MODELLING AND DISCRIMINATION STUDIES IN A CATALYTIC FLUIDIZED BED REACTOR

by

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A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

March, 1974

DOCTOR OF PHILOSOPHY (CHEMICAL ENGINEERING)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Modelling and Discrimination Studies in a Catalytic Fluidized Bed Reactor

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NUMBER OF PAGES: xvii, 359

SCOPE AND CONTENTS: The object of this research program was to develop a strategy and methodology for modelling existing large-scale chemical reactors by coupling bench-scale studies with plant data.

By way of example, the hydrogenolysis of n-butane on a 10% nickel on silica gel catalyst was carried out in a pilot-scale fluidized bed reactor (8 in. in diameter by 3 ft. bed depth). Integral reaction data were obtained from a small fixed bed reactor, packed with the same catalyst. A kinetic model, based on adsorption-desorption and reaction of activated hydrocarbon species, was developed and the ten kinetic parameters in it were estimated from the packed bed data. Statistical methods for the design of experiments for parameter estimation and for model discrimination were employed. This chemical kinetic model was used with a number of available two-phase mechanistic models to describe the fluid mechanical behaviour in fluidized beds. A catalyst activity and an interchange factor, which provides a prediction of the interchange of gas between the bubble and the emulsion phase in a fluidized bed were estimated from the plant data. Statistical methods were used to plan the experiments to allow a combination of maximum discrimination among models and a test of the

models over the full range of possible operating conditions. A model discrimination criterion which takes into account the effect of errors in parameter estimates is developed and applied to determine the best model for this system at two fluidized bed heights.

Fluidized bed models are evaluated in the light of this experience. Some of the problems associated with obtaining estimates of parameters in one experimental system and applying them in another are delineated. General guidelines are indicated for modelling large industrial-scale reactors.

ACKNOWLEDGEMENTS

The author wishes to thank all who contributed to this work. He is particularly indebted to:

His research director, Dr. T.W. Hoffman for his constructive suggestions and timely encouragement.

Dr. P.M. Reilly for his help and advice with statistics.

Mr. A. Orlickas for his work on the initial kinetic modelling.

Mr. R. Dunn and Mr. J. Newton for their help in the construction of the apparatus.

The Ontario Government and McMaster University for providing financial assistance in the form of Studentships.

The National Research Council and the Chevron Corporation for financial support of this research.

His wife Marilyn for her help and understanding.

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NOMENCLATURE

a	proportionality constant (equation 2.10)
A	cross sectional area of reactor ($cm.^2$)
A_i	area under chromatogram for component i
$\underline{A}$	variance-covariance matrix of $\underline{y}$ the observed responses from all trials
c	concentration of reacting component ($moles/cm.^3$)
c_o	initial concentration of reacting component ($moles/cm.^3$)
c_p	heat capacity ($cal./gm.\ ^oC.$)
C_i	concentration of component i ($gm.\ moles/cm.^3$)
D	diffusion coefficient ($cm.^2/sec.$)
d_p	diameter of particle (cm.)
$\bar{d}_p$	mean diameter of particle (cm.)
d_b	effective bubble diameter (cm.)
d_c	diameter of cloud region (cm.)
d_o	initial bubble diameter (cm.)
$E_e(t)$	contact time distribution
E	expectation operator
E_{DA}	eddy diffusivity ($cm.^2/sec.$)
F	fraction of C_4^* that cracks to C_3^* and C_1^*
F	flowrate ($cm.^3/sec.$)
$\underline{f}$	functional model
f	probability density function
f	number of hydrogen molecules retained by abosrbed butane species
$f_1 f_2$	prior and posterior density functions respectively for $\underline{\theta}$ (equation 3.18)

F	bubble emulsion interchange factor ($cm.^3/cm.^3 sec.$)
g	acceleration of gravity
G	superficial mass velocity ($gm./sec.\ cm.^2$)
h	height above distributor plate (cm.)
h	heat transfer coefficient ($cal./sec.\ cm.^2\ ^oC.$)
$\underline{I}$	identity matrix
j_D, j_H	Chilton-Colburn j factors for mass and heat transfer
k	thermal conductivity ($cal./sec.-cm.-^oC.$)
k	proportionality constant
k	Arrhenius rate constant
k_B	frequency factor for butane (moles/sec. vol. reactor atm.$^{-(m+n)}$
K	rate constant for reaction on the catalyst surface
K_{P1}	pre-exponential factor in propane rate expression in (moles/sec. vol. reactor atm.$^{-(m'+n')}$
K	bubble-to-emulsion interchange ($cm.^3/cm.^3$-sec.)
K_{p2}	pre-exponential factor in propane rate expression (dimensionless)
K_E	ratio of rates of reaction on the surface of the catalyst to rate of desorption for ethane (dimensionless)
k_E	pre-exponential factor in ethane rate expression (dimensionless)
K_{E2}	pre-exponential factor in ethane rate expression (moles/sec. vol. reactor atm.$^{-(m''+n'')}$
k_v	pseudo-first order rate constant for cracking of butane based on gross volume of catalyst particle (moles/sec. vol.)
k_G	mass transfer coefficient ($moles/sec.\ cm.^2$)
k/k_o	catalyst activity (dimensionless)
K_{CE}	interchange coefficient between cloud and emulsion
k_g	mass transfer coefficient ($gm.\ moles/sec.\ cm.^2\ atm.$)
L	characteristic length for Thiele modulus (cm.)

L	likelihood function
L	length or height of reactor bed (cm.)
L_{mf}	bed height at minimum fluidization (cm.)
m	number of models
m, m', m''	exponent on butane, propane and ethane partial pressure respectively
M	denotes model
n, n', n''	exponent of hydrogen partial pressure in butante, propane and ethane rate expression respectively
n_o	hole density on distributor grid ($cm.^{-2}$)
n	number of experimental runs
N	mass flux (gm. moles/sec. $cm.^2$)
N	number of bubbles per unit volume ($1/cm.^3$)
N	total number of observations ($n\ r$)
$P_{H.C.}$	partial pressure of hydrocarbon (atm.)
P_{H_2}	partial pressure of hydrogen (atm.)
P_i	partial pressure of component i (atm.)
$P(i,n-1)$	posterior probability of model i after n-1 experimental trials
p	number of parameters
$P(\underline{y})$	probability distribution function for $\underline{y}$
P	pressure (atm.)
Pr	Prandtl number ($C_p \mu/k$)
q	volumetric flowrate through bubble ($cm.^3/sec.$)
Q	heat flux (cal./sec. - $cm.^2$)
Q	q plus diffusive flow ($cm.^3/sec.$)
Q_E	cloud gas transfer per volume of cloud space in Partridge and Rowe model ($cm.^3/cm.^3$ - sec.)

r_i	rate of disapperance of component i (gm. moles/sec. - volume of packed bed)
r	number of responses per experimental trial
r_b	bubble radius (cm.)
R	universal gas law constant (atm. $cm.^3$/gm. moles $^oK.$)
Re	Reynolds number ($G\ d_p/\mu$)
S_i	selectivity of component i (moles of component i produced/moles of butane reacted)
S	cross sectional area of bubble phase ($cm.^2$)
$S(\underline{\theta})$	weighted sum of squares objective function
Sh	Sherwood number for transfer from a sphere of uniform surface composition
Sc	Schmidt number ($\mu/\rho D$)
t	time (sec.)
T	reacting temperature ($^oK.$)
$\underline{U}$	covariance matrix of the estimated parameters
U	superficial gas velocity (cm./sec.)
$U_{m.f.}$	minimum fluidization velocity (cm./sec.)
U_{br}	bubble rise velocity (cm./sec.)
$\bar{u}$	average superficial gas velocity (cm./sec.)
V_c	cloud overlap volume ($cm.^3$)
$\underline{V}$	variance-covariance matrix
V	volumetric flow through packed bed reactor ($cm.^3$/sec.)
V_b	bubble volume ($cm.^3$)
$\underline{v}$	matrix (equation 3.13)
$\underline{w}$	vector of observed minus predicted responses for all trials
$\underline{w}_u$	vector of observed minus predicted responses for u'th trial
x_i	mole fraction of component i
x	distance along packed bed reactor (cm.)

x	conversion
X	fluidized bed model interchange parameter
$\underline{X}$	matrix of partial derivatives of the responses with respect to the parameters for all trials
$\underline{X}_u$	matrix of partial derivatives of the responses with respect to the parameters for the u'th trial
$\underline{Y}$	vector of observations for all trials
$\underline{Y}_u$	vector of observations for the u'th trial
y	distance up a reactor (cm.)
$\bar{\underline{Y}}$	mean value of $\underline{Y}$
z	distance along a reactor (cm.)
$Z(\underline{\xi})$	Roth criterion objective function
$Z'(\underline{\xi})$	modified Roth criterion objective function

GREEK LETTERS

α	k^a/k^d (equation 2.6)
β	$P_{C_4}/(P_{H_2})^{[(10-f)/2]}$ (equation 2.7)
ΔE	activation energy (cal/gm. mole)
ΔH^o_{25}	standard heat of reaction (cal./gm. mole of butane reacted)
ΔP	partial pressure driving force for mass transfer to and from surface of catalyst particle (atm.)
ΔT	temperature driving force for heat transfer to and from surface of catalyst particle ($^oC.$)
ΔT_{max}	widest axial temperature observed in packed bed reactor ($^oC.$)
Δx	distance in control variable space
ΔY	discrimination provided by the i'th vector of control variables
$\underline{\epsilon}$	vector of errors for all trials
$\underline{\epsilon}_u$	vector of errors in $\underline{Y}_u$ for u'th experiment

$\epsilon_{m.f.}$	voidage of dense phase at incipient fluidization
η	effectiveness factor
$\underline{\eta}$	vector of predicted responses for all trials
$\underline{\eta}_u$	vector of predicted responses for the u'th trial
θ	fraction of catalyst surface covered by adsorbed species
θ^*	the interchange parameter equation 5.2 in the fluidized bed models
$\underline{\theta}$	vector of parameters
$\underline{\hat{\theta}}$	best estimate of $\underline{\theta}$
μ	gas viscosity (gm./cm. - sec.)
$\underline{\xi}_u$	vector of control variables for u'th experiment
ρ	density (gm./cm.^{3})
$\underline{\Sigma}$	variance-covariance matrix for the vector of respones for one experimental trial
$\underline{\tilde{\Sigma}}$	estimate of $\underline{\Sigma}$
ϕ	Thiele modulus

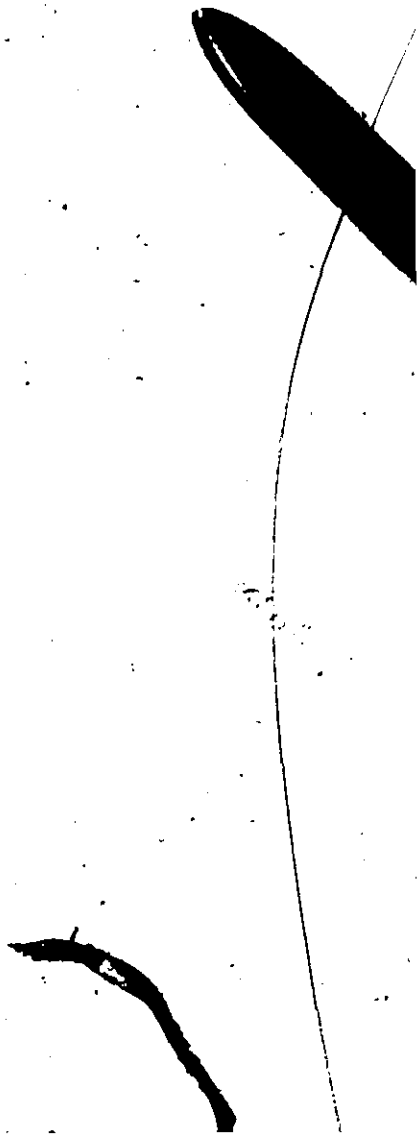
SUBSCRIPTS

H.C.	hydrocarbon
C_1	methane
C_2	ethane
C_3	propane
C_4	n-butane
H_2	hydrogen
b	bubble
e	emulsion
i, j	denotes particular response or component
m.f.	at minimum fluidiation
o	feed
p	particle

u	the u'th experimental trial

SUPERSCRIPTS

a	adsorption
d	desorption
r	reaction
T	transpose of a matrix
^	best estimate



1.0 DEVELOPING A REACTOR MODEL

Computer simulation of equipment and groups of equipment is now an established technique used in the chemical industry to aid in design, to identify bottlenecks in future expansions and to solve problems in optimization and control. Rather extensive experience with chemical process simulation (C7) has demonstrated that the reactor is often the most important and the most difficult to describe. Just as the model can be employed to improve the efficiency and to optimize the process, the engineer must improve his efficiency and optimize the use of his resources in the process of developing such a model.

The reactor model must be formulated so as to answer the specific questions posed for the study. Some degree of accuracy and precision is implied either formally or otherwise, Which, of a number of possible models, is the best must be determined and the necessary parameters estimated. The use of experimental design techniques and the assessment of errors in both the experimental measurements and the model predictions are essential. If all these considerations are not observed, the result will be a hopelessly inadequate model or, at the other extreme, a model that was too costly to develop and/or too costly to use.

The basic premise adopted at the outset is that deterministic or mechanistic models are to be preferred, as opposed to those based on empirical regressions of plant output-versus-input data. It is only in this way that a better understanding of the underlying basic phenomena can be obtained. This understanding will be essential if engineers are ever going to formulate meaningful design scale-up criteria.

In order to predict successfully the conversion and selectivity data over a wide range of operating conditions, a mathematical description is required of the fluid mechanics of the reactants and products within the reactor and the kinetics of the main chemical reactions. Since in many cases, the reactor model will be used within a larger simulation of the process or, at least, in some optimization program, these mathematical descriptions must not be so sophisticated that large expenditures of computer time are required.

In obtaining these mathematical models, the following procedures could be adopted:

(i) Evaluate the kinetic parameters in the mechanistic model for the main reactions in a bench-scale reactor, where the fluid mechanics of the reactants/products is relatively well-known. Then, a reactor fluid mechanical model is formulated in which some of the flow parameters may be estimated reasonably well a priori and other unknown parameters may be estimated from plant operating data. That is unknown parameters within the model are adjusted to make the model predict the measured conversion and selectivity data.

(ii) Evaluate the kinetic parameters as in (i) and determine the flow parameters in the fluid mechanical model by separate tracer analysis tests in the plant reactor, - again adjusting the parameters to give the measured response.

(iii) Determine the fluid mechanics as in (ii) and use the plant operating data to provide the kinetic parameters.

The actual choice depends to some extent, upon the ease with which the plant data can be obtained but, in general, should be determined in the light of which mechanism (the reaction or the fluid mechanics) is rate-controlling. Only the parameters in the rate-determining mechanism can be estimated precisely (H16).

The first approach is adopted here, since both the fluid mechanics and the reaction rate are important in determining the reactor performance. It is important to note the magnitude of the modelling problem when this scheme is adopted. Considerable resources will be required to develop the necessary experimental and analytical techniques for the bench-scale experiments and to generate sufficient data to build an adequate kinetic model. There will be uncertainty about the fluid mechanical behaviour in the reactor and perhaps incomplete knowledge of all other chemical reactions taking place. Furthermore, the plant data will, by its very nature, be less precise than that obtained from well controlled experiments. It therefore becomes imperative that the experimental program and the plant tests be well designed and the data be critically analyzed based on established statistical concepts.

This means that, after the various reasonable models have been formulated, parameters will have to be estimated and the best of the available models determined. Experimental design techniques should be employed so as to obtain the maximum of information from a minimum of experiments. Parameters should be estimated in a region where they are controlling and models should be discriminated among in a region where their responses are the most different. Both these procedures are accomplished by either fitting or comparing the experimentally

observed responses to the predicted responses of the model. In comparing these two quantities it must be realized that there are errors in both:

1) the measured response due toexperimental error

2) the predicted response due to imprecise knowledge of parameters estimated previously and inadequacies in the model.

The visualization of these error structures and their resulting effects is almost impossible when working with non-linear models and/or experimental systems with multiple response data (more than one measured response per experimental trial).

1.1 Objectives of the Present Study

Experience and proficiency in the development of reactor models has been shown to be expensive to obtain: in the cost of highly technical personnel, the experiments that must be performed and in computer time. It therefore becomes imperative that the effectiveness and the efficiency of these procedures must be improved by providing general and specific guidelines in the practice of modelling, just as these guidelines have been developed for design procedures over the past fifty years. Hence one of the main objectives of this investigation is to develop and test a methodology for obtaining models for existing chemical reactors and to indicate the relative importance of the various steps. The methodology should be based on understanding the basic underlying mechanisms of the phenomena occurring since this procedure should provide information relating to the scale-up problem in design.

A pilot-scale fluidized bed reactor, in which the catalytic hydrogenolysis

reaction of n-butane will be carried out, is chosen as a particular example of a reactor with a relatively complex series-parallel reaction scheme and complicated fluid mechanics. This system should provide a good test of any recommended methodology for reactor modelling.

The particular objective is to model this reactor system employing the methodology suggested in Section 1.0. This will involve determining chemical kinetic parameters in an appropriate model from the bench-scale reactor and fluid mechanic parameters in a reactor model from the fluidized bed data. An attempt will be made to obtain as much basic information as is deemed appropriate on these aspects from the data from these reactor systems. The data analysis will rely heavily on established statistical concepts.

2.0 THEORY AND REVIEW OF REACTION AND REACTOR MODELS

The engineer or scientist develops a model to answer questions. The statement and definition of the questions to be answered are of extreme importance although they are often lost and forgotten when the search for a model is begun. The questions to be answered dictate the level of sophistication required: too low and the questions cannot be answered, too high and the cost is too great.

There are two important rules that can be stated about model development that have been learned from experience. The first is to start simple. The second is, if possible, to separate and to measure independently as many as possible of the effects or phenomena that make up the model being developed.

This chapter of the thesis outlines the background information available for the models to be developed for this study. The final formulation of the models is presented in chapters four and five. There the exact models employed to answer the questions, as posed in the first chapter of the thesis, are presented.

A model must be good. It should be simple and it must fit. The first criterion "simple" implies cost, the second criterion "fit" implies accuracy. These two criteria are highly correlated and generally a more complex and costly model will fit better. The cost criterion, or rather the maximum allowable expenditure for a project is often specified (rigidly or otherwise) externally to the engineer. Many models are usually a-

vailable to describe the phenomena to be studied. The criterion of "fit" implies that the model must predict performance to some degree of accuracy or must fit data which were used to obtain it to some degree of accuracy.

The statistical techniques used to evaluate the goodness of fit are fully discussed in the third chapter of this thesis. However, a brief presentation must be included in the introduction to this chapter since modelling should not be discussed without some knowledge of the techniques used to describe fit. The standard measure of fit is the sum of squares of the deviations of the prediction of the models from the observed results. The mean squared deviation should not be too much greater than some value representing the experimental error plus the results of known errors in other parameters in the model. A second and equally important criterion is the complete randomness of residuals (observed values minus predicted values.) These should not be correlated with themselves (autocorrelation) or with any of the control variables (crosscorrelation.)

