's and Model 5's.

Carrá

$$H(X_p)_c = \frac{R_{EB} - 1/K_{eq}\, P_{STY}\, P_{H_2}}{P_{EB} + z\, P_{STY}} \qquad \text{G-47}$$

Again using equations 18-20

$$H(X_p)_c = \frac{(1-X_p) - \gamma\, (\alpha_S + \delta X_p)\, (\beta_S + \zeta X_p)}{(1-X_p) + Z\, (\alpha_S + \delta X_p)} \qquad \text{G-48}$$

$$\frac{AX^2 + BX + C}{X + E} \qquad \text{G-49}$$

where

$$A = \gamma\delta\zeta/(Z\delta-1) \qquad \text{G-50}$$

$$B = (1 + \gamma(\alpha_S\zeta + \beta_S\delta))/(Z\delta-1) \qquad \text{G-51}$$

$$C = (1=\gamma\alpha_S\beta_S))/(Z\delta-1) \quad \text{G-52}$$

$$E = (1 + b\alpha_S)/(Z\delta-1) \quad \text{G-53}$$

$$\int_o^{X_o} H(X_p)_c \, dX_p = \int_o^{X_o} \frac{AX_p^2 + BX_p + C}{X_p + E} \, dX_p \quad \text{G-54}$$

$$= \int_o^{X_o} AX_p + \frac{(-AE + B) X_p + C}{X_p + E} \, dX_p \quad \text{G-55}$$

$$= \int_o^{X_o} AX_p + (-AE + B) + (AE^2 - BE + C) \frac{1}{XE} \, dX_p \quad \text{G-56}$$

$$= \frac{1}{2} AX_0^2 + (-AE + B) X_o + (AE^2 - BE + C) \ln (1 + \frac{X_o}{E}) \quad \text{G-57}$$

So for Carra's kinetics

$$\int_o^{X_o} H(X_p)_c \, dX_p = \frac{1}{2} AX_{eq}^2 + (-AE + B) X_{eq} + (AE^2 - BE + C) \quad \text{G-58}$$

$$\ln (1 + \frac{X_{eq}}{E})$$

where $X_o \cong X_{eq}$

Model 5

$$H(X_p)_S = \frac{P_{EB} - 1/K_{eq}\ P_{STY}\ P_{H_2}}{P_{EB} + (y\ P_{STY})^2} \qquad \text{G-59}$$

Again using equations 18-20

$$H(X_p)_S = \frac{(1-X_p) - \gamma\ (\alpha_S + \delta X_p)\ (\beta_S + \zeta X_p)}{(1-X_p) + y^2\ (\alpha_S + \delta X_p)^2} \qquad \text{G-60}$$

$$H(X_p)_S = \frac{AX^2 + BX + C}{X^2 + DX + E}$$

where

$A = -\gamma\delta\zeta/y^2\delta^2 P_{EB,S} = \gamma\zeta/y^2\delta P_{EB,S}$

$B = -(1 + \delta\alpha_S\zeta + \gamma\beta_S\delta)/y^2\delta^2 P_{EB,S}$

$C = (1 - \gamma\alpha_S\beta_S)/y^2\delta^2 P_{EB,S}$

$D = (2b\alpha_S\delta P_{EB,s} - 1)/y^2\delta^2 P_{EB,S}$

$E = (1 + P_{EB,S}\ b\alpha^2{}_S)/y^2\delta^2 P_{EB,S}$

$$H(X_p) = A + \frac{(B - DA)\ X_p + (C - AE)}{X_p^2 + DX_p + E}$$

$$= A + \frac{AD-B}{2}\ \frac{2X + D}{X_p^2 + DX_p + E} +$$

$$\frac{1}{2}\ [-2AE + AD^2 - BD + 2C]\ \frac{1}{X_p^2 + DX + E}$$

For $D^2 - 4E < 0$ from the CRC Math Tables (29).

$$\int \frac{dx}{aX^2 + bx + c} = \frac{2}{\sqrt{4ac - b^2}} \tan^{-1}\left\{ \frac{2ax + b}{\sqrt{4ac - b^2}} \right\}$$

Using the previous information

$$\int_0^{X_o} H(X_p)\, dX_p = AX_o + \frac{1}{2}(-AD + B) \ln\left[\frac{X_o^2 + DX_o + E}{E}\right] +$$

$$\left[\frac{AD^2 - 2AE - BD + 2C}{\sqrt{4E - D^2}}\right]\left\{\tan^{-1} \frac{2X_o + D}{\sqrt{4E - D^2}} -\right.$$

$$\left.\tan^{-1} \frac{D}{\sqrt{4E - D^2}}\right\}$$

Appendix H

Interparticle Temperature Gradients

Invariably there will be a temperature gradient within the catalyst particle for the reaction is very endothermic. Lee (5), in his article showed that the potassium migrate toward the pellet centers because it was colder there. However we would like to have an idea how large of gradient we are neglecting by assuming the particle is isothermal. To do this we will look at the worst case, the reactor inlet with the reaction going to equilibrium in the catalyst particle.

Conditions:

$T = 900°K$

$P = 1.0$ atm

$S/o = 12.5$ (molar steam to oil ratio)

$\lambda_e = 10^{-3}$ cal/sec cm°K[1)]

$$\Delta H_{rxn} = (2.88 \times 10^7 + 1090\ T)\ \frac{\text{cal}}{\text{kg mol}}$$

$$= 2.98 \times 10^7\ \frac{\text{cal}}{\text{kg mol}} \text{ at } 900^0\text{K}$$

1) Assumed effective thermal conductivity suggested by Froment (16) p. 201.

Both the heat and mass balances for a catalyst particle are a function of the reaction rate. The reaction rate depends on the concentration and temperature profiles. By equating the reaction rate in both expressions and assuming the temperature and ethylbenzene concentration are at a minimum at the catalyst center, one obtains:

$$T - T^c = \frac{D_{eff}\,(-\Delta H)}{\lambda_e} (C_{EB} - C^c_{EB}) \qquad \text{H-2}$$

where

T = temperature, °K

c = center

D_{eff} = effective diffusivity

$-\Delta H$ = heat of reaction

λ_e = effective thermal conductivity

C_{EB} = concentration of ethylbenzene

From Appendix J

$$D_{eff} = 4.14 \times 10^{-3}\ m^2/hr \qquad \text{H-3}$$

With the center concentration being the equilibrium concentration:

$$(C_{EB} - C^c_{EB})$$

$$= C^o_{EB} \qquad \text{H-4}$$

$$= \frac{X_{eq}\ P_{EB}}{RT} \qquad \text{H-5}$$

$$(C_{EB} - C_{EB}^{c}) = \frac{(0.8513)\ (0.07407\ \text{atm})}{(82.057 \times 10^{-3}\ \frac{\text{m}^3\ \text{atm}}{\text{kg mol}\ ^{0}\text{K}})\ (900^{0}\text{K})}$$

$$= 8.54 \times 10^{-4}\ \text{kg mol/m}^3$$

Then

$$(T - T^{c}) = \frac{(4.14 \times 10^{-2}\ \text{m}^2/\text{hr})\ (2.98 \times 10^{7}\ \text{cal/kg mol})}{(10^{-3}\ \text{cal/cm}\ ^{0}\text{K sec})\ (3600\ \text{sec/hr})\ 100\ \text{cm/1 in.})}$$

$$(8.54 \times 10^{-4}\ \text{kg mol/m}^3$$

$$\Delta T = 2.93°\text{C}$$

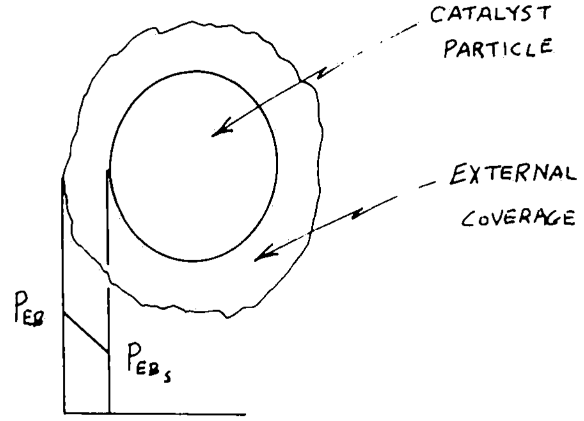
For Carrá and Forni's (7) activation energy

$$\frac{k}{k^{c}} = 1.09$$

So there is a 9% difference, which isn't that large considering the concentration in the pellet are closer to equilibrium.

Appendix I

External Mass Transfer Limitations



$$J = k_G\,(P_{EB} - P_{EB_S}) \qquad \text{I-1}$$

where

J = Molar flux to the catalyst particle, kg mol/m^2 sec

k_G = Gas (convective) mass-transfer coefficient

P_{EB} = The partial pressure of ethylbenzene in the bulk, atm

P_{EB_S} = The partial pressure of the ethylbenzene at the catalyst surface, atm

$$K_G = \frac{k_c}{R_g T} \qquad \text{I-2}$$

$$j_D = 0.357\,\frac{1}{\varepsilon}\,R_E^{-0.359} \qquad \text{Petrovic and Thodus} \qquad \text{I-3}$$

For gases $3 < R_E < 2000$

$$j_D = \frac{k_c \rho}{G} S_c^{2/3} \qquad \text{I-4}$$

$$S_c = \frac{\mu}{\rho D_{bulk}} \qquad \text{I-5}$$

$$R_E = \frac{D_p G}{\mu} \qquad \text{I-6}$$

where

k_c = Concentration mass transfer coefficient

R_G = Ideal gas constant,
82.057×10^{-3} m^3 atm/kgmol °K

T = Absolute temperature, °K

j_D = j factor for mass transfer

ρ = Gas density, kg/m^3

G = Mass flow rate, kg/m^2 sec

S_c = Schmidt number

μ = Gas viscosity, kg/m-sec

D_{bulk} = Bulk diffusivity, m^2/hr

ε = Catalyst void fraction

R_E = Reynolds number

D_p = Particle diameter, m

From equations 2, 3, 5

$$k_G = \frac{1}{R_G T} \frac{G}{\rho} S_c^{-2/3} (0.357) \frac{1}{\varepsilon} R_E^{-0.359} \qquad \text{I-7}$$

At 850°K and S/O (molar "steam to oil" rato) = 12.5

P = 1 atm

$\rho = 1.718 \text{ kg/m}^3$ Ideal gas law

$\mu = 0.1007$ kg/m-hr for steam

$D_{bulk} = 0.2192 \text{ m}^2\text{/hr}$ see Appendix J

For a 1/8" dia x 3/16 cylindrical particle

$D_{p_{eq}} = 5.522 \times 10^{-3}$ m

$\varepsilon = 0.4$

The following data is for a bench scale reactor (10).

$LHSV = 0.65 \text{ hr}^{-1}$

40% Conversion

S/O = 12.5

= 2.12 by wt

$P_{EB} = 0.0741$ atm

$$G = (S/O_{wt} + 1)\,(LHSV)\,\rho_{Liq}\,Vol/XA \qquad \text{I-8}$$

where

LHSV = Liquid hourly space velocity, hr^{-1}

ρ_{Liq} = Liquid density, kg/m^3

S/O_{wt} = Steam to oil ratio by weight

XA = Cross-sectional area, m^2

$$G = \frac{(1 + 2.12)\ (0.65\ \text{hr}^{-1})\ (0.867\ \text{g/cm}^3)\ \frac{1\ \text{kg}}{1000\ \text{g}}\ (90\ \text{cm}^3)}{\frac{\pi}{4}\ (2.54 \times 10^{-2}\ \text{m})^2}$$

$$= 312.3\ \text{kg/m}^2\ \text{hr}$$

$$R_E = \frac{(5.522 \times 10^{-3}\ \text{m})\ (312.3\ \text{kg/m}^2\ \text{hr})}{(0.1007\ \text{kg/hr m})}$$

$$= 17.13$$

So the Reynolds number is in the range where equation 3 is applicable.

$$S_c = \frac{(0.1007\ \text{kg/m hr})}{(1.718\ \text{kg/m}^3)\ (0.2192\ \text{m}^2/\text{hr})}$$

$$= 0.2674$$

Using these results in equation 7

$$k_G = \frac{(312.3\ \mathrm{kg/m^2\ hr})}{(82.057 \times 10^{-3}\ \mathrm{m^3\ atm/kgmol\ ^0K})\ (850^0\mathrm{K})\ (1.718\ \mathrm{kg/m^3})}$$

$$\times\ (0.2674)^{-2/3}\ (0.375)\ \frac{(17.13)}{(0.4)}^{-0.359}$$

$$= 2.021\ \mathrm{kg\ mol/hr\ m^2\ atm}$$

If mass transfer limitations are important the rate of reaction will be limited to the rate at which the ethylbenzene reaches the catalyst surface (i.e., J).

$$J = X\ \mathrm{LHSV}\ \frac{\rho_{Liq}}{MW}\ \frac{(\text{Particle Volume})}{(\text{Particle Surface Area})} \qquad \text{I-9}$$

$$= (0.40)\ (0.65\ \mathrm{hr^{-1}})\ \frac{(867\ \mathrm{kg/m^3})}{(105\ \mathrm{kg/kgmol})}\ \frac{4}{3}\ \pi\ (5.522 \times 10^{-3}\ \mathrm{m})^3$$

$$= 3.952 \times 10^{-3}\ \mathrm{kg\ mol/hr\ m^2}$$

From equation 1

$$P_{EB,S} = P_{EB} - \frac{J}{k_G} \qquad \text{I-10}$$

$$P_{EB,S} = 0.0741 - \frac{(3.952 \times 10^{-3}\ \mathrm{kgmol/hr\ m^2})}{(2.021\ \mathrm{kgmol/hr\ m^2\ atm})}$$

$$= 0.0741\ \mathrm{atm} - 1.96 \times 10^{-3}\ \mathrm{atm}$$

= 0.0721 atm

(differs by 3%)

Since almost no partial pressure gradient would be required for a mass transfer rate equal to the average reaction rate, external mass transfer is not important in a bench scale reactor.

Repeating this calculation for a plant reaction under the following conditions:

$G = 83{,}500$ lb/hr (22,630 lb EB/hr)

$T_{IN} = 897°K$

at 900°K

$D = 0.2444\ m^2/hr$

$\rho = 0.779\ kg/m^3$

$\mu = 2.568 \times 10^{-5}$ kg/m sec

for steam

$P_{EB} = 0.120$ atm

40.5% Conversion

Using the same catalyst data

$$R_E = \frac{(5.522\text{x}10^{-3}\text{m})(83{,}500\,\text{lb/hr})(0.454\,\text{kg/lb})\left(\frac{1\ \text{m}}{0.3048\,\text{ft}}\right)^2}{(2.568 \times 10^{-5}\ \text{kg/m sec})\ (3600\ \text{sec/hr})\ \frac{\pi}{4}\ (17.25\ \text{ft})}$$

= 104.3 within range for equation 5

$$S_c = \frac{(2.568 \times 10^{-5} \text{ kg/m sec})\ (3600 \text{ sec/hr})}{(0.779 \text{ kg/m}^3)\ (0.2444 \text{ m}^2\text{/hr})}$$

$$S_c = 0.4856$$

$$k_G = \frac{(1746 \text{ kg/m}^2 \text{ hr})}{(82.057 \times 10^{-2} \text{ m}^3 \text{ atm/kgmol } ^0\text{K})\ (397^0\text{K})\ (0.779 \text{ kg/m}^3)}$$

$$\times\ (0.4856)^{-2/3}\ (0.357)\ \left(\frac{(104.3)}{(0.40)}\right)^{-0.359}$$

$$= 8.295 \text{ kgmol/hr m}^2 \text{ atm}$$

$$J = \frac{(0.405)(22630 \text{ lb EB/hr})\ 1/3\ (5.522 \times 10^{-3} \text{m})}{(2.20 \text{ lb/kg})(105 \text{ kg/kgmol})\ \frac{\pi}{4}\ (5.26 \text{ m})^2}$$

$$= 3.357 \times 10^{-3} \text{ kg mol/m}^2 \text{ hr}$$

$$P_{EB,S} = \quad = \frac{3.357 \times 10^{-3}}{8.295}$$

$$= P_{EB} - 0.000405 \text{ atm}$$

Again, because the partial pressure gradient required for mass transfer is small the effects of external mass transfer are unimportant.

Appendix J

Diffusion, (Ordinary and Knudsen) Calculations

Bulk Bindary Diffusivity

Since the major components are ethylbenzene/styrene and water, it is assumed that it is a binary gas mixture. Ethylbenzene and styrene are of the same structure and have molecular weights of 106 and 104, respectively. Also equimolar counter diffusion of the EB/STY through the H_2O is assumed. From p. 548 of Reid (21), the diffusion coefficient equals:

$$D_{EB/STY,H_2O} = \frac{3}{16}\left[2\pi k_B T\left(\frac{1}{MW_{EB/STY}} + \frac{1}{MW_{H_2O}}\right)^{-1}\right]^{1/2} \frac{f_D}{n\pi\,\sigma_{EB/STY,H_2O}\,\Omega_D} \qquad J-1$$

where

k_B = Boltzmann's constant

T = absolute temperature

MW = molecular weight

n = number density of molecules in mixture

σ = characteristic length, Å

r_p = collision integral

f_D = correction term

Using the ideal gas law and assuming f_D equals 1, (it lies between 1 and 1.02 for mixtures of approximately equal molecular weight and between 1 and 1.1 otherwise), one obtains

$$D_{EB/STY,H_2O} = \left\{ 1.858 \times 10^{-3} \; T^{3/2} \frac{\left[\frac{1}{MW_{EB/STY}} + \frac{1}{MW_{H_2O}} \right]^{1/2}}{P\ (atm)\ \sigma_{EB/STY,H_2O}\ \Omega_D} \right\} \frac{cm^2}{sec} \qquad J-2$$

where P = pressure, atm

The mixing rules are

$$\varepsilon_{AB} = (\varepsilon_A \varepsilon_B)^{1/2} \qquad J-3$$

$$\sigma_{AB} = 1/2\ (\sigma_A + \sigma_B) \qquad J-4$$

The Neufeld et al. relation for the collision integral is:

$$\Omega_D = \frac{A}{T^{*B}} + \frac{C}{\exp\ (DT^*)} + \frac{E}{\exp\ (FT^*)} + \frac{G}{\exp\ (HT^*)} \qquad J-5$$

where

$A = 1.06036$

$B = 0.15610$

$C = 0.19300$

$D = 0.47635$

$E = 1.03587$

$F = 1.52996$

$G = 1.76474$

$H = 3.89411$

and

$$T^* = \frac{k}{\varepsilon} T \tag{J-6}$$

from p. 679 of Reid (21)

$$\sigma_{H_2O} = 2.641 \text{ Å}$$

$$\left.\frac{\varepsilon}{k}\right|_{H_2O} = 809.1^0\text{K}$$

Using the values for benzene for EB/STY

$$\sigma_{EB/STY} \cong 5.349 \text{ Å}$$

$$\frac{\varepsilon}{k}_{EB/STY} \cong 412.3^0\text{K}$$

Using the mixing rules, (equations 3 and 4)

$$\sigma_{EB/STY,H_2O} = 1/2\ (5.349 + 2.641)\ \text{Å}$$

$$= 3.995\ \text{Å}$$

$$\frac{\varepsilon}{k}_{EB/STY,H_2O} = [(412.3)\ (809.1)]^{1/2}\ {}^0\text{K}$$

$$= 577.6°\text{K}$$

At 900°K

$$T^* = \frac{(900^0\text{K})}{(577.6^0\text{K})}$$

$$= 1.56$$

Substituting this into equation 5

$$\Omega_D = 1.181$$

Using equation 2 at a pressure of 1 atm

$$D_{EB/STY,H_2O} = \left[\frac{1.858\ \text{x}\ 10^{-3}\ \left[\frac{1}{105} + \frac{1}{18}\right]^{1/2}}{(3.995)^2\ (1.181)}\ \frac{(900^0\text{K})^{3/2}}{1\ \text{atm}}\right]\frac{\text{cm}^2}{\text{sec}}$$

$$= 0.679\ \text{cm}^2/\text{sec}$$

$$= 0.244\ \text{m}^2/\text{hr}$$

Note that in the program these calculations were redone for the particular temperature and pressure.

In a similar way the binary diffusion coefficients for all the combinations of ethylbenzene, styrene, hydrogen and steam can be calculated.

Knudsen Diffusivity

The Knudsen diffusivity is a function of molecular weight, temperature and average pore radius. Hill (27) (p. 433) gives the following relations:

$$D_K = 2/3\ \bar{r} \left(\frac{8\ R_G T}{\pi MW} \right)^{1/2} \qquad \text{J-7}$$

$$D_K = 9.7 \times 10^{+3}\ \bar{r}\ (T/MW)^{1/2}\ \text{cm/sec}^2 \qquad \text{J-8}$$

where

$\bar{r}$ = average pore radius, cm

T = absolute temperature, °K

MW = molecular weight, g/mol

For Shell 105 and similar iron oxide catalysts (10 and 11):

$$\bar{r} \cong 2.3 \times 10^{-5}\ \text{cm}$$

So for ethylbenzene at 900°K

$$D_K = \left[\frac{(9.7 \times 10^3)\ (2.3 \times 10^{-5}\ \text{cm})}{(106.16)^{1/2}} (900^0\text{K})^{1/2} \right] \text{cm}^2/\text{sec}$$

$$= 0.650\ \text{cm}^2/\text{sec}$$

$$= 0.234\ \text{m}^2/\text{hr}$$

Diffusivity in the Mixture:

Both ordinary and Knudsen diffusivities contribute to the actual diffusivity. Forment and Bischoff (30) suggest the following relation to combine the two:

$$\frac{1}{D_{i,M}} = \sum_{j=1}^{n} 1/D_{i,j}\ (y_i - \alpha y_i) + 1/D_{Ki} \qquad \text{J-9}$$

$$\alpha = \frac{N_j}{N_i} \qquad \text{J-10}$$

where

$D_{i,M}$ = the diffusivity of component i in the mixture

$D_{i,j}$ = the binary diffusivity for components i and j

y_i = the mole fraction of component i

N_i = the molar flux of component i

D_{Ki} = the Knudsen diffusivity for component i

Effective Diffusivity:

All of the previous calculations have not accounted for the irregular and tortous nature of the catalyst pore structure. In order to account for this two factors are introduced. They are the void fraction and a tortorsity factor. Introducing the void fraction into the molar flux equation

$$(\text{i.e., } N_i = \varepsilon\, D_{i,M} \frac{dC_i}{dz} \qquad \text{J-11}$$

accounts for the fact that the flux is not going through the whole catalyst surface but only the fraction where there are voids. The tortorsity factor is included because the catalyst pores are not straight cylinders as proposed in the single pore model but for this interconnecting passage. So

$$N_i = \frac{\varepsilon}{\tau} D_{i,M} \frac{dC_i}{dz} \qquad \text{J-12}$$

Defining

$$D_{i,eff} = \frac{\varepsilon}{\tau} D_{i,M} \qquad \text{J-13}$$

$$N_i = D_{i,eff} \frac{dC_i}{dz} \qquad \text{J-14}$$

Thus the effective diffusivity is

$$D_{i,eff} = \frac{\varepsilon}{\tau} D_{i,M}$$

(Note: Some author introduce this correction factor in the calculation or bulk of Knudsen diffusivities.)

Thus the effective diffusivity can be calculated for each component inside the porous catalyst. A computer subroutine was written to carry out the function.

Appendix K

Economics Analysis of Major Raw Materials and Energy Costs

The cost to produce a pound of styrene is calculated based on a constant fixed cost, raw materials cost and approximate energy costs. This appendix contains the assumptions made for this analysis.

Fixed Cost

The fixed costs were estimated as $190 per hour.