The use of a model in one physical system after its parameters have been evaluated in another physical system presents another problem in the analysis of errors. Often it is not just the precision to which the parameters and the model were initially estimated that is the real criterion of fit. The transformation of a model from one system to another requires that the experimenter consider how the lack of fit from the first system will affect the precision of the predictions made in the second system. If the ultimate goal of a project is the prediction of responses in the second system, then it is how the lack of fit in the first

model or the tolerances on the parameters actually get translated into the second system that is important. This will also be discussed in Chapter 3.

The formulation of mechanistic models and the determination of parameters, defined as estimated or adjustable, is an established technique in chemical engineering. An abundance of models incorporating various effects are available to the engineer. The easy access to high speed computers with large storage facilities has greatly increased the number of models that can be economically used to describe an event or process. Almost all models describing an event in a macro sense are approximate at best. They cannot be said to be "the truth" and even the most complex model incorporating a multitude of effects and phenomena will not stand up under very close scrutiny. The question is: "What effects to include?" Perhaps the only explanation is enough physically reasonable effects to provide answers to the questions that have been posed. The measures of model fit, in a statistical sense, have only been briefly presented here, but are fully discussed in Chapter 3. Experience is perhaps the best guide in the formulation of a model (mechanistic or otherwise).

"Start Simple" is the single best guideline for model formulation. A great deal of time and money has often been spent to describe effects which do not significantly contribute to the predicting performance of the model for the situation being studied. Some start has to be made with a model and with data. During this initial step, the engineer becomes familiar with both some model of the system and the system itself.

There are very many effects or phenomena which could be included in a computation scheme. Only those needed to answer the questions that have been asked should be included. If a particular response of the system affecting those answers is significantly sensitive to an effect, the effect should be incorporated in the model. For example if there is an experimentally observed pressure gradient evaluate a simple constant pressure model using both the inlet and then the outlet pressure. If no significant difference results in the predicted values, there is no need to incorporate a pressure gradient in the model. This check can be easily made without the expense of initially including the pressure gradient in the computation scheme. Use of either a large number of adjustable parameters or unrealistic physical parameters should be avoided.

As stated in the first chapter, an actual fluidized bed reactor is to be modelled by estimating a parameter which reflects the gas flow patterns within the reactor. In order to accomplish this, the kinetics of the reaction must also be modelled and the kinetic parameters estimated. The procedure followed is to estimate separately the kinetic parameters in a packed bed reactor where the flow of gas can be accurately described. Background information and a literature survey of kinetic, packed bed and fluidized bed models are presented in sections 2.1, 2.2 and 2.3 respectively.

2.1 HYDROGENOLYSIS OF N-BUTANE

The hydrogenolysis of paraffinic hydrocarbons in excess hydrogen over a metal catalyst produces lower molecular weight paraffins. The product of complete hydrogenolysis in excess hydrogen is methane.

Hydrogenolysis of small paraffinic hydrocarbons is generally well understood. The catalysis literature includes many studies of various hydrocarbons over a large number of metals on an assortment of supports covering a varying range of conversion. However, specific rate constants, activation energies and reaction orders for a particular hydrocarbon over the desired catalyst and support are usually not available with any degree of accuracy. Also, many studies only present limited conversion and selectivity data. Conclusions concerning the catalyst stability and activity vary widly among the various studies.

The only published work for n-butane over a nickel catalyst was carried out by Anderson and Baker (A1) and was done at low pressures. A summary of the studies reported to date for n-butane, propane and ethane are shown in Table 2.1. Very little specific information concerning the hydrogenolysis of n-butane over 10.% nickel on silica gel can be obtained from these results.

Taylor, Sinfelt and Yates (T2) investigated the ethane hydrogenolysis reaction at low conversions. A recent study by Kikucki and Morita (K6) with n-pentane over 8.% nickel on silica gel reported selectivities but activation energies were not evaluated. Some generalities can be obtained from the published data summarized in Table 2.1. The rate of hydrogenolysis is inversely dependent on the partial pressure of hydrogen. There is an

TABLE 2.1 HYDROGENOLYSIS OF PARAFINNIC HYDROCARBONS OVER NICKEL CATALYST

	AUTHORS	TYPE OF CATALYST	°C.	$P_{H.C.}^{m}$ m =	$P_{H_2}^{n}$ n =	-ΔE kcal.	H_2/H.C. RATIO	PRESS.	CONVERSION
ETHANE	Anderson et al. (A1) (1963)	Ni. Film	254 - 273			58	12	50 Torr.	<10.%
	Taylor et al. (T2) (1965)	Ni. on Silica Gel 1.%	287	.8	-1.1	28.7			
		Ni. on Silica Gel 5.%	218	.6	-1.8	38.2	3 - 10	Atm.	<1.%
		Ni. on Silica Gel 10.%	177	1.0	-2.2	40.6			
	Yates et al. (Y1) (1964)	10.% Ni. on Kieselguhr	187 - 227	1.0	-2.0	40	3 - 10	Atm.	<.5%
	Morikawa et al (M1) (1963)	15.% Ni. on Kieselguhr	172 - 184		-2.5	43	5 - 1.1	1 Atm.	Up to 100.%
	Kemball et al. (K5) (1948)	15.% Ni. on Kieselguhr	182	0.7	-1.2	52	>1		
						40	<1		
	Tajbl (T3) (1969)	58.% Ni. on Kieselguhr	182	0.7	-1.2	46.4	1.1 - 15		1. - 27.%
PROPANE	Shepard (S3) (1969)	Co-ppt. 75% Ni. on Alumina	200 - 350	1.0	-2.0	50	7		≤1.%
	Anderson et al. (A1) (1963)	Ni. Film	217 - 267			31	12	50 Torr.	<10.%
	Morikawa et al. (M2) (1937)	15.% Ni. on Kieselguhr	138 - 172	.92	-2.6	34			
n-BUTANE	Anderson et al. (A1) (1963)	Ni. Film	184 - 209			34		50 Torr.	

approximate proportionality between the rate of reaction and the partial pressure of the hydrocarbon. The activation energy is very high. The specific activity of the catalyst depends on the method of preparation and the temperature of reduction. Nickel catalysts are strongly specific to the fracture of the terminal carbon-carbon bond.

The magnitude of the activation energy seems to depend on the state of dispersion of the nickel on the catalyst support. Taylor, Sinfelt and Yates (T2) increased the nickel surface area from 0.7 to 13.6 $m.^2/gm.$ by increasing the weight percent nickel from 1.% to 10.%. The activation energy for ethane hydrogenolysis increased from -28.7 to -40.0 kcal./gm. mole. Shepard (S3), however, did not observe such an increase in activation energy although he was able to increase the surface area from 5. to 56. $m^2/gm.$ This was done by varying the reduction temperature of the co-precipitated nickel and alumina catalyst from 340. to 1160°C.

The activity of the catalyst has been defined as the number of molecules or moles reacting per catalyst site per unit of time. The activity with reference to a standard activity is, therefore, the ratio of rate constants under similar reacting conditions. The specific activity is usually taken with respect to the surface area of active metal catalyst exposed to the reacting species. Schuit and Van Reifen (S4) performed various investigations of nickel on silica catalysts. They report that the percentage reduction is a function of the reducing temperature for various concentrations of nickel. At very high temperatures sintering can also occur. Shepard (S3) found that for most catalysts the activity varied directly with the metal surface area as measured by hydrogen chemisorption. He could not detect any trend in activity with crystal size. Sinfelt, however, (S5) varied the

crystal size from 29 to 88 Angstroms by varying the pre-treatment temperature from 370°C to 700°C. He did observe a decrease in the specific activity of his nickel catalyst from 1070. to 56. for the hydrogenolysis of ethane. Yates (Y2) studying ethane over a rhodium catalyst, found a maximum catalyst activity with smaller crystallite size.

RATE EXPRESSIONS

There are two approaches commonly used to formulate the mathematical expressions to describe the rate of reaction for the hydrogenolysis of short chain paraffinic hydrocarbons. The first, as proposed by Hougen and Watson (H1) involves the description of all the possible reaction, desorption and adsorption rate expressions. The whole matrix of equations is combined to give the overall rate expression. The matrix of rate expressions for the hydrogenolysis of n-butane which includes some 30 parameters can be found in reference 02. This is a very large number of parameters to be estimated. A second approach as suggested by Cimino, Boudart and Taylor (C2) assumes an equilibrium between the gaseous and adsorbed hydrocarbon, and that the reaction of the adsorbed hydrocarbon is the rate determining step. It is this analysis that is used in the present study and leads to the general relationship:

$$r_{H.C.} = k_{H.C.} \exp\left(\frac{-\Delta E_{H.C.}}{RT}\right) P_{H.C.}^{m} P_{H_2}^{n} \qquad 2.1$$

where $r_{H.C.}$ is the rate of disappearance of the hydrocarbon

$k_{H.C.}$ is the frequency factor

$\Delta E_{H.C.}$ is the activation energy

m and n are constants

$P_{H.C}$ and P_{H_2} are the partial pressures of the hydrocarbon and hydrogen

respectively.

The derivation of this rate expression for the hydrogenolysis of n-butane (02) is presented here to indicate the assumptions that are made.

n-Butane, upon or after adsorption loses hydrogen atoms according to the process:

$$C_4H_{10} \rightleftharpoons (C_4H_f)^a + \left(\frac{10-f}{2}\right) H_2 \qquad 2.2$$

It is assumed that the adsorbed hydrocarbon reacts with gaseous hydrogen in the reaction step according to the process:

$$(C_4H_f)^a + H_2 \rightarrow \text{Methane, ethane and propane adsorbed species} \qquad 2.3$$

The process represented by equation 2.2 is assumed to be in equilibrium. Equating the rates of adsorption and desorption:

$$k'^a P_{C_4} (1-\theta) = k'^d P_{H_2}^{\frac{(10-f)}{2}} \theta \qquad 2.4$$

where k'^a = rate constant for adsorption

$= k^a \exp(-\Delta E^a/RT)$

k'^d = rate constant for desorption

$= k^d \exp(-\Delta E^d/RT)$

$\Delta E^a, \Delta E^d$ = activation energies for adsorption and desorption respectively

θ = fraction of surface covered with adsorbed butane species

P_{C_4}, P_{H_2} = partial pressures of n-butane and hydrogen respectively

Solving for θ in equation 2.4:

$$\theta = \frac{\alpha\beta}{1+\alpha\beta} \qquad 2.5$$

where $\alpha = k^a/k^d$ 2.6

$$\beta = P_{C_4}/P_{H_2}^{[(10-f)/2]} \quad 2.7$$

over a restricted range of pressures:

$$\theta \propto \alpha^x \beta^x \quad 2.8$$

where $0 < x < 1$

The proportionality is used in 2.8 because, although the expression:

$$\theta = \alpha^x \beta^x \quad 2.9$$

for an appropriate value of x, predicts the same trends as 2.5, over a restricted pressure range the values of θ will not be predicted the same. The proportionality factor is included to compensate for this:

Thus

$$\theta = a\, \alpha^x\, \beta^x \quad 2.10$$

where a is a function of x.

This proportionality is not clearly stated in either the original paper by Taylor et al. (C2) or in a later development by Bond (B2).

Assuming that the rate of hydrogenolysis of n-butane is the slow step, and that the adsorbed butane molecules react with the gaseous hydrogen molecules, the rate of reaction of n-butane may be described by:

$$r \propto \theta\, P_{H_2}^{-n} \quad 2.11$$

Expanding

$$r \propto a\, \alpha^x\, P_{C_4}^x\, P_{H_2}^{1-x(10-f)/2} \quad 2.12$$

Therefore

$$r = K\, a\, \alpha^{x}\, P_{C_4}^{x}\, P_{H_2}^{n} \qquad 2.13$$

where K = rate constant for reaction on the surface of the catalyst

$= k^{r} \exp(-\Delta E^{r}/RT)$

ΔE^{r} = activation energy for reaction in the surface

$n = 1-x\,[(10-f)/2]$

Thus equation 2.13 may be written simply substituting k^{r} for $k a^{x}$ as:

$$r = K^{r}\, P_{C_4}^{x}\, P_{H_2}^{n} \qquad 2.14$$

This simplified rate expression, known as the power rate law, is used in this study to describe the hydrogenolysis of n-butane. The expansion of this rate expression to include the entire network of possible reactions for this specific case is presented in Chapter 4 of this thesis. This section will also include the exact definition of the parameters that must be estimated to completely describe the reaction network.

2.2 PACKED BED REACTORS

The physics of packed bed reactors is well understood and has been extensively studied. This type of integral reactor is commonly used both in industry for the production of chemicals and in research for the estimation of kinetic parameters. It is the latter case, where the flow profile can be accurately described, that is of interest in this study. The only problem facing the experimenter is that of reducing the mass and energy equations describing the reactor and reaction to the simplest form and still retain the desired accuracy.

Two extensive review papers, one by Froment (F1) (81 references), and the second by Hlavacek (H2) (146 references) provide an excellent coverage of the topic. These two papers present the mass and energy equations for the one-dimensional case with and without axial mixing and for the two-dimensional model which also includes radial temperature and concentration profiles. A discussion of the methods of numerical solution and the use of packed beds for kinetic parameter estimation is also presented. Another very good review article is given by Beek (B3).

If the effects of axial mixing are small, and radial concentration and temperature gradients can be neglected, a simple one-dimensional model may be sufficient to describe the reactor. Both Carberry (C1) and Satterfield and Sherwood (S2) discuss the importance of mass and heat transfer rates in and around the catalyst particles on the controlling step in the reaction. Satterfield and Sherwood present j_d and j_h curves in order to calculate the effect of mass and heat transfer limitations. Peterson (P2) gives a summary

of the effects and importance of axial mixing in packed bed reactors. The one dimensional model with no axial mixing is used in this study. The exact equations including the kinetic model are given in Chapter 4 of the thesis. The calculation of particle diffusion and mass transfer limitations and the importance of radial terms and axial mixing are given in Appendix E.

2.3 FLUIDIZED BED REACTORS

Fluidization, as stated by Kunii and Levenspiel (L1) is the operation by which fine solids are transformed into a liquid-like state through contact with a gas or liquid. This method of contact has some unusual properties, some of which are very advantageous and others which present considerable problems in their application to reaction engineering. The fluid-like property of the solid particles facilitates the circulation of the solids between reactors, the transfer of large quantities of heat with immersed heat exchanger tubes and the application of continuous automatic control. The solids bed is close to isothermal, and the heat and mass transfer rate between gas and particles are high when compared to other methods of contacting. On the negative side, the residence time of solids is very non-uniform, extensive by-passing of gas may occur, and the attrition of friable solids and the erosion of pipes and vessels is a problem. Experience has shown that these reactors are difficult to model.

Historically, the first commercial reactor was patented by Fritz Winkler in 1922 for the gasification of powdered coal. The Second World War marked the beginning of large scale interest in these reactors for the production of high octane gasoline from kerosene and light oil. A number of books are now available describing the phenomena of fluidization

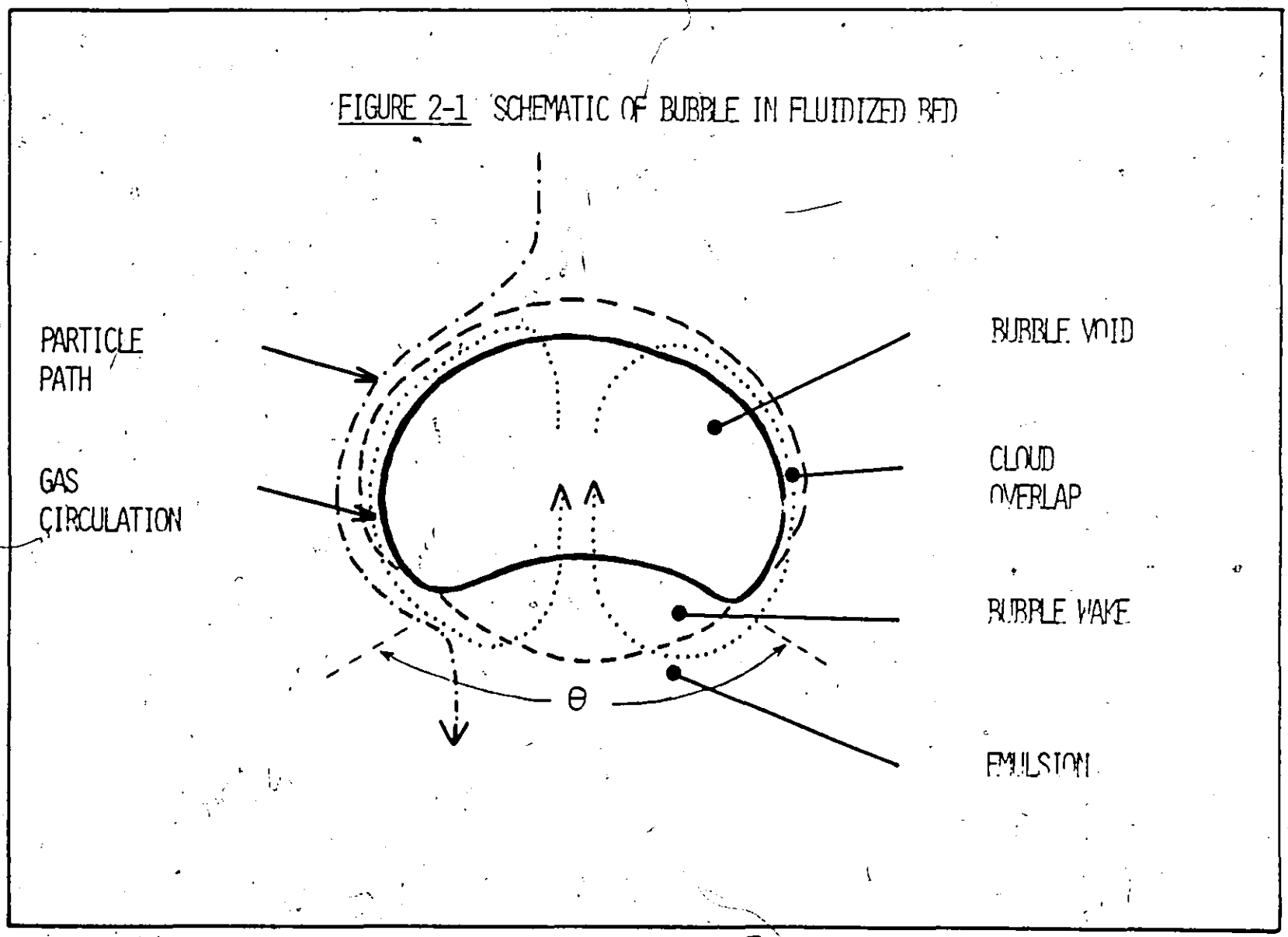
and its use in chemical reactors (D1)(L1)(O3)(Z1)(D3).

Because of the present intense interest in fluidized bed reactors, and with the availability of modern high-speed computers, many mechanistic models have been developed to describe the behaviour of fluids and solid particles and hence the conversion and product distribution for a given chemical reactor. All these models and their various assumptions and adjustable parameters are variations of the basic two-phase bubble model. Before this model is discussed, a more detailed description of the flow of reactant feed gas within the reactor will be presented.

In a fluidized bed reactor the gaseous reactants are fed into the bottom of a bed of fine catalyst or catalyst-impregnated particles. Under good fluidization conditions, most of the gas moves up the bed as bubbles which form at the bottom. As the bubbles proceed upwards they grow in size, coalesce, break-up and coalesce. The remainder of the feed gas flows in the emulsion or particulate phase to keep the particles suspended in a fluidized state. Since the reaction may only occur on the catalyst, the problem is to describe the interchange between the gas in the emulsion and the gas which forms the bubbles. The existence of two distinct regions, an emulsion or dense phase, and a bubble or up-flow phase, suggests that the reactor may be described by a two-phase model.

Considerable effort has been expended on studying single bubbles rising in an infinite medium of catalyst under incipiently fluidized conditions (D1)(J1)(M3). These studies suggest that there are three regions associated with the bubble or up-flow phase as shown in Figure 2.1 (L1). First, there is the bubble void containing almost no catalyst. The gas within the bubble circulates; this circulating flow includes the other

FIGURE 2-1 SCHEMATIC OF BUBBLE IN FLUIDIZED BED



two regions: (i) the wake which is filled with catalyst, and amounts to about one third the size of the bubble void; (ii) the bubble cloud, which is a region of emulsion phase (perhaps with slightly greater voidage (L3) surrounding the bubble void, which contains the circulating gas flowing from the bubble void and which travels upward with the void. The cloud region decreases in size as the bubble size increases (P3). As the bubble moves up the bed the bubble diameter grows, the bubble rise velocity increases, and as a consequence the relative amount of cloud gas decreases. In large reactor systems where the bubbles may be quite large, the cloud phase is a very small fraction of the bubble volume.

Since reaction occurs only by contact of gas with the catalyst, the transfer of reactant from the gas bubbles to the emulsion phase is important in fluidized bed reactors. This transfer has been shown to occur by the following mechanism for a single bubble (K1) (Figure 2.2): molecular diffusion and bulk flow transfer occur between the bubble and the gas surrounding the bubble followed by transfer by molecular diffusion between the cloud and the emulsion. Some models have assumed infinite transfer rate between cloud and the emulsion (D1) while others have assumed infinite transfer between the bubble and the cloud (that is uniform concentration in cloud and bubble) (P4). All these models assume that the bubbles remain discrete entities throughout their rise through the bed. It is well known that coalescence, bubble break-up, wake shedding and gas by-passing from bubble to bubble occur; these phenomena will contribute to the exchange process and should be included in many more sophisticated models. Van Deemter (V2) includes an axial diffusion term which in a general way would take some

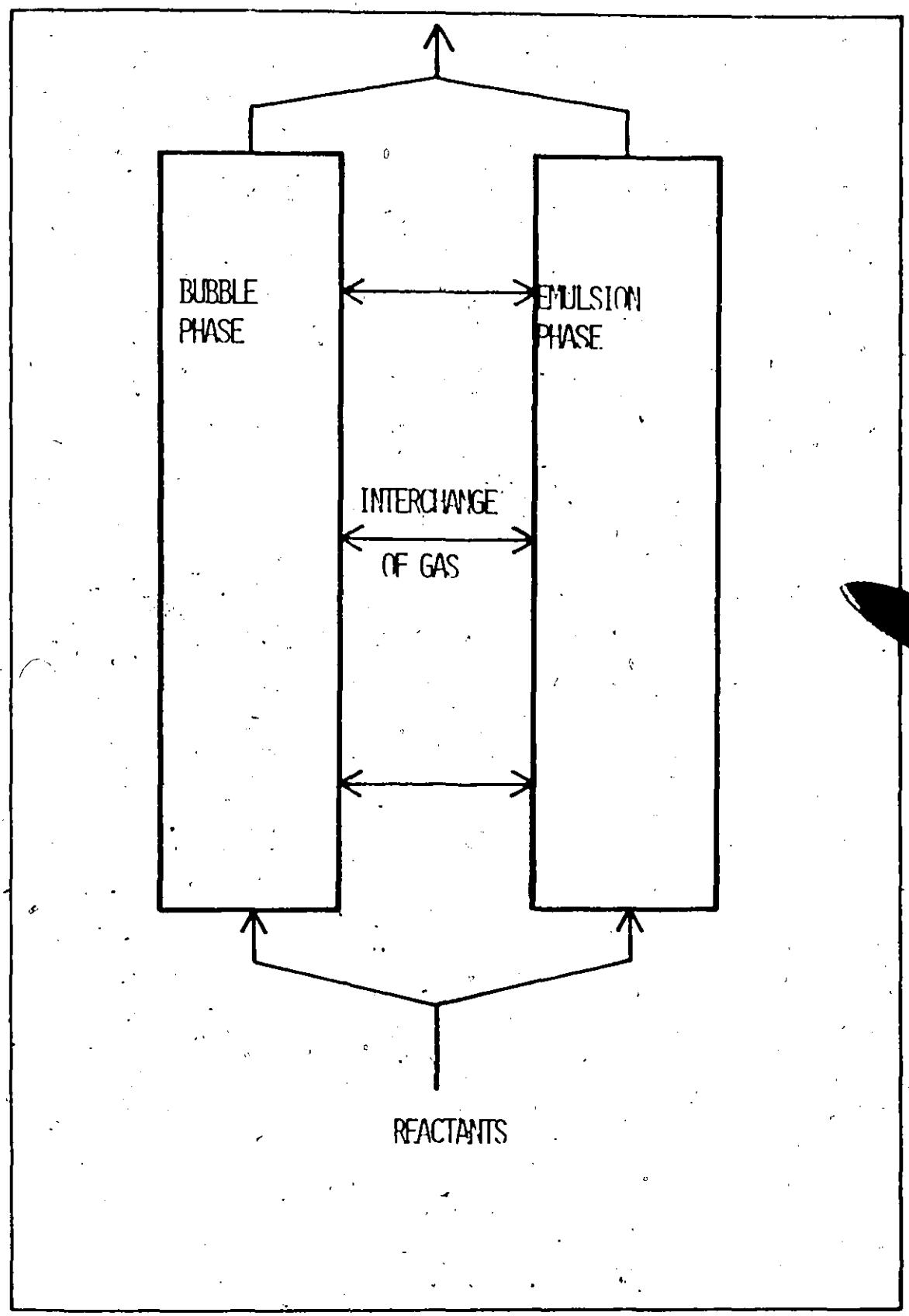


FIGURE 2.2 TWO PHASE MODEL FOR FLUIDIZED BED REACTOR

of these effects into account.

The general form of the two-phase model for steady state can now be formulated. At any height in the reactor assuming radial uniformity of concentrations within each phase, the following equation is written to describe each of the two phases as shown in Figure 2.2:

net axial diffusion	+	net axial bulk flow	+	net interchange between phases	+	net reaction	=	0

Many two-phase models have been proposed. They can be characterized by three considerations:

(i) the make-up of the bubble phase

(ii) the flow pattern in the emulsion phase

(iii) the mode of interchange between the two

In all cases, the bubble is assumed to be perfectly mixed and to rise up the reactor in plug flow. This phase includes the bubble void (through which some catalyst particles may rain) and depending upon the model can include the wake or the cloud or both. A number of assumptions can be made concerning the emulsion phase: it can be perfectly mixed; it can pass in plug flow from bottom to top; or the gas within the emulsion can be assumed stagnant (K3). More realistically, the Kunii and Levenspiel model (K1) assumes that the downflow of solids, which compensates for the upflow of solids in the wake and cloud of the bubble, carries gas downward in plug flow.

The gas flow and the interchange between the bubble and emulsion phases has been investigated as suggested by Kato and Wen (K3) by two

methods. One approach involves the use of tracer techniques while the other involves the adjusting of model parameters to fit experimentally observed chemical conversions. Gilliland and Mason (G1) first used the tracer technique. It has also been employed by other investigators (D2, I1, K8, K9, M4, W1). The method of determining the flow parameters by comparing the observed and the predicted conversion was first used by Shen and Johnstone (S6). This method has proven popular with many other workers (G2, I2, K10, K11, K12, M5, O1). Even with these two techniques, there are some fluid mechanic properties of fluidized beds and bubbles which must be described before a model can be formulated.

The following section deals with the description of bubbles in a fluidized bed. This information concerning bubble size, bubble velocity, gas interchange and other parameters must be understood before the specific two-phase bubble models can be formulated.

2.3.1. DESCRIPTION OF BUBBLES IN FLUIDIZED BEDS

The description of the behaviour of the gas in the bubbles is necessary in order to predict the performance of a reactor by a two-phase bubbling model. Many bubble characteristics must be described. A large number of studies using X-rays, probes, tracers and high speed photography have been undertaken to study single bubbles, single streams of bubbles and swarms of bubbles in both wide and very narrow beds of many different catalyst particles. One must only look at a freely bubbling thin two-dimensional bed to appreciate the complexity of the flow. Few if any experimenters in this field would state that their (or any other) model

accurately describes the truth since all the phenomena that are occurring are not included. Even if such a model did exist, it would be so complex and so time-consuming to compute even on the fastest computers, that it would likely be of little value to the engineer who wished to model a specific reactor.

The use of fluidized bed reactor models for scale-up or a priori predictions is at best a process of limited accuracy. This is particularly true in cases where the reaction rate is very high and the fluid mechanic aspects of the model are the limiting or rate-controlling step. Simulation of an existing reactor is a different matter. As mentioned above, current two-phase models differ essentially on how they treat the bubble-to-emulsion exchange process. Moreover, this exchange parameter is not only important in the overall reactor description, but also the least well known. Hence, it becomes convenient and appropriate to make this interchange parameter an adjustable one in the model and use the analysis of the chemical species as the responses to determine its best value. In this way, this parameter accounts for all the mechanisms such as coalescence and wake shedding that contribute to the gas interchange.

This section presents a summary of the existing knowledge and a description of bubble characteristics. The most complete presentation of this information along with references is contained in the book by Kunii and Levenspiel (L1). Only work by the main investigators describing the phenomena needed to formulate the two-phase models is presented. The formulation of existing reactor models and the exact bubble descriptions

used in each case will be presented in section 2.3.2.

BUBBLE SHAPE

The shape of a single rising bubble is quite well established (D1, P5, M3). Small bubbles are almost spherical while large bubbles as shown in Figure 2.1 are somewhat irregular spherical caps and flattened with an indentation in the bottom. This has been observed directly in the two-dimensional beds and with the use of X-ray photography in larger thicker beds. The angle θ as shown in Figure 2.1 has been examined by several workers (P5, R2) and in general is between 110° and 160°. Most models assume a spherical bubble which may or may not include the bubble wake, which contains catalyst. Although violent distortion of the bubble occurs as it breaks up and coalesces, the spherical bubble model is still used.

BUBBLE SIZE AND GROWTH

As bubbles rise through a fluidized bed they grow. The exact mechanism for growth is not well understood but the growth rate is more than would be accounted for by pressure expansion as the bubbles rise through the bed. Bubble break-up and coalescence are also occurring. At any one height in the bed, there are bubbles of more than one diameter. It has been stated that in commercial beds equipped with internals, the bubble size is close to constant except for a small region close to the inlet (L1). It is generally agreed that there is some maximum stable bubble size but its magnitude for a specific catalyst, reactor and flow is in great dispute (D1, L1). Actual observation in the specific reactor is still the most

accurate method for an individual case.

There are four general methods used to obtain the appropriate bubble-size distribution or average bubble size for a specific reactor.

(i) The bubble size can be estimated by matching observed experimental responses with model predictions for a given gas interchange mechanism.

(ii) The bubbles inside a reactor can be photographed using X-ray techniques.

(iii) The bubbles in a thin two-dimensional bed, filled with the catalyst to be studied, can be photographed and then measured. These data can be used to calculate a bubble size distribution for the three-dimensional case.

(iv) The bubble size distribution can be estimated by measuring bubble size inside a column with capacitance probes.

The accuracy or usefulness of any of these techniques can be criticized.

The use of a constant effective bubble size which is essentially an estimated parameter could be considered to be a simplification of unnecessary restriction. Bubbles may grow from less than a centimeter at the distributor to almost the column diameter at the top of the bed. However, they may also be close to one constant size for a reactor with internal packing or heat exchanger tubes.

The estimation of a bubble size distribution with height using two-dimensional bed data can also be criticized. The accuracy of the conversion from the two-dimensional case which can be seen, to the larger three-dimensional bubbling reactor in which only the emerging bubbles at the

upper surface can be seen has been questioned. This method does, however, attempt to take into account the effect of the type of catalyst which is being fluidized, and this can be an important factor.

X-ray studies become difficult for the analysis of bubble sizes in large diameter reactors. For smaller reactors this method should provide the best description of bubble sizes. Unlike capacitance probe methods, the bubbles are not disturbed by the measurement. The use of probes to determine the size of bubbles within a reactor may be impossible when studying a large industrial unit.

The use of a general correlation for the mean bubble size with height as a function of gas flow and particle size is also questionable. The correlation of Kobayashi (K13) for a drilled distributor plate:

$$d_B = 1.4 \rho_p d_p \left(\frac{U}{U_{mf}}\right) h + d_o \qquad 2.16$$

was obtained from his own work using capacitance probes at various column heights. d_o is the intial bubble size at the distributor plate.

BUBBLE RISE VELOCITY

The absolute rise velocity of a single bubble in a bed at incipient fluidization as first suggested by Nicklin (N1) for gas-liquid system is:

$$U_{br} = 0.711 \ (g d_b)^{1/2} \qquad 2.17$$

Later, Davidson and Harrison used this same expression for fluidized beds. Equation 2.17 generally is used for bubbles of size d_b in freely bubbling beds. Studies on single bubbles and streams of bubbles (D4, H3, R2, P5, T4) show a range of 0.55 to 0.85 for the proportionality constant

but 0.711 is generally used: Recent work by Grace and co-workers (G3) shows that the interaction of bubbles causes an upwards acceleration as well as lateral movement of trailing bubbles.

BUBBLE SOLID CONTENT

Solids have been observed in the bubble void by three investigators (T4, K14, K13) and they report a concentration of from 0.2 to 1.0% by volume. The main interest in the modelling of reactors is the size of the wake and the cloud region as shown in Figure 2.1. Models can be written to include none, one or both with the bubble void assuming the gas included within this bubble associated phase is completely mixed.

A commonly used model to predict the magnitude of the cloud radius relative to the bubble radius for a three dimensional bubble (D5) is:

$$\frac{d_c}{d_b} = \left(\frac{U_{br} + 2\,\frac{U_{mf}}{E_{mf}}}{U_{br} - \frac{U_{mf}}{E_{mf}}} \right)^{1/3} \qquad 2.18$$

Work by Murry (M3) for single bubbles probably provides a more accurate description of the cloud thickness and is being used in some more recent investigations.

The bubble wake represents about a quarter of the upflow phase. X-ray studies by Rowe and Partridge (P5) list previous work including probe studies and present data on bubble shape and wake angle for a number of solids. Bubble-bubble interaction in freely bubbling beds causes bubble and wake distortion. The validity of conclusions relating to multiple bubble behaviour from single bubble studies can be questioned.

The solids transported to the top of the bed in the bubble wake can cause flow reversal in the emulsion phase as the solids are deposited at the top of the bed by the bursting bubble. Tracer studies have verified this phenomenon (L4). The gas flow necessary to produce zero emulsion flow, or flow reversal has been given as U/U_{mf} 2.7 - 6.0 (L4) and U/U_{mf} 6. - 11. (L1). The reverse flow in the emulsion, coupled with poor distributor design can produce gross circulation in the emulsion phase (L1).

GAS INTERCHANGE

The understanding of the mechanisms and magnitude of gas interchange is considered by many to be the key to understanding and accurately predicting a priori the performance of fluidized beds. The interchange has been studied by a number of techniques:

(i) Stimulus response studies using a pulse injection of tracer gas and then interpretation of the cross flow or interchange from the response.

(ii) Fitting the predicted conversion of a model to the experimentally observed conversion.

Several semi-theoretical models have been proposed (D1, L1, Z1, B4, O4, G6, H8) to describe direct gas interchange. Davidson and Harrison (D1) considered the circulation rate of gas in and out of the bubble to be:

$$q \left(\frac{cm^3}{sec}\right) = 3U_{mf} \pi r_b^2 \qquad 2.19$$

Davidson also proposed employing Baird's correlation (B4) initially developed to describe mass transfer from liquid bubbles to describe a diffusive

contribution for the bubble-to-emulsion interchange.

$$k_g = 0.975\, D^{1/2}\, d_b^{-1/4} g^{1/4} \qquad 2.20$$

Note the difficulty in evaluating one unique interchange coefficient in a multicomponent system if this diffusion mechanism represents a major contribution to the interchange process. Partridge and Rowe (P4) proposed the use of a mass transfer coefficient similar to that used to describe a bubble of immiscible liquid rising through another liquid. Kunii and Levenspiel (L1) developed a three phase model (bubble, cloud, emulsion) with mass transfer resistances in series to describe gas interchange. In their scheme, the Davidson model (D1) is used to describe the interchange between the bubble void and the cloud, and then the Higbie penetration model (L1, H4) is used to describe the gas interchange between the cloud and the emulsion. None of these semi-theoretical models account for interchange due to cloud and wake shedding or bubble break-up and coalescence. However, they all do generally suggest a volumetric interchange rate per unit volume of bubble which is inversely proportional to the bubble diameter.

Kato and Wen (K3) suggest instead, after reviewing the results of Kobyashi's (K9) bubble-bubble studies, that the model:

$$\frac{\text{cm}^3 \text{ interchanged}}{\text{cm}^3 \text{ of bubble-sec}} = \frac{11}{d_b} \qquad 2.21$$

should be used where d_b is the bubble diameter in centimeters. This is consistent with other observations in that the interchange is inversely proportional to the bubble diameter. Toei (T5) in working with single bubbles suggests that the constant of proportionality is between 3. and 6.

In modelling situations where one fluid mechanic parameter is to be estimated to describe an existing reactor, this description of the interchange may be useful. The proportionality constant in equation 2.21 could be estimated. Note that a diffusion coefficient is not included; this is because for larger bubbles and most gases, the diffusional mechanism, as calculated by equation 2.20 is small. In addition the diffusion coefficient may be very difficult to predict for multi-component mixtures. Drinkhamer (D7) in his comparison of the interchange predictions of the various models includes the diffusion coefficient.

Orcutt and Carpenter in a recent paper (O4) have proposed a scheme to account for bubble coalescence. The vertical coalescence of bubbles occurs when a trailing bubble is accelerated and captured by the leading bubble. The coalescence phenomenon will affect the bubble rise velocity, the number and size distribution and the concentration of gas in the bubbles at any point in the bed. Hence, this phenomenon plays an important part in bubble-emulsion interchange; how important it is has not been demonstrated.

BED EXPANSION

The presence of bubbles causes the bed to expand above the level at minimum fluidization. This can be readily calculated knowing the gas flow and the bubble rise velocity (D1):

$$\frac{L-L_{mf}}{L} = \frac{U - U_{mf}}{0.711(g\bar{d}_b)^{1/2}} \qquad 2.22$$

$\bar{d}_b$ is the mean bubble diameter for the whole bed. This assumes that the emulsion voidage remains at ε_{mf} even when bubbles are present. Expansion may also occur below the minimum fluidization velocity as the voidage increases from the settled bed voidage.