Raw Materials Cost

Table XIII of the text should be consulted for the raw materials cost. The cost of the ethylbenzene recovered in-house from the C_8 distillation columns was estimated from plant data. No credit is presently given for toluene and benzene produced.

The vent gas produced is used in the plants' boiler. The boiler efficiency was found to be 85% in a plant study. The heat content of the vent gas is 367 Btu/std ft^3. From these two pieces of information and the energy cost in Table XVIII the credit for the vent gas is calculated.

The energy cost was again obtained from the Houston Plant Production Manager.

Energy Costs

Figure K-1 shows a schematic representation of the plant showing the major energy consumers. Table K-I gives the energy requirements and temperatures for areas shown in Figure K-1 and compares them with those calculated by the computer program under design conditions.

Table K-I

Energy Requirements and Related Temperatures for the Design Case and a Simulation of the Design Case (30)

	Design	Simulation1)
Boiler Duty (ΔH_{bal})	23.7 10^6 Btu/hr	22.9 10^6 Btu/hr
Steam Temperature (T_{steam})	710°C	700°C
Reactor Inlet Temperature (T_{inlet})	629°C	629°C
Reactor Effluent Temperature (T_{eff})	566°C	587°C
Condenser Duty (ΔH_{cond})	108 10^6 Btu/hr	100 10^6 Btu/hr
Recycle Column Duty ($\Delta H_{recycle}$)	49.6 10^6 Btu/hr	51.2 10^6 Btu/hr
Recycle Flow Rate	204.4 lb mol/hr	193.3 lb mol/hr
B/T Column Duty ($\Delta H_{B/T}$)	5.4 10^6 Btu/hr	5.6 10^6 Btu/hr
Finishing Column Duty (ΔH_{finish})	3.9 10^6 Btu/hr	4.0 10^6 Btu/hr

1) The design was very conservative. To simulate the design conversions, the kinetics for the main reactions were reduced by a factor of 25.

Following is a discussion of how the heat duties for the simulated case were calculated including the assumptions made.

Looking at the heat duties in the design case the largest one is the condenser duty. This heat loss is mainly

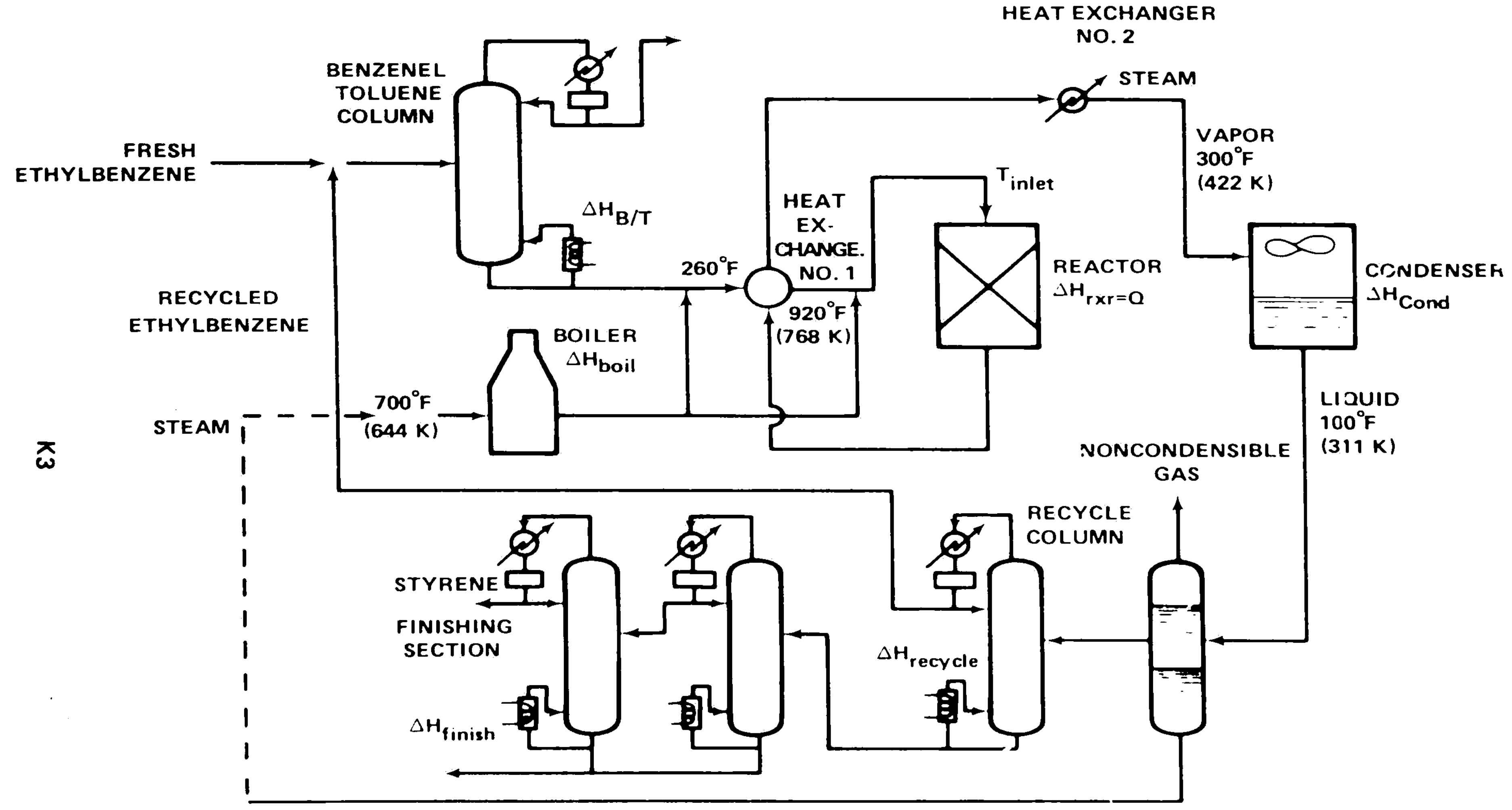


Figure K-1 A SCHEMATIC REPRESENTATION OF THE PLANT SHOWING THE AREAS THAT CONSUME THE MAJORITY OF THE ENERGY the latent heat of the water and aromatics. The actual effluent temperature to the condenser has only a small influence on the actual heat duty.

The second largest heat duty is the reboiler duties of the recycle column. This value should be proportional to the amount of material recycled.

When using a basis of the energy to produce 1 lb of styrene under different operating conditions, the energy requirements for the B/T column and the finishing section should be constant. This is approximately true for the B/T column because most of the B/T does not come from the recycle but is in the EB stream from the refinery. The finishing section processes the styrene and thus within a reasonable range should require the same amount of energy per pound of styrene.

Energy Requirements

To summarize what was said above in equation form:

1) $$\Delta H_{boil} = (\text{flow rate})\,(H^{v}_{T_{steam}} - H^{v}_{700^{0}F})$$

(See next page for the calculation of T_{steam}.)

2) $$\Delta H_{cond} = (\text{flow of } H_2O)\,(H^{v}_{300^{0}F} - h^{l}_{100^{0}F})_{H_2O} + (\text{flow of aromatics})\,(H^{v}_{300^{0}F} - h^{l}_{100^{0}F})_{\text{aromatics}}$$

3) $$\Delta H_{recycle} = \frac{(\text{recycle flow rate})\ (49.4\ 10^6\ \text{Btu/hr})}{(204.390\ \text{lb mol/hr})}$$

$$= (\text{recycle flow rate})\ (0.242\ 10^6\ \text{Btu/lb mol})$$

4) $$\Delta H_{B/T} = (5.4\ 10^6\ \text{Btu})/(8546\ \text{lb}_{STY})$$

$$= 632\ \text{Btu/lb}_{STY}$$

5) $$\Delta H_{finish} = (3.9 \times 10^6\ \text{Btu})/(8546\ \text{lb}_{STY})$$

$$= 456\ \text{Btu/lb}_{STY}$$

The assumption implied in this equation and the rest of the analysis are listed on page K7.

Boiler

Once an inlet temperature and the EB and H_2O flow rates are chosen the injection steam temperature can be calculated from an energy balance. But to be rigerous one should take the effluent temperature, the feed inlet temperature to heat exchanger 1, and the overall heat transfer coefficient to calculate the feed temperature. This would become a very involved calculation.

In the design case, with a steam to oil ratio of 12/1 mole or 2.71 wt the approach was 130°F. If the steam to oil ratio was lowered the approach would go down.

For the design

$$q_1 = q_2$$

$$m_1 Cp_1 \Delta T_1 = m_2 Cp_2 \Delta T_2$$

$$m_2/m_1 = S/O + 1; \ \Delta T_1 = 660°F; \ \Delta T_2 = 210°F$$

$$\Delta T_{approach} = 130°F$$

$$T_{EB} = T_{eff} - \Delta T_{approach}$$

$$T_{EB} \approx T_{eff} - \Delta T_{approach} \left[\frac{(S/O + 1)_{design}}{(S/O + 1)} \right]^n$$

where $n < 1$

The reason I would include a n is that just because one cuts the effluent flow rate by 1/2 does not mean the heat transfer is cut by 1/2. The design effluent exit temperature approach is 580°F.

Let $n = 0.8$.

$$T_{EB} \approx T_{eff} - \frac{1012^0F}{(S/O_M + 1)^{0.8}}$$

$$\approx T_{eff} - \frac{562^0C}{(S/O_M + 1)^{0.8}}$$

This assumption is justified because we are only looking at the approximate difference in styrene production cost under different operating conditions. Under design conditions this heat exchanger is transferring less than 7% of the total energy lost in the plant.

Condenser

From Standard Steam Tables

$$(H^{v}_{300^{0}F} - h^{l}_{100^{0}F})_{H_2} = 20.2\ 10^{3}\ \text{Btu/lb mol}$$

and approximating the aromatics of ethylbenzene

$$(H^{v}_{300^{0}F} - h^{l}_{100^{0}F})_{\text{aromatics}} = 24.2\ 10^{3}\ \text{Btu/lb mol}$$

Assumptions

The assumptions involved in this analysis to evaluate the relative merits of different operating costs and reactor configurations.

a) The two dominate energy uses are energy lost in the condenser and used in the recycle column reboilers, (108 & 50 10^6 Btu/hr Design, see Table K-1).

b) The calculation of condenser duty can be based on condensing and cooling vapor at 300°F to liquid at 100°F because the latent heat term dominates and the heat exchanger capacity is enough to get the effluent temperature close to 300°F.

c) The recycle columns combined reboiler duty is proportional to the recycle flow rate.

d) The heat content of the effluent and the heat exchanger area is sufficient to heat the recycled steam up to 700°F.

e) To raise the reactor inlet temperature by 50°F requires ~2.5 10^6 Btu/hr. Therefore, since this is less than 1% of the energy requirements, it is assumed the additional heat lost to the condenser when operating with a higher effluent temperature and the inaccuracies of using the approximation for the ethylbenzene temperature are not significant.

So the cost to produce styrene can be approximated by the following equation.

Styrene Production Cost = [Raw Materials Cost) -
(Vent Gas Credit)]
\+ [Fixed Cost] +
[Fixed Energy Cost] +
[Variable Energy Cost]

where

(Raw Materials Cost) = F_{EB} (15.71 ¢/lb)

(Vent Gas Credit) = (\$1.306/10^3 std ft^3)
[2.5 (vent gas predicted)] 1)

---

1) The 2.5 is to account for the reactor model under predicting the production of vent gas by a factor of 2.5.

[Fixed Costs] = \$190/hr
[Fixed Energy Costs] = $[(5.4) + (3.9)\ 10^6$ Btu/hr] $(\$3.56/10^6$ Btu)/(0.85 efficiency) (8513 lb styrene/hr)

= 0.458 ¢/lb_{STY}

[Variable Energy Costs] = $[\Delta H_{bal} + \Delta H_{stage} + \Delta H_{recycle}$ $(3.56/10^6$ Btu)/(0.85 efficiency)

To be able to compare the different cases a cost to produce 1 pound of styrene will be used. Thus, all the terms except the fixed cost and fixed energy cost will be divided by the pounds of styrene produced.