2.3.2 CURRENT FLUIDIZED BED MODELS

Many mechanistic models have been proposed to describe the performance of fluidized bed reactors. All attempt to describe the phenomenon occurring in the bubble and emulsion phases as presented in section 2.3. In all models, the bubble rise velocity, bubble size, interchange, coalescence, flow in the emulsion phase and other necessary gas flow descriptions are modelled. A summary of many of the available models that have been employed to predict the performance of actual fluidized bed reactors is given in Table 2.2

Table 2.2 provides a convenient method of displaying some of the many different models and observing the many schemes for describing and interpreting the associated phenomena. This list is by no means complete. Kunii and Levenspiel (L1) discuss many of the published models in their book and there must be many models that were developed but not published. The first four models are discussed in detail as these were the ones chosen for investigation and subsequent discrimination studies in this thesis. These models, as originally presented by their authors, are summarized. The exact form of these basic models and the modifications made for their use in this study are detailed in Chapter 5.

TABLE 2.2a CURRENT FLUIDIZED BED MODELS

MODEL	PHASES	UPFLOW PHASE		DENSE PHASE	
		BUBBLE MODEL	MIXING	SOLIDS MIXING	GAS FLOW AND MIXING
Orcutt, Davidson, Pigford (O1)	1 Bubble 2 Emulsion	Spherical bubbles, no solids, constant size	Perfectly mixed bubble void	NO	$U_{m.f.}$, perfectly mixed $U_{m.f.}$, plug flow upwards
Partridge, Rowe (P3, P4)	1 Bubble, Cloud 2 Emulsion	Murray model, 2-dimensional measurements	Perfectly mixed bubble and cloud	NO	$U_{m.f.}$, plug flow upwards
Kunii, Levenspiel (K1, K2)	1 Bubble 2 Cloud, wake 3 Emulsion	Davidson model, constant size	Bubble perfectly mixed cloud and wake	YES	Calculated, plug flow, allows flow reversal
Kato, Wen (K3)	1 Bubble, Cloud 2 Emulsion	Spherical bubble and cloud, Kobayashi size	Perfectly mixed cloud and bubble	YES	Mixing in compartments, no vertical flow
Latham (L4)	1 Bubble, Wake 2 Emulsion	Davidson model, no cloud	Perfectly mixed bubble and wake	YES	Calculated, reverse plug flow
Van-Deemter (V1)	1 Bubble, Cloud 2 Emulsion	Davidson Model, Volume Fractions of Phases Used	No Perfect Mixing between bubble and cloud	YES	Determined, reverse plug flow
May (M6) Van-Deemter(V2) Mireur (M7)	1 Bubble 2 Emulsion	Spherical bubbles, no cloud	Perfect Mixing in Bubble Void	NO	$U_{m.f.}$, mixing by diffusion coefficient

TABLE 2.2b CURRENT FLUIDIZED BED MODELS

MODEL	INTERCHANGE BETWEEN PHASES	PARAMETER TO BE DETERMINED
Orcutt Davidson Pigford	Bubble Circulation (Davidson) $q = 3/4 \mu_{m.f.} \pi D_e^2$ Diffusion From Bubble (Baird) $k_G = 0.975 D_e^{-\frac{1}{2}} D_G^{\frac{1}{2}} g^{\frac{1}{4}}$	Effective Bubble Diameter
Partridge Rowe	Mass Transfer Coeff $h_m = D\ Sh\ d_c$ where $Sh = 2.0 + 0.69\ Sc^{1/3}\ Re_c^{1/2}$	Correlation for size, number and Velocity of Bubbles with height
Kunii Levenspiel	Bubble to Cloud Transfer same as Orcutt Cloud to Emulsion. Higbie Penetration Model $K_{CE} \approx 6.78 \quad DU_b/d_b^3$	Effective Bubble Diameter
Kato Wen	Gas Interchange per volume of bubble $F_o = 11\ /D_B$	None
Latham	Dimensionless Interchange Parameter $X = NQH/Uga$	Effective Bubble Diameter
Van-Deemter	Mass Transfer Coeff't for Bubble-Cloud and Cloud-Emulsion Transport. Effective Mass Transfer Coeff't. Accounts for Wake Shedding	Mass Transfer Coefficients, Volume Fraction of Phases
May, Van-Deemter, Mireur	Number of Times Emulsion Gas Exchanges with Bubble Gas is Used to Characterize Gas Transfer	Crossflow Parameter and Diffusion Coefficient for Emulsion Phase

ORCUTT-DAVIDSON-PIGFORD (01)

Orcutt et al. studied the first order decomposition of ozone over microspherical catalyst impregnated with ferric oxide (1960, 1962). Gas in excess of that required for minimum fluidization is assumed to pass through the bed in solid-free bubbles of constant size. The remaining fraction of gas "f" flows through the emulsion and can be described by a contact time distribution Ee(t). For a given rate constant r, the conversion can be calculated from equation 2.23

$$1-X = f + (1-f) \int_0^\infty \exp(-rt)\, E_e(t)\, dt \qquad 2.23$$

Two bubble flow models are presented for the limiting cases of plug flow and completely mixed flow in the emulsion phase. Interchange between the two phases is predicted using the Davidson circulation model (D1) and the Baird molecular diffusion model (B4). The bubble size or effective bubble size must be determined for the reactor to be modelled.

An analytical solution for the case of plug flow in the emulsion can be obtained if the reaction is first order and only the conversion is calculated. For a complex reaction numerical integration techniques must be employed. The model, assuming a completely mixed emulsion can be calculated very quickly, even for a complex reaction where a product distribution is predicted. This is due, not only to the assumption of complete mixing in the emulsion, but also to the lack of solids (and thus reaction) in the bubble. The calculation time is orders of magnitude less than that for the plug-flow-emulsion case where an integration technique must be used to obtain a solution.

PARTRIDGE-ROWE (P3, P4, Y3)

Partridge and Rowe developed a model first used to describe the first order reaction of a gas diluted with an inert going to a single product (1966). In their model to describe the fluid mechanical behaviour, all gas in excess of that required for minimum fluidization forms bubbles which grow as they rise through the reactor. The remaining gas flows upwards in plug flow through the emulsion at the minimum fluidization velocity. The Murray bubble model is used to describe the cloud. Perfect mixing is assumed between the gas in the bubble void and the cloud. The interchange of gas between the bubble and the emulsion is described using a Sherwood number and is based on the theory for a sphere rising in a fluid.

The distinct feature of this model is that the bubble size distribution along the axis of the reactor is calculated using observations of bubble size with height from two-dimensional bed experiments with the same catalyst. An effective mean bubble size is calculated at different heights up the two-dimensional bed by analyzing photographs of the bed at the required flow. This information is then converted to the equivalent bubble size for the three-dimensional case to describe the bubbles that would occur in the reactor under study.

Because of the plug flow of gas through the emulsion and the reaction which occurs in the bubble, the model must be solved, as suggested by its authors, by some integration technique. A two-phase model with growing bubbles containing some catalyst would seem to be an improvement over the model of Orcutt et al with its constant bubble size and solidless bubbles.

The extension of two-dimensional observations of bubble sizes to a three-dimensional system can be strongly criticized and therefore this poses a serious limitation on the direct use of their model.

KATO-WEN (K3)

Kato and Wen present a model which is claimed to have no adjustable parameters (1969). They use this model to predict the experimental results of a number of experimenters. The bed is divided into a number of compartments whose height is equal to the mean size of the bubbles at that height. Each compartment contains a bubble phase and an emulsion phase. The gas bubbles flow in plug flow through the emulsion phase which is assumed to be completely mixed within each compartment.

The spherical bubbles are surrounded by spherical clouds of radius calculated by the Davidson model (D5). The bubble growth is predicted by the correlation of Kobayashi (K13) which is based on three-dimensional bubble observations. The emulsion phase voidage is constant up to the bed height at minimum fluidization.

Kato and Wen recommend using an interchange coefficient, F, representing the volumetric interchange of gas between bubbles and the emulsion per unit volume of bubble per second as given by:

$$F = 11/d_B$$

This coefficient is entirely empirical being based on Kobayashi's experiments. Note that it contains no effect of the exchanging gases, particularly no diffusion coefficient.

The partitioning of the bed into zones for the purpose of calculation allows for a more rapid calculation than by most integration techniques. The assumption of complete mixing within each emulsion zone is unique to this model.

KUNII-LEVENSPIEL (K1, K2)

Kunii and Levenspiel have proposed a three-phase bubble model in which the cloud is a separate phase (1968). A constant effective bubble size must be determined for the reactor to be investigated. They claim that a constant bubble size should adequately describe deep beds or beds with internals that effectively control bubble size.

The Davidson model (D5) is used to describe the cloud size. The direction (upward or downward) of the plug flow of gas in the emulsion phase is determined by the circulation of solids entrained in the bubble wake. The resistance to gas interchange from bubble to emulsion is calculated from two resistances in series between the three phases. The gas transfer from the bubble to the cloud is described by the Davidson circulation model (D1) and the Baird diffusion model (B4). The transfer between the cloud and the emulsion is described by the thin layer Higbie penetration model (H4).

An analytical expression arises for calculating the conversion if a first order reaction is assumed. If the reaction is not first order or the product distribution must be predicted, the differential equations describing the concentration of the reactants must be solved by numerical integration. The addition of the third phase, the cloud, greatly increases the calculation

time. If the downflow of gas in the emulsion phase is included, the computation time is further increased since a two-point boundary value problem must be solved. Again, for the Baird diffusion model, the determination of an effective diffusivity in a multicomponent system of changing composition may be difficult.

The exact form of these models employed to predict the performance of the reactor to be studied is presented in Chapter 5. The models will be used in a simulation mode and one fluid mechanical parameter will be estimated using data obtained from the observed conversion and product distribution.

3.0 STATISTICAL TECHNIQUES

Statistical techniques enable one to make quantitative inferences about the truth. Statistical analysis is often considered to be too difficult for the problem studied or that the problem being studied is too simple to require the analysis. It is not for window dressing. The great power of proper statistical analysis lies in its ability to prevent the experimenter from deceiving himself, not in its possibilities for deceiving others.

The need for statistical analysis can be simply explained: The measured value of the dependent variable at an experimental trial is not in general the true value of the quantity measured. An error, from one of a multitude of sources and of unknown magnitude, makes up some part of the recorded response. These errors cannot be removed completely. Thus, the experimenter must rely on some form of statistical analysis to efficiently reach his goal (if indeed this is possible) and to honestly and unbiasedly report his findings. Almost all of the techniques necessary have been available for many years. Blame for their lack of use is both with the experimentalist and with the statistician. The experimentalist has often been uncompromising in his mistrust of these techniques and reluctant to spend valuable time for their implementation which he considers almost to be wasted. Indeed, he often has great faith in his intuitive ability to appreciate what the effects of all the errors will be and to react and to plan accordingly. To him, this is much more efficient. The statisticians on the other hand have often presented theorems and techniques which are perfect and precise in their own language of integrals, spaces, matrices and tables; unfortunately, this language is in many instances almost incomprehensible to all but the faithful. He is often unwilling to

compromise and contaminate his theory by making concessions requested by the experimenter to solve a specific problem.

One solution to the problem is to have the experimenter become his own statistician. A more efficient solution is to enlighten both parties. The experimentalist is rapidly converted when he can understand the basic statistical techniques and can be shown the power and efficiency of these techniques. The statistician too, sees the benefit of the relationship to himself when shown what problems can be solved.

The learning process by the experimenter can be very infectuous. The appearance of more and more "readable" statistics papers is very encouraging. The best paper to date is that of Box and Hunter, entitled "The Experimental Study of Physical Mechanisms" (B13). This paper should be required reading for every experimentalist. It deals with the basics of data analysis, the presentation of parameter estimates and conclusions based on models, as well as experimental design for parameter estimation and for model discrimination. It stresses the importance of the visual scrutiny of the data and the analysis of residuals. It also points out the importance of the interaction and joint analysis of results by both the experimenter and the statistician. Both can draw important conclusions from the data that the other might miss or be unable to interpret. This interaction will result in a far more efficient and rapid attainment of the goals of any project.

This chapter presents the statistical nomenclature used in this thesis. It deals with experimental data with more than one response or observation per experimental trial. The presence of errors is analyzed and the variance-covariance matrix of the responses is dealt with. The

procedure of parameter estimation is discussed and the use of confidence regions, instead of point estimates, presented. Methods of experimental design for both efficient and effective parameter estimation and model discrimination are summarized. Finally, the concept of the total experimental redesign is explained to show how, through a sensitivity analysis, the experimenter can identify the major sources of error that will hinder his progress.

The use of statistical techniques must be an essential part of any experimental study. In neglecting their use, the experimenter reduces his efficiency, reduces his chances of drawing precise and accurate conclusions and increases the probability of deceiving himself and others.

3.1 MULTIPLE RESPONSE DATA

In the search to investigate underlying physical mechanisms, the engineer will often postulate a mechanistic model. Of course, he only tentatively assumes it, he never accepts such a model uncritically. Primarily due to the speed and availability of modern computers, he is now able to investigate more complex models for more complex systems. It is inevitable that he would now try to investigate phenomena that yield more than one observation, result or response per single experiment or experimental trial. The statistical techniques for the analysis of multivariate observations, as suggested by the limited number of texts on the subject for example references A2, K15, and H5, are still relatively unknown compared to univariate analysis. The notation however, is similar in form to that used in the univariate case and is explained in the following paragraphs.

A mechanistic model is proposed:

$$\underset{}{Y_u} = \underset{}{\eta_u}(\underset{}{\xi_u}, \underset{}{\theta}) + \underset{}{\varepsilon_u} \qquad u = 1,2...n \qquad 3.1$$

where $\underset{}{Y_u}$ is the vector of observed experimental responses for the u'th experiment and $\underset{}{\eta_u}$ and $\underset{}{\varepsilon_u}$ are the vectors of predicted responses[t] and experimental errors respectively for the u'th experiment. This assumes that the model describes the physical system exactly. The vector of r predicted responses is given by some function:

$$\underset{rxl}{\eta_u}\ (\underset{}{\xi_u}, \underset{}{\theta}) = [f_i, (\underset{}{\theta}, \underset{}{\xi_u})] \qquad i = 1,2...r \qquad 3.2$$

where $\underset{}{\xi_u}$ is the vector of control variables for the u'th experimental trial and $\underset{}{\theta}$ is the vector of parameters for the model f. The quantity in square brackets is the i'th element of the rxl vector.

Multiple response* data produces r observations or responses per experimental trial. However, for normally distributed data the error structure is described by $\frac{(r)(r+1)}{2}$ quantities per trial (the variance-covariance matrix). Define one single vector of responses for all n trials:

$$\underset{nrxl}{Y} = \begin{bmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_n \end{bmatrix} \qquad 3.3$$

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* The terms response and dependent variable are used synonymously whether referring to predicted, "true" or measured value.

[t] The term "predicted" response has been used to mean the "expected" response.

Then its variance-covariance matrix* $\underset{nrxnr}{\underline{V}}(\underline{y})$ becomes:

$$\underset{nrxnr}{\underline{V}}(\underline{y}) = \begin{bmatrix} \underline{\Sigma} & \underline{0} & \underline{0} & \cdots & \underline{0} \\ \underline{0} & \underline{\Sigma} & \underline{0} & \cdots & \\ \underline{0} & \underline{0} & \underline{\Sigma} & \cdots & \\ \vdots & & & & \vdots \\ \underline{0} & \cdots & & \cdots & \underline{\Sigma} \end{bmatrix} = \underline{A} \qquad 3.4$$

where $$\underset{rxr}{\underline{\Sigma}} = \underline{V}(\underline{y}_u) \qquad u = 1,2,\ldots n \qquad 3.5$$

is the variance-covariance matrix of an individual vector of observations and $\underline{0}$ is a rxr null vector. The $\underline{y}_u$ vectors are assumed to have the same variance-covariance matrix and to be independent of each other.

For single response data many distribution forms have been investigated for describing the error structure. Most often, one assumes that the error is normally distributed. If this distribution does indeed describe

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* The covariance matrix, sometimes called the variance-covariance matrix or dispersion matrix is defined for a vector random variable $\underset{mxl}{\underline{z}}$ as:

$$\underset{mxm}{V(\underline{z})} = [Cov(z_i,z_j)] = E\{[\underline{z} - E(\underline{z})][\underline{z} - E(\underline{z})]^T\} \qquad 3.6$$

where the operator E stands for the expected value. The expected value of a vector random variable is the vector of expected values of the elements of the random variable each of which may be considered the limiting average value for an indefinitely large number of trials. It is defined as:

$$E(z_i) = \int_{-\infty}^{\infty} z_i \, Pr(z_i) \, dz_i \qquad 3.7$$

where $p(z_i)$ is probability density function of z_i.

the error structure, then the least squares estimate of parameters is also the maximum likelihood estimate (likelihood function defined equation 3.17). In the multivariate case, the multivariate normal distribution is so far the only distribution that has been investigated to any great degree. The form of the probability density function is similar to that for the single response case:

$$p(\underline{y}) = \frac{1}{(2\pi)^{N/2}|\underline{A}|^{1/2}} \exp\{-\tfrac{1}{2}(\underline{y}-\underline{\eta}(\underline{\theta}))^T \underline{A}^{-1}(\underline{y}-\underline{\eta}(\underline{\theta}))\} \qquad 3.8$$

where $\underline{\eta}$ is defined as the expectation of $\underline{y}$ and N=nr. The expected value of the error is zero and its variance-covariance matrix is given by $\underline{A}$. Equation 3.8 can be written in the alternate form:

$$p(\underline{y}) = \frac{1}{(2\pi)^{N/2}|\underline{\Sigma}|^{n/2}} \exp\{-\tfrac{1}{2}\sum_{u=1}^{n}(\underline{y}_u-\underline{\eta}_u(\underline{\xi}_u,\underline{\theta}))^T\underline{\Sigma}^{-1}(\underline{y}_u-\underline{\eta}_u(\underline{\xi}_u,\underline{\theta}))\} \qquad 3.9$$

The error variance-covariance matrix can be used for several purposes. It is needed to provide an independent estimate of the lack of fit of model predictions. It can be used to establish confidence regions for the parameter estimates. It is also needed to weight properly the experimental responses when using the likelihood function to obtain parameter estimates.

3.2 PARAMETER ESTIMATION

There are three basic aspects of parameter estimation that the experimenter must deal with: the design of experiments, the weighting of responses and finally, searching for the parameters. The first, the design of experiments, is the most important. The damage caused by poorly designed experiments is irreparable. This most important topic, which is often overlooked, is presented in section 3.4. The second problem, the weighting of

the experimental responses, is easier for the single response experiment. For the multiple response experiments, however, the individual responses may be of different numerical magnitudes and do not in general have the same weights because their variances and covariances may have any permissible values. Finally, a technique of search must be chosen. The parameters to be estimated should be transformed to make the derivative of the objective function with respect to the parameters to be of the same order of magnitude for convenience. Direct search or local linearization can be used. If more than one parameter is to be estimated, some criterion of parameter grouping for efficient searching must be used (02). Also, the experimenter must ensure that the measured responses he is using are linearly independent (B7). Before the searching procedure can be discussed, the experimenter must fully understand the importance of and the actual procedure of weighting.

WEIGHTING

If there were no errors, the weighting of the experimental responses would not be necessary. Even if the structure of the errors were exactly known, as in the case of many statistics papers with synthetic data generated from a true model and known error structure, the task would be much simpler. The experimenter in his search for parameter estimates is confused and hindered by three main types of errors. All, depending on their relative magnitudes, can be important. They are:

1. experimental error
2. inaccurate parameter estimates used for the model predictions
3. incorrect models.

The experimenter must estimate the effect of the magnitude of each and proceed accordingly if he does not wish to fool himself, both with the parameters he has estimated and the degree of confidence he has in them.

The first, experimental error, is perhaps the best known and the easiest with which to deal. It can be well defined by performing properly randomized and replicated experiments. Randomization of replicate experiments is essential since this first type of error is the random experimental error. The technique of randomization is well understood (D9). The need for proper replication is not well appreciated. The taking of a second sample and analyzing it is not sufficient. At some later time, the experimenter must return to the operating condition and physically reset all the control variables to the same settings. Then, the sample will reflect, not only the error in analysis, but also the inability to detect differences in operation that cannot be seen even though all the instruments and the operating settings are exactly the same. These may include temperature profiles, feed concentration differences, catalyst activity, slight calibration changes and a multitude of other effects. If a systematic error is detected, it must, of course, be identified and corrected.

From replicated experimental trials the variance-covariance matirx can be estimated:

$$\underline{\Sigma} = \frac{1}{n} \sum_{u=1}^{n} (\underline{y}_u - \bar{\underline{y}}) \quad (\underline{y}_u - \bar{\underline{y}})^T \qquad 3.10$$

where $\bar{\underline{y}}$ is the mean for the experimental trials performed. If there are enough data to assume that the estimate is equal to the true value it may be used to weight the data when employing the maximum likelihood method to estimate the parameters. In this case the maximum likelihood estimates of the parameters are obtained by maximizing the likelihood function:

$$\exp\left\{-\tfrac{1}{2}\sum_{u=1}^{n}(\underline{y}_u-\underline{\eta}_u(\underline{\xi}_u,\underline{\theta}))^T\ \tilde{\Sigma}^{-1}\ (\underline{y}_u-\underline{\eta}_u(\underline{\xi}_u,\underline{\theta}))\right\} \qquad 3.11$$

The quadractic form in the exponent takes into account both the magnitude of the responses $\underline{y}$ and also the magnitude of the error in each response. It should be noted that this equation assumes a constant variance-covariance matrix over the entire range of operating conditions. To ensure this, several sets of randomized replicates should be performed and the variance-covariance matrix for each calculated (equation 3.10) and compared.

The Plackett test (P9) can be used to evaluate the homogeneity of the variance-covariance matrix. Both the variance and the covariance elements are tested. The technique is somewhat cumbersome. The Bartlett test (K16) can be employed to investigate the homogeneity of the individual variance elements of the variance-covariance matrix if the errors are normally distributed. The test is very sensitive to departures from normality. If the variances are not homogeneous then the data can be transformed to a form which will overcome this difficulty. Common transformations include logarithms, exponentials and inverses. Box and Cox (B5) have developed a specific method of dealing with a family of such transformations for the single response case but not for multiple responses. Practical application to multivariate systems is tedious.

An estimate of the variance-covariance matrix is desirable, even in the initial stages of parameter estimation as will be seen. At this stage, the experimenter should not expend a large effort in obtaining the very best estimate however. Primarily, he will not know at what conditions to perform experiments. Thus replicated trials can be performed at several conditions dictated by the experimental design. Then he will have a reasonable estimate of the variance-covariance matrix and its constancy can be evaluated over the entire response surface used to obtain the final

parameter estimates. In the initial stages, perhaps only a rough estimate of the diagonal elements or variances would be necessary. It is unlikely that the approximation:

$$\tilde{\underline{\Sigma}} = k\,\underline{I} \qquad 3.12$$

would be reasonable where k is some guessed variance and $\underline{I}$ is an rxr identity matrix. From his knowledge of the system, the experimenter may be able to provide a reasonable estimate of the variance of each of the responses but perhaps not good estimates of the covariances among them.

Box and Draper (B6) propose a method for parameter estimation when the variance-covariance matrix of a single measurement is unknown. If the experimenter has no knowledge of $\underline{\Sigma}$, then this method should be used. It assumes a uniform prior probability for the parameters to be estimated over the parameter region where the likelihood takes on appreciable values. It also assumes that the errors are independent from one trial to another, normally distributed and with expectation zero. Parameters are chosen so as to minimize the determinant of the matrix $\underline{v}$ where:

$$\underline{v} = \sum_{u=1}^{n} (\underline{y}_u - \underline{\eta}_u(\underline{\xi}_u, \underline{\theta}))\,(\underline{y}_u - \underline{\eta}_u(\underline{\xi}_u, \underline{\theta}))^T \qquad 3.13$$

The paper also develops expressions for the Bayesian posterior density function of the parameters estimated. If the model is assumed perfect then the matrix $\underline{V}$ can be used in estimating the variance-covariance matrix:

$$\tilde{\underline{\Sigma}} = \frac{1}{n-\binom{p}{r}}\,\tilde{\underline{v}} \qquad 3.14$$

where $\tilde{\underline{v}}$ is the matrix $\underline{v}$ which has the smallest determinant and p is the number of parameters estimated.

SEARCHING FOR PARAMETERS

Box et al. (B7) in a recent paper point out that incorrect parameter

estimates will be obtained if there is a linear relationship among the measured responses. The most common example of dependent responses is that which arises when the experimenter makes the sum of the mole fractions from an analysis equal to 1.0. In the case where moderately smooth transformations are used their linear relationships could be expected to produce a badly conditioned estimation situation.

Three common search methods for finding an extremum are: grid search and directed search including local linearization. The simplest but the least efficient to use is the grid search. Values are calculated at various discrete grid points in parameter space. The grid spacing is then decreased in the region of the minimum until the minimum is located.

A more efficient search method, especially where ridges are present, was developed by Rosenbrock (R3, R4). The parameters are initially varied one at a time and the effect of these changes on the objective function are noted. After encountering a failure (increased objective function) in all directions, the axes which determine the direction of movement are rotated and the parameters are varied together.

The simplex search technique is perhaps the best for parameter estimation when a high degree of correlation exists among the parameters. In searching for p parameters, p+1 initial values of the objective function are evaluated. In the case of a two parameter search, the three points would form a triangle in two dimensional space. The next pair of parameters is chosen by projecting from the vertex of the poorest value of the objective function through the centroid of the remaining vertices.

This search technique allows for movement of all parameters early in

the searching procedure. The simplex search, like the Rosenbrock search is easily used.

The method of linearization is perhaps the most difficult of the three and is often less fool proof than direct search methods. The model is linearized about the initial estimates of the parameters using a Taylor expansion and neglecting second and higher order derivatives (B8). The partial derivatives of each of the responses with respect to all the parameters are determined numerically for each data point. A matrix equation is written involving the observations, the model and the derivatives. Then, using linear least squares theory, the equation is solved for the best estimate of the parameters. The procedure is iterative since new derivatives may be calculated at each new point as the parameter estimates are updated. The method is not simple to use and the calculation of the large number of derivatives can be very expensive for complex models and large amounts of data. Also, linearization of the models far from the best estimates of the paramters may cause considerable trouble.

Searching for one parameter at a time using direct search techniques is very inefficient, particularly in cases where parameters are highly correlated. Searching for more than four or five parameters at one time can also be very inefficient (although the simplex technique should be far better than the Rosenbrock method with this number of parameters). The method which appears to be most efficient is to choose two or three highly correlated parameters and then to simultaneously search on them. Other sets are chosen until all the parameters have been estimated at least once. This procedure is repeated until the best estimates of the parameters (based on some appropriate criterion) are determined.

The grouping of some correlated parameters such as activation energies and reaction frequency factors is usually obvious. The correlation matrix of the parameter estimates can be used most efficiently for determining the grouping of parameters. It is obtained form the covariance matrix of the estimated parameters which is:

$$\left[\sum_{u=1}^{n} \underset{u}{X}^{T} \; \underset{}{\Sigma}^{-1} \; \underset{u}{X}\right]^{-1} \qquad 3.15$$

where

$$\underset{rxp}{X_u} = \left[\frac{\partial f_i(\underset{u}{\xi}, \underset{}{\theta})}{\partial \theta}\right]_{\theta=\underline{\theta}} \qquad 3.16$$

and $\underline{\theta}$ is the best current estimate of the parameters $\underline{\theta}$. The resulting p dimensional square matrix (p parameters) is then divided row and column by the square root of the diagonal elements. The resulting matrix is the correlation matrix of the parameter estimates. The off-diagonal elements represent the degree of correlation between the parameters for the respective row and column. The best grouping of parameters for efficient simultaneous searching can then be easily determined.

The analysis of residuals is also an essential part of the parameter estimation procedure. It is not sufficient to test on the basis of some magnitude of the weighted sum of squares. There must be no obvious cross nor auto-correlation among the residuals. That is, the residuals must be randomly scattered about zero. The residuals must be plotted against the control variables and against the observed experimental responses. As well, it is also advisable to plot them against time, batch number and other such quantities. This can be easily done at the end of a search stage using standard computer programs to produce "dot" diagrams. The analysis of the correlation of the residuals with the variables increases the efficienty of the search

by visually displaying systematic lack of fit which the experimenter can often correct by adjusting the appropriate parameters other than those being estimated before resuming the next stage of the search.

After the best parameter estimates have been obtained, the experimenter may want to know how precisely he has estimated the parameters. This can be readily obtained by an analysis of the confidence contours or likelihood ratios for his parameter estimates. This is discussed in the next section.

3.3 CONFIDENCE REGIONS

The best estimates of the parameters can be found using the methods described in section 3.2. These are point estimates. In some cases (usually very few) they are sufficient. The experimenter can be far more informative if he can also provide a measure of how good, how precise or how much better his best * values are over any other set of parameters. This valuable information can be presented by defining the region of "confidence" or the degree of "confidence". The region or area of confidence can be described by likelihood or by Bayesian methods.

The likelihood analysis is based on a calculation of a likelihood ratio for two or more cases and these are compared. The magnitude of an individual likelihood is a function of the error in the measurements (or an

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* In this work the word "best" is not used as the absolute best when applied to estimates of model parameters. The least squares estimator has been used for parameters because even in the non-linear case they are unbiased and with minimum variance at least approximately. Unbiased estimates have been used for the variance-covariance matrix.

estimate of it) and the data. Consider the case of experimental data $\underline{y}$ with error normally distributed with mean zero and known variance-covariance matrix $\underline{\Sigma}$. The likelihood function for any set of parameters $\underline{\theta}$ is:

$$L(\underline{\theta}|\ \underline{y},\underline{\xi},\underline{\Sigma}) \equiv L = \frac{1}{(2\pi)^{N/2}|\underline{\Sigma}|^{n/2}} \exp\left[-\frac{1}{2}\sum_{u=1}^{n}(\underline{y}_u-\underline{\eta}_u(\underline{\xi}_u,\underline{\theta}))^T\underline{\Sigma}^{-1}(\underline{y}_u-\underline{\eta}_u(\underline{\xi}_u,\underline{\theta}))\right] \quad 3.17$$

where n is the total number of experiments performed. This likelihood can then be compared to the maximum likelihhod value calculated using the the parameter estimates producing the minimum weighted least squares. Since only the ratio of the likelihood values is of interest, the exponential factor in the likelihood is the only one that need be calculated. A likelihood ratio of 10 is ordinarily taken as showing a real difference while a ratio of 100 denotes a strong preference for one set of parameters over another. Using this technique and choosing sets of parameters different from the best estimates of the parameters, confidence regions can be accurately defined. References to likelihood methods in general are B10 and J2.

The Bayesian analysis is based on the subjective interpretation of probability and Bayes' Theorem. The experimenter, before starting an experiment is able to assume an appropriate prior distribution for the parameter(s) to be estimated. After performing one or more experiments, he can update the probability density function of the parameters by using Bayes' Theorem:

$$f_2(\underline{\theta}\ /\underline{y},\underline{\xi},\underline{\Sigma}) \ \alpha\ \ f_1(\underline{\theta}) \times f_3(\underline{y}/\underline{\theta},\underline{\xi},\underline{\Sigma}) \quad 3.18$$

where f_2 is the posterior probability density function of the parameters

$\underline{\theta}$ with variance-covariance matrix $\underline{\Sigma}$. $\underline{y}$ are the new experimental responses for the control variables $\underline{\xi}$. f_1 is the prior density function as defined previously and f_3 is a likelihood. In this way, subsequent experments are used to update the previous degree of belief in the distribution or confidence regions of the estimated parameters.

These two techniques provide a way of more completely presenting the parameter estimates. These two techniques are superior to any method which simply reports a point estimate or even to one which reports a simple interval estimate. One essential part of both of these techniques as applied in our situation is a knowledge or at least a good estimate of the variance-covariance matrix.

Bayesian and likelihood techniques can also be employed to discriminate among possible models and to express a measure of confidence in these models. However, as stated by Box and Hunter (B8), "The damage of poor design is irreparable; no matter how ingenious the analysis, little information can be salvaged from poorly planned data".

3.4 EXPERIMENTAL DESIGN

Considerable study has been given to the field of experimental design. This work can be conveniently divided into two sections: for parameter estimation and for model discrimination. Some combined criteria have also been proposed (H6). In this study there are two experimental design problems to be solved. For practical reasons parameters had to be estimated in the packed bed reactor where the model was known. Secondly, in the fluidized bed reactor, experiments had to be designed for model discrimination.

3.4.1 PARAMETER ESTIMATION

If experiments are not carefully planned, the operating conditions may be so situated in the control variable space that the estimates which can be obtained for the parameters are not only imprecise but also highly correlated. There has been considerable investigation of the design of experiments for models which are non-linear in the parameters (B11, C5, K17, A3, D6, K18). These workers have attempted to reduce the hypervolume in p parameter space which defines some region of confidence for the parameters.

The multiple response - multiple parameters design is a simple extension of the one parameter - one response case. In the latter case, the experimenter attempts to choose the operating or control variables so that the derivative:

$$\left[\frac{\partial \text{ (response)}}{\partial \text{ (parameter)}}\right]^2 \qquad 3.19$$

is maximized (B11). In this way, the effect of the experimental error leading the experimenter to an incorrect estimate of the parameter will be minimized. For one parameter and r responses the effect of the error on each response must be considered. Even though the derivative as written in equation 3.19 might be large for one response, the expected experimental error might also be large thus negating the effect of a large derivative. Thus each derivative is weighted by the inverse of the variance expected for that response (D10). To design experiments for r responses and p parameters, the control variables are chosen so as to maximize:

$$\left|\sum_{u=1}^{n+1} \underline{X}_u^T \, \tilde{\underline{\Sigma}}^{-1} \, \underline{X}_u\right| \qquad 3.20$$

where $\tilde{\underline{\Sigma}}$ and $\underline{X}_u$ are as defined previously. The derivatives, in the case of most complex non-linear models, are determined numerically. The derivatives for the conditions presently being considered, the n+1 'th

trial, must be determined.

If only one experiment is to be performed, a directed search can determine the set of control variables that will maximize the determinant defined by equation 3.20. Often it is more practical from an experimental point of view to design and perform a block of experiments. This is only slightly less efficient (B15) than the sequential approach of designing one experiment, performing it, analyzing the new parameter estimates and then if warranted, repeating the procedure.

If one experiment is to be designed, a directed search over the control variable space will yield the conditions for the best experiment. If a block of experiments is to be performed a Monte Carlo procedure could be employed to select possible sets of operating conditions and the best ones selected. A similar method is described in Cochran & Cox (C9). Although this is not as efficient as a direct search for determining the best possible sets of operating conditions, it may require substantially less computation time and the resulting sets of operating conditions should be reasonably close to the best sets. A number of sets of operating conditions can be randomly chosen and the best ones selected.

These methods of experimental designs are based on the criterion that the total uncertainty in all the parameters is minimized. In some cases, this may not suit the requirements of the estimation situation. This present study has indicated that if the parameters that are estimated are to be used in another model, a different criterion should be employed. This criterion includes in the analysis the effect of the uncertainity in the

parameters on the precision of the predictions of the second model. That is, the sensitivity of the final model to the parameters that are being estimated from another experimental system must be considered when designing the experiments in this system. Elaboration of this point may be found in Chapter Six and Appendix K.

3.4.2 MODEL DISCRIMINATION

The experimenter is usually faced with a number of models that may describe the physical system to be investigated. They may represent different postulated reaction paths, flow patterns, reaction orders, or any of a number of possible mechanisms. When modelling a system in which a number of models may apply, each with different parameters to be estimated, it is desirable to reduce the number of models being considered. In this way, the more probable models, and their parameters, can be defined with greater precision with less computation and experimentation. This discrimination procedure only guarantees that the best model of those proposed will be chosen to fit the experimental data over the investigated range of independent variables. Formalizing the discrimination procedure will hasten the choice of the best model from among those proposed. This best model may still be inadequate if it is not a good one in the sense that it does not predict the experimental responses within the experimental error.

Experimental design for model discrimination is simply a formal procedure for choosing operating conditions so that when the experiment is analyzed the greatest possible difference among the models can be detected.

As in the case of experimental design for parameter estimation, the choice of the operating conditions is also affected by the error in measuring the responses and by the uncertainty in the predictions arising from errors in the parameter estimates. Some criteria for experimental design for this purpose attempt to balance separation between models and errors in prediction stemming from these sources.

Reilly (R5) presents a summary of some of the methods with examples of the criteria used for experimental design for model discrimination. These are: The Roth criterion (R7), the Box and Hill (B12) criterion and the expected entropy criterion (R5). These criteria increase in complexity as listed above and differ in their treatment of the error structure. In all cases, the prior degree of belief or probability of the model, based on all the previous experiments, is used for weighting.

The Roth criterion, presented in his thesis (R7) is the simplest and easiest to apply. No direct reference is made to the effect of any errors. As it was initially written for the single response case operating conditions $\underline{\xi}$ are chosen to maximize:

$$Z(\underline{\xi}) = \sum_{i=1}^{m} P(j,n-1) \left[P(i,n-1) \prod_{\substack{j=1 \\ j\neq 1}}^{m} \left|\eta_j(\underline{\xi}) - \eta_i(\underline{\xi})\right|\right] \qquad 3.21$$

for the n'th trial to be performed. P(i,n-1) is the posterior Bayesian probability of the i'th model after the previous n-1 experimental trials have been completed and m is the number of models. A criterion similar to equation 3.21 can be proposed for the multiple response case by including the product of differences between each of the responses?

$$z'(\underline{\xi}) = \sum_{i=1}^{m} \sum_{\substack{j=1 \\ j \neq i}}^{m} [\{P(i,n-1)+P(j,n-1)\}\left((\underline{\eta}_i-\underline{\eta}_j)^T \underline{\Sigma}^{-1}(\underline{\eta}_i-\underline{\eta}_j)\right)] \qquad 3.22$$

The quantity within the curved brackets is multiplied by the sum of the prior probabilities of models i and j. The inverse of the variance-covariance matrix is used to weight the expected responses of the i and j model for the chosen operating conditions $\underline{\xi}$.