Appendix L

Program Listing and Sample Data Sets

Program Listing

```
      PROGRAM STYRER (INPUT,TAPE 5=INPUT,OUTPUT,TAPE 3=OUTPUT)
C         THIS PROGRAM MODELS A FIXED-BED CATALYTIC CHEMICAL REACTOR.
C     IT HAS BE SPECIFICLY USED FOR INVESTIGATING THE DEHYDROGENATION
C     OF ETHYLBENZENE TO STYRENE.  IT WAS WRITTEN BY CHARLES M. SHEPPARD
C     AS PART OF HIS MASTERS THESIS ON "KINETIC AND REACTOR MODELS FOR
C     ETHYLBENZENE DEHYDROGENATION REACTION."
C         THE PROGRAM USES EPISODE, A PUBLISHED INTERGRATION PACKAGE TO
C     INTERGRATE THE DIFFERENTIAL COMPONENT, MOMENTUM AND ENERGY BALANCES.
C     IMSL LIBRARY SUBROUTINES ARE ALSO USED TO CORRELATE RATE EQUATIONS
C     AND CATALYST DEACTIVATION WITH AGE.  A LIBRARY WAS ADDED TO THE
C     PROGRAM CONTAINING THE ABREVIATED NAMES OF THE COMMON COMPONENTS
C     ENCOUTERED, THEIR MOLECULAR WEIGHT AND HEAT CAPACITY DATA.  WITH
C     WITH THE EXCEPTION OF THE LIBRARY AND THE CALCULATION OF CONVERSION
C     (IN SUBROUTINE PRINT) THIS PROGRAM IS A GENERAL REACTOR MODEL.
C          FOR AN EXPLINATION OF THE VARIOUS PROGRAM OPTIONS SEE
C     SUBROUTINE MODE.  THE FUNCTION OF EACH OF THE SUBROUTINES IS
C     EXPLAINED WITHIN THE SUBROUTINE.

      COMMON/T/Z,NF,NR /IO/NIN,NOUT
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
      COMMON /INT/ NEQN,DSTEP,ITYPE,ERROR,EPS,Z0(25),ZF(25),DELTAZ,
     + IERROR,MF,INDEX
      COMMON /PLOT/ AGE(25),RXREFF(25,15),CONV(2,6,25),SELTV(2,4,25)
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      DIMENSION LABEL(20)
      INTEGER DSTEP ,ERROR,  FLAG
      NR=0
      NIN=5
      NOUT=3
      NTRIAL=1

   10 CONTINUE
      NF=1
      N=NR+1
      READ(NIN,100) LABEL
      READ(NIN,105) Z0(N),ZF(N),DEL
      NOSET=NR
      IF(Z0(N).LT.0.0) GO TO 20
      DELTAZ=DEL
      READ(NIN,110) NEQN,DSTEP,ITYPE, ERROR,          EPS
      NR=NR + 1
      DSTEP=DSTEP+100000000
      IERROR=3
      MF=22
      INDEX=1
      IF(ZF(N).GT.0.0) GO TO 15
      ZF(N)=-ZF(N)
      MF=2
   15 WRITE(NOUT,115) NR,LABEL,Z0(N),ZF(N),DELTAZ
      WRITE(NOUT,120) NEQN,DSTEP,IERROR,MF,INDEX,EPS

C     EBRXR IS THE REACTOR MODEL.
      CALL EBRXR
      GO TO 10

   20 CONTINUE
      IF(M100.NE.-1) GO TO 40

C     THE MEASURED CONVERSION (OUTLET TEMPERATURE AND PRESSURE,
C     AND CATALYST AGE IF APPROPIATE) IS READ BELOW.
      DO 30 N=1,NOSET
C     MEASURED CONVERSION:  STYRENE      TOLUENE     BENZENE
      READ(NIN,103)     CONV(1,2,N),CONV(1,4,N),CONV(1,5,N)
      CONV(1,2,N)=100.0*CONV(1,2,N)
      CONV(1,4,N)=100.0*CONV(1,4,N)
      CONV(1,5,N)=100.0*CONV(1,5,N)
      TOUT(N,1)=TIN(N)
      POUT(N,1)=PIN(N)
      IF(M10.GE.3) READ(NIN,103)TOUT(N,1),POUT(N,1)
      IF(M1.EQ.5) READ(NIN,103)AGE(N)
      CONV(1,1,N)=CONV(1,2,N) + CONV(1,4,N) + CONV(1,5,N)
      SELTV(1,1,N)=100.0*CONV(1,2,N)/CONV(1,1,N)
      SELTV(1,2,N)=100.0*CONV(1,4,N)/CONV(1,1,N)
      SELTV(1,3,N)=100.0*CONV(1,5,N)/CONV(1,1,N)
   30 CONTINUE
      IF((M1.EQ.2).OR.(M1.EQ.3)) CALL OPTM
      IF(M1.EQ.2) CALL OPTM2
   40 CONTINUE
      NR=NOSET
      WRITE(NOUT,90)MODES
      CALL SUMMRY
      IF((M1.EQ.5).AND.(NOSET.GE.4)) CALL AGING
      STOP

   90 FORMAT(1H1,10X,36H SUMMARY OF CONVERSION & SELECTIVITY,
     *13H WITH MODES =,I5,///)
  100 FORMAT(20A4)
  103 FORMAT(F10.0)
  105 FORMAT(8F10.0 )
  110 FORMAT(4I5,5X,F10.0)
  115 FORMAT(1H1, 9X,8H RUN NO.,I3,3H - ,20A4,//,10X,
     1 34H INITIAL VALUE OF REACTOR DEPTH = ,E10.4,//,10X,
     2   32H FINAL VALUE OF REACTOR DEPTH = ,E10.4,//,10X,
     335H PRINT INTERVAL OF REACTOR DEPTH = ,E10.4, /)
  120 FORMAT(10X,47H NUMBER OF FIRST ORDER DIFFERENTIAL EQUATIONS =,I5,
     1//,10X,55H INITIAL PRINT INTERVAL/MINIMUM INTERGRATION INTERVAL =
     +,I14,//,10X,30H EPISODE PARAMETERS:  IERROR =,I3,/,
     +31X,5H MF =,I3,/,31X,8H INDEX =,I3,//,
     5 10X,29H MAXIMUM INTERGRATION ERROR =,E10.4,//)

      END


      SUBROUTINE EBRXR
C     THIS SUBROUTINE RUNS THE REACTOR MODEL.
C THAT IS IT CALL THE NECESSARY INTERGRATION PROGRAMING
      COMMON/T/Z,NF,NR /IO/NIN,NOUT
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
      COMMON /INT/ NEQN,DSTEP,ITYPE,ERROR,EPS,Z0(25),ZF(25),DELTAZ,
     + IERROR,MF,INDEX
      COMMON /TWOSTG/ TIN2(25), ZSTAGE(25), STEAM(25)
      DIMENSION Y0(15)
      INTEGER DSTEP,ERROR

C     FOR A TWO STAGE REACTOR THE POINT OF THE TEMPERATURE INCREASE
C     (ZSTAGE), THE TEMPERATURE OF THE SECOND STAGE (TIN2), AND THE
C     AMOUNT OF STEAM INJECTED (STEAM) MUST ALL BE SET.

      IF(M10.LE.3) ZSTAGE(NR)=ZF(NR) + 10.0

      INDEX=1
      Z=Z0(NR)
      ZSTEP=DELTAZ/DSTEP
      ZOUT=Z0(NR) + DELTAZ
      IFN=ABS( (ZF(NR)-Z0(NR))/DELTAZ ) + 1.5
```

```
C     INITAL INITIALIZE THE VARIALBELS.
      CALL INITAL

C     IF M1=4 THE EFFECTIVENESS FACTOR WILL BE CALCULATED AT
C    REACTOR INLET CONDITIONS.
      IF(M1.EQ.4) CALL RATES
C     IF M10=0 THE EXIT TPPERATURE IS CALCULATED ASSUMING THERE
C    IS NO HEAT LOSS.
      IF(M10.EQ.0) RETURN

      CALL PRINT
      DO 20 INTERG=2,IPR
      CALL VARCH (NEQN,Y0)
C     DRIVE IS EPISODE"S MAIN (DRIVING) SUBROUTINE.
      CALL DRIVE (NEQN,Z,ZSTEP,Y0,ZOUT,EPS,IERROR,MF,INDEX)
      IF(INDEX.LT.0)  WRITE(NOUT,125)INDEX
      CALL CHVAR (NEQN,Y0,ZOUT)
      CALL PRINT
      ZOUT=ZOUT + DELTAZ
C     FOR A TWO STAGE REACTOR HTEXCH (HEAT EXCHANGE) IS CALLED TO
C    INTIALIZE THE CONDITIONS AT THE SECOND BED"S INLET.
      IF((ZOUT.GT.ZSTAGE(NR)).AND.((ZOUT-DELTAZ).LT.ZSTAGE(NR)))
     + CALL HTEXCH
      IF((ZOUT.GT.ZSTAGE(NR)).AND.((ZOUT-DELTAZ).LT.ZSTAGE(NR)))
     + ZSTEP=DELTAZ/DSTEP
   20 CONTINUE
      IF(M1.EQ.6) CALL OUTIES

  125 FORMAT(10X,21H WARNING *** INDEX = ,I2,4H ***)
      RETURN
      END
C
C
      SUBROUTINE VARCH (NEQN,Y0)
C     THIS IS AN INTERFACE SUBROUTINE.
C     IT INTERFACES EPISODE WITH THE OLD DSS/2 PROGRAMING.
C     DSS/2 WAS INTERGRATION PACKAGE THAT WAS PREVIOUSLY USED.
      COPMON/Y/TDEGK,P,F(15)
      DIPENSION Y0(NEQN)

      Y0(1)=TDEGK
      Y0(2)=P
      DO 10 N=3,NEQN
      Y0(N)=F(N-2)
   10 CONTINUE
      RETURN
      END

      SUBROUTINE CHVAR (NEQN,Y,ZNEW)
C     THIS IS AN INTERFACE SUBROUTINE.
C     IT INTERFACES EPISODE WITH THE OLD DSS/2 PROGRAMING.
      COMMON/Y/TDEGK,P,F(15)  /T/Z
      DIMENSION  Y(NEQN)

      Z=ZNEW
      TDEGK=Y(1)
      P=Y(2)
      DO 10 N=3,NEQN
      F(N-2)=Y(N)
   10 CONTINUE
      RETURN
      END
C
C
      SUBROUTINE DIFFUN (NEQN,ZZ,Y,DY)
C       THIS SUBROUTINE IS CALLED BY EPISODE.  IT SUPPLIES THE
C     INTERGRATION PACKAGE WITH NUMMERICAL ESTIMATES OF THE DERIVATIVES
C    FOR THE DIFFERENTIAL COMPONENT,MOMENTUM AND ENERGY BALANCES.
C    THE STRUCTURE OF THIS PROGRAM IS SUCH THAT THESE DERIVATIVES ARE
C    ACTUALLY CALCULATED IN THE SUBROUTINE DERV.
      COMMON/T/Z,MF,NR /IO/NIN,NOUT/Y/TDEGK,P,F(15) /F/DT,DP,DF(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
      COPMCN /EPCCM2/YMAX(15)
      DIMENSION Y(NEQN),DY(NEQN)

      Z=ZZ
      TDEGK=Y(1)
      P=Y(2)
      DO 10 N=3,NEQN
      F(N-2)=Y(N)
   10 CONTINUE

      CALL DERV

      DY(1)=DT
      DY(2)=DP
      DO 20 N=3,NEQN
      DY(N)=DF(N-2)
   20 CONTINUE

      DO 30 I=1,NOCOMP
      YMAX(I)=AMAX1(ABS(Y(I)),1.0E-20)
   30 CONTINUE
C
      RETURN
      END


      SUBROUTINE INITAL
C     IN THIS SUBROUTINE THE VALUES OF THE INTERGRATION VARIBLES
C    ARE SET BEFORE EACH INTERGRATION.  THESE VALUES ARE INITIALLY
C    READ IN SUBROUTINE READ.
      COMMON /T/Z,MF,NR /Y/TDEGK,P,F(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15)
      INTEGER FLAG
C
      IDIFF=0
      IF(MF.GE.0) CALL READ
      ICOUNT=0
      TDEGK=TIN(NR) + 273.15
      P=PIN(NR)
      DO 10 I=1,NOCOMF
   10 F(I)=F0(NR,I)
      CALL DERV
      RETURN
      END
C
C
      SUBROUTINE MODE
      COPMCN /IO/NIN,NOUT
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
      INTEGER PMODES


C     MODES IS THE PARAMETER THAT CONTROLS THE OPERATION OF THE PROGRAM.
C    IT HAS THREE PARTS :
C    M100 WHICH IS THE NUMBER IN THE HUNDRETHS PLACE INCLUDING THE SIGN.
```

```
C        CONTILS THE DATA READ BY THE PRJGRAM
C  M10 IS THE NUMBER IN THE TENS PLACE  AND CONTROLS THE TYPE OF REACTOR
C       SIMULATED.
C  M1 IS THE NLMBLR IN THE ONES PLACE AND CONTROLS THE WAY THE RESULTS
C      ARE ANALYZED.
C                                   DATA FORMAT
C       M100
C         1             DATA INPUT IN SI UNITS FLOWS IN KGMOL/HR
C         2             OPERATING DATA INPUT IN PLANT UNITS
C     (- SIGN MEANS DATA IS READ TO COMPARE REACTOR EFFLUENT
C        WITH EG CONVERSION & T P DATA FOR M100=1)
C
C       M10                        REACTOR OPERATION
C         1             ISOTHERMAL AND ISOBARIC
C         2             ISOTHERMAL AND THE PRESSURE DROP CALCULATED
C         3             1 STAGE ADIBATIC WITH PRESSURE DROP CALCULATED
C         4             2 STAGE ADIBATIC WITH INLET TEMPERATURE TO THE
C                       SECOND BED SPECIFED, PRESSURE DROP CALCULATED
C         5             2  STAGE ADIBATIC WITH THE INTERSTAGE INJECTION
C                       STEAM TEMPERATURE SPECIFED PRESSURE DROP CALCULATE
C
C                              ANALYSIS OF THE RESULTS
C       M1
C         1             SIMULATION RESULTS PRESENTED.
C         2             KINETIC CONSTANTS FOR THE THREE MAIN REACTIONS ARE
C                       FIT ONE PIECE OF DATA AT A TIME AND THEN THE ARRHE
C                       EQUATION IS FIT
C         3             KINETIC CONSTANTS ARE FIT MINIMIZING THE DIFFERENCE
C                       EXPERIMENTAL AND PREDICTED CONVERSIONS FITTING ALL
C                       THE DATA SIMULTANIOUSLY.  (M1=2 IS BETTER FOR FINE
C                       TUNING THE KINETICS)
C         4             AN EFFECTIVENESS FACTOR IS CALCULATED AT THE
C                       REACTOR INLET CONDITIONS THEN THE SIMULATION
C                       PROCEEDS FOR THE SPECIFED KINETICS.
C                       (SEE KINETIC OPTIONS FOR THE USE OF AN EFFECTIVE-
C                           NESS FACTOR THOUGHOUT THE REACTOR)
C         5             CATALYST ACTIVITY IS CORRELATED AS A FUNCTION OF A
C                       ( THIS PRESENTLY ONLY CAN BE DONE WITH M100=-2)
C         6             AN ECONOMIC ANALYSIS OF THE REACTORS OPERATION IS
C                        DONE. ( THIS IS MOST SUITALBE FOR M10>2)
C
      PMODES=MODES
      IF(MODES.LT.0) PMODES=-MODES
      M100=MODES/100
      M10=PMODES/10 - (PMODES/100)*10
      M1=PMODES - 10*M10 - (PMODES/100)*100
C
      IF((PMODES.GT.266).OR .(PMODES.LT.111)) WRITE(NOUT,100)
      IF(PMODES.GT.200) GO TO 20
      IF(PMODES.LT.100)M100=1
      IF((M10.GT.5).OR.(M10.LT.1)) WRITE(NOUT,110)
      IF((M10.GT.5).OR.(M10.LT.1)) M10=3
      IF(((M1.EQ.2).OR.(M1.EQ.3).OR.(M1.EQ.5)).AND.(M100.NE.-1))
     * WRITE(NOUT,120)
      IF(((M1.EQ.2).OR.(M1.EQ.3).OR.(M1.EQ.5)).AND.(M100.NE.-1))
     * M100=-1
      RETURN

 20   CONTINUE
      IF(M100.NE.-2) WRITE(NOUT,130)
      M100=-2
      IF((M10.GT.5).OR.(M10.LT.0)) WRITE(NOUT,110)
      IF((M10.GT.5).OR.(M10.LT.0)) M10=3
      IF(M10.NE.3) WRITE(NOUT,140)
      IF((M1.EQ.2).OR.(M1.EQ.3)) WRITE(NOUT,140)
      IF((M1.EQ.2).OR.(M1.EQ.3)) M1=1
      IF((M1.EQ.6).AND.(M10.LE.2)) WRITE(NOUT,150)
      RETURN

 100  FORMAT(/,15X,34H THE MODE OF PROGRAM OPERATION WAS ,
     *51H INCORRECTLY SPECIFED, DEFUALT VALULS WILL BE USED.)
 110  FORMAT(/,15X,26H INVALID REACTOR OPERATION,
     *52H PARAPETER SPECIFIED, AN ADIBATIC REACTOR SIMULATED.)
 120  FORMAT(/,15X,40H FOR THE SPECIFIED ANALYSIS OF THE DATA,,
     *49H CONVERSION DATA FOR COMPARISON MUST BE SUPPLIED.,
     */,15X,56H IT WAS ASSUMED THAT THIS DATA IS PROVIDED AT THE END OF,
     *14H THE DATA SET.)
 130  FORMAT(/,15X,37H PRESENTLY REACTOR EFFLUENT DATA MUST,
     *13H BE SPECIFED.)
 140  FORMAT(/,15X,42H THE USUSAL REACTOR OPERATION MODE IS THAT,
     *28H OF A 1 BED ADIBATIC REATOR.)
 150  FORMAT(/,15X,112H IT IS MORE TYPICAL FOR THE ECONOMIC ANALYSIS OF
     *THE REACTOR OPERATION TO BE PERFORMED WITH AN ADIBATIC REACTOR.)
      END

      SUBROUTINE READ
C    ALL INPUT DATA ( NOT INCLUDING THE INTERGRATION PARAMETERS AND
C   MEASURED CONVERSION DATA) IS READ IN THIS SUBROUTINE.
      COMMON/T/Z,NF,NR /IO/NIN,NOUT/Y/TDEGK,P,F(15) /F/DT,DP,DF(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     *M10,M1
      COMMCN/HEAT/CPS(4,15),CP(15),HRXN0(15),HRXN1(15)
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     *INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON/RXRCAT/DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP,EQDIA
      COMMCN/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      COMMON /TWOSTG/ TIN2(25), ZSTAGE(25), STEAM(25)
      DIMENSION FOIN (15), NAMEIN(15), WTPER(15), VOLPER(15)
      INTEGER CATNO,FLAG,HPR,RXRPR
      REAL KEQ,LAMDA,K0,LENP,LHSV,MW

C    THIS PRCGRAM IS PRESENTLY DESIGNED TO HANDLE THE 13
C    COPPONENT WHICH, ALONG WITH THEIR MOLECULAR WEIGHTS, ARE
C    LISTED BELOW
      DATA MW/106.168,104.152,92.141,78.114,18.015,2.016,16.043,28.054,
     *44.01,28.01,106.168,14.0,118.2,2*0.0/
      DATA NAME/4HEB  ,4HSTY ,4HTOL ,4HBEN ,4HH20 ,4HH2  ,4HCH4 ,4HC2H4,
     *4HCO2 ,4HCO  ,4HXYL ,4HCH2 ,4HPARF,2*4H    /
C
C
      CATNO=1
      IF(NR.EQ.NOSET) GO TO 60
      IF(NR.EQ.1) GO TO 10
      KPR=-1
      RXRPR=-1
      HPR=-1
      GO TO 40

 10   CONTINUE
      READ(NIN,100) MODES
      WRITE(NOUT,90) MODES
      CALL MODE

C  READ PRINT INDICATORS
C  THESE SECTIONS (HEAT, KINETIC AND REACTOR & CATALYST DATA)
C  WILL BE PRINTED IF THE RESPECTIVE INDICATOR EQUALS 0
        READ(NIN,100)HPR,KPR,RXRPR
C   THE NUMBER OF COMPONENTS AND THE NUMBER OF REACTIONS IS READ.
        READ(NIN,100)NOCOMP,NORXN
C  HEAT DATA READ
C
```

```
      READ(NIN,105)(HRXNO(J),HRXNI(J),J=1,NORXN)

C  KINETIC DATA READ
C     THE KINETIC OPTION (KOPT) HAS THREE PARTS.
C    THE SIGN, THE TENS DIGIT AND THE ONES DIGIT  (+/-, K10, INHBNO)
C       +/-              FORM
C        +           K(J)=EXP( K0(J) - EA(J)/T )
C        -           K(J)=K0(J)*EXP( EA(J)/T )
C       K10              OPTION
C        0           NORMAL SIMULATION
C        1           NONIDEALITY FACTOR USED.
C        2           KINETICS FOR A DIFFERENT CATALYST IN THE SECOND
C                    REACTOR BED READ AND USED.
C        3           EFFECTIVENESS FACTOR USED IN THE CALCULATION OF THE
C                    KINETICS.  (ONLY PROGRAMED FOR INHBNO = 2 OR 5)
C     INHBNO             INHIBITOR
C        1           NONE
C        2           THAT PROPOSED BY CARRA - PEB + B0*PSTY
C        3           THAT PROPOSED BY LEBEDEV - (1.+B0*EXP(LANDA/T)*PSTY)**2
C        4           MODEL 4 INHIBITOR - (PEB + B0*PSTY)**2
C        5           MODEL 5 INHIBITOR - PEB + (B0*PSTY)**2

      READ(NIN,100)KOPT
      NEFF=1
      IF(KOPT.LT.0) NEFF=-1
      IF(KOPT.LT.0) KOPT=-KOPT
      K10=KOPT/10
      INHBNO=KOPT - K10*10
      IF((K10.EQ.2).AND.(M10.LT.4)) WRITE(NOUT,92)
      IF((K10.EQ.2).AND.(M10.LT.4)) K10=0
      IF((K10.EQ.3).AND.(INHBNO.NE.2).AND.(INHBNO.NE.5)) WRITE(NOUT,94)
      IF((K10.EQ.3).AND.(INHBNO.NE.2).AND.(INHBNO.NE.5)) K10=0
      IF(INHBNO.NE.1) READ(NIN,105) B0,LANDA
      IF(INHBNO.NE.1) READ(NIN,100) INHIB
      IF((K10.EQ.3).AND.(LANDA.LT.0.01)) LANDA=10.0
      IF(NEFF.LT.0) KOPT=-KOPT
      READ(NIN,105)(K0(1,J),EA(1,J), J=1,NORXN)
      IF(K10.EQ.2) READ(NIN,105)(K0(2,J),EA(2,J), J=1,NORXN)
C   COEFF IS THE COEFFICIENT MATRIX WHICH CONTAINS THE
C    THE REACTION STOICHIOMETRY.
      DO 30 J=1,NORXN
      READ(NIN,107)(COEFF(J,I),I=1,NOCOMP)
30    CONTINUE
C
C  READ REACTOR AND CATALYST DATA
      READ(NIN,105) DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP
      XAREA=3.14159*(DIARXR/2.)**2
      EQDIA=3./(2./DIAP + 1./LENP)/100.
      RADIUS=0.5* (1.5/DIAP + 1./LENP)/100.
C
C  READ OPERATING CONDITIONS
40    CONTINUE
      IF((M100.EQ.2).OR.(M100.EQ.-2)) CALL READ2
      IF((M100.EQ.2).OR.(M100.EQ.-2)) GO TO 65
      READ(NIN,105)TIN(NR),PIN(NR)
      IF(M10.GE.4) READ(NIN,105) TIN2(NR),ZSTAGE(NR),STEAM(NR)
      IF(NR.EQ.1) NF=2
C
      IF(NF.EQ.2) READ(NIN,103)(F0IN(I),NAMEIN(I),I=1,NOCOMP)
C   IN THE DO LOOPS BELOW THE BOOK KEEPING OF WHICH COMPONENT
C   NAME HAS WHICH NUMBER IS DONE
      DO 55 I=1,15
      DO 50 J=1,NOCOMP
50    IF(NAME(I).EQ.NAMEIN(J)) F0(NR,I)=F0IN(J)
55    CONTINUE
C     WRITE(NOUT,109)
      GO TO 65
60    CONTINUE
      NXPPR=0
      KPR=0
      IF(M10.GE.3) MPR=0
65    CONTINUE
C
C  FLAG IS USED TO KEEP TRACK OF NEGATIVE STREAMS THAT ARE SET TO ZERO
C    AVEWT (AVERAGE WEIGHT) IS USED TO CALCULATE THE WEIGHT
C    PERCENT (WTPER) AND THE DENSITY
      FTOTAL=0.
      AVEWT=0.0
      DO 70 I=1,NOCOMP
      F(I)=F0(NR,I)
      FLAG(I)=1
      IF(NAME(I).EQ.4HH2O ) RATIO=F0(NR,I)/F0(NR,1)
      FTOTAL=FTOTAL + F0(NR,I)
      AVEWT=AVEWT + F(I)*MW(I)
70    CONTINUE

C     VOLUME AND WEIGHT PERCENT OF THE * LIQUID * COMPONENTS
C    IN THE FEED ARE CALCULATED BELOW.
      DO 71 I=1,15
      VOLPER(I)=0.0
      WTPER(I)=0.0
71    CONTINUE
C
      TVOL=0.0
      TWT=0.0
      DO 72 I=1,7
      II=I
      IF(I.EQ.6)II=11
      IF(I.EQ.7)II=13
      TVOL=TVOL + F(II)
      VOLPER(II)=F(II)
      TWT=TWT +F(II)*MW(II)
      WTPER(II)=F(II)*MW(II)
72    CONTINUE
      DO 73 I=1,NOCOMP
      VOLPER(I)=VOLPER(I)/(TVOL-F(5)) * 100.0
      WTPER(I)=WTPER(I)/( TWT - F(5)*MW(5) ) * 100.0
73    CONTINUE
      AVEWT=AVEWT/FTOTAL
      TDEGK=TIN(NR) +273.15
      P=PIN(NR)
C     THE IDEAL GAS DENSITY, THE LIQUID HOURLY SPACE VELOCITY OF
C    ETHYLBENZENE, THE VISCOSITY (PDROP) AND IDEAL GAS HEAT CAPACITY
C    (CPCALC) ARE CALCULATED THROUGH THE FOUR STATEMENTS BELOW.
      DENSTY=82.057 E-6*TDEGK/P * AVEWT
      LHSV=((FTOTAL-F0(NR,5))*MW(1)/867.0)/(HEIGHT*XAREA)
      CALL PDROP (DPDZ)
      CALL CPCALC (CPMIX)
C
C  WRITE OPERATING CONDITIONS
      WRITE(NOUT,110)TIN(NR),PIN(NR),DENSTY,VISC,VELCTY,LHSV,RATIO
      IF(M10.EQ.4) WRITE(NOUT,112)TIN2(NR),STEAM(NR),ZSTAGE(NR)
      IF(M10.EQ.5) WRITE(NOUT,114)TIN2(NR),STEAM(NR),ZSTAGE(NR)
      WRITE(NOUT,115)(I,NAME(I),F0(NR,I),WTPER(I),VOLPER(I),MW(I),I=1,
     *NOCOMP)
      WRITE(NOUT,117)FTOTAL
      IF(NXXPR.NE.0)GO TO 75

C  WRITE REACTOR AND CATALYST DATA
      WRITE(NOUT,120) DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP,EQDIA,
     *RADIUS
   75 IF(KPR.NE.0) GO TO 80
```

```
C WRITE KINETIC DATA
      WRITE(NOUT,120)(J,K0(1,J),EA(1,J), J=1,NORXN)
      IF(K10.EQ.2) WRITE(NOUT,130)(J,K0(2,J),EA(2,J), J=1,NORXN)
      WRITE(NOUT,124)KOPT
      IF(INHBND.NE.1) WRITE(NOUT,125)B0,LANDA,INHIB
      WRITE(NOUT,133)(NAME(I),I=1,NOCOMP)
      DO 85 J=1,NORXN
   85 WRITE(NOUT,135)J,(COEFF(J,I),I=1,NOCOMP)
88     IF (M10.EQ.2) WRITE(NOUT,150)
      IF(M10.EQ.1) WRITE(NOUT,160)
      IF((M10.LE.2).OR.(HPR.NE.0)) RETURN
C WRITE HEAT DATA
      WRITE(NOUT,137)
      WRITE(NOUT,138)CPMIX,(NAME(I),(CPS(J,I),J=1,4),I=1,NOCOMP)
      WRITE(NOUT,140)(J,HRXN0(J),HRXN1(J),J=1,NORXN)
C
C
90    FORMAT(10X,32H THE PROGRAM MODE OF OPERATION = ,I5,///)
92    FORMAT(15X,58H X KINETIC OPTION OF 2 CATALYST HAS BEEN REQUESTED,
     +,/,10X,56H WITHOUT SPECIFYING THE REACTOR OPERATION FARAMETER AS A
     +,/,10X,34H TWO BED REACTOR. K10 WAS SET TO 0,/)
94    FORMAT(15X,48H THE EFFECTIVENESS FACTOR CAN ONLY BE CALCULATED
     +,/,10X,39H FOR INHIBITORS 2 AND 5 BY THIS PROGRAM,/)
  100 FORMAT(I5)
  103 FORMAT(F10.0,6X,A4)
  105 FORMAT(F10.5)
  107 FORMAT(15F4.1)
  110 FORMAT(//,10X,36H THESE ARE THE OPERATING CONDITIONS:  ,//,
     +20X,20H INLET TEMPERATURE =,F10.2,2H C,/,20X,17H INLET PRESSURE =,
     +,F10.3,4H ATM,/,20X,15H FEED DENSITY =,F10.3,
     + 9H KG/CU M ,/,20X,16H FEED VICOSITY = ,E10.4,
     +9H KG/M-SEC ,/,20X,28H SUPERFICAL INLET VELOCITY = ,F10.3,
     +7H M /SEC  ,/,20X
     +38H LIQUID HOURLY SPACE VELOCITY (LHSV) =,F10.3,5H 1/HR,/,20X,
     +,39H MOLAR RATIO OF STEAM TO ETHYLBENZENE = ,F10.3,////)
 112  FORMAT(15X,27H FOR THE SECOND REACTOR BED,/,
     +20X,20H INLET TEMPERATURE =,F10.2,2H C,/,
     +20X,17H STEAM INJECTED =,F10.3,9H KGMOL/HR,/,
     +20X,33H DEPTH OF THE FIRST REACTOR BED =,F10.3,///)
 114  FORMAT(15X,27H FOR THE SECOND REACTOR BED,/,
     +20X,32H TEMPERATURE OF STEAM INJECTED =,F10.2,2H C,/,
     +20X,17H STEAM INJECTED =,F10.3,9H KGMOL/HR,/,
     +20X,33H DEPTH OF THE FIRST REACTOR BED =,F10.3,///)
 115  FORMAT(25X,10H COMPONENT ,3X,16H MOLAR FLOW RATE ,
     +2X,15H WEIGHT PERCENT,2X,15H VOLUME PERCENT,4X,10H MOLECULAR,/,
     +40X,11H (KGMOL/HR),2(6X,12H OF ORGANICS),,7X,7H WEIGHT,/,
     +15(/,25X,I5,3H = ,A4,5X,F8.3,3F17.3))
  117 FORMAT(/,25X,6H TOTAL,11X,F8.3,/)
  120 FORMAT(/////,10X,13H REACTOR DATA,//,20X,11H DIAMETER =,E10.4,
     +2H M,/,20X,23H CROSS-SECTIONAL AREA =,E10.4,6H SQ M ,/,20X,
     +23H CATALYST BED HEIGHT =  ,E10.4,3H M ,///,
     +10X,14H CATALYST DATA,//,20X,15H BULK DENSITY =,E10.4,8H KG/CU M,/
     +,20X,13H VOID SPACE =,F6.4,/,20X,
     +20H PARTICAL DIAMETER =,E10.4,3H CM,/,20X,18H PARTICAL LENGTH =,
     +E10.4,3H CM,/,20X,22H EQUIVALENT DIAMETER =,E10.4,2H M,/
     +,20X,27H VOLUME EQUIVALENT RADIUS =,E10.4,2H M,/)
C
 124  FORMAT(/,20X,29H THE KINETIC OPTION IS NUMBER,I3)
  125 FORMAT(/,20X,5H B0 =,E10.4,/20X,8H LANDA =,E10.4,/,
     +20X,10H THE FIRST,I3,37H REACTIONS INCLUDE THE INHIBITOR TERM,/)
  128 FORMAT(////,10X,13H KINETIC DATA ,//,20X,
     +7H RXN NO,2X,27H K0 (KGMOL/KGCAT-HR-ATM**N),4X,7H EA (K),/,
     +10X,10(I5,5X,2E20.7,/10X))
  130 FORMAT(////,10X,43H KINETIC DATA FOR THE SECOND BED"S CATALYST//,
     +20X,7H RXN NO,2X,27H K0 (KGMOL/KGCAT-HR-ATM**N),4X,7H EA (K),/,
     +10X,10(I5,5X,2E20.7,/10X))
```

```
  133 FORMAT(20X,19H COEFFICIENT MATRIX,//,30X,10H COMPONENT ,//,10X,
     +7H RXN NO,2X,14(A4,2X),I2,/)
  135 FORMAT(12X,I4,15F6.1,/)
C
  137 FORMAT(////,10X,10H HEAT DATA)
  138 FORMAT(//,20X,34H THE FEED MIXTURE HEAT CAPACITY IS,F10.3,
     +16H CAL/KGMOL-DEG K,//,
     + 21X,5H COMP,3X,15H CAL/KGMOL-DEGK,2X,19H CAL/KGMOL-DEG K**2,
     +3X,19H CAL KGMOL-DEG K**3,3X,19H CAL/KGMOL-DEG K**4,/,
     +15(/,22X,A4,4(6X,E10.4,4X)))
  140 FORMAT(///,20X,22H HEAT OF REACTION DATA,//22X,7H RXN NO,
     +,8X,6H HRXN0,6X,2H +,7X,26H HRXN1     * T(K)  =  HRXN,
     +12H (CAL/KGMOL),//,
     +10(20X,I5,2(10X,E10.4),/))
  145 FORMAT(//,20X,36H THE FEED MIXTURE HEAT CAPACITY IS =,F10.3,
     +16H CAL/KGMOL-DEG K,//)
 150  FORMAT(////,20X,36H ISOTHERMAL OPERATION OF THE REACTOR,//)
 160  FORMAT(////,20X,47H ISOTHERMAL & ISOBARIC OPERATION OF THE REACTOR
     +,///)
      RETURN
      END

C
C
      SUBROUTINE READ2
C     THIS SUBROUTINE READS THE OPERATING DATA IN THE FORM AND UNITS
C    USED IN THE PLANT.  THAT IS AGE (#STYRENE/#CATALYST),
C    TEMPERATURE (F), PRESSURE (PSIG), STEAM AND FEED RATES (#/HR),
C    VENT GAS FLOW (STD CU FT/HR),AND FEED AND EFFLUENT COMPOSITIONS
C    (LIQUID PERCENT).
      COMMON/T/Z,NF,NF /IO/NTW,NOUT
      COMMON/PARM/MOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
      COMMON /PLOT/ AGE(25),RXRCFF(25,15),CONV(2,6,25),SELTV(2,4,25)
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      DIMENSION WTPER(2,6),LIQPER(2,6),SPGRAV(6),TLIQ(2)
      REAL MW,LIQPER,MOLES
      DATA SPGRAV/0.780,0.794,0.775,0.818,0.812,0.836/

      DO 10 I=1,NOCOMP
      F0(NR,I)=1.0E-10
      RXRCFF(NR,I)=0.0
 10   CONTINUE

C     THE REACTOR CONDITIONS, STEAM RATE AND FEED RATE ARE READ BELOW.
C    THE DATA MAY BE READ IN TWO DIFFERENT FORMATS:
C    1  THE OPERATING CONDITIONS ON THE FIRST CARD AND THE FEED
C       AND EFFLUENT COMPOSITIONS (LIQ PER) ON THE NEXT 2 CARDS.
C    2  EACH PIECE OF DATA ON A SEPARATE CARD, WITH THE FEED AND
C       EFFLUENT IN WT PERCENT.
      READ(NIN,105)AGE(NR),TINF,TOUTF,PSI,DELTAP,STEAM,FEED,VENT
      L=1
      IF(TINF.LT.1.0) L=-1
      IF(TINF.LT.1.0) READ(NIN,100)TINF,TOUTF,DELTAP,STEAM,FEED,VENT,PSI

C    THE OPERATING CONDITIONS ARE CONVERTED FROM ENGLISH UNITS
C    INTO SI UNITS.
      TIN(NR)=( TINF  - 32.0 )/1.8
      TOUT(NR,1)=( TOUTF  - 32.0 )/1.8
      PIN(NR)=1.0 + PSI/14.7
      POUT(NR,1)=1.0 + ( PSI  - DELTAP )/14.7
      DPATM=DELTAP/14.7
      WRITE(NOUT,110)NR,AGE(NR),TINF,TIN(NR),TOUTF,TOUT(NR,1),
     +DELTAP,DPATM,STEAM,FEED,VENT,PSI,PIN(NR)
```

```
C     THE FEED AND EFFLUENT COMPOSITIONS ARE READ BELOW.
C    THEN THE COMPONENT FLOW RARES ARE CALCULATED

      IF(L.EQ.1) GO TO 60
      READ(NIN,100)(WTPER(1,I),I=1,6),(WTPER(2,I),I=1,6)
      WRITE(NOUT,120)((WTPER(J,I),J=1,2),I=1,6)

      AVEMW=0.0
      DO 20 J=1,2
      TLIQ(J)=0.0
      DO 30 I=1,6
      LIQPER(J,I)=WTPER(J,I)/SPGRAV(I)
      TLIQ(J)=TLIQ(J) + LIQPER(J,I)
 30   CONTINUE
 20   CONTINUE
C
      DO 40 J=1,2
      DO 50 I=1,6
      LIQPER(J,I)=LIQPER(J,I)/TLIQ(J)
 50   CONTINUE
 40   CONTINUE
      GO TO 70
 60   CONTINUE
      READ(NIN,107) ((LIQPER(J,I),I=1,6),J=1,2)
      WRITE(NOUT,130)((LIQPER(J,I),J=1,2),I=1,6)

 70   CONTINUE
      INOUT=1
 80   CONTINUE
      AVEMW=LIQPER(INOUT,4)*MW(1) + LIQPER(INOUT,6)*MW(2) +
     + LIQPER(INOUT,2)*MW(3) + LIQPER(INOUT,1)*MW(4) +
     + LIQPER(INOUT,5)*MW(11) + LIQPER(INOUT,3)*MW(13)
      IF(INOUT.EQ.2) FEED=FEED - 4.28*GAS
      MOLES=FEED/AVEMW * 0.454

      F0(NR,1)=LIQPER(INOUT,4)*MOLES
      RXREFF(NR,1)=LIQPER(2,4)*100.0
      F0(NR,2)=LIQPER(INCUT,6)*MOLES
      RXREFF(NR,2)=LIQPER(2,6)*100.0
      F0(NR,3)=LIQPER(INOUT,2)*MOLES
      RXREFF(NR,3)=LIQPER(2,2)*100.0
      F0(NR,4)=LIQPER(INOUT,1)*MOLES
      IF(F0(NR,4).LT.1.0E-10) F0(NR,4)=1.0E-10
      RXREFF(NR,4)=LIQPER(2,1)*100.0
      F0(NR,11)=LIQPER(INOUT,5)*MOLES
      RXREFF(NR,11)=LIQPER(2,5)*100.0
      F0(NR,13)=LIQPER(INOUT,3)*MOLES
      RXREFF(NR,13)=LIQPER(2,3)*100.0
      F0(NR,5)=STEAM/MW(5) * 0.454


      IF(M10.NE.0) GO TO 90
      GAS=VENT*1.196
      CALL HTLOSS (INOUT,GAS)
      IF(INCUT.EQ.2) GO TO 80
 90   CONTINLE

C     THE PLANT CONVERSION DATA IS CALCULATED FROM THE EFFLUENT
C    COPPOSITION.
      CONV(1,2,NR)=100.0*( LIQPER(2,6) - LIQPER(1,6) )/LIQPER(1,4)
      CONV(1,4,NR)=100.0*( LIQPER(2,2) - LIQPER(1,2) )/LIQPER(1,4)