The deficiency of the Roth criterion is the failure to include the effect of error in the predicting ability of the model. The Box-Hill criterion includes the effect of the prediction error in the models. The Box-Hill criterion (B12, H7) is based on Shannon's (S7, K19) entropy approach to information theory. The entropy is analagous to thermodynamic entropy and is a measure of the randomness or uncertainity. This criterion considers uncertainty in both the experimental responses and the model predictions. The maximum expected decrease in entropy for the total system is the criterion used to choose the next experiment with operating conditions $\underline{\xi}$.

The third criterion involves the calculation of the expected entropy change rather than using the upper bound as in the Box-Hill criterion. Reilly (R5) presents a method for calculating the integral necessary for defining the expected entropy change.

Many methods of designing experiments for model discrimination are available. The importance of including the effects of experimental error and prediction error can easily be seen. Comparisons of the various methods have generally shown that all the methods select the same or very nearly

the same conditions as the best for the next experiment to be performed (R5). If more than one experiment is to be designed, all the criteria would choose the same experiment to be repeated. This can be considered to be a weakness if other sets of very different operating conditions exist that are expected to provide almost as good a discrimination. This problem and a proposed solution to it for the design of blocks of experiments is fully discussed in Chapter Six.

The mathematical techniques described in section 3.4 are very important and must represent part of any experimental investigation. The investigation of physical systems is usually an iterative procedure of conjecture, design, experiment and analysis. Thus, a procedure of total experimental redesign, of which experimental design as described here is an important step, should be followed. A formal description of the various aspects of total experimental redesign is given in the next section.

3.5 TOTAL EXPERIMENTAL REDESIGN

The experimental cycle of design-experiment-analyze is well known. The necessary techniques to avoid the irreparable damage caused by poor design of experimental operating conditions are well understood. A multitude of statistical techniques are available to obtain the maximum information from the experimental data. The experimental cycle is iterative and the error that could limit the attainment of the final goal can come from any of a multitude of sources. Thus, a total redesign of the total experimental cycle should be undertaken, formally or informally, before each "experiment" step of the cycle is begun. This simply involves a sensitivity analysis of all the possible contributing sources of errors. The total number of possible errors are too many and their individual magnitudes are too difficult to estimate without some form of sensitivity analysis.

The errors will generally affect the results of an experiment in one of two ways. Estimated parameters or model predictions may be imprecise and have a larger than desired variance or confidence region associated with them. Secondly, the parameters or the model predictions may be systematically higher or lower than the true parameter values or model predictions. There are many errors which may cause these effects but they can generally be grouped into five categories:

1. Improper Experimental Conditions
2. Deficiencies in the Model
3. Uncertainty in Parameters Assumed to be Known
4. Experimental Apparatus
5. Analytical Techniques

The effect and magnitude of any of these can usually be readily and simply determined by using a sensitivity analysis. The analysis is performed by observing the magnitude of the change in a parameter estimate or a model prediction for a small change in one of the above sources of error. By comparing the magnitudes of the various contributing errors the experimenter can efficiently concentrate on reducing those with major contributions and not spend valuable time and money on those that are negligible. As given here this analysis ignores interactions. If they are expected a reasonable number of them can be investigated by similar methods.

Deficiencies in the models are closely related to experimentally observable conditions. These may include temperature or pressure gradients, non-ideal mixing patterns, inconsistency in packing or any number of conditions that are not described by the model presently being used. The first step is

to determine if they would affect the results and conclusions of the study if they were included in the model. This can usually be easily determined without major changes to the model. If, for example, a pressure gradient is observed, the conclusions from the model can be compared using first the inlet pressure and then the outlet pressure in the model calculation. If there is an appreciable effect of the pressure, it must be included in the model or else the apparatus redesigned to eliminate the pressure drop. It may be very unwise to neglect investigating the sensitivity of an effect which the experimenter "feels" is unimportant for his case. A quick, even order of magnitude, check by sensitivity analysis will usually provide a more objective and honest appraisal of the importance of a specific phenomena or effect.

One of the most common weaknesses in experimental studies is the failure to assess the degree of uncertainty in parameters that are assumed to be known. Commonly, parameters or phenomena are independently determined in one system for use in a second system from which the main conclusions will be made. The precision to which these values were first determined, plus the sensitivity of the conclusions to be drawn to errors in these parameters must be assessed. If not, time consuming and costly experiments and analysis which may never be able to provide the answers might be performed and wasted. Errors introduced in this way are commonly neglected in many experimental studies, and may bring about the total failure of the project before it is even begun. Indeed, often the identification of this error is never made.

Inaccuracies in experimental techniques, or in recording phenomena which are occurring, can also lead to inaccurate or imprecise conclusions.

The effects of calibration errors, random or systematic, are well known as possible sources of considerable error. A simple sensitivity analysis will provide a guide as to the order of magnitude of their affect on the study being performed. Also, just because a phenomena is not observed does not mean it does not occur. Improperly positioned thermocouples in a packed bed reactor may not detect the true temperature profile and presence of a hot spot. This could lead to estimated values of the apparent activation energies much larger than actually occur. Again, a simple sensitivity analysis can provide an estimate of the seriousness of an imprecise measurement of the temperature profiles.

The method of analysis of the experimental responses must also be carefully investigated. An estimate of the expected random error inherent in the method of analysis may show that the error may be of the same order of magnitude as the response. It may be possible that the interpretation of the results is very sensitive to the accuracy of the response being measured. If this is found to be important, a new and more accurate method of analysis must be designed. Many experimenters have discovered late in a study that the method of analysis, thought to be accurate, was insufficient to provide the clear answers that were sought.

Thus a sensitivity analysis performed early in an experimental study can save far more time and wasted experimentation than it takes to perform. It may indeed show that the error structure and the errors inherent in the system being studied will not allow conclusions of the desired accuracy and precision to be obtained.

4.0 ESTIMATION OF KINETIC PARAMETERS

Both the kinetics of the reaction and the flow of reactants through a reactor must be described if a mechanistic model is to be employed to predict the performance of a reactor. One could attempt to define and to estimate the required parameters for both phenomena using the results of the fluidized bed experiments. This approach to the problem was not used in this study since there would be a large expenditure of computer time using the fluidized bed models. The full justification for estimating the kinetic parameters independently of the fluidized bed is presented in Chapter 5.

It was decided instead to estimate the kinetic parameters separately in a system where the flow within the reactor was accurately known and only the kinetic model and the associated kinetic parameters were unknown.

A packed bed reactor was chosen to study the kinetics of the reaction. The modelling of these reactors is common practice and the flow and temperature can be described quite accurately as shown in Appendix F. Thus, with the flow of gas through the reactor accurately known and the temperatures throughout the reactor measured the only unknown would be the kinetic model and the associated parameters. In this way, the kinetics can be investigated without the added complication of uncertainty in the flow of the reactants which most certainly would complicate the analysis if performed using the fluidized bed data.

At the beginning of the overall study very little information was available concerning both the performance of the fluidized bed and the

hydrogenolysis of n-butane. Two simultaneous studies were initiated to gather the primary information concerning both these topics. The initial study of the kinetics was performed by A. Orlickas (02).

The work reported in this chapter covers the total kinetic study. A summary of the initial work by Orlickas is presented in section 4.1. The initial investigation of the performance of this first kinetic model in the fluidized bed models, as reported in Chapter 5, indicated that further investigation of the kinetics was necessary. A chronological description of the total investigation of the kinetics would be very disjointed. Thus, the various aspects of the parameter estimation are divided into sections and all studies performed are reported in the appropriate sections. These sections include: the experimental apparatus, the reactor and reaction models, the design of experiments, the estimation of parameters and the analysis of confidence in the model. The justifications for the extension to the more rigorous and complex models and analysis are presented in the appropriate sections.

4.1 PREVIOUS WORK

The initial packed bed reactor study for the purpose of formulating a kinetic model and estimation of the necessary parameters was carried out by Mr. Algis Orlickas (02). The resultant model and the estimated parameters were incorporated into several fluidized bed models and used for the initial study of the fluidized bed. These studies, as presented in the next chapter, clearly indicated that further investigation of the kinetics would be necessary and should be expected to improve the modelling of the fluidized bed.

Catalyst was prepared and a bench scale packed bed reactor constructed. A kinetic model was formulated and incorporated into a reactor model to describe the conversion and selectivity of the integral reactor. A series of experiments was performed using n-butane and also propane as feed. A block factorial experimental design was performed at three levels of temperature, flowrate and reactant concentration. Standard centre point replicate experiments were performed to monitor the changing catalyst activity. The required kinetic parameters were estimated and a technique developed for the grouping of parameters during the search. Models for the changing catalyst activity were also investigated. Individual confidence regions were estimated for each parameter and an error analysis of the observed mole fractions of the reactor effluent data was performed.

This study represented the initial stage of work reported in this chapter.

4.2 EXPERIMENTAL PROCEDURE

A schematic of the flow system and packed bed reactor is shown in Figure 4.1. The reaction was carried out at essentially atmospheric pressure by the downflow of reactants through a 0.276 cm. I.D. by 19.0 cm. long packed bed of 10.% nickel on silica gel catalyst. All lines except for the reactor and preheater were 1/8 in. O.D. copper tubing so as to reduce dead volume. The reactor effluent was sampled by means of a gas sample valve and analyzed by gas chromatography (Appendix C).

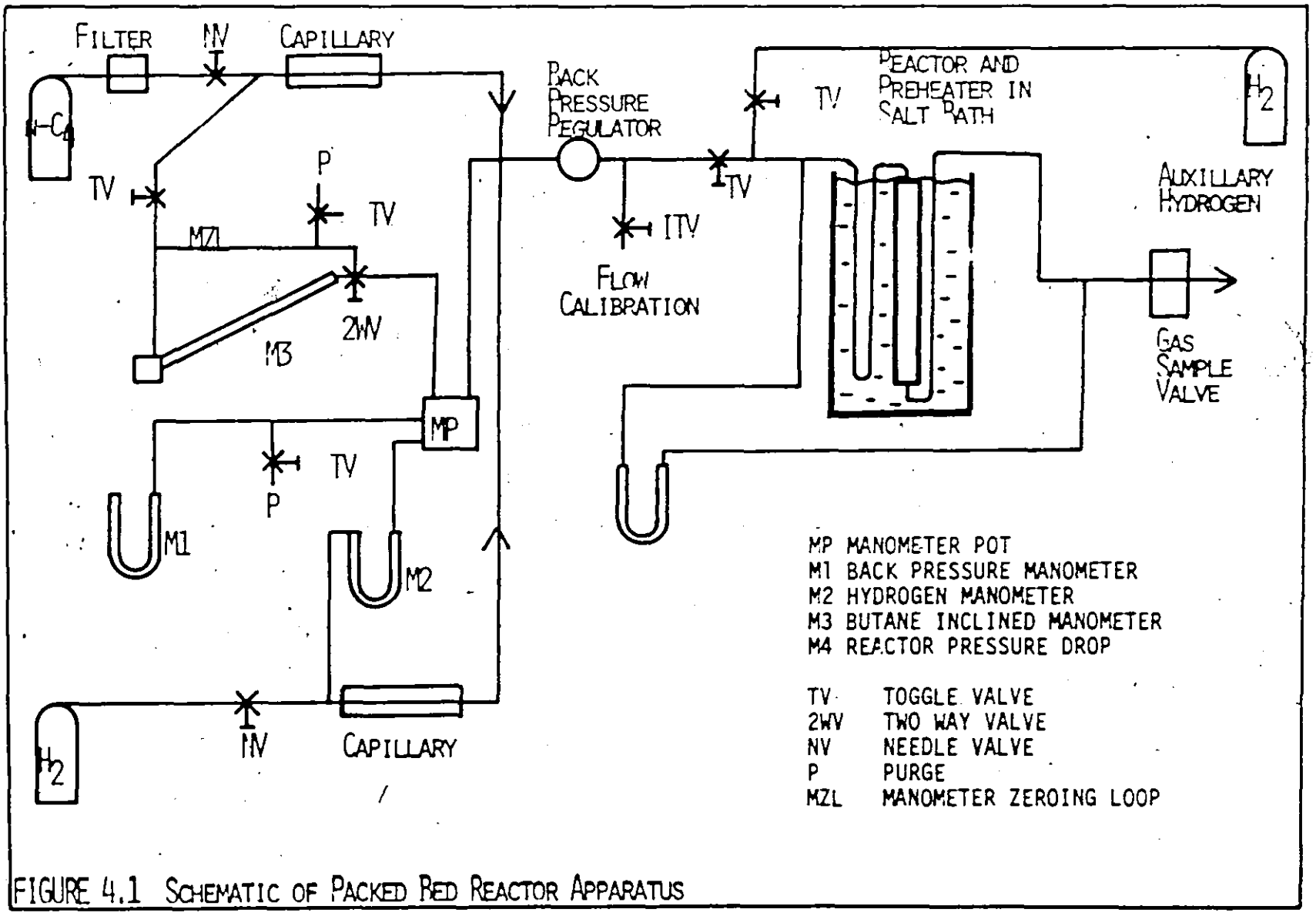


FIGURE 4.1 SCHEMATIC OF PACKED BED REACTOR APPARATUS

FEED SYSTEM

The flowrate of feed gas was measured by means of the pressure drop across a capillary and controlled with a needle valve. The calibration procedure and curves are given in Appendix A. A constant pressure of 11.90 in. of mercury as measured on a mercury manometer was manually maintained using a Fairchild-Hiller model 10BP back-pressure regulator. Thus any slight change in the reactor pressure drop caused by changing the flowrate would not affect the calibrations of the two flow meters. The feed gas was taken from high pressure cylinders. The same gases were used for both packed bed and fluidized bed studies. The hydrogen was of minimum purity of 0.9999 and was purchased from Canadian Liquid Air. The n-butane was Matheson C.P. grade with a minimum purity of 0.99. Chromatographic analysis indicated only iso-butane (0.004) and a trace of propane.

Many modifications were made to the original apparatus. Because of the low flow rates of gas and the need to change operating concentrations quickly the dead volume in the system had to be reduced to a minimum. All lines were 1/8 in. O.D. copper and two purge valves were added to the feed system. Because of the low n-butane flow and since Meriam oil adsorbes n-butane, thus, changing its density, an inclined mercury manometer was used to monitor the n-butane flow. An auxillary hydrogen cylinder was added to supply an uninterrupted, oxygen free, supply of hydrogen to the reactor so that the capillary flow meter calibrations could be checked during a run.

REACTOR

The reactor and feed preheating coils were immersed in a constant

temperature bath. Heat was supplied to the bath by two 1500. watt Chromalox immersion heaters which were manually controlled with a Variac transformer. Hitec heat transfer salt (E.I. Dupont Corp.) with a melting point of 275°F. was the fluid in the bath. Hitec is a eutectic mixture of potassium nitrate, sodium nitrate and sodium nitrite and can be used to 1100°F. A two-bladed stirrer was immersed in the insulated bath to produce a uniform temperature throughout the bath. The preheater coil is approximately 3. ft. of 1/8 in. O.D. stainless steel tubing completely immersed in the salt bath.

The reactor was 0.276 in. I.D., 3/8 in. O.D. stainless steel held vertically and completely immersed in the salt bath. The catalyst was supported on a 200 mesh stainless steel screen held by a Swagelock fitting at the bottom. The reacting gas was introduced at the top of the bed and flowed downward. The reactor was substantially modified and altered throughout the series of experiments. The reactor used in the initial study was 25.0 cm. long and contained three 1/16 in. ceramo chromel-alumel thermocouples which were inserted through the reactor wall from the sides and silver soldered. They were located at 1., 9. and 17. cm. from the top of the reactor and were positioned on the centerline of the reactor. For the temperature range over which the reaction rate was to be studied, the bed was too long. Also a more accurate measure of the temperature profile was needed. The bed was shortened to 19.0 cm. and thermocouples placed at 1.0, 3.6, 6.2, 11.4 and 16.5 cm. from the top of the bed along the centre-line. An additional thermocouple was placed on the inside wall of the reactor at 11.4 cm. Stainless steel Swagelock fittings were used only at the top and

bottom of the reactor and the feed and exit tubing were connected by silver solding to reduce the chance of leaks.

EFFLUENT GAS ANALYSIS

The product gas from the reactor was analyzed with a gas chromatograph equipped with a Varian Aerograph plunger-type gas sample valve. The analysis was changed a number of times to increase the accuracy and to reduce the analysis time from 19. to 5. minutes. A complete description of the calibration procedure and the series of analysis schemes that were used are given in Appendix C.

REACTOR OPERATION

The catalyst was dried at 200.°C. for three hours. The reactor tube was vibrated with a hand vibrator while filling with catalyst to the required depth (± 0.2 cm.). The feed preheater was attached and the reactor leak tested. The hydrogen feed was turned on and the reactor slowly (15. min.) lowered into the hot salt bath to avoid the sudden vaporization of water adsorbed during the filling of the reactor. The catalyst was reduced at 550.°F. for eight hours using the auxiliary hydrogen cylinder. The salt bath temperature was lowered to about 400.°F. and left overnight. A similar conditioning process is carried out for the fluidized bed reactor except that the temperature dropped to almost room temperature overnight. This difference should be unimportant since no oxygen is allowed to contact the catalyst and the catalyst activity is determined by the upper conditioning temperature (S4).

The feed system is purged of oxygen which would immediately oxidize the catalyst. For one day before an experimental trial both the hydrogen and the n-butane are fed through the feed system and exhausted to remove any oxygen from the system.

The desired reacting conditions are obtained by adjusting the hydrogen and n-butane flows and the reactor temperature as measure by the thermocouples. Care must be taken to ensure that the hydrogen-to-n-butane feed ratio never drops below 3.0. At a ratio lower than this, carbon deposition on the catalyst may occur. This would be detected by a rapid increase in the reactor pressure drop and the catalyst bed would have to be replaced. Both the desired hydrogen and n-butane flows and the back-pressure on the feed system of 11.90 in. of mercury are set. The desired reactor temperature is set by adjusting the heater Variac control. The thermocouples in the reactor are monitored on a 12-point chart recorder. The thermocouple 3.6 cm. from the top of the reactor is also continuously monitored on a digital volt meter. This is the thermocouple closest to the possible hot-spot and is the best indicator of the thermal steady-state of the reactor. Since about 0.025 mv. is equivalent to 1.0°F. the digital voltmeter provides an excellent indication of temperature drift and thus the heat input to the salt bath can very quickly be adjusted to obtain steady state. The digital voltmeter also provides a check of the calibration of the strip chart recorder.

A sample is taken after four minutes if no visible change is observed in the feed flows (as indicated by the manometers) or the back-

pressure and the temperature drift is less than 0.003 mv. per minute. A check is made to ensure that the chromatograph filament current is correctly set. The pressure drop across both capillary flow meters is recorded along with the reactor pressure drop. The flowrate of the reactor effluent is measured using a soap bubble flow meter.

4.3 KINETIC AND REACTOR MODELS

The background information and a literature survey of packed bed reactors and the hydrogenolysis of small paraffins is presented in sections 2.1 and 2.2. The specific models used in this study and the justification of the assumptions made are presented in this section. Their evolution is traced as they were modified in the iterative procedure of experimental redesign.

4.3.1 HYDROGENOLYSIS OF N-BUTANE

In the presence of excess hydrogen there will be no formation of coke or unsaturated hydrocarbons. There are six reactions that can be written to describe the family of reactions that can occur.

$$C_4H_{10} + H_2 \longrightarrow C_3H_8 + CH_4 \qquad 4.1$$

$$C_4H_{10} + H_2 \longrightarrow 2C_2H_6 \qquad 4.2$$

$$C_3H_8 + H_2 \longrightarrow C_2H_6 + CH_4 \qquad 4.3$$

$$C_2H_6 + H_2 \longrightarrow 2CH_4 \qquad 4.4$$

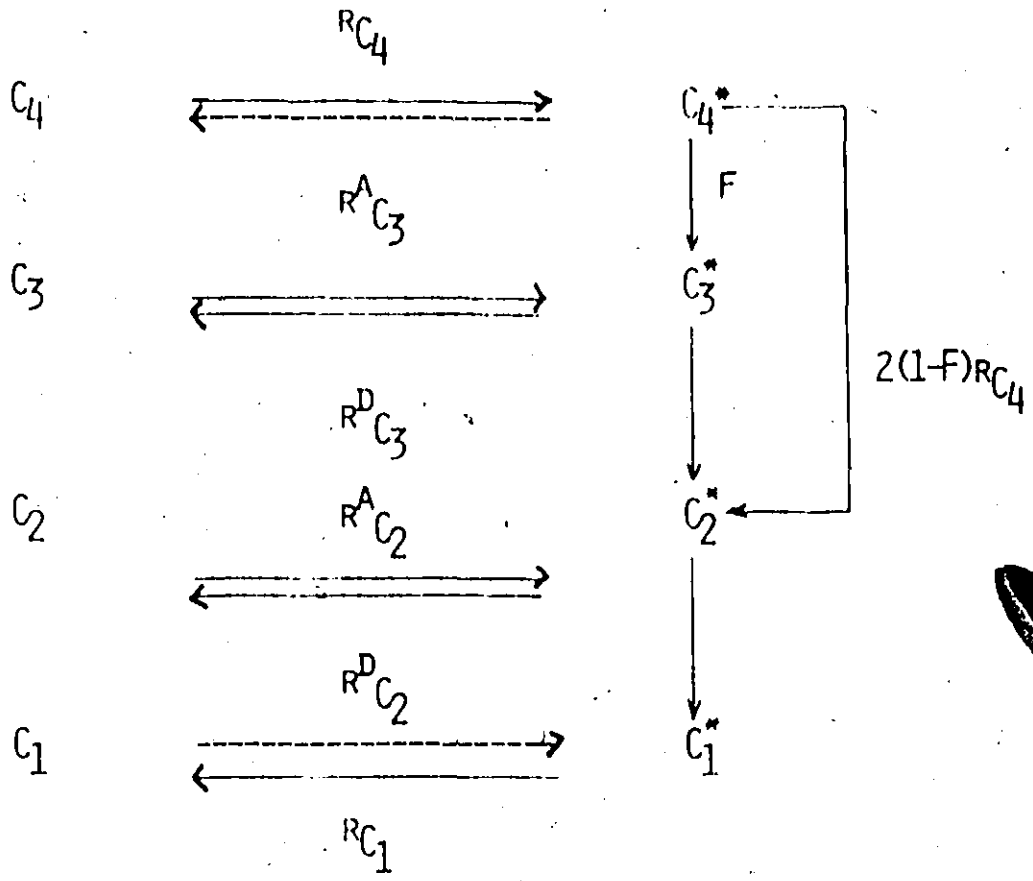
$$C_4H_{10} + 3H_2 \longrightarrow 4CH_4 \qquad 4.5$$

$$C_3H_8 + 2H_2 \longrightarrow 3CH_4 \qquad 4.6$$

In order to describe the reaction rate of butane, in an integral reactor, it is necessary to know the hydrogen concentration at every point. Since the hydrogenolysis of the products, propane and ethane, (equations 4.3, 4.4 and 4.6) occurs simultaneously, it will be necessary to include these reactions in the description as well since they also consume hydrogen. Moreover, there are other interactions, such as surface coverage by adsorbed molecules, that will affect the butane kinetic model. Therefore, a full or partial description of the other reactions is necessary in order that the parameters estimated from the experimental, integral bed data be meaningful.

Reactions 4.5 and 4.6, as such, were assumed not to occur because of the low probability of breaking two or three of the carbon-carbon bonds simultaneously. A schematic diagram of these reaction paths is shown in Figure 4.2 (as suggested by Professor R. B. Anderson and Dr. J. C. Kempling studying these same reactions on a ruthenium catalyst). For simplicity this diagram shows only the major compounds that are involved in the reaction paths. The compounds labelled C_1, C_2, C_3 and C_4 are the hydrocarbon species in the gas phase. The compounds labelled C_1^*, C_2^*, C_3^* and C_4^* represent the hydrocarbon species that are absorbed on the surface of the catalyst. All hydrocarbon cracking is assumed to occur through the breaking, one at a time, of the carbon-carbon bonds of these highly active adsorbed complexes. Rate expressions are developed to describe the reaction paths shown in Figure 4.2 with solid lines. Only the adsorption of butane and the desorption of methane paths are excluded, since in the rate

FIGURE 4.2 OVERALL REACTION SCHEME FOR HYDROGENOLYSIS OF N-BUTANE



R_{C_4} = RATE OF CRACKING OF BUTANE

$R^A_{C_3}$ = RATE OF ADSORPTION OF PROPANE

$R^D_{C_3}$ = RATE OF DESORPTION OF PROPANE

$R^A_{C_2}$ = RATE OF ADSORPTION OF ETHANE

$R^D_{C_2}$ = RATE OF DESORPTION OF ETHANE

R_{C_1} = RATE OF PRODUCTION OF METHANE

F = FRACTION OF C_4^* THAT CRACKS TO C_3^* AND C_1^*

——→ REACTION PATHS CONSIDERED

- - - - - - - - - - - - - - → ASSUMED = 0

equations yet to be developed net rates will be considered for these compounds.

One basic change only was made to the kinetic model. The results of the initial experiments indicated that the rate of adsorption of ethane (previous believed to be small) was important. The initial experiments were not sufficient to estimate this rate. The ethane mole fraction predicted in the reactor effluent was significantly higher than that measured when the experiments at a high rate of reaction and low hydrogen content were analyzed. Further investigation of the gas concentrations predicted by the fluidized bed reactor models indicated that these conditions of low hydrogen concentration and extensive reaction were very common in the emulsion phase. The readsorption of ethane must be incorporated into the kinetic model and the rate parameters accurately estimated. The rate equations developed here are essentially those of Orlickas (02) but with the readsorption of ethane included.

ASSUMPTIONS

The following assumptions were necessary since no method was available for observing the particular phenomena:

(i) Steady-state prevails on the catalyst surface, that is, rate of change of the active species on the catalyst surface is zero. This assumption requires that an equal number of active species of a particular type disappear through reaction and desorption as are formed through reaction and adsorption.

(ii) The fraction F representing the amount of C_4^* species that reacts to form C_3^* plus C_1^* species is 0.9 and is constant with temperature

and catalyst activity. From Figure 4.2 it may be noted that if F is not specified, an infinite number of sets of solutions could be obtained to describe the reaction scheme. F could not be predicted from experimental analysis of the effluent gas. It was estimated by Orlickas by extrapolating the selectivities of propane, ethane and methane to zero conversion of n-butane. If all the carbon-carbon bonds of the adsorbed n-butane species were broken with equal ease, F would be 0.667 . However, both the experimental observations and all the literature data indicate that a nickel catalyst is more selective to the fracture of the terminal carbon-carbon bond. It must be pointed out that any value of F between 0.7 and 0.9 would probably produce an equally valid, from a simulation point of view, set of kinetic parameters estimates. F was chosen as 0.9 since no measurement technique was available to provide better estimates. Moreover, it must be emphasized that the primary purpose of the kinetic model was to simulate rather than to uncover fundamental mechanisms.

(iii) The catalyst activity is defined as the ratio of the rate of reaction at any time to the rate of reaction at similar experimental operating conditions and at a time at which the activity is defined as the known or reference activity. Catalyst activity is assumed to be directly related to the number of active sites on the catalyst surface. All sites are assumed to have the same catalytic properties. A more detailed description of the proposed model for catalyst activity changes is given by Orlickas (02). The catalyst activity is assumed to have a linear effect on all rate processes involved in the reaction, and, therefore,

a factor for activity is included in all rate expressions. This factor is the ratio of the rates or frequency factors at the operating conditions under study to those at a standard operating condition. The catalyst activity for an experimental trial is determined from a standard experiment performed just before and just after that trial. The activity is reflected by both but more strongly by the activity of the experiment following the trial. The catalyst activity (k/k_o) for the n'th experiment was defined for this study as:

$$(k/k_o)_n = [(k/k_o)_{n-1} + 2.(k/k_o)_{n+1}]/3. \qquad 4.7$$

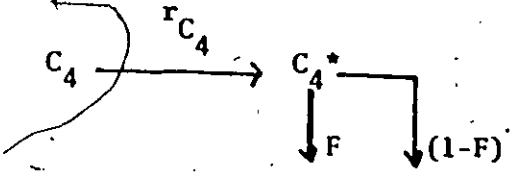
where the subscripts n-1 and n+1 refer to the previous and following experiments respectively at a standard operating condition. The method of calculating the catalyst activity from the experiments at a standard condition is included in section 4.5 where the method of parameter estimation is presented. Again it must be emphasized that the primary purpose of the kinetic model was to simulate rather than to uncover fundamental mechanisms.

(iv) First order adsorption, desorption and reaction kinetics with respect to the hydrocarbons were assumed. Literature data indicated these orders of reaction were close to first order. This assumption greatly reduced the number of parameters to be estimated.

RATE EXPRESSIONS

Figure 4.2 can be broken down into sections according to components and the equations describing adsorption, desorption and reaction formulated.

n-BUTANE



The net rate of disappearance of butane is described by the analysis first proposed by Cimino, Boudart and Taylor (C2):

$$r_{C_4} = \frac{k}{k_o} \cdot k_B \cdot \exp(-\Delta E_B/RT)\ P_{C_4}^{\ m} P_{H_2}^{\ n} \qquad 4.8$$

where r_{C_4} = rate of reaction (moles/sec.gm. catalyst)

ΔE_B = activation energy for butane reaction (cal./gm. mole)

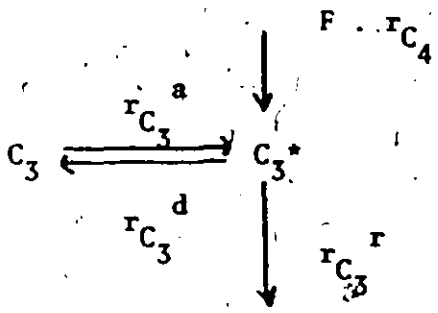
k_B = frequency factor for butane reaction (moles/sec.gm. catalyst atm.$^{-(m+n)}$)

P_{C_4}, P_{H_2} = partial pressures of butane and hydrogen, respectively (atm.)

m,n = constants

The term k/k_o represents the catalyst activity as previously defined.

PROPANE



Separate rate expressions are required to describe the adsorption and desorption of propane. The rate of adsorption can be described by:

$$r_{C_3}^{a} = \frac{k}{k_o} \; k_{C_3}^{a} \cdot \exp(-\Delta E_{C_3}^{a}/RT) P_{C_3}^{m'} P_{H_2}^{n'} \qquad 4.9$$

where $r_{C_3}^{a}$ = rate of adsorption of propane (moles/sec.gm. catalyst

$k_{C_3}^{a}$ = frequency factor (moles/sec.gm.cat.atm.$^{-(m'+n')}$

$\Delta E_{C_3}^{a}$ = activation energy for adsorption (cal./gm.mole)

P_{C_3} = partial pressure of propane (atm.)

m', n' = constants

Let K_{P2} represent the ratio of the rate of reaction on the surface to the rate of desorption

$$K_{P2} = \frac{r_{C_3}^{r}}{r_{C_3}^{d}} = \frac{k_{C_3}^{r} \exp(-\Delta E_{C_3}^{r}/RT) \cdot \theta_3^*}{k_{C_3}^{d} \exp(-\Delta E_{C_3}^{d}/RT) \cdot \theta_3^*} \qquad 4.10$$

where $r_{C_3}^{r}$ and $r_{C_3}^{d}$ = rates of reaction and desorption (moles/sec. gm. catalyst)

$k_{C_3}^{r}$, $k_{C_3}^{d}$ = frequency factors (moles/sec.gm. catalyst)

$\Delta E_{C_3}^{r}, \Delta E_{C_3}^{d}$ = activation energies for reaction and desorption (cal./gm. mole)

θ_3^* = fraction of active surface sites covered by C_3^* species

Equation 4.10 can be condensed to:

$$K_{P2} = k_{P2} \exp(-\Delta E_{P2}/RT) \qquad 4.11$$

where $k_{P2} = k_{C_3}^{r}/k_{C_3}^{d}$

$$-\Delta E_{P2} = -\Delta E_{C_3}{}^{r} + \Delta E_{C_3}{}^{d}$$

From a mass balance on C_3^* assuming pseudosteady state on the surface:

$$F \cdot r_{C_4} + r_{C_3}{}^{a} = r_{C_3}{}^{d} + r_{C_3}{}^{r} = r_{C_3}{}^{d} + K_{P2} \cdot r_{C_3}{}^{d} \qquad 4.12$$

Therefore:

$$r_{C_3}{}^{d} = \frac{F \cdot r_{C_4} + r_{C_3}{}^{a}}{(1. + K_{P2})} \qquad 4.13$$

The net rate of desorption of propane is defined as:

$$r_{C_3} = r_{C_3}{}^{d} - r_{C_3}{}^{a} \qquad 4.14$$

Combining equation 4.13 with equation 4.14

$$r_{C_3} = \frac{F \cdot r_{C_4} - K_{P2} r_{C_3}{}^{a}}{(1. + K_{P2})} \qquad 4.15$$

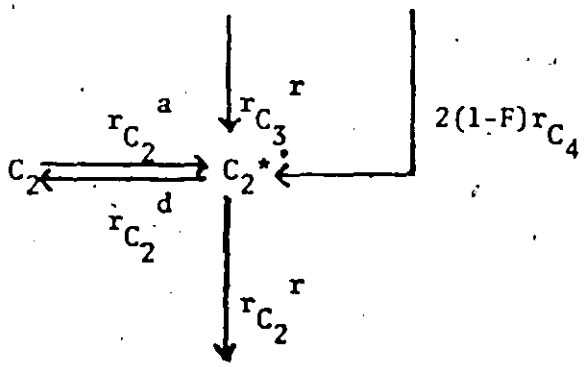
Therefore the rate of production of propane may be represented by:

$$r_{C_3} = \frac{F \cdot r_{C_4} - \frac{k}{k_o} \cdot K_{P1} \cdot \exp(-\Delta E_{P1}/RT) P_{C_3}{}^{m} P_{H_2}{}^{n}}{1. + k_{P2} \cdot \exp(-\Delta E_{P2}/RT)} \qquad 4.16$$

where $K_{P1} = K_{P2} \cdot k_{C_3}{}^{a}$

$$-\Delta E_{P1} = -\Delta E_{C_3}{}^{r} + \Delta E_{C_3}{}^{d} - \Delta E_{C_3}{}^{a}$$

ETHANE



The rate expressions including the adsorption and desorption are essentially the same as those for propane. The rate of adsorption can be described by:

$$r_{C_2}^{\ a} = \frac{k}{k_o} \cdot k_{C_2}^{\ a} \cdot \exp(-\Delta E_{C_2}^{\ a}/RT) P_{C_2}^{\ m''} P_{C_2}^{\ n''} \qquad 4.17$$

where $r_{C_2}^{\ a}$ = rate of adsorption of ethane (moles/sec.gm. catalyst)

$k_{C_2}^{\ a}$ = frequency factor (moles/sec.gm. catalyst atm.$^{-(m''+n'')}$)

$\Delta E_{C_2}^{\ a}$ = activation energy for adsorption (cal./gm. mole)

P_{C_2} = partial pressure of ethane (atm.)

m'', n'' = constants

Let K_E represent the ratio of the rate of reaction on the surface to the rate of desorption:

$$K_E = \frac{r_{C_2}^{\ r}}{r_{C_2}^{\ d}} = \frac{k_{C_2}^{\ r} \exp(-\Delta E_{C_2}^{\ r}/RT) \cdot \theta_2^*}{k_{C_2}^{\ d} \exp(-\Delta E_{C_2}^{\ d}/RT) \cdot \theta_2^*} \qquad 4.18$$

where $r_{C_2}^{\ r}, r_{C_2}^{\ d}$ = rates of reaction and desorption (moles/sec.gm.catalyst

$k_{C_2}^{\ r}, k_{C_2}^{\ d}$ = frequency factors (moles/sec.gm. catalyst)

$\Delta E_{C_2}^{\ r}, \Delta E_{C_2}^{\ d}$ = activation energies for reaction and desorption (cal./gm. mole)

θ_2^* = fraction of active surface sites covered by C_2^* species

Equation 4.18 can be condensed to

$$K_E = k_E \exp(-\Delta E_E/RT) \qquad 4.19$$

where $k_E = k_{C_2}^{\,r}/k_{C_2}^{\,d}$

$$-\Delta E_E = -\Delta E_{C_2}^{\,r} + \Delta E_{C_2}^{\,d}$$

From a mass balance on C_2^* assuming pseudosteady state on the surface:

$$2(1-F)\, r_{C_4} + r_{C_3}^{\,r} + r_{C_2}^{\,a} = r_{C_2}^{\,d} + r_{C_2}^{\,r} = r_{C_2}^{\,d}(1+K_E) \qquad 4.20$$

Therefore:

$$r_{C_2}^{\,d} = \frac{2(1-F)r_{C_4} + r_{C_3}^{\,r} + r_{C_2}^{\,a}}{1 + K_E} \qquad 4.21$$

The net rate of desorption of ethane is defined as:

$$r_{C_2} = r_{C_2}^{\,d} - r_{C_2}^{\,a} \qquad 4.22$$

Combining equation 4.21 with equation 4.22

$$r_{C_2} = \frac{2(1-F)r_{C_4} + r_{C_3}^{\,r} - \bar{k}_o \cdot K_{E2} \cdot \exp(-\Delta E_{E2}/RT) P_{C_2}^{\,m''} P_{H_2}^{\,n''}}{1 + k_E \exp(-\Delta E_E/RT)} \qquad 4.23$$

where $K_{E2} = K_E \cdot k_{C_2}^{\,a}$

$$-\Delta E_{E2} = -\Delta E_{C_2}^{\,r} + \Delta E_{C_2}^{\,d} - \Delta E_{C_2}^{\,a}$$

METHANE AND HYDROGEN

By overall mass balance on equations 4.1 to 4.6 and assuming pseudosteady state, the rate equations for the production of methane and disappearance of hydrogen are:

$$r_{C_1} = 4\ r_{C_4} - 3\ r_{C_3} - 2\ r_{C_2} \qquad 4.24$$

$$r_{H_2} = 3\ r_{C_4} - 2\ r_{C_3} - r_{C_2} \qquad 4.25$$

SUMMARY

The rate equations given by 4.8, 4.16, 4.23, 4.24 and 4.25 are needed to describe the hydrogenolysis of n-butane. Assumed values were used for five of the kinetic parameters:

$$m,\ m',\ m'',\ \Delta E_{P1},\ \Delta E_{E2}$$

The values of m, m' and m" were assumed equal to one. This appeared to be a reasonable assumption in light of the reported literature in which the rates of reaction appeared essentially first order with respect to the hydrocarbon partial pressures. The values of ΔE_{P1} and ΔE_{E2} differ only from ΔE_{P2} and ΔE_E by the respective energy of activation for the rate of adsorption for propane and ethane. Limited literature studies indicated that it is very difficult to estimate this rate independently and that a value of 10. k.cal./mole was a reasonable estimate for the adsorption step for both gases. Thus for the purpose of parameter estimation:

$$\Delta E_{P1} = \Delta E_{P2} - 10{,}000 \qquad 4.26$$

$$\Delta E_{E2} = \Delta E_E - 10{,}000 \qquad 4.27$$

and values of ΔE_{P2} and ΔE_E were estimated using these relationships.