      CONV(1,5,NR)=100.0*( LIQPER(2,1) - LIQPER(1,1) )/LIQPER(1,4)
      CONV(1,1,NR)=CONV(1,2,NR) + CONV(1,4,NR) + CONV(1,5,NR)
      SELTV(1,1,NR)=100.0*CONV(1,2,NR)/CONV(1,1,NR)
      SELTV(1,2,NR)=100.0*CONV(1,4,NR)/CONV(1,1,NR)
      SELTV(1,3,NR)=100.0*CONV(1,5,NR)/CONV(1,1,NR)
      RETURN

 100  FORMAT(F10.0)
 105  FORMAT(8F10.0)
 107  FCRMAT(6F10.0)
 110  FCRMAT(///,30X,12H TEST NUMBER,I5,/,30X,
     +15H #STY PROD/#CAT,F7.1,///,35X,11H PLANT DATA,/,35X,
     +11H **********,//,
     +20X,22H RX INLET TEMPERATURE ,F8.1,2H F,F8.1,2H C,/,
     +20X,22H RX OUTLET TEMPERATURE ,F8.1,2H F,F8.1,2H C,/,
     +20X,6H RX DP,F24.2,4H PSI,F6.3,4H ATM,/,
     +20X,11H STEAM RATE,F19.1,5H #/HR,/,
     +20X,18H REACTOR FEED RATE,F12.1,5H #/HR,/,
     +20X,9H VENT GAS,F21.1,6H MSCFH,/,
     +20X,17H REACTOR PRESSURE,F13.2,4H PSI,F6.2,4H ATM,//)
 120  FORMAT(///,35X,10H TEST DATA/,35X,10H *********,///,
     +35X,11H WT PERCENT,/,34X,5H FEED,3X,4H EFF,/,
     +20X,8H BENZENE,4X,2F7.2,/,20X,8H TOLUENE,4X,2F7.2,/,
     +20X,10H PARAFFINS,2X,2F7.2,/,20X,3H EB,9X,2F7.2,/,
     +20X,12H M-P XYLENES,2F7.2,/,20X,8H STYRENE,4X,2F7.2,//)
 130  FORMAT(///,35X,10H TEST DATA/,35X,10H *********,///,
     +35X,12H LIQ PERCENT,/,34X,5H FEED,3X,4H EFF,/,
     +20X,8H BENZENE,4X,2F7.2,/,20X,8H TOLUENE,4X,2F7.2,/,
     +20X,10H PARAFFINS,2X,2F7.2,/,20X,3H EB,9X,2F7.2,/,
     +20X,12H M-P XYLENES,2F7.2,/,20X,8H STYRENE,4X,2F7.2,//)
      END


      SUBROUTINE DERV
C     THIS SLBROUTINE CCATAINS THE COMPONENT,ENERGY AND MOMENTUM
C    BALANCES IN DIFFERENTIAL FORM.
      COMMON/Y/TOLGK,P,F(15) /F/DT,DP,DF(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODE1,M100,
     +M10,M1
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHBNO,CATNO,INHIH,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON/RXRCAT/DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LEAP,EBDIA
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      INTEGER CATNO,FLAG
      REAL KEQ,LAMDA,K0,MW
C
      IDIFF=IDIFF + 1
      FTOTAL=0.0
      DC 10 I=1,NOCOMP
      IF(F(I).LT.0.0) FLAG(I)=-1
      IF(F(I).LT.0.0) F(I)=1.0E-10
      FTOTAL=FTOTAL + F(I)
   10 CCATINLE
C     THESE ARE THE DIFFERENTIAL MOMENTUM, COMPONENT AND ENERGY BALANCES
C    THE ORDER IS IMPORTANT.
      DP=0.0
      IF(M10.EQ.1) GO TO 15
      CALL FDROF (DPDZ)
      DP=-DPDZ
   15 CALL RATES
      DO 20 I=1,NOCOMP
      DF(I)=RATE(I) * PBULK * XAREA
   20 CONTINUE
C
      DT=0.0
      IF(M10.LE.2) RETURN
      CALL CPCALC (CPMIX)
      CALL ENERGY (GEN)
```

```
      DT=GEN/(CPMIX*FTOTAL)
      RETURN
      END
C
C
      SUBROUTINE PDROP (DPDZ)
C
C     THIS SUBROUTINE USES THE ERGUN PRESSURE DROP EQUATION.
C    IDEAL GAS IS ASSUMED TO CALCULATE THE VELOCITY CHANGE DUE TO CHANGES
C    IN THE TEMPERATURE, PRESSURE AND NUMBER OF MOLES
C    VISCOSITY IS ASSUMED TO BE THAT OF WATER AND IS CALCULATED
C    BY AN EQUATION FROM REID
      COMMON/T/Z,NF,NR /Y/TDEGK,P,F(15)
      COMMON/REACAT/DIAREA,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP,EQDIA
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     *,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     *M10,M1
      INTEGER FLAG
      REAL MW
      DATA VISC0,VISC1/283.15,658.25/
C
      IF(IDIFF.GT.0) GO TO 10
      RG=82.057 E-3
      VELCTY=FTOTAL*RG*TDEGK/(XAREA*PIN(NR)*3600.0)
      VOLCH=VELCTY*PIN(NR)/(FTOTAL*TDEGK)
      G0=DENSTY*VELCTY*XAREA
 10   CONTINUE

      VELCTY=VOLCH*FTOTAL*TDEGK/P
      VISC=10.**(VISC1*(1./TDEGK - 1.0/VISC0) - 3.)
      TERM1=150.*(1.-EPSILN)**2/EPSILN**3 *VELCTY*VISC/EQDIA**2
      TERM2=1.75*(1.-EPSILN)/EPSILN**3 *G0*VELCTY/(EQDIA*XAREA)
      DPDZ=TERM1 + TERM2
C  CHANGE PRESSURE FROM PA TO KPA
      DPDZ=DPDZ/1000.
C  CHANGE PRESSURE FROM KPA TO ATM
      DPDZ=DPDZ/101.3
      RETURN
      END
C
C
      SUBROUTINE RATES
C     THIS SUBROUTINE CALCULATES THE RATES IN KGMOL OF COMPONENT I
C    PER ( KG OF CATALYST - HOUR )
C    THE REACTIONS ARE ASSUMED TO BE IRREVERSIBLE AND MECHANISTIC.
C    TO SIMULATE A REVERSIBLE REACTION TWO REACTION MUST BE USED
C    WITH THE RATIO OF THEIR RATE CONSTANTS BEING THE EQUILBRIUM
C    CONSTANT.
      COMMON /KIN/ K1(3,25)
      COMMON/T/Z,NF,NR /IO/NIN,NOUT/Y/TDEGK,P,F(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     *M10,M1
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     *INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     *,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      INTEGER CATNO,FLAG
      REAL KEQ,LAMDA,K,K0,K1,MW,NIDL
      DIMENSION K(15),PP(15)
      DATA ETA,NIDL,LCOUNT /1.0,1.0,-1/
C
C  KINETIC DATA READ
C     THE KINETIC OPTION (KOPT) HAS THREE PARTS.
C    THE SIGN, THE TENS DIGIT AND THE ONES DIGIT  (+/-, K10, INHBNO)
C       +/-                 FORM
C       +           K(J)=EXP( K0(J) - EA(J)/T )
C       -           K(J)=K0(J)*EXP( EA(J)/T )
C      K10                  OPTION
C       0           NORMAL SIMULATION
C       1           NONIDEALITY FACTOR USED.
C       2           KINETICS FOR A DIFFERENT CATALYST IN THE SECOND
C                   REACTOR BED READ AND USED.
C       3           EFFECTIVENESS FACTOR USED IN THE CALCULATION OF THE
C                   KINETICS.  (ONLY PROGRAMED FOR INHBNO = 2 OR 5)
C     INHBNO              INHIBITOR
C       1           NONE
C       2           THAT PROPOSED BY CARRA - PEB + B0*PSTY
C       3           THAT PROPOSED BY LEBEDEV - (1.+B0*EXP(LAMDA/T)*PSTY)**2
C       4           MODEL 4 INHIBITOR - (PEB + B0*PSTY)**2
C       5           MODEL 5 INHIBITOR - PEB + (B0*PSTY)**2

      DO 10 I=1,NOCOMP
      PP(I)=P*F(I)/FTOTAL
   10 CONTINUE

      DENOM=1.0
      IF(INHBNO.EQ.2) DENOM=PP(1) + B0*PP(2)
      IF(INHBNO.EQ.3) DENOM=(1.0 + B0*EXP(LAMDA/TDEGK)*PP(2) )**2
      IF(INHBNO.EQ.4) DENOM=( PP(1) + B0*PP(2) )**2
      IF(INHBNO.EQ.5) DENOM= PP(1) + (B0*PP(2))**2
C
C    IN THE NESTED DO LOOPS BELOW THE RATE OF EACH REACTION
C   IN THIS VOLUME ELEMENT IS CALCULATE
C
      DO 20 J=1,NORXN
C  THE PTERM IS THE PRODUCT OF THE PARTICAL PRESSURES OF THE REACTANTS
C  SURFACE
      PTERM=1.
      DO 30 I=1,NOCOMP
      IF(COEFF(J,I).LT.-0.0001) POWER=-COEFF(J,I)
   30 IF(COEFF(J,I).LT.-0.00001) PTERM=PTERM*PP(I)**POWER
C
      K(J)=EXP(  K0(CATNO,J) - EA(CATNO,J)/TDEGK )
      IF(KOPT.LT.0) K(J)=K0(CATNO,J)*EXP(-EA(CATNO,J)/TDEGK)


C     IF( (KOPT.NE.1).AND.(J.EQ.NORXN).AND.(NORXN.LE.9) )
C    *K(J)=K(J)*P/TDEGK**3
      RXRATE(J)=K(J)*PTERM
      IF(J.LE.INHIB) RXRATE(J)=RXRATE(J)/DENOM
   20 CONTINUE
C
C    EQUILIBRIUM CALCULATION ARE BASED ON ONLY THE MAIN
C   REACTION PROCEEDING FROM THIS POINT IN THE REACTOR.
      KEQ=K(1)/K(2)
      BETA=KEQ*FTOTAL/P
      SUMP=0.
      PROD=1.
      DO 60 I=1,NOCOMP
      IF(COEFF(1,I).GT.0.) SUMP=SUMP + F(I)
      IF(COEFF(1,I).GT.0.) PROD=PROD*F(I)
   60 CONTINUE
      SUMP=SUMP + BETA
      GAMA=(SUMP**2 +4.*(BETA*F(1) - PROD))**0.5 - SUMP
      XEQ=(F(2)+0.5*GAMA)/F0(NR,1)

C     THE COMMANDS BELOW ARE FOR CALCULATING THE EFFECTIVENESS
C    FACTOR AT THE REACTOR INLET.
      IF((M1.EQ.4).AND.(ICOUNT.NE.LCOUNT))
     * CALL EFFECT (PHI,XPEQ,ETAS,K,PP)
      IF((M1.EQ.4).AND.(ICOUNT.NE.LCOUNT))
```

```
     + WRITE(NOUT,100)PHI,XPEQ,ETAS
      LCCUNT=ICOUNT

      IF(K10.EQ.1) CALL NIDEAL (NIDL)
      IF(K10.EQ.3) CALL EFFECT (PHI,XPEQ,ETA,K,PP)
      DO 55 J=1,INHIB
55    KXRATE(J)=KXRATE(J)*ETA*NIDL

C     THE RATE OF FORMATION OF EACH COMPONENT IS CALCULATED BELOW
      DO 40 I=1,NOCOMP
      RATE(I)=0.0
      DO 50 J=1,NORXN
      RATE(I)=RATE(I) + COEFF(J,I)*KXRATE(J)
   50 CONTINUE
   40 CONTINUE

      KI(1,NR)=K(1)
      DO 70 L=2,3
70    KI(L,NP)=K(L+1)

100   FORMAT(12X,3(F10.4,3X))
      RETURN
      END
C
C
      SUBROUTINE NIDEAL (NIDL)
      COMMON /PLOT/ AGE(25)
      REAL NIDL
C     THIS SUBROUTINE SUPPLIES A FACTOR TO ACCOUNT FOR THE CATALYST AND
C     REACTOR NONIDEALITIES.

      NIDL=0.85

C     IF A CORRELATION OF CATALYST ACTIUVITY WITH AGE (IE #STY PROD/#CAT)
C     WAS FOUND IT COULD BE USED IN THIS SUBROUTINE.
      RETURN
      END
C
C
      SUBROUTINE EFFECT (PHI,XPEQ,ETA,K,PP)
C     THIS SUBROUTINE CALCULATES AN EFFECTIVENESS FACTOR.
      COMMON/T/Z,NF,NR /IO/NIN,NOUT/Y/TDEGK,P,F(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODES,NI00,
     +M10,M1
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON/RXRCAT/DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP,EQDIA
      COMMON /FEED/ MW(15)
      REAL K,KEQ,LENP,LAMDA,L,IDM
      DIMENSION K(15),PP(15),DM(15),DAB(15,15),DK(15),Y(15)
C
C     FIRST THE DIFFUSIVITIES ARE CALCULATED
C
      DO 10 I=1,NOCOMP
      Y(I)=FF(I)/P
 10   CONTINUE

      CALL DIFUSE  (DAB,DK)
      DO 20 II=1,3
      I=II
      IF(I.EQ.3) I=6
      IDM=0.0
      DO 30 J=1,6
      IF(I.NE.J)
     + IDM=IDM +( Y(J) - COEFF(1,J)/COEFF(1,I)*Y(I) )/DAB(I,J)
 30   CONTINUE
      DM(I)=1./(IDM + 1./DK(I) )
 20   CONTINUE
C
C
      RG=82.057 E-3
      L=EQDIA/6.
      PHISQ=(K(1)*PBULK)*L**2*RG*TDEGK/(DM(1)*PP(1))
      PHI=PHISQ**.5
C
C     THE DRIVING FORCE FOR THE RLACTION IS OF THE FORM:
C                   PEB - PSTY PH2 / KEQ
C          H(X) =   --------------------
C                   PEB + B0 ( PSTY )**N
C
C                   ( N = 1 OR 2 )

C                       OR
C
C                   (1-X) - GAMA(ALPHA + DELTA X)(BETA + ZETA X)
C          H(X) =   ----------------------------------------------
C                           (1-X) + B0*PEB (ALPHA + DELTA X)**N
C     PUTING THE DRIVING FORCE IN THE FORM:
C
C                   AX**2 + BX + C
C          H(X) =   --------------
C                     X**N + DX +E
C
C              ( IF N=1 D=0 )

      ALPHA=PP(2)/PP(1)
      BETA=PP(6)/PP(1)
      DELTA=DM(1)/DM(2)
      ZETA=DP(1)/DM(6)
      GAMA=PP(1)/KEQ
C
      U=B0*DELTA - 1.0
      IF(INHBNO.EQ.5) U=B0*DELTA**2*PP(1)
      A=-GAMA*DELTA*ZETA/U
      B=-( 1. + GAMA*(ALPHA*ZETA + BETA*DELTA) )/U
      C=(1. - GAMA*ALPHA*BETA)/U
      D=0.0
      IF(INHBNO.EQ.5) D=(2*B0*PP(1)*ALPHA*DELTA - 1.)/U
      E=(1.0 + B0*ALPHA)/U
      IF(INHBNO.EQ.5) E=(1. + B0*PP(1)*ALPHA**2)/U
C
      XPEQ=(-B - (B**2 -4.*A*C)**.5 )/(2.*A)
C
      CALL INTGRL (A,B,C,D,E,SHX,XPEQ)
C
      H0=C/E
C
      ETA=(2.*SHX)**.5/(PHI*H0)
      IF((PHI.LT.1.0).AND.(ETA.GT.1.0)) ETA=1.0
      IF((ETA.LT.0.0).OR.(ETA.GT.1.0)) WRITE(NOUT,100)ETA
      IF(M1.EQ.4) WRITE(NOUT,110)ETA,XPEQ,PHI
C     RETURN
C     WRITE(NOUT,120)K(1),PBULK,L,RG,TDEGK,DM(1),PP(1)
C     WRITE(NOUT,130)ALPHA,BETA,DELTA,ZETA,GAMA,A,B,C,D,E
      WRITE(NOUT,140)PHI,XPEQ,ETA,SHX,H0,DM(1),PP(1)
C
      RETURN
 100  FORMAT(/,10X,20H **** WARNING ETA = ,G10.4)
 110  FORMAT(//,20X,34H THE EFFECTIVENESS FACTOR AT INLET,
     +14H CONDITIONS =  ,G10.4,/
     +,25X,37H WITH A PORE EQUILIBRIUM CONVERSION =,G10.4,/,
     +25X,22H AND A THEIL MODULUS =,G10.4,/)
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120   FORMAT(18X,*K(I) = *,F10.4,/,18X,*PBULK = *,F10.4,/,
     +18X,*L = *,G10.3,* M*,/,18X,*GAS CONSTANT = *,G10.4,/,
     +18X,*T (K) = *,F10.2,/,18X,*DIFFUSIVITY = *,G10.4,* SQ M/HR*,/,
     +18X,* EB PARTIAL PRESSURE = *,F10.4,* ATM*,/)
130   FORMAT(/,20X,*ALPHA*,5X,*BETA*,5X,*DELTA*,5X,*ZETA*,6X,*GAMA*,/,
     +20X,5G12.4,//,
     +25X,*A*,11X,*B*,11X,*C*,11X,*D*,11X,*E*,/,
     +20X,5G12.4,/)
140   FORMAT(12X,7G13.5)
      END
C
C
      SUBROUTINE DIFUSE (DAB,DK)
C       THIS SUBROUTINE CALCULATES THE DIFFUSIVITIES OF
C    THE COMPONENTS USING THE LENORD JONES 12-6 POTENTIAL
C    FOR THE BULK DIFFUSIVITY AND THE STANDARD EQUATION FOR THE
C    KNUDSEN DIFFUSIVITY.  THE LENORD JONES PARAMETER FOR BENZENE
C    WAS USED FOR ALL THE AROMATICS.
      COMMON/Y/TDEGK,P,F(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
      COMMON/RATE/BO,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +IAHBNO,CATNO,IAHTB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON/RXRCAT/DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP,EQDIA
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      REAL KEQ,LENP,LAPDA,MW
      DIMENSION DAB(15,15),DK(15),EOK(15),SIGMA(15)
      DATA AA,BB,CC,DD,EE,FF,GG,HH /1.06036,0.1561,0.193,0.47635,
     +1.03587,1.52996,1.76474,3.89411/
      DATA EOK /4*412.3,809.1,59.7,9*1.0/
      DATA SIGMA /4*5.349,2.641,2.827,9*1.0/
C
      RBAR=2.3 E-5
      TAL=LAPDA
      DC 10 I=1,6
      DK(I)=9.70 E+3*0.36*RBAR*(TDEGK/MW(I))**.5
      DK(I)=EPSILN*DK(I)/TAU
      IF(I.EQ.6) RETURN
      IP1=I+1
      DO 20 J=IP1,6
      TSTAR=TDEGK/(EOK(I)*EOK(J))**.5
      OMEGA=AA/TSTAR**BB + CC/EXP(DD*TSTAR) + EE/EXP(FF*TSTAR)
     +  + GG/EXF(HH*TSTAR)
      DAB(I,J)=6.6888E-4*(TDEGK)**1.5*(1./MW(I) + 1./MW(J))**.5
     + /  (P*OMEGA*(SIGMA(I) + SIGMA(J))/2.)
      DAB(I,J)=EPSILN/TAU*DAB(I,J)
      DAB(J,I)=DAB(I,J)
20    CONTINUE
10    CONTINUE
C
      RETLRN
      END
C
C
      SUBROLTINE INTGRL (A,B,C,D,E,SMX,X0)

      IF((D.GT.-0.001).AND.(D.LT.0.001)) GO TO 10

      Q=(4*E-D**2)**.5

      TERM1=A*X0
      TERM2=(-A*D + B)/2 * ALOG( (X0**2 + D*X0 + E)/E )
      TERM3=( A*D**2 - 2.*A*E - B*D + 2.*C )/Q *
     + ( ATAN( (2.*X0 + D)/Q ) - ATAN( D/Q ) )
      SMX=TERM1 + TERM2 + TERM3
      RETLRN

10    CONTINUE
      TERM1=A/2.*X0**2
      TERM2=(B-A*E)*X0
      TERM3=(C + A*E**2 - B*E)*ALOG(1.0 + X0/E)

      SMX=TERM1 + TERM2 + TERM3
      RETLRN
      END

      SUBROUTINE CPCALC (CPMIX)
C    HEAT CAPACITY DATA IS FROM REID, PRAUSNITZ & SHERWOOD*S BOOK
      COMMON/Y/TDEGK,P,F(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP
      COMMCN/HEAT/CPS(4,15),CP(15),HRXN0(15),HRXN1(15)
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL
      REAL MW
C    THE HEAT CAPACITY FOR THE COMPONENT 13 (PARAFFINS) IS
C    THAT OF N-OCTANE.
      DATA CPS/-10924.0,168.9,-0.1149,0.3107E-4,-6747.0,147.1,-0.09609
     +,2.373E-5,-5817.0,122.4,-0.06605,1.173E-5,-8101.0,113.3,-0.07206,
     +1.703E-5,7701.0,0.4595,0.002521,-0.59E-7,6483.0,2.215,-0.003298,
     +1.826E-6,4598.0,12.45,0.00286,-2.703E-6,909.0,37.4,-0.01994,4.192E
     +-6,4728.0,17.54,-0.01338,4.097E-6,7373.0,-3.07,0.006662,-3.037E-6
     +,6494.5,147.35,-0.08504,1.827E-5,4*0.0,
     +-1456.0,184.2,-0.1002,2.115E-5,8*0.0/
C
      CPNEW=0.0
      DO 10 I=1,NOCOMP
      CP(I)=CPS(1,I)+CPS(2,I)*TDEGK+CPS(3,I)*TDEGK**2+CPS(4,I)*TDEGK**3
      CPNEW=CPNEW + CP(I)*F(I)/FTOTAL
   10 CCNTINLE
      CPMIX=CPNEW
      RETURN
      END
C
C
      SUBROUTINE ENERGY (GEN)
C     THIS SUBROUTINE DOES A DIFFERENTIAL ENERGY BALANCE.
C    THE REACTION RATES (CALCULATED IN *RATES*) FOR THIS ELEMENT
C    AND FIRST ORDER HEAT OF REACTION DATA IS USED TO CALCULATE
C    A HEAT OF GENERATION (OR CONSUMTION) TERM, GEN.
      COMMON/Y/TDEGK,P,F(15)
      CCPMCN/PARM/NCSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN
      COMMON/HEAT/CPS(4,15),CP(15),HRXN0(15),HRXN1(15)
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15)
      COMMON/RXRCAT/DIARXR,XAREA,HEIGHT,PBULK,EPSILN,DIAP,LENP,EQDIA
      REAL LAMDA,K0
C
      GEN=0.0
      DO 10 J=1,NORXN

      GEN=GEN - RXRATE(J)*(HRXN0(J) + HRXN1(J)*TDEGK)
   10 CONTINUE
C   GEN HAS UNITS OF CAL/HR
      GEN= FBULK * XAREA * GEN
      RETURN
      END
C
C
      SUBROUTINE PRINT
      COMMON/T//,NF,NR /IO/NIN,NOUT/Y/TDEGK,P,F(15)
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,M1
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      COMMON /PLOT/ AGE(25),RXREFF(25,15),CONV(2,6,25),SELTV(2,4,25)
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
     +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
      COMMON /COST/ MFURN(25),MSTAGE(25),MCOND(25),MRCYCL(25),VENT(25)
     +,EBUSED(25),STYPRD(25),STYCST(25),PROFIT(5,25)
      INTEGER CATNO,FLAG
      REAL MW
      DIMENSION FLOW(15,60),TEMP(60),PRES(60),X(6),SEL(4),WTPER(15)
     +, VOLPER(15)
C
      NCONV=3
      ICOUNT=ICOUNT + 1
      IF((ICOUNT.EQ.1).AND.((M1.EQ.1).OR.(M1.GE.4))) WRITE(NOUT,100)
C
      XTOTAL=0.0
      DO 10 K=1,NCONV
      X(K)=0.0
      IF(ICOUNT.GT.1) X(K)=(F(K+1) - F0(NR,K+1) )/ F0(NR,1)
      XTOTAL=XTOTAL + X(K)
 10   CONTINUE
      DO 20 K=1,NCONV
      SEL(K)=X(K)/XTOTAL
 20   CONTINUE
C
      IF((M1.EQ.1).OR.(M1.GE.4))
     +WRITE(NOUT,105)ICOUNT,Z,TDEGK,P,XTOTAL,X(1),XEQ,(SEL(K),K=1,NCONV)
C
      TEMP(ICOUNT)=TDEGK
      IF((TEMP(ICOUNT).GT.TEMP(ICOUNT-1)).AND.(ICOUNT.NE.1)) WRITE(NOUT,
     +97)
      PRES(ICOUNT)=P
      NEG=1
      DO 40 I=1,NOCOMP
      IF(FLAG(I).LT.0)NEG=-1
      IF(FLAG(I).LT.0) WRITE(NOUT,95)I
      FLAG(I)=1
   40 FLOW(I,ICOUNT)=F(I)
C
      IF(ICOUNT.LT.IPR) RETURN
C
      TOUT(NR,2)=TDEGK - 273.15
      POUT(NR,2)=P
      CONV(2,1,NR)=100.0*XTOTAL
      CONV(2,2,NR)=100.0*X(1)
      CONV(2,3,NR)=100.0* XEQ
      CONV(2,4,NR)=100.0*X(2)
      CONV(2,5,NR)=100.0*X(3)
      DO 50 K=1,NCONV
      SELTV(2,K,NR)=100.0*SEL(K)
      EBUSED(NR)=F0(NR,1) - F(1)
      STYPRD(NR)=F(2) - F0(NR,2)
 50   CONTINUE
      IF((M1.EQ.2).OR.(M1.EQ.3)) RETURN
C
      WRITE(NOUT,110)(NAME(I),I=1,NOCOMP)
      DO 60 K=1,IPR
      WRITE(NOUT,112)K,(FLOW(I,K),I=1,NOCOMP)
   60 CONTINUE

      DO 71 I=1,15
      VOLPER(I)=0.0
      WTPER(I)=0.0
 71   CONTINUE
C
      TVOL=0.0
      TWT=0.0
      DO 72 I=1,7
      II=I
      IF(I.EQ.6)II=11
      IF(I.EQ.7)II=13
      TVOL=TVOL + F(II)
      VOLPER(II)=F(II)
      TWT=TWT +F(II)*MW(II)
      WTPER(II)=F(II)*MW(II)
 72   CONTINUE
      DO 73 I=1,NOCOMP
      VOLPER(I)=VOLPER(I)/(TVOL-F(5)) * 100.0
      WTPER(I)=WTPER(I)/( TWT - F(5)*MW(5) ) * 100.0
 73   CONTINUE

      WRITE(NOUT,115)(I,NAME(I),F(I),WTPER(I),VOLPER(I),RXREFF(NR,I),I=1
     +,NOCOMP)
      WRITE(NOUT,117)FTOTAL

C     THE VENT GAS FLOW RATE IS CALCULATED ASSUMING IDEAL GAS,
C    AND STANDARD CONDITIONS (E6 60 F & 1 ATM).
      VENT(NR)=0.0
      DO 85 I=6,10
      VENT(NR)=VENT(NR) + F(I)
 85   CONTINUE
      VENT(NR)=VENT(NR)*520.0*8.7315E-3
      WRITE(NOUT,140)VENT(NR)
C
   95 FORMAT(5X,14H STREAM NUMBER,I3,27H 'S FLOW RATE WENT NEGITIVE)
   97 FORMAT(20X,39H WARNING *** THE TEMPERTURE WENT UP ***,)
  100 FORMAT(1H1,//,10X,36H CONVERSION PROFILE DOWN THE REACTOR,//,
     +2X,5H STEP,4X,
     +6H DEPTH,3X,12H TEMPERATURE,3X,9H PRESSURE,6X,6H TOTAL,5X,
     +8H STYRENE,
     +4X,11H EQUILBRIUM,4X,8H STYRENE,5X,8H TOLUENE,5X,8H BENZENE,,
     +/,12X,4H (M),8X,4H (K),9X,6H (ATM),4X,
     +3(11H CONVERSION,2X),3(12H SELECTIVITY,1X),/)
  105 FORMAT(5X,I2,9(F10.4,3X))
 110   FORMAT(1H1,40X,32H COMPONENT FLOW RATES (KGMOL/HR),///,
     +2X,5H STEP,3X,13(A4,5X),/)
 112   FORMAT(4X,I2,3F9.3,F8.3,F10.3,8F9.3)
 115   FORMAT(1H1,25X,10H COMPONENT ,3X,16H MOLAR FLOW RATE ,
     +2X,15H WEIGHT PERCENT,2(2X,15H VOLUME PERCENT),/,
     +40X,11H (KGMOL/HR),3(6X,12H OF ORGANICS),/,
     +94X,9H IN PLANT,/,
     +15(/,25X,I5,3H ) ,A4,5X,F8.3,3(5X,F12.3)))
  117 FORMAT(/,25X,6H TOTAL,11X,F8.3,/)
 140   FORMAT(/,20X,9H VENT GAS,F21.2,6H MSCFM,/)
       RETURN
       END
C
C
       SUBROUTINE HTEXCH
C        THIS SUBROUTINE INITAILIZES THE INLET CONDITIONS FOR THE
C    SECOND REACTOR BED.  THE REACTOR INLET TEMPERATURE MAY BE SPECIFED
C    FOR INTERSTAGE HEATING BY HEAT EXCHANGER OR STEAM INJECTION; OR
C    THE STEAM TEMPERATURE MAY BE SPECIFIED FOR INTERSTAGE HEATING
C    BY STEAM INJECTION.   IT IS ASSUMED THAT THE PRESSURE DROP DUE
C    TO THE INTERSTAGE HEATING CAN BE NEGLECTED.
       COMMON/T/Z,NF,NR /TO/NIN,NOUT/Y/TDEGK,P,F(15)
       COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL
       COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODES,M100,
      +M10,M1
       COMMON/HEAT/CPS(4,15),CP(15),HRXN0(15),HRXN1(15)
       COMMON /TWOSTG/ TIN2(25), ZSTAGE(25), STEAM(25)
```

```
      COMMON /INT/ NEQN,DSTEP,ITYPE,ERROR,EPS,Z0(25),ZF(25),DELTAZ,
     + IERROR,MF,INDEX
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHMRO,CATNO,IAMIN,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON /COST/ HFURN(25),HSTAGE(25),HCOND(25),HRCYCL(25),VENT(25)
     +,EBUSED(25),STYPRD(25),STYCST(25),PROFIT(5,25)
      INTEGER CATNO
      REAL K0,KEQ,LAMDA,PW
      DIMENSION H(15)
C
      INDEX=1
C     IF THE SECOND BED IS PACKED WITH A DIFFERENT CATALYST,
C    THE KINETIC INDEX (CATNO) IS SET TO 2.
      IF(K10.EQ.2) CATNO=2
      CALL ENTHPY (TDEGK,HIN)
      IF(M10.EQ.5) GO TO 40
      T2=TDEGK
C     THE SECOND STAGE INLET TEMPERATURE HAS BEEN SPECIFIED,
C    AND IS SET IN THE EQUATION BELOW
      TDEGK=TIN2(NR) + 273.15
C     IF STEAM < 1, THE INTERSTAGE HEATING IS DONE BY HEAT EXCHANGER.
      IF(STEAM(NR).LT.1.0) GO TO 90

C     SINCE THE INTERSTAGE HEATING IS DONE BY STEAM INJECTION,
C    THE STEAM > 0) THE INJECTION STEAM TEMPERATURE IS CALCULATED
C    USING A TRIAL AND ERROR ENERGY BALANCE.  NOTE REID'S IDEAL
C    GAS HEAT CAPACITIES ARE USED TO CALCULATE ENTHALPY.
      HEFF=0.0
      DO  5 I=1,NOCOMP
      H(I)=CPS(1,I)*(T2-TDEGK) + CPS(2,I)*(T2**2-TDEGK**2)/2. +
     + CPS(3,I)*(T2**3-TDEGK**3)/3. + CPS(4,I)*(T2**4-TDEGK**4)/4.
      HEFF=HEFF - F(I)*H(I)
    5 CONTINUE
      TINJ=TDEGK + HEFF/(STEAM(NR)*9530.0)
      TOTAL=FTOTAL + STEAM(NR)
      T2=TDEGK
      DELTAT=5.0
      K=0
C
   10 CONTINUE
      K=K + 1
      HINJ=STEAM(NR)*( CPS(1,5)*(T2-TINJ) + CPS(2,5)*(T2**2-TINJ**2)/2.
     + + CPS(3,5)*(T2**3-TINJ**3)/3. + CPS(4,5)*(T2**4-TINJ**4)/4. )
C
      TOLD=TINJ
      DELTAH=HEFF + HINJ
      IF(K.EQ.1) GO TO 30
      CHNEW=OLDDH - DELTAH
      IF(K.EQ.2) GO TO 30
      IF((CHNEW/CHOLD).LT.0.0) DELTAT=DELTAT/2.
      IF(DELTAT.LT.0.02) GO TO 90
   30 CONTINUE
      DIR=1.0
      IF(DELTAH.LT.0.0) DIR=-1.0
      TINJ=TINJ + DIR*DELTAT
      CHOLD=CHNEW
      OLDDH=DELTAH
      IF(K.LT.100) GO TO 10
      PERH=DELTAH/HEFF * 100.0
      WRITE(NOUT,100)PERH
      GO TO 90
C
C
   40 CONTINUE
      IF(STEAM(NR).LT.1.0) WRITE(NOUT,95)
      IF(STEAM(NR).LT.1.0) GO TO 90
C     THE INJECTION STEAM'S TEMPERATURE HAS BEEN SPECIFIED,
C    AND THE SECOND STAGE INLET TEMPERATURE IS CALCULATED BY
C    A TRIAL AND ERROR ENERGY BALANCE.
      TINJ=TIN2(NR) + 273.15
      TOTAL=FTOTAL + STEAM(NR)
      T2=STEAM(NR)/TOTAL*TINJ + FTOTAL/TOTAL*TDEGK
      DELTAT=5.0
      K=0
C
   50 CONTINUE
      K=K + 1
      HEFF=0.0
      DO 60 I=1,NOCOMP
      H(I)=CPS(1,I)*(T2-TDEGK) + CPS(2,I)*(T2**2-TDEGK**2)/2. +
     + CPS(3,I)*(T2**3-TDEGK**3)/3. + CPS(4,I)*(T2**4-TDEGK**4)/4.
      HEFF=HEFF + F(I)*H(I)
   60 CONTINUE
      HINJ=STEAM(NR)*( CPS(1,5)*(T2-TINJ) + CPS(2,5)*(T2**2-TINJ**2)/2.
     + + CPS(3,5)*(T2**3-TINJ**3)/3. + CPS(4,5)*(T2**4-TINJ**4)/4. )
C
      TOLD=T2
      DELTAH=HEFF + HINJ
      IF(K.EQ.1) GO TO 70
      CHNEW=OLDDH - DELTAH
      IF(K.EQ.2) GO TO 70
      IF((CHNEW/CHOLD).LT.0.0) DELTAT=DELTAT/2.
      IF(DELTAT.LT.0.02) GO TO 80
   70 CONTINUE
      DIR=1.0
      IF(DELTAH.GT.0.0) DIR=-1.0
      T2=T2 + DIR*DELTAT
      CHOLD=CHNEW
      OLDDH=DELTAH
      IF(K.LT.100) GO TO 50
      PERH=DELTAH/HEFF * 100.0
      WRITE(NOUT,100)PERH
C
   80 CONTINUE
      TDEGK=T2
   90 CONTINUE
      F(5)=F(5) + STEAM(NR)
      TSTAGE=TDEGK - 273.15
      WRITE(NOUT,110)TSTAGE
      IF(STEAM(NR).GT.1.0) WRITE(NOUT,120)TINJ
      CALL ENTHPY (TDEGK,HOUT)
      HSTAGE(NR)=(HOUT-HIN) * 1.0 E-6

      TB=644.2
      IF((M10.EQ.4).AND.(STEAM(NR).GT.1.0)) HSTAGE(NR)=1.0 E-6 *
     + STEAM(NR)*(CPS(1,5)*(TINJ-TB) + CPS(2,5)*(TINJ**2-TB**2)/2.
     + + CPS(3,5)*(TINJ**3-TB**3)/3. + CPS(4,5)*(TINJ**4-TB**4)/4. )

      WRITE(NOUT,130)HSTAGE(NR)
      RETURN
C
   95 FORMAT(15X,40H WARNING THE INLET TEMPERATURE WAS TO BE
     +,34H CALCULATED BY A ENERGY BLANCE FOR,/,10X,
     +59H INTERSTAGE HEATING BY STEAM INJECTION, BUT THE AMOUNT OF
     +,/,50) STEAM WAS TO LOW. THE STEAM TEMPERATURE WAS USED AS THE
     +,19H INLET TEMPERATURE.,//)
  100 FORMAT(/,10X,44H **** WARNING THE INTERSTAGE STEAM INJECTION,
     +43H SUBROUTINE DID NOT CONVERGE ON TEMPERATURE,/,10X,
     +20H ENTHALPY IS OFF BY ,F8.2,8H PERCENT,/)
  110 FORMAT(/,10X,35H THE SECOND REACTOR BED BEGINS HERE,
     +,/,10X,24H THE INLET TEMPERATURE =,F10.2,2H C)
  120 FORMAT(10X,24H THE STEAM TEMPERATURE =,F10.2,2H C)
```

```
 130    FORMAT(10X,39H THE HEAT ADDED BY INTERSTAGE HEATING =,
       +G10.4,9H MMCAL/HR)
        END
 C
 C
        SUBROUTINE DUTIES
 C   THIS SUBROUTINE CALCULATES THE HEAT DUTY OF THE FURNANCE, THE
 C   HEAT LOST IN THE CONDENSER AND THE RECYCLE COLUMES REBOILER DUTY.
        COMMON/T/2,NF,NR /IO/NIN,NOUT/Y/TDEGK,P,F(15)
        COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORKN,ICOUNT,MODES,M100,
       +M10,M1
        COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
       +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
        COMMON/HEAT/CPS(4,15),CP(15),HRXN0(15),HRXN1(15)
        COMMON /COST/ HFURN(25),HSTAGE(25),HCOND(25),HRCYCL(25),VENT(25)
       +,EBUSED(25),STYPRD(25),STYCST(25),PROFIT(5,25)
        DIMENSION H(15)

 C    FH20 IS THE STEAM INJECTED INTO THE ORGANIC PHASE (IE OIL)
 C    BEFORE IT GOES THROUGH THE HEAT EXCHANGER.
        FH20=210.5
        TOIL=TDEGK - 700./(F0(NR,5)/F0(NR,1))**0.8
        TINK=TIN(NR) + 273.15
        HOIL=0.0

        DO  5 I=1,NOCOMP
        H(I)=CPS(1,I)*(TOIL-TINK) + CPS(2,I)*(TOIL**2-TINK**2)/2. +
       + CPS(3,I)*(TOIL**3-TINK**3)/3. + CPS(4,I)*(TOIL**4-TINK**4)/4.
        FLOW=F(I)
        IF(I.EQ.5) FLOW=FH20
        HOIL=HOIL - FLOW*H(I)
   5    CONTINUE
        FSTM=F0(NR,5) - FH20
        TAQ=TDEGK + HOIL/(FSTM*9530.0)
        DELTAT=4.0
        K=0
 C
  10    CONTINUE
        K=K + 1
        HSTM=FSTM*(CPS(1,5)*(TAQ-TINK) + CPS(2,5)*(TAQ**2-TINK**2)/2.
       1+ CPS(3,5)*(TAQ**3-TINK**3)/3. + CPS(4,5)*(TAQ**4-TINK**4)/4.)
 C
        DELTAH=HOIL - HSTM
        IF(K.EQ.1) GO TO 30
        CHNEW=OLDDH - DELTAH
        IF(K.EQ.2) GO TO 30
        IF((CHNEW/CHOLD).LT.0.0) DELTAT=DELTAT/2.
        IF(DELTAT.LT.0.02) GO TO 40
  30    CONTINUE
        DIR=1.0
        IF(DELTAH.LT.0.0) DIR=-1.0
        TAQ=TAQ + DIR*DELTAT
        CHOLD=CHNEW
        OLDDH=DELTAH
        IF(K.LT.150) GO TO 10
        PERH=DELTAH/HOIL * 100.0
        WRITE(NOUT,100)PERH
 C
  40    CONTINUE
        TB=644.2

        HF=FSTM*(CPS(1,5)*(TAQ-TB) + CPS(2,5)*(TAQ**2-TB**2)/2.
       + + CPS(3,5)*(TAQ**3-TB**3)/3. + CPS(4,5)*(TAQ**4-TB**4)/4. )
        HFURN(NR)=HF*1.0E-6
 C
 C      THIS NEXT SECTION CALCULATES THE HEAT LOST IN THE CONDENSER.
 C    THERE ARE ONLY TWO IMPORTANT TERMS.  THE HEAT OF THE WATER AND
 C    THE HEAT OF THE AROMATICS CONDENSING FROM 300 F TO 100 F.
        AROMTC=0.0
        DO 50 II=1,5
        I=II
        IF(I.EQ.5) I=11
        AROMTC=AROMTC + F(I)
  50    CONTINUE
 C
        DHARCP=13.433 E+6
        DHH20=11.23 E+6
        HCOND(NR)=AROMTC*DHAROM + F(5)*DHH20
        HCOND(NR)=HCOND(NR)*1.0 E-6

 C      THE NEXT SECTION CALCULATES THE REBOILER DUTY FOR THE
 C    RECYCLE COLUMES.  IT IS BASED ON THE HEAT DUTY BEING PROPORTIONAL
 C    THE RECYCLE RATE

        AROMTC=AROMTC - F(2)
        REBOIL=134.16
        HRCYCL(NR)=AROMTC*REBOIL

 C    A SUMMARY TABLE OF THE HEAT DUTY REQUIRED IS WRITTEN.
        WRITE(NOUT,110)HFURN(NR),HSTAGE(NR),HCOND(NR),HRCYCL(NR)
        WRITE(NOUT,120)TOIL,FSTM,TAQ
        RETURN

 100    FORMAT(/,10X,31H **** WARNING THE FURNANCE DUTY,
       +43H SUBROUTINE DID NOT CONVERGE ON TEMPERATURE,/,10X,
       +20H ENTHALPY IS OFF BY ,F8.2,8H PERCENT,/)
 110    FORMAT(///,25X,23H SUMMARY OF HEAT DUTIES,/,
       +/,10X,21H FURNANCE HEAT DUTY =,4X,G12.3,9H MMCAL/HR,
       +/,10X,23H INTERSTAGE HEAT DUTY =,2X,G12.3,9H MMCAL/HR,
       +/,10X,22H CONDENSER HEAT DUTY =,3X,G12.3,9H MMCAL/HR,
       +/,10X,20H RECYCLE HEAT DUTY =,5X,G12.3,9H MMCAL/HR,//)
 120 FORMAT(10X,17H A TEMPERATURE OF,F8.3,
       +37H K IS ASSUMED FOR THE PREHEATED FEED.,/,
       +10X,17H INTO THIS STREAM,F8.2,21H KGMOL/HR OF STEAM AT,
       +/,10X,F8.3,42H K IS INJECTED TO RAISE THE TEMPERATURE TO ,
       +,/,10X,31H THE REACTOR INLET TEMPERATURE.,//)
        END

 C
        SUBROUTINE HTLOSS  (INOUT,GAS)
 C        THIS SUBROUTINE IS USED TO DETECT ANY HEAT LOSSES IN THE REACTOR
 C     IT DOES THIS BY CALCULATING THE ENTHALPY INTO THE REACTOR,
 C     (INCLUDING THE HEAT OF FORMATION CONTRIBUTION) AND THEN CALCULATING
 C     THE EFFLUENT TEMPERATURE THAT AT THE EFFLUENT COMPOSITION
 C     CORRESPONSES TO THE SAME ETHALPY.
        COMMON/T/2,NF,NR /IO/NIN,NOUT /Y/TDEGK,P,F(15)
        COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP
        COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
       +,F0(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
        DIMENSION HFORM(15)
        DATA HFORM /13.917,40.34,17.5,24.0,-57.102,0.0,-15.9,
       +14.522,-93.964,-27.199,60.995,0.0,-38.71,0.0,0.0/

        IF(INCLT.EQ.2) GO TO 20
        HFIN=0.0
        DO 10 I=1,NOCOMP
        HFIN=HFIN + F0(NR,I)*HFORM(I)*1.0E+6
        F(I)=F0(NR,I)
  10    CONTINUE
 C
        TINK=TIN(NR) + 273.15
```

```
      CALL ENTHPY (TINK,HFIN)
      HIN=HIN + HFIN
      INOUT=2
      RETURN
C
20    CONTINUE
C     THE AMOUNT OF GAS PRODUCED IS CONVERTED INTO KGMOL/HR
      FO(NR,6)=0.82*GAS
      FO(NR,7)=0.08*GAS
      FO(NR,8)=0.01*GAS
      FO(NR,9)=0.09*GAS
      FO(NR,5)=FO(NR,5) - 2.*FO(NR,9)
C
      HFOUT=0.0
      DO 30 I=1,NOCOMP
      HFOUT=HFOUT + FO(NR,I)*HFORM(I)*1.0E+6
      F(I)=FO(NR,I)
30    CONTINUE
C
      K=0
      TOUTK=TOUT(NR,1) + 273.15
      DELTAT=5.0
C
40    CONTINUE
      K=K+1
      CALL ENTHPY (TOUTK,HOUT)
      IF(K.EQ.1) HOUT1=HOUT
      HOUT=HOUT + HFOUT
      DELTAH=HIN - HOUT
      CRITRA=ABS(DELTAH/HIN)
      IF(K.EQ.1) GO TO 70
      CHNEW=OLDDH - DELTAH
      IF(K.EQ.2) GO TO 70
      IF((CHNEW/CHOLD).LT.0.0) DELTAT=DELTAT/2.
      IF(DELTAT.LT.0.02) GO TO 80
70    CONTINUE
      DIR=1.0
      IF(DELTAH.LT.0.0) DIR=-1.0
      TOUTK=TOUTK + DIR*DELTAT
      CHOLD=CHNEW
      OLDDH=DELTAH
      IF(K.LT.100) GO TO 40
      PERM=DELTAH/HIN * 100.0
      WRITE(NOUT,100)PERM

80    CONTINUE
      TOUT(NR,2)=TOUTK - 273.15
      TOUTF=(TOUTK - 273.15)*1.8 + 32.0
      WRITE(NOUT,110)TIN(NR),HIN,HOUT1,TOUT(NR,2),TOUTF
      INOUT=1
      RETURN

100   FORMAT(/,10X,41H WARNING THE HEAT LOSS SUBROUTINE DID NOT
     *,17H CONVERGE OFF BY ,F7.2,8H PERCENT)
110   FORMAT(///,10X,22H HEAT LOSS CALCULATION,//,10X,
     *17H INLET CONDITIONS,/,15X,14H TEMPERATURE =,F8.3,2H C,/,
     *,15X,11H ENTHALPY =,G11.4,7H CAL/HR,//,10X,
     *16H EXIT CONDITIONS,/15X,18H ACTUAL ENTHALPY =,G11.4,
     *,7H CAL/HR,/,15X,23H ADJUSTED TEMPERATURE =,F8.3,3H C ,
     *F8.3,2H F,//)
      END
C
      SUBROUTINE ENTHPY (T,ENTH)
C
C     THIS SUBROUTINE CALCULATES THE TOTAL ENTHALPY OF THE
C    COMPONENT AT THE POINT WHEN IT IS CALLED.  IT USES
C     REID*S IDEAL GAS HEAT CAPACITIES AND A BASE TEMPERATURE
C     OF 0 K.
        COMMON /Y/TDEGK,P,F(15)
        COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP
        COMMON /HEAT/CPS(4,15),CP(15)
        DIMENSION H(15)
C
        ENTH=0.0
        DO 10 I=1,NOCOMP
        H(I)=CPS(1,I)*T+CPS(2,I)*T**2/2.+CPS(3,I)*T**3/3.+CPS(4,I)*T**4/4.
        ENTH=ENTH + H(I)*F(I)
 10     CONTINUE
        RETURN
C
        END
C
C
C
C
         SUBROUTINE SUMMRY
C       THIS SUBROUTINE PRINTS A SUMMARY TABLE OF THE RESULTS.
C      THE TOTAL, STYRENE, EQUILIBRIUM, TOLUENE AND BENZENE
C      CONVERSIONS ARE IN ARRAY "CONV", SO PLOTTING THE RESULTS AND
C      EXPERIMENTAL VALUES WOULD NOT BE DIFFICULT.
C
         COMMON /T/Z,WF,NR   /IO/NIN,NOUT
         COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODES,M100,
        *M10,M1
         COMMON /PLOT/ AGE(25),RXREFF(25,15),CONV(2,6,25),SELTV(2,4,25)
         COMMON/FEED/MW(15),TIN(25),PIN(25),DENSTY,VELCTY,FTOTAL,FLAG(15)
        *,FO(25,15),NAME(15),VISC,TOUT(25,2),POUT(25,2)
         INTEGER FLAG
         REAL MW
         DIMENSION CONST(8),RSD(3)
C
         IF(M10.GT.2) WRITE(NOUT,95)
         WRITE(NOUT,110)
         DO 10 N=1,NOSET
         WRITE(NOUT,105)N,TIN(N),PIN(N),(CONV(2,K,N),K=1,3),SELTV(2,1,N)
         IF(M100.LT.0)
        * WRITE(NOUT,105)N,TIN(N),PIN(N),(CONV(1,K,N),K=1,3),SELTV(1,1,N)
 10      CONTINUE
C
         WRITE(NOUT,100)
         DO 20 N=1,NOSET
         WRITE(NOUT,105)N,TOUT(N,2),POUT(N,2),(CONV(2,K,N),K=4,5),
        *(SELTV(2,K,N),K=2,3)
         IF(M100.LT.0)
        * WRITE(NOUT,105)N,TOUT(N,1),POUT(N,1),(CONV(1,K,N),K=4,5),
        *(SELTV(1,K,N),K=2,3)
 20      CONTINUE
C      PLOTING SUBROUTINE CALLS SHOULD FOLLOW
         IF(M100.GT.0) GO TO 30
         NTRIAL=1
         NCALB=0
         NRSD=3
         IM1=M1
         M1=3
         CALL RESID(CONST,NRSD,NCALB,RSD)
         M1=IM1
         WRITE(NOUT,115)(RSD(I),I=1,3)
 30      CONTINUE
         IF(M1.EQ.6) CALL COST
         IF(NR.LT.2) RETURN
         WRITE(NOUT,120)
         NR=NOSET
```

```
      CALL READ
      RETURA
 95   FORMAT(28X,30H THESE RUNS ARE NOT ISOTHERMAL,/ )
 100  FORMAT(///,2X,7H RUN NO,2X,12H TEMPERATURE,2X,
     +9H PRESSURE,2(5X,8H TOLUENE,5X,8H BENZENE),/,
     +12X,8H OUT (C),5X,10H OUT (ATM),2X,
     +2(11H CONVERSION,2X),2(12H SELECTIVITY,1X),/)
 105  FORMAT(5X,I2,5X,F8.2,F13.3,4F13.2)
 110  FORMAT(///,2X,7H RUN NO,2X,12H TEMPERATURE,2X,
     +,9H PRESSURE,6X,6H TOTAL,6X,8H STYRENE,
     +4X,11H EQUILBRIUM,4X,8H STYRENE,4X,/,
     +12X,8H  IN (C),5X,9H IN (ATM),4X,
     +3(11H CONVERSION,2X),(12H SELECTIVITY,1X),/)
 115  FCRMAT(//,
     +7X,40H THE AVERAGE ABSOLUTE DIFFERENCE BETWEEN    ,
     +51H THE STYRENE EXPERIMENTAL & PREDICTED CONVERSIONS =,E11.5,/
     +7X,40H THE AVERAGE ABSOLUTE DIFFERENCE BETWEEN    ,
     +51H THE TOLUENE EXPERIMENTAL & PREDICTED CONVERSIONS =,E11.5,/
     +7X,40H THE AVERAGE ABSOLUTE DIFFERENCE BETWEEN    ,
     +51H THE BENZENE EXPERIMENTAL & PREDICTED CONVERSIONS =,E11.5,//)
 120  FORMAT(///,10X,17H FOR THE LAST RUN)
      ENC


      SUBROUTINE COST
C     THIS SUBROUTINE CALCULATES THE COST TO PRODUCE A POUND OF STYRENE.
C    THE RAW MATERIALS COST (IE ETHYLBENZENE), VENT GAS CREDIT,
C    AND THE MAJOR VARIBLE AND FIXED ENERGY COSTS ARE INCLUDED IN
C    THE CALCULATION.
      COPMCN /IO/NIN,NOUT
      COMMON /FEED/MW(15)
      COMMON /PARM/ NOSET
      COPMON /COST/ HFURN(25),HSTAGE(25),HCOND(25),HRCYCL(25),VENT(25)
     +,EBUSED(25),STYPRD(25),STYCST(25),PROFIT(5,25)
      DIMENSION STYLBS(25),STYPR(5)
      REAL MW
      DATA EBRCST,ENCST,EFF,VNTCST /15.7,356.0,0.85,130.6/
      DATA STYPR /25.0,30.0,35.0,40.0,45.0/
C
      FIXED=19000.0
      FIXEN=0.450
      WRITE(NOUT,100)
C
      DO 10 N=1,NOSET
C    THE MAXIMUM AMOUT OF ETHYLBENZENE RECOVERED FROM THE C8
C    COLUPE IS 12540 LBS/HR (TOTAL FLOW OF 13555 LBS/HR).
      EBLBS=EBUSED(N)*MW(1)/0.454
      STYLBS(N)=STYPRD(N)*MW(2)/0.454

      FIXCST=FIXED/STYLBS(N)
      RAWCST=EBLBS*EBRCST/STYLBS(N)
C     THE REACTOR MODEL"S PREDICTION OF VENT GAS PRODUCTION IS
C    LOW BY A FACTOR OF THREE (WHICH IS WHY THERE IS A FACTOR
C    CF 3 IN THE EQUATIOA BELOW).
      VNTCRD=2.5*VENT(N)*VNTCST/STYLBS(N)

C    CONVERTING THE HEAT DUTIES FROM MMCAL TO MMBTU
      HFURN(N)=HFURN(N)/252.0
      HSTAGE(N)=HSTAGE(N)/252.0
      HCOND(N)=HCOND(N)/252.0
      HRCYCL(N)=HRCYCL(N)/252.0
      CFURN=ENCST/EFF * HFURN(N) / STYLBS(N)
      CSTAGE=ENCST/EFF * HSTAGE(N) / STYLBS(N)
      CCOND=ENCST/EFF * HCOND(N) / STYLBS(N)
      CRCYCL=ENCST/EFF * HRCYCL(N) / STYLBS(N)
      VAREN=CFURN + CSTAGE + CCOND + CRCYCL
```

```
      STYCST(N)=RAWCST - VNTCRD + FIXCST + VAREN + FIXEN
      WRITE(NOUT,110)N,STYCST(N),RAWCST,VNTCRD,FIXCST,FIXEN,CFURN,CSTAGE
     +,CCOND,CRCYCL

      DO 20 M=1,5
      PROFIT(M,N)=( STYPR(M) - STYCST(N) ) * STYLBS(N) / 100.0
 20   CCNTINUE
 10   CCNTINUE

      WRITE(NOUT,120)(STYPR(M),M=1,5)
      WRITE(NOUT,130)(N,STYLBS(N),(PROFIT(M,N),M=1,5),N=1,NOSET)


      RETURN
 100  FORMAT(//4X,4H RUN,X,8H STYRENE,7X,3H EB,9X,5H VENT,8X,6H FIXED,
     +7X,6H FIXED,5X,9H FURNANCE,3X,11H INTERSTAGE,2X,10H CONDENSER,4X
     +,8H RECYCLE,/,5X,3H NO,2X,5H COST,8X,5H COST,7X,7H CREDIT,
     +7X,5H COST,4X,5(13H ENERGY COST ),
     +/,4X,9(5X,7H (C/LB),X),//)
 110  FORMAT(4X,I3,9G13.4)
 120  FORMAT(//,4X,4H RUN,3X,8H STYRENE,15X,25H PROFIT AT A STYRENE SELL
     +13HING PRICE OF:,/,
     +5X,3H NO, 2X,9H PRODUCED,6X,5(F5.2,5H C/LB,3X),/,
     +10X,9H (LBS/HR),1X,5(6X,7H (K/HR)),/)
 130  FORMAT(4X,I3,6F13.2)
      END


      SUBROUTINE KINICS
C    THIS SUBROUTINE DOES A LEAST SQUARES FIT OF THE LN OF THE REACTION
C    RATE CONSTANT VERSES RECIPRICAL TEMPERATURE.  THE SLOPE EQUALS
C    THE ACTIVATION ENERGY DEVIDED BY R.
      COMMON /KIN/ K1(3,25)
      COMMON /T/Z,NF,NR /IO/NIN,NOUT
      COPMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODES,N100,
     +N10,P1
      COMMON/RATE/N0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,INNONO

      DIPENSION FREQ(6), ACT(6)
      REAL K1,K0,LAMDA,KEQ
      INTEGER CATNO,FLAG

      IF(M).EQ.1) GO TO 20

      WRITE(NOUT,100)
      WRITE(NOUT,110)

      NSET=NOSET
      IMOD=0

      CALL LSTSQ (1,NSET,IMOD,FREQ(1),ACT(1) )
      CALL LETSC (2,NSET,IMOD,FREQ(2),ACT(2) )
      CALL LSTSQ (3,NSET,IMOD,FREQ(3),ACT(3) )

      WRITE(NOUT,100)
      WRITE(NOUT,120)
      IMOD=1
      CALL LSTSQ (1,NSET,IMOD,FREQ(4),ACT(4) )

 20   CONTINUE
      NSET=15
      IF(NOSET.LE.NSET) GO TO 10
C       THIS SECTION REFITS THE TOLUENE AND BENZENE REACTIONS
C    USING ONLY THE FIRST NSET POINTS.  THUS THE DATA THAT
C    ONLY THE TOTAL CONVERSION AND STYRENE SELECTIVITY ARE
```

```
C     NEED NOT BE INCLUDED IN THE FIT.
      WRITE(NOUT,100)
      WRITE(NOUT,130)
      NSET=15
      IMOD=0
      CALL LSTSQ (2,NSET,IMOD,FREQ(5),ACT(5) )
      CALL LSTSQ (3,NSET,IMOD,FREQ(6),ACT(6) )
C
      IF(M1.EQ.2) KB(1,1)=FREQ(1)
      IF(M1.EQ.2) EA(1,1)=ACT(1)
      KB(1,2)=KB(1,1) -15.282
      EA(1,2)=EA(1,1) - 14599.0
      KB(1,3)=FREQ(5)
      EA(1,3)=ACT(5)
      KB(1,4)=FREQ(6)
      EA(1,4)=ACT(6)

      DO 30 NR=1,NOSET
      CALL CBRXR
   30 CONTINUE
      IF(M1.EQ.1) RETURN
      WRITE(NOUT,90)MODES
      WRITE(NOUT,140)
      NR=NOSET
      CALL SUMMRY

  10  CONTINUE
      IF(INMONO.NE.2) GO TO 45
C      IN THE SEGMENT BELOW A ONE PARAMETER FIT OF THE MAIN REACTION*S
C    FREQUENCY FACTOR IS DONE USING CARRA*S ACTIVATION ENERGY.
      KB(1,1)=FREQ(4)
      EA(1,1)=ACT(4)
      KB(1,2)=KB(1,1) -15.282
      EA(1,2)=EA(1,1) -14599.0
      KB(1,3)=FREQ(2)
      EA(1,3)=ACT(2)
      KB(1,4)=FREQ(3)
      EA(1,4)=ACT(3)
      DO 40 NR=1,NOSET
      CALL CBRXR
   40 CONTINUE
      WRITE(NOUT,90)MODES
      WRITE(NOUT,150)
      NR=NOSET
      CALL SUMMRY

 45   CONTINUE
      KB(1,1)=FREQ(1)
      EA(1,1)=ACT(1)
      KB(1,2)=KB(1,1) -15.282
      EA(1,2)=EA(1,1) -14599.0
      DO 50 NR=1,NOSET
      CALL CBRXR
   50 CONTINUE
C
 90   FORMAT(1H1,10X,36H SUMMARY OF CONVERSION & SELECTIVITY,
     *13H WITH MODES =,I5,//)
 100  FORMAT(1H1,30X,30H LEAST SQUARES FIT OF THE KINETIC DATA,//)
 110  FORMAT(10X,33H FITTING THE SLOPE AND INTERSEPT:)
 120  FORMAT(10X,42H USING THE LITERATURE ACTIVATION ENERGY OF,
     *40H 45.8 KCAL/MOL AND FITTING THE FREQUENCY FACTOR:)
 130  FORMAT(10X,51H FITTING THE SLOPE AND INTERSEPT FOR THE FIRST 15,
     *7H POINTS)
 140  FORMAT(15X,46H 2 PARAMETER FIT OF ALL POINTS FOR THE STYRENE
     *,35H REACTION & THE FIRST 15 POINTS FOR,
     *32H THE TOLUENE & BENZENE REACTIONS)
 150  FORMAT(15X,46H 1 PARAMETER FIT OF ALL POINTS FOR THE STYRENE
     *,9H REACTION,/15X,44H & A 2 PARAMETER FIT FOR THE FIRST 15 POINTS,
     *36H FOR THE TOLUENE & BENZENE REACTIONS)
      RETURN
      END


      SUBROUTINE LSTSQ (LRXN,NSET,IMOD,FREQ,ACT)
C     THIS SUBROUTINE DOES A LINEAR LEAST SQUARES FIT OF THE
C    APPARENT REACTION RATE CONSTANTS USING THE ARRHENIUS EQUATION.
      COMMON /KIN/ K1(3,25)
      COMMON /FEED/MW(15),TIN(25)
      COMMON /IO/ NIN,NOUT
      DIMENSION XY(25,2),ALBAP(3),DES(5),ANOVA(14),PRED(25,7),STAT(9)
      REAL K1,MW

      IPRED=0
      ALBAP(1)=0.05
      ALBAP(2)=0.1
      ALBAP(3)=0.01
      IER=0

      DO 30 N=1,NSET
      XY(N,1)=1.0/(TIN(N) + 273.15)
      XY(N,2)=ALOG(K1(LRXN,N))
      IF(IMOD.NE.0) XY(N,1)=(TIN(N) + 273.15)
      IF(IMOD.NE.0) XY(N,2)=(TIN(N) + 273.15)*ALOG(K1(LRXN,N)) + 23050.0
 30   CONTINUE
      N=NSET
      CALL RLONE(XY,25,N,IMOD,IPRED,ALBAP,DES,ANOVA,STAT,PRED,25,N,IER)
      IF(IER.NE.0) WRITE(NOUT,110)IER
      LP1=LRXN + 1
      IF(LRXN.EQ.1) LP1=1
      FREQ=STAT(5)
      ACT=-STAT(1)
      IF(IMOD.NE.0) FREQ=STAT(5)
      IF(IMOD.NE.0) ACT=23050.0
      WRITE(NOUT,130)(LP1,K1(LRXN,N),TIN(N),N=1,NSET)
      WRITE(NOUT,140)STAT(5),STAT(1),DES(5)
      WRITE(NOUT,105)LP1,(STAT(I),I=1,9)
      WRITE(NOUT,105)LP1,(DES(I),I=1,5)
      WRITE(NOUT,105)LP1,(ANOVA(I),I=1,7)
      WRITE(NOUT,105)LP1,(ANOVA(I),I=8,14)
      WRITE(NOUT,120)

      RETURN

  105 FORMAT(5X,I2,9E13.7)
 110  FORMAT(10X,21H ***** WARNING IER = ,I4,//)
 120  FORMAT(//)
  130 FORMAT(////,10X,13H KINETIC DATA ,//,20X,
     *7H RXN NO,2X,27H K  (KGMOL/KGCAT-HR-ATM**N),4X,7H   T (C),/,
     *10X,25(I5,5X,2E20.5,/10X))
 140  FORMAT(///,15X,12H INTERSEPT =,F5.3,//,15X,8H SLOPE =,
     *E11.4,//,15X,26H CORRELATION COEFFICIENT =,F6.4,//)
      END

      SUBROUTINE AGING
C     THIS SUBROUTINE DOES A LEAST SQUARES FIT OF THE CATALYST*S
C    ACTIVITY WITH AGE (IE G STY PRODUCED PER G OF CATALYST).
C    IF A GOOD CORRELATION IS FOUND, THE INTERSEPT WOULD EQUAL
C    THE NONIDEALITIES OF THE REACTOR AND THE SLOPE WOULD EQUAL
C    THE DEACTIVATION WITH AGE.

      COMMON /IO/ NIN,NOUT /T/Z,NF,NR
      COMMON /PARM/NOSET
```

```
      COMMON /PLOT/ AGE(25),RXREFF(25,15),CONV(2,6,25),SELTV(2,4,25)
      DIMENSION XY(25,2),ALBAP(3),DES(5),ANOVA(14),PRED(25,7),STAT(9)
     +,ACTVTY(25)

      WRITE(NOUT,130)
      AVEACT=0.0
      DO 10 N=1,NOSET
      ACTVTY(N)=CONV(1,2,N)/CONV(2,2,N)
      AVEACT=AVEACT + ACTVTY(N)
      XY(N,2)=ACTVTY(N)
      XY(N,1)=AGE(N)
      WRITE(NOUT,140)N,N,AGE(N),ACTVTY(N)
 10   CONTINUE
      AVEACT=AVEACT/NOSET

      IPRED=0
      ALBAP(1)=0.05
      ALBAP(2)=0.1
      ALBAP(3)=0.01
      IER=0
      M=NOSET
      IMOD=0

      CALL RLONE(XY,25,M,IMOD,IPRED,ALBAP,DES,ANOVA,STAT,PRED,25,M,IER)
      IF(IER.NE.0) WRITE(NOUT,110)IER
      WRITE(NOUT,150)STAT(5),STAT(1),DES(5),AVEACT
      WRITE(NOUT,105)N,(STAT(I),I=1,9)
      WRITE(NOUT,105)N,(DES(I),I=1,5)
      WRITE(NOUT,105)N,(ANOVA(I),I=1,7)
      WRITE(NOUT,105)N,(ANOVA(I),I=8,14)
      WRITE(NOUT,120)


      WRITE(NOUT,170)

      DO 20 N=1,NOSET
      ACTVTY(N)=CONV(1,2,N)/CONV(2,2,N)
      XY(N,2)=ACTVTY(N) - 1.
      XY(N,1)=ALOG( -AGE(N)/400.0 ) - 1.0
      WRITE(NOUT,140)N,N,AGE(N),ACTVTY(N)
 20   CONTINUE

      IPRED=0
      ALBAP(1)=0.05
      ALBAP(2)=0.1
      ALBAP(3)=0.01
      IER=0
      M=NOSET
      IMOD=1

      CALL RLONE(XY,25,M,IMOD,IPRED,ALBAP,DES,ANOVA,STAT,PRED,25,M,IER)
      IF(IER.NE.0) WRITE(NOUT,110)IER
      XINT=1.0
      WRITE(NOUT,160)XINT,STAT(1),DES(5)
      WRITE(NOUT,105)N,(STAT(I),I=1,9)
      WRITE(NOUT,105)N,(DES(I),I=1,5)
      WRITE(NOUT,105)N,(ANOVA(I),I=1,7)
      WRITE(NOUT,105)N,(ANOVA(I),I=8,14)
      WRITE(NOUT,120)
      RETURN

 105  FORMAT(5X,I2,9E13.7)
 110  FORMAT(10X,21H ***** WARNING IER = ,I4,//)
 120  FORMAT(//)
 130  FORMAT(1H1,//,10X,34H LEAST SQUARES FIT OF THE CATALYST,
     +20H ACTIVITY AS FUNCTION OF AGE,//,
     +10X,7H RUN NO,5X,8H TEST NO,10X,4H AGE,12X,9H ACTIVITY,/,
     +35X,15H RETY PROD/RCAT,/)
 140  FORMAT(8X,I5,9X,I5,F18.2,F20.4)
 150  FORMAT(///,15X,12H INTERSEPT =,F5.3,//,15X,8H SLOPE =,
     +E11.4,//,15X,26H CORRELATION COEFFICIENT =,F6.4,//,
     +15X,19H AVERAGE ACTIVITY =,F6.3,///)
 160  FORMAT(///,15X,12H INTERSEPT =,F5.3,//,15X,8H SLOPE =,
     +E11.4,//,15X,26H CORRELATION COEFFICIENT =,F6.4,//)
 170  FORMAT(1H1,45H ONE PARAMETER FIT OF ACTIVITY VERSES LN AGE,///)
      END


      SUBROUTINE OPTP
C     THIS SUBROUTINE USES A IMSL SEARCH PACKAGE.  IT CAN EITHER BE USED
C     TO FIND THE BEST KINETIC CONSTANTS (KO"S OR KO"S & EA"S)
C     FOR A SET OF DATA OR FOR EACH INDIVIDUAL POINT.
C     WHEN EACH INDIVIDUAL POINT IS FIT AN ARRANHEIUS PLOT CAN BE MADE.
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,M100,
     +M10,MI
      COMMON /IO/ NIN,NOUT /T/Z,NF,NR
      COMMON/RATE/B0,LAMDA,KO(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      EXTERNAL RESID
      DIMENSION PARM(4), CONST(8), RSD(5),XJAC(5,5),XJTJ(15), WORK(50)
     +, C(8)
      INTEGER CATNO
      REAL KEQ,LAMDA,KO
C
      IOPT=1
      NRSD=3
      NCALB=3
      NSIG=8
      EP=1.0 E-8
      DELTA=0.0
      MAXFN=50
      IXJAC=NRSD
      WRITE(NOUT,100)NRSD,NCALB,IXJAC,IOPT
      WRITE(NOUT,110)NSIG,EP,DELTA,MAXFN

      IF(NCALB.GE.4) C(NCALB)=80
      DO 10 N=2,4
      C(N-1)=KO(1,N)
      IF(NCALB.GE.6) C(N+2)=EA(1,N)
 10   CONTINUE

      DO 5 NRUN=1,NOSET
      NTRIAL=1
      NOPT=0

      DO 15 N=1,NCALB
      CONST(N)=C(N)
 15   CONTINUE
 20   NOPT=NOPT + 1
      NP=NRUN
      CALL ZXSSQ (RESID,NRSD,NCALB,NSIG,EP,DELTA,MAXFN,IOPT,PARM,CONST,
     +SSQ,RSD,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      IF(IER.NE.0) WRITE(NOUT,120) IER
      WRITE(NOUT,130)INFER,NTRIAL,SSQ
      IF((INFER.EQ.0).AND.(NOPT.LE.10)) GO TO 20
      IF(M1.EQ.3) RETURN
      NR=2
      IF((5*(NRUN/5)-NRUN.EQ.0).OR.(NRUN.EQ.NOSET))
     +CALL SUMMRY
 5    CONTINUE
      CALL KINTCS
      RETURN
```

```
100   FORMAT(1H1,20X,32H OPTIMIZATION PROGRAM PARMETERS ,///10X,
     + 26H THE NUMBER OF RESIDUALS = ,I5,//,10X,
     + 30H THE NUMBER OF CALABRATION CONSTANTS =  ,I5,//,10X,
     +20H THE ROW DIMENSION OF XJAC = ,I5,//,10X,
     + 29H THE INPUT OPTION PARAMETER = ,I5,//)
110   FORMAT(10X,35H THESE ARE THE CONVERGENCE CRITERIA ,//15X,
     +7H OPTION ,10X,6H VALUE, 10X,12H DISCRIPTION ,
     +/,19X,2H 1,10X,I3,
     +/19X,2H 2, 6X,E10.3,
     +/19X,2H 4, 6X,F10.3,,
     +//,10X,8H MAXFN =,I5,/)
120   FORMAT(5X,20H ***** WARNING IER = ,I4)
130   FORMAT(/,10X,8H INFER =,I3,6X,9H NTRIAL =,I4,6X,6H SSQ =,E10.4,/)
      END


      SUBROUTINE RESID (CONST,NRSD,NCALB,RSD)
C     THIS SUBROUTINE CALCULATES THE AVERAGE ABSOLUTE DIFFERENCE
C   BETWEEN THE MODEL"S CONVERSION AND THE EXPERIMENTAL VALUES.
C   THE THREE CONVERSION IT LOOKS AT ARE STRYENE, TOLUENE, AND BENZENE

      COMMON /T/Z,NF,NR /IO/NIN,NOUT
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODES,M100,
     +M10,M1
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON /PLOT/ AGE(25),RXEFF(25,15),CONV(2,6,25),SELTW(2,4,25)
      COMMON /KIN/ K1(3,25)
      DIMENSION CONST(NCALB), RSD(NRSD)
      INTEGER CATNO
      REAL KEQ,LAMDA,K0,K1

      IF(NCALB.EQ.0) GO TO 20
      IF(NCALB.GE.4) B0=CONST(NCALB)
      DO 5 N=2,4
      K0(I,N)=CONST(N-1)
      IF(NCALB.GE.6) EA(1,N)=CONST(N+2)
5     CONTINUE
      K0(1,1)=15.282 + K0(1,2)
      EA(1,1)=14599.0 + EA(I,2)
      IF(NTRIAL.EQ.1) GO TO 20
      NF=+1
      IF(M1.EQ.2) GO TO 35
      DO 10 NR=1,NOSET
      CALL EBRXR
   10 CONTINUE
C
   20 CONTINUE
      IF(M1.EQ.2) GO TO 43
      DO 30 I=1,NRSD
   30 RSD(I)=0.0
      REL=1.0
C     IF IREL = 1 THE ERROR IS RELATIVE OTHERWISE IT IS ABSOLUTE
      IREL=1
      IF(NCALB.EQ.0) IREL=0

      DO 40 NR=1,NOSET
      IF(IREL.EQ.1)  REL=CONV(1,2,NR)/2.0
      RSD(1)=RSD(1) + ABS(CONV(1,2,NR) - CONV(2,2,NR))/(NOSET*REL)
      IF(IREL.EQ.1) REL=CONV(1,4,NR)
      RSD(2)=RSD(2) + ABS(CONV(1,4,NR) - CONV(2,4,NR))/(NOSET*REL)
      IF(IREL.EQ.1) REL=CONV(1,5,NR)
      RSD(3)=RSD(3) + ABS(CONV(1,5,NR) - CONV(2,5,NR))/(NOSET*REL)
   40 CONTINUE
      GO TO 45

35    CONTINUE
      CALL EBRXR
43    CONTINUE
      IREL=0
      REL=1.0
      IF(IREL.EQ.1)  REL=CONV(1,2,NR)/2.0
      RSD(1)= ABS(CONV(1,2,NR) - CONV(2,2,NR))/REL
      IF(IREL.EQ.1) REL=CONV(1,4,NR)
      RSD(2)= ABS(CONV(1,4,NR) - CONV(2,4,NR))/REL
      IF(IREL.EQ.1) REL=CONV(1,5,NR)
      RSD(3)= ABS(CONV(1,5,NR) - CONV(2,5,NR))/REL

45    CONTINUE
      SSQ=0.0
      DO 50 I=1,NRSD
50    SSQ=SSQ + RSD(I)**2
C
      IWP=5
      IF((IREL.EQ.1).AND.(NTRIAL.EQ.1)) WRITE(NOUT,95)
      IF((IWP*(NTRIAL/IWP)-NTRIAL).NE.0) GO TO 60
      WRITE(NOUT,100)
      WRITE(NOUT,105)NTRIAL,(RSD(I),I=1,NRSD)
      WRITE(NOUT,110)
      WRITE(NOUT,105)NR,(K1(I,NR),I=1,NCALB)
      IF(M1.EQ.3) NR=2
      IF(M1.EQ.3) CALL SUMMRY
   60 NTRIAL=NTRIAL + 1
C
      RETURN
95    FORMAT(//,20X,35H A RELATIVE ERROR WAS USED WITH THE ,
     +33H STYRENE CONVERSION WEIGHTED BY 2)
100   FORMAT(//,3X,6H TRIAL,15X,4H RSD)
  105 FORMAT(4X,I3,9E13.6)
110   FORMAT(5X,3H NR,5X,3H K1,8X,3H K2,8X,3H K3)
      END


       SUBROUTINE OPTM2
C     THIS SUBROUTINE USES A IMSL SEARCH PACKAGE.  ONCE THE BEST
C    KINETIC CONSTANTS ARE FOUND FOR THE MAIN REACTION. THIS
C    SUBROUTINE CAN BE CALLED (USING M1=2) TO RECALIBRATE THE
C    SIDE REACTIONS.
       COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,NODES,M100,
      +M10,M1
       COMMON /IO/ NIN,NOUT /T/Z,NF,NR
       COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
      +INHBNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
       EXTERNAL RESID2
       DIMEASION PARM(4), CONST(8), RSD(5),XJAC(5,5),XJTJ(15), WORK(50)
      +, C(8)
       INTEGER CATNO
       REAL KEQ,LAMDA,K0
C
       M1=1
       IOPT=1
       NRSD=2
       NCALB=2
       NSIG=8
       EP=0.00001
       DELTA=0.0
       MAXFN=50
       IXJAC=NRSD
       WRITE(NOUT,100)NRSD,NCALB,IXJAC,IOPT
       WRITE(NOUT,110)NSIG,EP,DELTA,MAXFN
```

```
      C(1)=K0(1,3)
      C(2)=K0(1,4)

      DO 5 NRUN=1,NOSET
      NTRIAL=1
      NOPT=0

      CONST(1)=C(1)
      CONST(2)=C(2)
20    NOPT=NOPT + 1
      NR=NRUN
      CALL ZXSSQ (RESID2,NRSD,NCALB,NSIG,EP,DELTA,MAXFN,IOPT,PARM,CONST,
     +SSQ,RSD,XJAC,IXJAC,XJTJ,WORK,INFER,IER)
      IF(IER.NE.0) WRITE(NOUT,120) IER
      WRITE(NOUT,130)INFER,NTRIAL,SSQ
      IF((INFER.EQ.0).AND.(NOPT.LE.5)) GO TO 20
      NR=2
      IF((5*(NRUN/5)-NRUN.EQ.0).OR.(NRUN.EQ.NOSET))
     *CALL SUMMRY
5     CONTINUE
      CALL KINTCT
      RETURN

100   FORMAT(1H1,20X,32H OPTIMIZATION PROGRAM PARMETERS ,///10X,
     + 34H THE SIDE REACTIONS ARE CALIBRATED ,//,10X,
     + 26H THE NUMBER OF RESIDUALS = ,I5,//,10X,
     + 38H THE NUMBER OF CALABRATION CONSTANTS =  ,I5,//,10X,
     +28H THE ROW DIMENSION OF XJAC = ,I5,//,10X,
     + 29H THE INPUT OPTION PARAMETER = ,I5,//)
110   FORMAT(10X,35H THESE ARE THE CONVERGENCE CRITERIA ,//15X,
     +7H OPTION ,10X,6H VALUE, 10X,12H DISCRIPTION ,
     +/,19X,2H 1,10X,I3,
     +/19X,2H 2, 6X,E10.3,
     +/19X,2H 4, 6X,E10.3,,
     +//,10X,8H MAXFN =,I5,/)
120   FORMAT(5X,20H ***** WARNING IER = ,I4)
130   FORMAT(/,10X,8H INFER =,I3,6X,9H NTRIAL =,I4,6X,6H SSQ =,E10.4,/)
      END


      SUBROUTINE RESID2 (CONST,NRSD,NCALB,RSD)
C     THIS SUBROUTINE CALCULATES THE AVERAGE ABSOLUTE DIFFERENCE
C    BETWEEN THE MODEL"S CONVERSION AND THE EXPERIMENTAL VALUES.
C    IT IS USED IN CONJUNCTION WITH OPTM2 TO CALIBRATE THE BENZENE
C    AND TOLUENE FORMATION REACTIONS.  THUS IT ONLY COMPARES THESE
C    REACTION"S CONVERSIONS.

      COMMON /T/Z,NF,NR /IO/NIN,NOUT
      COMMON/PARM/NOSET,NTRIAL,IPR,IDIFF,NOCOMP,NORXN,ICOUNT,MODES,MI00,
     +M10,M1
      COMMON/RATE/B0,LAMDA,K0(2,15),EA(2,15),RXRATE(15),KOPT,K10,
     +INHNO,CATNO,INHIB,KEQ,XEQ,RATE(15),COEFF(15,15)
      COMMON /PLOT/ AGE(25),RXNEFF(25,15),CONV(2,6,25),SELTV(2,4,25)
      COMMON /KIN/ K1(3,25)
      DIMENSION CONST(NCALB), RSD(NRSD)
      INTEGER CATNO
      REAL KEQ,LAMDA,K0,KI

      K0(1,3)=CONST(1)
      K0(1,4)=CONST(2)

      NF=-1
      IF(NTRIAL.NE.1) CALL TBRXN
      RSD(1)=ABS( CONV(1,4,NR) - CONV(2,4,NR) )/CONV(1,4,NR)
      RSD(2)=ABS( CONV(1,5,NR) - CONV(2,5,NR) )/CONV(1,5,NR)
      SSQ=RSD(1)**2 + RSD(2)**2
      IF(NTRIAL.EQ.1) WRITE(NOUT,95)
C
      IWR=5
      IF((IWR*(NTRIAL/IWR)-NTRIAL).NE.0) GO TO 60
      WRITE(NOUT,100)
      WRITE(NOUT,105)NTRIAL,(RSD(I),I=1,NRSD)
      WRITE(NOUT,110)
      WRITE(NOUT,105)NR,(K1(I,NR),I=1,2)
60    NTRIAL=NTRIAL + 1
C
      RETURN
95    FORMAT(//,20X,27H A RELATIVE ERROR WAS USED.)
100   FORMAT(//,3X,6H TRIAL,15X,4H RSD)
105   FORMAT(4X,I3,9E13.6)
110   FORMAT(5X,3H NR,5X,3H K2,8X,3H K3)
      END
C THE DATA GOES HERE
```

Sample Data Set 1: Isothermal Reactor Operation Using the Ergun Pressure Drop Equation

```
100=SAMPLE DATA SET 1, SIMULATING AN ISOTHERMAL REACTOR USING SHELL DATA
110= 0.0          1.0      0.020
120=   14 1000     6    1  REL   .00001
130=  121  MODES
140=    0  HPR
150=    0  KPR
160=    0  RXRPR
170=   12 NOCOMP
180=    9  NORXN
190=20843000.0               HRIN0 & HRIN1 STARTS
200=1090.0
210=-20843000.0
220=-1090.0
230=25992000.0
240=-1900.0
250=-12702000.
260=-3150.0
270=19602000.0
280=2110.0
290=50460000.0
300=3960.0
310=0.0
320=0.0
330=-10002000.
340=2500.0
350=10002000.
360=-2500.0
370=    5   KOPT         MODEL 5
380=100.0
390=0.0
400=    5     INHIB
410=38.052             STYRENE  MODEL 5   22 APRIL 82 KINETICS
420=33178.2
430=22.858              REVERSE RXN
440=18579.2
450=39.94              BENZENE
460=37697.8
470=47.93              TOLUENE
480=43984.8
490=4.84          1/2 C2H4 + H20 = CO + 2H2
500=4418.0
510=4.84              CH4 + H20 = CO + 3H2
520=4418.0
530=7.0                  CH2 + H2 = CH4
540=1.0
550=16.88           CO + H20 = CO2 + H2
560=88.07
570=21.21            CO2 + H2 = CO + H20
580=567.0
```

```
590=-1.01.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0               COEFF MATRIX
600=1.0 -1.00.0 0.0 0.0 -1. 0.0 0.0 0.0 0.0
610=-1. 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0
620=-1. 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
630=0.0 0.0 0.0 0.0 -1. 2.0 0.0 -.5 0.0 1.0
640=0.0 0.0 0.0 0.0 -1. 3.0 -1. 0.0 0.0 1.0
650=0.0 0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 0.0 0.0 -1.
660=0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 1.0 -1.
670=0.0 0.0 0.0 0.0 1.0 -1. 0.0 0.0 -1. 1.0 0.0 0.0 0.0
680= 1.1230              DIARXR
690=1.000              XAREA
700=1.000            HEIGHT
710=1447.0            PBULK
720=0.325             EPISLON
730=0.4800        DIA      PARTICAL
740=0.790         LENP
750=550.00              TIN
760=1.00         PIN ATM
770=5.317            EB
780=0.00000001       STY
790=0.00000001       TOL
800=0.00000001       BEN
810=66.4625          H20
820=.000000001       H2
830=.000000001       CH4
840=.000000001       C2H4
850=.000000001       CO2
860=.000000001       CO
870=.000000001       XYL
880=.000000001       CH2
890= ISOTHERMAL TESTING OF SHELL 105 CATALYST
900= 0.0          1.0      0.020
910=   14 1000     6    1  REL   .00001
920=560.0              TIN
930=1.00               PIN
940= ISOTHERMAL TESTING OF SHELL 105 CATALYST
950= 0.0          1.0      0.020
960=   14 1000     6    1  REL   .00001
970=570.0              TIN
980=1.00               PIN
990= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1000= 0.0          1.0      0.020
1010=   14 1000     6    1  REL   .00001
1020=580.0              TIN
1030=1.00               PIN
1040= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1050= 0.0          1.0      0.020
1060=   14 1000     6    1  REL   .00001
1070=590.0            TIN
1080=1.00               PIN
1090=END OF RUNS
1100=    1.0
```

Sample Data Set 2: Isothermal Isobaric Reactor Operation With Kinetic Constants Calibrated by Comparing Predicted Conversions to Manufacturers' Data

```
100=SAMPLE DATA SET 2, SIMULATING AND FITTING ISOTHERMAL DATA FOR SHELL 105
110= 0.0           1.0     0.020
120=    14 1000    6    1 REL  .00001
130= -112  MODES
140=     0  HPR
150=     0  KPR
160=     0  RXRPR
170=    12 NOCOMP
180=     9  NORXN
190=28843000.0              HRXN0 & HRXN1 STARTS
200=1090.0
210=-28843000.0
220=-1090.0
230=25992000.0
240=-1900.0
250=-12702000.
260=-3150.0
270=19602000.0
280=2110.0
290=50460000.0
300=3960.0
310=0.0
320=0.0
330=-10802000.
340=2500.0
350=10802000.
360=-2500.0
370=     5   KOPT           MODEL 5
380=100.0
390=0.0
400=     5      INHIB
410=38.052             STYRENE  MODEL 5   22 APRIL 82 KINETICS
420=33178.2
430=22.850              REVERSE RXN
440=18579.2
450=39.94              BENZENE
460=37697.8
470=47.93              TOLUENE
480=43984.8
490=4.84           1/2 C2H4 + H2O = CO + 2H2
500=4418.0
510=4.84              CH4 + H2O = CO + 3H2
520=4418.0
530=7.0                 CH2 + H2 = CH4
540=1.0
550=16.88            CO + H20 = CO2 + H2
560=88.07
570=21.21             CO2 + H2 = CO + H2O
580=567.0
590=-1.01.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0                  COEFF MATRIX
600=1.0 -1.00.0 0.0 0.0 -1. 0.0 0.0 0.0 0.0
610=-1. 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0
620=-1. 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
630=0.0 0.0 0.0 0.0 -1. 2.0 0.0 -.5 0.0 1.0
640=0.0 0.0 0.0 0.0 -1. 3.0 -1. 0.0 0.0 1.0
650=0.0 0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 0.0 0.0 -1.
660=0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 1.0 -1.
670=0.0 0.0 0.0 0.0 1.0 -1. 0.0 0.0 -1. 1.0 0.0 0.0 0.0
```

```
690=1.000                  XAREA
700=1.000              HEIGHT
710=1447.0              PBULK
720=0.325              EPISLON
730=0.4800         DIA       PARTICAL
740=0.790          LENP
750=550.00               TIN
760=1.00          PIN ATM
770=5.317             EB
780=0.00000001        STY
790=0.00000001        TOL
800=0.00000001        BEN
810=66.4625           H2O
820=.000000001        H2
830=.000000001        CH4
840=.000000001        C2H4
850=.000000001        CO2
860=.000000001        CO
870=.000000001        XYL
880=.000000001        CH2
890= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
900= 0.0           1.0     0.020
910=    14 1000     6    1  REL  .00001
920=560.0                TIN
930=1.00                 PIN
940= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
950= 0.0           1.0     0.020
960=    14 1000     6    1  REL  .00001
970=570.0                TIN
980=1.00                 PIN
990= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
1000= 0.0          1.0     0.020
1010=    14 1000    6    1  REL  .00001
1020=580.0               TIN
1030=1.00                PIN
1040= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
1050= 0.0          1.0     0.020
1060=    14 1000    6    1  REL  .00001
1070=593.0            TIN
1080=1.00                PIN
1090= ISOTHERMAL  TESTING OF SHELL 105 CATALYST   DATA SET 2
1100= 0.0          1.0     0.020
1110=    14 1000    6    1  REL  .00001
1120=580.0               TIN
1130=0.3401                 PIN
1140= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
1150= 0.0          1.0     0.020
1160=    14 1000    6    1  REL  .00001
1170=587.0               TIN
1180=0.680                PIN
1190= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
1200= 0.0          1.0     0.020
1210=    14 1000    6    1  REL  .00001
1220=599.5               TIN
1230=1.36                PIN
1240= ISOTHERMAL  TESTING OF SHELL 105 CATALYST
1250= 0.0          1.0     0.020
1260=    14 1000    6    1  REL  .00001
1270=606.0               TIN
1280=1.7007                 PIN
```

```
1290=  UNITED CATALYST"S DATA  LHSV = 1.  S/O (BY WT) = 1.5  DATA SET 3
1300= 0.0            -1.0      0.020
1310=    14 1000     6    1  REL     0.0001
1320=566.0               TIN
1330=01.272                PIN
1340=8.167             EB
1350=0.00000001        STY
1360=0.00000001        TOL
1370=0.00000001        BEN
1380=72.2500           H2O
1390=.000000001        H2
1400=.000000001        CH4
1410=.000000001        C2H4
1420=.000000001        CO2
1430=.000000001        CO
1440=.000000001        XYL
1450=.000000001        CH2
1460= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1470= 0.0             1.0      0.020
1480=    14 1000     6    1  REL     0.0001
1490=593.0               TIN
1500=01.272                PIN
1510= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1520= 0.0            1.0      0.020
1530=    14 1000     6    1  REL     0.0001
1540=621.1             TIN
1550=01.272                PIN
1560=  UNITED CATALYST"S DATA  LHSV = 1.  S/O (BY WT) = 1.5  DATA SET 4
1570= 0.0            1.0      0.020
1580=    14 1000     6    1  REL     0.0001
1590=566.0               TIN
1600=01.272                PIN
1610= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1620= 0.0             1.0      0.020
1630=    14 1000     6    1  REL     0.0001
1640=593.0               TIN
1650=01.272                PIN
1660= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1670= 0.0            1.0      0.020
1680=    14 1000     6    1  REL     0.0001
1690=621.1             TIN
1700=01.272                PIN
1710=  UNITED CATALYST"S DATA  LHSV = 2.  S/O (BY WT) = 2.5  DATA SET 5
1720= 0.0            -1.0      0.020
1730=    14 1000     6    1  REL     0.0001
1740=566.0             TIN
1750=1.272                 PIN
1760=16.33             EB
1770=0.00000001        STY
1780=0.00000001        TOL
1790=0.00000001        BEN
1800=240.830           H2O
1810=.000000001        H2
1820=.000000001        CH4
1830=.000000001        C2H4
1840=.000000001        CO2
1850=.000000001        CO
1860=.000000001        XYL
1870=.000000001        CH2
1880= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1890= 0.0             1.0      0.020
1900=    14 1000     6    1  REL     0.0001
1910=593.0               TIN
1920=1.272                 PIN
..
1930= ISOTHERMAL TESTING OF SHELL 105 CATALYST
1940= 0.0            1.0      0.020
1950=    14 1000     6    1  REL     0.0001
1960=621.11            TIN
1970=1.272               PIN
1980=  UNITED CATALYST"S DATA  LHSV = 2.  S/O (BY WT) = 1.5  DATA SET 6
1990= 0.0            -1.0      0.020
2000=    14 1000     6    1  REL     0.0001
2010=566.00              TIN
2020=0.680           PIN ATM
2030=16.33             EB
2040=0.00000001        STY
2050=0.00000001        TOL
2060=0.00000001        BEN
2070=144.466           H2O
2080=.000000001        H2
2090=.000000001        CH4
2100=.000000001        C2H4
2110=.000000001        CO2
2120=.000000001        CO
2130=.000000001        XYL
2140=.000000001        CH2
2150= ISOTHERMAL TESTING OF SHELL 105 CATALYST
2160= 0.0            1.0      0.020
2170=    14 1000     6    1  REL     0.0001
2180=593.0               TIN
2190=0.680               PIN
2200= ISOTHERMAL TESTING OF SHELL 105 CATALYST
2210= 0.0            1.0      0.020
2220=    14 1000     6    1  REL     0.0001
2230=621.1             TIN
2240=0.680               PIN
2250=END OF RUNS
2260=   -1.0
2270=0.4002                      T=550.0 C     SET 1
2280=0.0187
2290=0.0152
2300=0.4519            T=560
2310=0.0245
2320=0.0178
2330=0.5023                         T=570.0 C
2340=0.03164
2350=0.0211
2360=0.5537          T=580
2370=0.0417
2380=0.0244
2390=0.609                          T=593.0 C
2400=0.059
2410=0.0315
2420=0.6342                      T=580 C  P=5 PSIA      SET 2
2430=0.042
2440=0.0238
2450=0.6237         T=587  P-10 PSIA
2460=0.0504
2470=0.0273
2480=0.5929        T=599.5  P=20 PSIA
2490=0.07
2500=0.0364
2510=0.574                       T=606 C  P=25 PSIA
2520=0.084
2530=0.042
..

  1,f,2540-30000
```

```
2540=0.409                           T=566 C    SET 3
2550=0.01753
2560=0.00947
2570=0.529                              T=593 C
2580=0.0373
2590=0.0157
2600=0.607                      T=621 C
2610=0.07515
2620=0.0278
2630=0.4360                    T=566  SET 4
2640=0.0215
2650=0.0099
2660=0.5559                       T=593
2670=0.0492
2680=0.0139
2690=0.6100                    T=621 C
2700=0.0006
2710=0.0346
2720=0.339             T=566 P=18.7    SET 5
2730=0.0004
2740=0.0046
2750=0.519               T=593  P=18.7
2760=0.0261
2770=0.0109
2780=0.647                T=621 S/O=2.5
2790=0.0504
2800=0.0216
2810=0.376            T=566     SET 6
2820=0.0052
2830=0.0020
2840=0.561            T=593
2850=0.019
2860=0.000
2870=0.603            T=621
2880=0.0416
2890=0.0154
```

Sample Data Set 3: Adiabatic Reactor Operation to Simulate the USS Chemicals Reactor Reading in Plant Data (compositions in mole percent).

```
100=SAMPLE DATA SET 3, SIMULATING AN ADIABATIC REACTOR USING PLANT DATA
110= 0.0           1.22     0.0400
120=    14 1000     6     1  REL  .00001
130= -235  MODES
140=     0  HPR
150=     0  KPR
160=     0  RXRPR
170=    13 NOCOMP
180=     9  NORXN
190=28843000.0               HRXN0 & HRXN1 STARTS
200=1090.0
210=-28843000.0
220=-1090.0
230=25992000.0
240=-1900.0
250=-12702000.
260=-3150.0
270=19602000.0
280=2110.0
290=50460000.0
300=3960.0
310=0.0
320=0.0
330=-10802000.
340=2500.0
350=10802000.
360=-2500.0
370=     5   KOPT           MODEL 5
380=100.0
390=0.0
400=     5     INHIB
410=38.052              STYRENE  MODEL 5   22 APRIL 82 KINETICS
420=33178.2
430=22.850               REVERSE RXN
440=18579.2
450=39.94               BENZENE
460=37697.0
470=47.93               TOLUENE
480=43984.0
490=4.04          1/2 C2H4 + H2O = CO + 2H2
500=4410.0
510=4.04              CH4 + H2O = CO + 3H2
520=4410.0
530=7.0                   CH2 + H2 = CH4
540=1.0
550=16.80           CO + H20 = CO2 + H2
560=80.07
570=21.21            CO2 + H2 = CO + H2O
580=567.0
```

```
590=-1.01.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0              COEFF MATRIX
600=1.0 -1.00.0 0.0 0.0 -1. 0.0 0.0 0.0 0.0
610=-1. 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0
620=-1. 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
630=0.0 0.0 0.0 0.0 -1. 2.0 0.0 -.5 0.0 1.0
640=0.0 0.0 0.0 0.0 -1. 3.0 -1. 0.0 0.0 1.0
650=0.0 0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 0.0 0.0 -1.
660=0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 1.0 -1.
670=0.0 0.0 0.0 0.0 1.0 -1  0.0 0.0 -1. 1.0 0.0 0.0 0.0
680= 4.851               DIARXR
690=21.927              XAREA
700=1.219           HEIGHT
710=1447.0           PBULK
720=0.325           EPISLON
730=0.3175       DIA      PARTICAL
740=0.370        LENP
750=304.      1144.0    1037.0    14.0      2.9       68400.    30000.    63.
760=0.0       2.16      1.62      79.74     16.04      0.44
770=1.21      5.05      1.17      42.67     15.46      34.4
780=  HOUSTON PLANT DATA SHEET DEC 1 1978  (PREVIOUS RUN JAN 1 1978)
790= 0.0           1.22     0.0400
800=    14 1000     6     1  REL  .00001
810=1610.     1170.     1060.     21.       3.0       93400.    44400.    93.
820=0.0       1.14      0.92      80.22     15.03      2.69
830=1.15      3.68      0.69      44.00     13.97      33.01
840=STYRENE REACTOR TEST  3/ 6/79
850= 0.0           1.22     0.0400
860=    14 1000     6     1  REL  .00001
870=1965.     1154.     1040.     13.       2.4       55900.    27600.    54.
880=0.0       0.66      1.01      82.27     15.20      0.70
890=1.01      2.41      0.92      47.89     14.44     33.01
900=  HOUSTON PLANT DATA SHEET JUNE 7 1981
910= 0.0           1.22     0.0400
920=    14 1000     6     1  REL  .00001
930=1.0       1164.     1049.     9.        0.0       55400.    27000.    60.
940=0.0       0.71      3.26      71.81     23.24      0.97
950=1.01      4.63      3.36      38.71     21.75      32.12
960=  HOUSTON PLANT DATA SHEET JULY 2 1981
970= 0.0           1.22     0.0400
980=    14 1000     6     1  REL  .00001
990=1.0       1164.     1044.     12.       1.6       62400.    27600.    67.5
1000=0.0       1.63      6.58      75.94     15.36      0.49
1010=1.42      4.63      5.81      36.54     14.77      36.84
1020=END OF RUNS
1030=-1.0
```

Sample Data Set 4: Adiabatic Reactor Operation to Simulate the Polymer Corporation Reactor Reading in Plant Data (compositions in weight percent)

```
100=SAMPLE DATA SET 4, SIMULATING AN ADIABATIC REACTOR USING SHEEL"S DATA
110= 0.0          1.22    0.0400
120=   14 1000     6    1  REL  .00001
130= -231  MODES
140=     0  HPR
150=     0  KPR
160=     0  RXRPR
170=    13 NOCOMP
180=     9  NORXN
190=28843000.0                HRXN0 & HRXN1 STARTS
200=1090.0
210=-28843000.0
220=-1090.0
230=25992000.0
240=-1900.0
250=-12702000.
260=-3150.0
270=19602000.0
280=2110.0
290=50460000.0
300=3960.0
310=0.0
320=0.0
330=-10802000.
340=2500.0
350=10802000.
360=-2500.0
370=     5   KOPT          MODEL 5
380=100.0
390=0.0
400=     5      INHID
410=38.052              STYRENE  MODEL 5   22 APRIL 82 KINETICS
420=33178.2
430=22.050               REVERSE RXN
440=18579.2
450=39.94               BENZENE
460=37697.0
470=47.93               TOLUENE
480=43984.0
490=4.84
500=4418.0
510=4.84              CH4 + H2O = CO + 3H2
520=4418.0
530=7.0                  CH2 + H2 = CH4
540=1.0
550=16.88            CO + H20 = CO2 + H2
560=88.07
570=21.21             CO2 + H2 = CO + H2O
580=567.0
590=-1.01.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0                 COEFF MATRIX
600=1.0 -1.00.0 0.0 0.0 -1. 0.0 0.0 0.0 0.0
610=-1. 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0
620=-1. 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
630=0.0 0.0 0.0 0.0 -1. 2.0 0.0 -.5 0.0 1.0
640=0.0 0.0 0.0 0.0 -1. 3.0 -1. 0.0 0.0 1.0
650=0.0 0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 0.0 0.0 -1.
660=0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 1.0 -1.
670=0.0 0.0 0.0 0.0 1.0 -1. 0.0 0.0 -1. 1.0 0.0 0.0 0.0
```

```
690=2.9830               XAREA
700=1.610            HEIGHT
710=1447.0            PBULK
720=0.325            EPISLON
730=0.3175       DIA       PARTICAL
740=0.370        LENP
750=0.0
760=1201.0            TINF
770=1100.0             TOUT F
780=1.18              DP
790=18000.0           STEAM
800=9000.0            FEED
810=0.0               VENT
820=20.14              PSI G
830=0.206           FEED BENZENE
840=1.982                TOLUENE
850=0.204                PARAFFINS
860=95.704               ETHYLBENZENE
870=0.0                  XYLENE
880=1.702                STYRENE
890=2.924           EFFLUENT BENZENE
900=4.665                    TOLUENE
910=0.421                    PARAFFINS
920=51.53                    ETHYLBENZENE
930=0.0                      XYLENE
940=40.463                   STYRENE
950=SHEEL"S MAY DATA
960= 0.0          1.61    0.0322
970=   14 1000     6    1  REL  .00001
980=0.0
990=1199.93              TINF
1000=1099.1               TOUTF
1010=1.18                 DP
1020=18000.0              STEAM
1030=9000.0               FEED
1040=0.0                  VENT
1050=20.14                PSI
1060=0.65               BEN FEED
1070=2.55
1080=0.05
1090=95.40
1100=0.0
1110=1.35
1120=3.35               BEN EFF
1130=5.45
1140=0.15
1150=50.25
1160=0.0
1170=40.0
```

```
1180=SHEEL"S JUNE DATA
1190= 0.0            1.61     0.0322
1200=    14 1000     6     1   REL   .00001
1210=0.0
1220=1196.92          TINF
1230=1098.0             TOUT F
1240=1.18               DP
1250=18000.0            STEAM
1260=9000.0             FEED
1270=0.0                VENT
1280=20.14              PSI
1290=0.139
1300=2.721                   TOL FEED
1310=0.179
1320=94.987
1330=0.0
1340=1.974
1350=2.417                  BEN EFF
1360=4.900
1370=.396
1380=53.316
1390=0.0
1400=38.963
1410=SHEEL"S POLY-29 DATA
1420= 0.0            1.61     0.0322
1430=    14 1000     6     1   REL   .00001
1440=0.0
1450=1201.0             TINF
1460=0.0              TOUT UNKNOWN
1470=0.0              DP
1480=15965.5           STEAM
1490=8593.24           FEED
1500=0.0               VENT
1510=17.79             PSI
1520=0.197                 BEN FEED
1530=3.924
1540=0.0
1550=94.509
1560=0.0              XYL
1570=1.200            STY
1580=2.61             BEN EFF
1590=6.50
1600=0.0
1610=48.64
1620=0.0
1630=43.15
1640=END OF RUNS
1650=-1.0
```

Sample Data Set 5: Simulating a Two-Stage Reactor Packed With Shell 105 and 015 Catalyst and Doing an Economic Analysis for Different Inlet Temperatures, Heating Methods, and Steam-to-Oil Ratios

```
100= SAMPLE DATA SET 5 TWO BED ADIBATIC REACTOR SIMULATION  SHELL 105 & 015
110= 0.0             2.00    0.0400
120=    14 1000      6     1  REL  .00001
130=   146    MODES
140=      0   HPR
150=      0   KPR
160=      0   RXRPR
170=    13 NOCOMP
180=     9  NORXN
190=28843000.0                HRXN0 & HRXN1 STARTS
200=1090.0
210=-28843000.0
220=-1090.0
230=25992000.0
240=-1900.0
250=-12702000.
260=-3150.0
270=19602000.0
280=2110.0
290=50460000.0
300=3960.0
310=0.0
320=0.0
330=-10802000.
340=2500.0
350=10802000.
360=-2500.0
370=    25   KOPT            MODEL 5
380=100.0
390=0.0
400=     5      INHIB
410=38.052                STYRENE  MODEL 5   22 APRIL 82 KINETICS
420=33178.2
430=22.850                 REVERSE RXN
440=18579.2
450=39.94                 BENZENE
460=37697.0
470=47.93                 TOLUENE
480=43984.0
490=4.84            1/2 C2H4 + H2O = CO + 2H2
500=4418.0
510=4.84                CH4 + H2O = CO + 3H2
520=4418.0
530=7.0                    CH2 + H2 = CH4
540=1.0
550=16.88             CO + H20 = CO2 + H2
560=88.07
570=21.21               CO2 + H2 = CO + H2O
580=567.0
590=42.329               STYRENE RXN  SHELL 015  23 APRIL 82 KINETICS
600=37504.0
610=27.127               REVERSE REACTION
620=22905.0
630=61.41                BENZENE REACTION
640=58132.3
650=61.64                TOLUENE REACTION
660=57550.9
670=4.84            1/2 C2H4 + H2O = CO + 2H2
680=4418.0
690=4.84             CH4 + H2O = CO + 3H2
700=4418.0
710=7.0                  CH2 + H2 = CH4
720=1.0
730=16.88          CO + H20 = CO2 + H2
740=88.07
750=21.21           CO2 + H2 = CO + H2O
760=567.0
770=-1.01.0 0.0 0.0 0.0 1.0 0.0 0.0 0.0 0.0                  COEFF MATRIX
780=1.0 -1.00.0 0.0 0.0 -1. 0.0 0.0 0.0 0.0
790=-1. 0.0 0.0 1.0 0.0 0.0 0.0 1.0 0.0 0.0
800=-1. 0.0 1.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1.0
810=0.0 0.0 0.0 0.0 -1. 2.0 0.0 -.5 0.0 1.0
820=0.0 0.0 0.0 0.0 -1. 3.0 -1. 0.0 0.0 1.0
830=0.0 0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 0.0 0.0 -1.
840=0.0 0.0 0.0 0.0 -1. 1.0 0.0 0.0 1.0 -1.
850=0.0 0.0 0.0 0.0 1.0 -1. 0.0 0.0 -1. 1.0 0.0 0.0 0.0
860= 4.851                 DIARXR
870=21.927                XAREA
880=2.00               HEIGHT
890=1447.0              PBULK
900=0.325              EPISLON
910=0.3175        DIA       PARTICAL
920=0.370         LENP
930=593.0                TIN
940=2.0                   PIN
950=593.0                TIN
960=1.0000001         Z STEAM
970=0.0
980=167.249          EB
990=3.6280           STY
1000=1.6910           TOL
1010=0.00000001       BEN
1020=1520.0           H2O
1030=.000000001       H2
1040=.000000001       CH4
1050=.000000001       C2H4
1060=.000000001       CO2
1070=.000000001       CO
1080=12.443           XYL
1090=.000000001       CH2
1100=4.958            PARF
1110= TWO BED STUDY   VARY T INLET
1120= 0.0           2.00    0.0400
1130=    14 1000     6     1  REL    0.0001
1140=628.33               TIN
1150=2.0                   PIN
1160=628.33               TIN
1170=1.0000001        Z STEAM
1180=0.0                   STEAM INTO THE SECOND STAGE
1190= TWO BED STUDY   VARY T INLET
1200= 0.0           2.00    0.0400
1210=    14 1000     6     1  REL  .00001
1220=650.0            TIN
1230=2.0                  PIN
1240=650.0            TIN
1250=1.0000001        Z STEAM
1260=0.0                  STEAM INTO THE SECOND STAGE
```

```
1270= TWO BED STUDY   VARY T INLET
1280= 0.0          2.00    0.0400
1290=   14 1000    6    1  REL  .00001
1300=675.0              TIN
1310=2.0                   PIN
1320=675.0              TIN
1330=1.0000001          Z STEAM
1340=0.0                   STEAM INTO THE SECOND STAGE
1350= TWO BED STUDY   STEAM INJECTION
1360= 0.0          2.00    0.0400
1370=   14 1000    6    1  REL  .00001
1380=593.0                TIN
1390=2.0                   PIN
1400=593.0                TIN
1410=1.0000001          Z STEAM
1420=730.0                   STEAM
1430= TWO BED STUDY   STEAM INJECTION   VARY T INLET
1440= 0.0          2.00    0.0400
1450=   14 1000    6    1  REL    0.0001
1460=628.33               TIN
1470=2.0                    PIN
1480=628.33               TIN
1490=1.0000001          Z STEAM
1500=730.0                   STEAM
1510= TWO BED STUDY   STEAM INJECTION   VARY T INLET
1520= 0.0          2.00    0.0400
1530=   14 1000    6    1  REL  .00001
1540=650.0              TIN
1550=2.0                   PIN
1560=650.0              TIN
1570=1.0000001          Z STEAM
1580=730.0                   STEAM
1590= TWO BED STUDY   STEAM INJECTION   VARY T INLET
1600= 0.0          2.00    0.0400
1610=   14 1000    6    1  REL  .00001
1620=675.0              TIN
1630=2.0                   PIN
1640=675.0              TIN
1650=1.0000001          Z STEAM
1660=730.0                   STEAM
1670= TWO BED STUDY  STEAM TO OIL RATIO OF 13   VARY T INLET
1680= 0.0         -2.00    0.0400
1690=   14 1000    6    1  REL    0.0001
1700=593.0                TIN
1710=2.0                PIN
1720=593.0                TIN
1730=1.0000001          Z STEAM
1740=0.0              STEAM INTO SECOND STAGE
1750=167.249            EB
1760=3.6200             STY
1770=1.6910             TOL
1780=0.00000001         BEN
1790=2250.0             H2O
1800=.000000001         H2
1810=.000000001         CH4
1820=.000000001         C2H4
1830=.000000001         CO2
1840=.000000001         CO
1850=12.443             XYL
1860=.000000001         CH2
1870=4.958              PARF
```

```
1880= TWO BED STUDY  STEAM TO OIL RATIO OF 13   VARY T INLET
1890= 0.0          2.00    0.0400
1900=   14 1000    6    1  REL    0.0001
1910=628.33              TIN
1920=2.0                 PIN
1930=628.33              TIN
1940=1.0000001        Z STEAM
1950=0.0            STEAM INTO SECOND STAGE
1960= TWO BED STUDY  STEAM TO OIL RATIO OF 8  VARY T INLET
1970= 0.0          2.00    0.0400
1980=   14 1000    6    1  REL  .00001
1990=650.0            TIN
2000=2.0                PIN
2010=650.0            TIN
2020=1.0000001        Z STEAM
2030=0.0            STEAM INTO SECOND STAGE
2040= TWO BED STUDY  STEAM TO OIL RATIO OF 8  VARY T INLET
2050= 0.0          2.00    0.0400
2060=   14 1000    6    1  REL  .00001
2070=675.0            TIN
2080=2.0                PIN
2090=675.0            TIN
2100=1.0000001        Z STEAM
2110=0.0            STEAM INTO SECOND STAGE
2120=END OF RUNS
2130=-1.0
```

Vita

The author was born April 29, 1958, to William H. and Virginia B. Sheppard in Woodbury, NJ. He attended Lehigh University in Bethlehem, PA, for both his undergraduate and graduate work in Chemical Engineering. A Bachelor of Science degree was received on June 1, 1980, with Honors; and a Master of Science degree was received on June 6, 1982, as part of a Master's Degree Cooperative Education Program with U. S. Steel Research.