The kinetic parameters which must be estimated from experiments are:

$$k_B,\ \Delta E_B,\ n,\ K_{P1},\ K_{P2},\ \Delta E_{P2},\ n',\ K_{E2},\ K_E,\ \Delta E_E,\ n''$$

The kinetic parameters and equations will be combined with the fluid mechanical, the material and the energy balance equations for both reactors. The kinetic parameters will be estimated from packed bed experiments where the flow equations can be accurately described. They will be used in the fluidized bed models to assess the predictions of the various models for that reactor.

4.3.2 PACKED BED REACTOR

The kinetic parameters defined in section 4.3.1 were estimated by searching for the values which minimized the sum of squares of the difference between observed values and values predicted from a packed bed reactor model. The predicted values are obtained by solving the appropriate differential equations describing the reactor and reactions. This section describes both the specific packed bed reactor model and the assumptions made to formulate it.

The reactor model used first was the standard simple integral packed bed model: homogeneous, isothermal, isobaric and including only bulk axial flow. On the basis of sensitivity analysis it was modified to include axial temperature and pressure profiles before being used for the final estimation of the kinetic parameters. The model assumptions and their justifications are presented below.

SPECIFIC ASSUMPTIONS FOR MODEL

(i) The packed bed is assumed statistically homogeneous with all changes in the bed occurring continuously and smoothly. The bed diameter and the mean particle size are 0.70 cm. and 162μ respectively. Hlavacek (H2)

reports that a heterogeneous packed bed can be treated as a continuum if the tube diameter is greater than 10 particle diameters and the depth greater than 6.

(ii) The gas is assumed to flow in plug flow. Beek (B3) reports that if the particles are small the velocity profile is flat at least over the central portion of the cross-section. The exact solution to this problem is still unresolved.

(iii) Concentration gradients in the radial direction are assumed negligible. The packed bed encourages radial mixing and the diffusion path is small because of the small tube radius (0.35 cm.).

(iv) Axial diffusion can be neglected when compared to bulk flow. The detailed calculations supporting this assumption are given in Appendix F.

(v) There is no interparticle or intraparticle mass transfer limitations and the heat transfer rate is sufficient to keep the particles at the same temperature as the gas. Calculations supporting these assumptions are given in Appendix F.

(vi) The pressure drop across the reactor is linear as expected in a laminarly flowing system. The maximum observed pressure drop for the data used for parameter estimation was 0.17 atmospheres. Table 4.1 shows the effect of pressure on the model predictions of conversion and selectivity of ethane and propane for a constant pressure model. Both predictions are for the same conditions except for the reactor total pressure. At higher temperatures and more n-butane in the feed, the differences in the predictions are even greater. There was no measurable pressure drop or reaction when the empty reactor was run under these conditions.

ATM.	$P^{o}_{H_2}/P^{o}_{C_4}$	ml./sec.	°C.	CONV.	S_2	S_3
1.067	4.0	1.7	253.	80.9	0.254	0.398
1.134	4.0	1.7	253.	74.5	0.242	0.438

TABLE 4.1 EFFECT OF PRESSURE ON MODEL PREDICTIONS

(vii) There is no blank reaction. Experimental tests with the empty reactor at conditions far more severe than those used for parameter estimation showed no reaction.

(viii) The gases in the reactor are assumed to obey the ideal gas law.

(ix) The axial temperature profile through the reactor can be approximated by linear interpolation between the observed thermocouple measurements and the radial temperature gradients are small. The temperature profile for the most severe experiment used in the parameter estimation is shown in Figure 4.3. The first thermocouple measured the feed gas temperature above the catalyst bed. The sharpest temperature gradient is between there and the thermocouple 1.0 cm. into the bed. This is due to the fact that only the salt bath was used to preheat the feed. The thermocouple 3.6 cm. into the bed is the best indication of the magnitude of any hot spot. The magnitude and position of a hot spot will vary depending on the reaction conditions. Excluding the first 1.0 cm. of the bed, the maximum temperature range for the bed was 4.8 ^{o}C but for most of the data used for parameter estimation the range was less than half of this. The observed temperature profile is that which would be expected quantitatively in a packed bed reactor and the thermocouples were concentrated near the entrance so as to measure the critical region. The maximum observed temperature gradient between 1.0 cm. and 3.6 cm. is 1.0 °C. per cm. along the axis of the reactor. The radial temperature gradient was not measured. The well stirred heat transfer medium around the reactor would provide cooling. Based on the maximum observed axial temperature

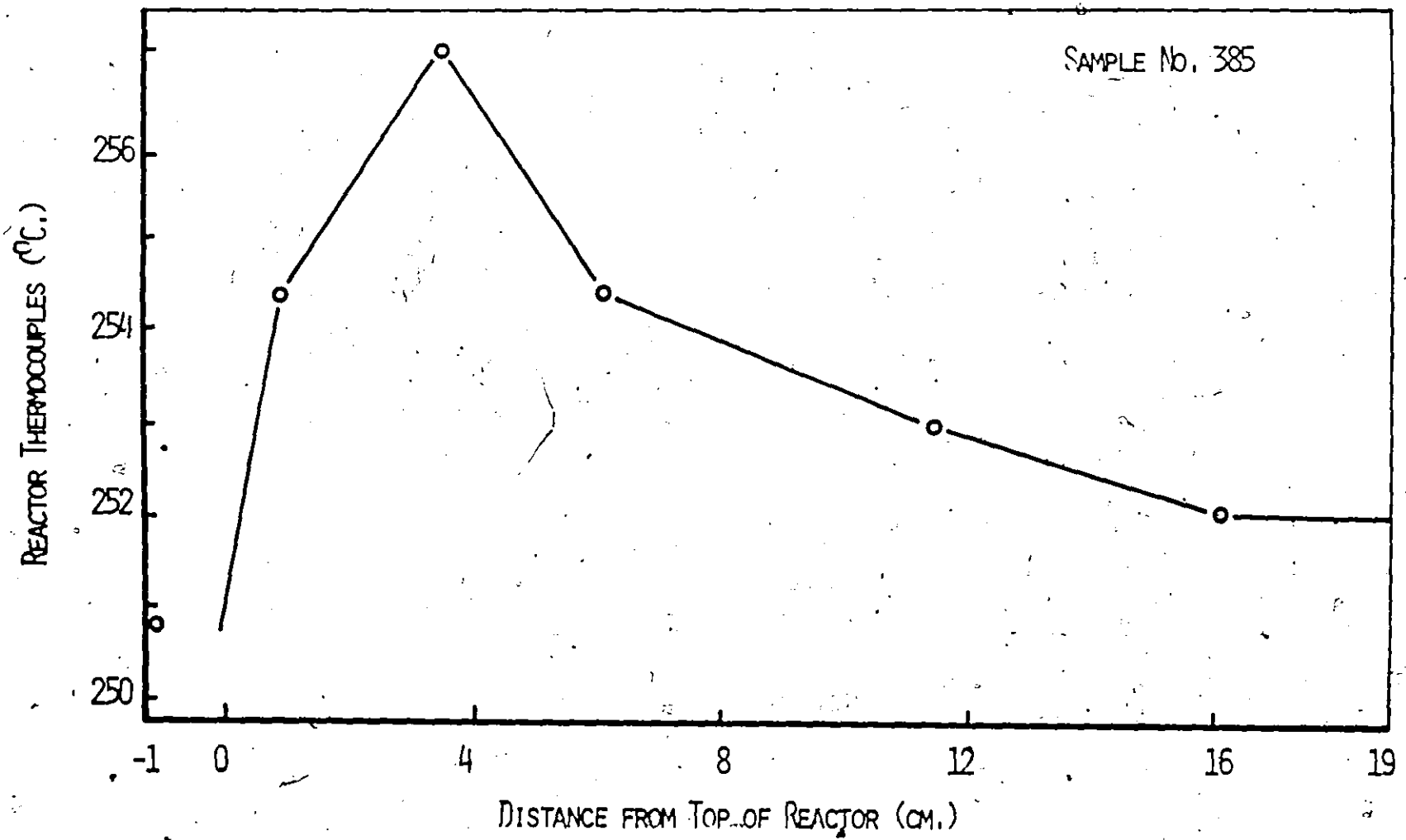


FIGURE 4.3 REACTOR THERMOCOUPLES AND ASSUMED REACTOR PROFILE FOR MOST SEVERE EXPERIMENT USED FOR PARAMETER ESTIMATION

gradient of 1.0°C. per cm. and the reactor radius of 0.35 cm. a rough estimate of the axial temperature gradient between 1.0 and 3.6 cm. along the reactor might be 0.35°C.

MODEL

From a mass balance on a differential height of a packed bed reactor:

$$\frac{dc}{dx} = \frac{-r_v}{u} \qquad 4.28$$

where C = concentration of reactant (gm. moles/cm.^{3})

$-r_v$ = rate of disappearance of reactant (gm.moles/sec.cm.^{3})

u = superficial velocity (cm/sec.)

x = length along reactor (cm.)

since $u = \frac{V}{A}$ and $C = \frac{P}{RT}$ 4.29

$$\frac{dP}{dx} = \frac{(R.T.A.)}{V} \cdot (-r_v) \qquad 4.30$$

where P = partial pressure of reactant (atm.)

T = temperature (°K.)

R = gas constant (atm. cm.^{3}/gm. mole °K.)

A = reactor cross sectional area (cm.^{2})

V = volumetric flow (cm.^{3}/sec.)

METHOD OF SOLUTION

The equations describing the rates of disappearance of the five components (4.8, 4.16, 4.23, 4.24, 4.25) were combined with equation 4.30 giving five coupled non-linear differential equations. These were

simultaneously integrated using a fourth order Runge-Kutta numerical integration technique. The step size was allowed to vary in order to monitor and to correct for the integration error and to increase the step if justified. The maximum allowable error was 10^{-6} atmospheres.

For calculational purposes the reactor was considered as six reactors in series. Each section was bounded by a thermocouple and the linear temperature profile, as shown in Figure 4.3, defined the temperature at any point in that section. A uniform linear pressure profile representing the total reactor pressure drop described the total pressure along the reactor. The average execution time for one reactor calculation required 0.5 second on a C.D.C. model 6400 computer.

4.4 DESIGN OF EXPERIMENTS

The statistical techniques for the design of experiments is only one, although a very important one, of the considerations in the total design or redesign of experiments for parameter estimation. This procedure requires the expenditure of time by the experimenter. Many recent studies on this subject indicate that these techniques should be applied as soon as possible, even after only a very few exploratory experiments have been completed and only the crudest estimates of the parameters obtained. Indeed, the poorest of estimates from the literature or the experimenter's intuition may be sufficient for all but a few of the parameters. Then, the experimenter can very early design and begin the right experiments for parameter estimation and/or model discrimination.

The preliminary packed bed experiments were performed according to a block factorial design (02). There was a large amount of uncertainty

about the reaction rates and catalyst activity as well as the dependability of the initial apparatus. Orlickas performed his set of experiments over two levels of flow and feed concentration and three levels of temperature. Each experimental trial was replicated and was followed by a trial at a standard condition (midpoint) to monitor the catalyst activity. All the data were obtained over a continuous ninety-six hour operation. The operating conditions are shown in Table 4.2. The preliminary kinetic model that was first entertained was of the polynomial type and so an orthogonal experimental design was chosen as a convenient initial experimental design to be performed. Analysis of the data and the requirements of the fluidized bed models indicated that a regression model would not be adequate. By attempting to investigate the effect of the independent variables over the total possible range, some of the operating conditions proved to be too severe. This is a very common occurrence during initial experimentation when a wide range of operating conditions are being explored. However, these experiments provided sufficient data for the formulation of a kinetic model and initial estimates of the required parameters.

Further experiments were necessary to obtain a more precise and accurate description of the kinetics of the reaction. These new experiments were necessary for a number of reasons:

(i) The temperature profile was not adequately defined since only three thermocouples were used in the experimental reactor. The original model assumed the reactor was isothermal since relatively small

	OPERATING CONDITIONS			
	FOR TWELVE TRIALS			FOR MID POINT
TEMPERATURE ($^{o}C.$)	246	258	282	258
RATIO (H_2^{o}/C_4^{o})	4.0	9.0		6.5
FLOW (ml./sec.)	1.0	1.8		1.4

TABLE 4.2 DESIGN OF EXPERIMENTAL TRIALS FOR INITIAL PARAMETER ESTIMATION

temperature differences were recorded.

(ii) The original reactor model was isobaric.

(iii) Experimental conditions close to those predicted to be occurring in the emulsion phase of the fluidized bed models must be investigated. Experiments with much lower hydrogen concentration and more extensive reaction must be used for parameter extimation. Moreover, the original experimental range was not sufficient to allow a reasonable estimation of the readsorption of ethane, a step which was occurring at a significant rate in the fluidized bed.

(iv) The original method of chromatographic analysis, as given in Appendix C, was not sufficiently accurate for experimental trials at high conversion.

(v) Uncertainty existed as to the exact catalyst voidage in the initial trials. This value and the corresponding value for the fluidized bed are critical if the kinetics are determined in the one reactor and then used in the other.

Because of these inadequacies the previous experiments could not be used to develop a revised kinetic model.

The criteria used for the design of the experiments as given by equation 3.14 was

$$\max \left| \sum_{u=1}^{n+1} \underline{X}_u \underline{\Sigma} \underline{X}_u^T \right| \qquad 4.31$$

over the control variables of temperature, feed ratio and flowrate. Strictly speaking for the design of experiments with a multivariate response $\underline{\Sigma}$ must be known. In this case, not knowing $\underline{\Sigma}$ an estimate was used. To obtain

this matrix five groups of three replicated experiments were performed with the modified apparatus and exit gas analysis technique. The experimental operating conditions were chosen to cover the expected ranges of temperature, flow and concentrations to be selected by the experimental design technique. In most cases the exact settings of these variables could only be determined once the reactor was operating since conditions of 50.% to 98.% conversion and at low hydrogen concentrations were beyond the range of the data used to develop the initial model.

Although an estimate of experimental covariance requires operating replicate experiments, that is, under conditions of identical settings of the control variables, some variation did occur within each set of three experiments. To compensate for this, minor adjustments were made to the observed responses. An average value of the control variables was calculated for each set of three replicates. Predicted model responses were calculated for each of the three actual control variable settings and for the average control variable settings. The differences between the calculated responses for the average control variable settings and those for the three actual experimental trials were determined. These differences were subtracted from the value of the measured experimental responses for each of the three experiments. The control variables for each experiment as well as the calculated average control variables are shown in Table 4.3a. It can also be seen from Table 4.3a that the adjustment made to each of the measured responses is very slight. The estimated variance-covariance matrix is shown in Table 4.3b. It is not distorted by known and detectable differences in the control variables and provides an

OPERATING CONDITIONS					RAW RESPONSE			ADJUSTED		
RUN	$P^{o}_{C_4}$	$P^{o}_{H_2}$	ml. sec.	°C.	CONV.	S_2	S_3	CONV.	S_2	S_3
224	.1275	.9426	2.01	270.43	.9956	.2401	.1936	.9974	.2402	.1880
225	.1315	.9382	2.01	270.38	.9959	.2439	.1882	.9960	.2434	.1884
226	.1293	.9409	2.01	270.75	.9960	.2542	.1759	.9943	.2547	.1789
AVG.	.1299	.9403	2.01	270.52						
229	.1138	.9582	2.24	260.57	.5798	.2325	.4838	.5695	.2320	.4863
231	.1119	.9615	2.28	260.57	.5799	.2213	.4769	.5807	.2213	.4772
232	.1090	.9637	2.29	260.44	.5635	.2212	.4852	.5750	.2216	.4820
AVG.	.1109	.9620	2.26	260.53						
233	.2168	.8360	1.53	255.56	.7720	.2215	.3764	.7611	.2198	.3825
234	.2153	.8379	1.53	255.57	.7615	.2330	.3822	.7546	.2320	.3860
235	.2158	.8457	1.57	255.56	.7380	.2332	.3856	.7574	.2360	.3758
AVG.	.2160	.8397	1.54	255.56						
246	.1274	.9101	1.04	260.26	.9218	.2500	.3204	.9179	.2494	.3240
247	.1257	.9117	1.04	260.25	.9253	.2485	.3237	.9244	.2485	.3244
248	.1264	.9110	1.04	260.11	.9194	.2478	.3204	.9216	.2479	.3181
AVG.	.1265	.9107	1.04	260.21						
255	.2134	.8426	1.60	260.59	.9612	.2323	.2294	.9604	.2317	.2319
256	.2112	.8448	1.61	260.62	.9510	.2318	.2351	.9550	.2333	.2282
257	.2122	.8438	1.60	260.61	.9500	.2337	.2358	.9511	.2341	.2340
AVG.	.2123	.8437	1.60	260.61						

TABLE 4.3a DATA FOR ESTIMATION OF VARIANCE-COVARIANCE MATRIX FOR PACKED BED EXPERIMENTAL DESIGN

CONVERSION	S_2	S_3
0.15225	-0.13544	-0.05618
-0.13544	0.33687	-0.06184
-0.05618	-0.06184	0.19344

TABLE 4.3b ESTIMATED VARIANCE-COVARIANCE MATRIX OF CONVERSION AND SELECTIVITIES OF ETHANE AND PROPANE FOR EXPERIMENTAL DESIGN

estimate of the error in replicated experimental trials performed at the exact same settings of the control variables.

Preliminary experimental design selection indicated that better designs could be obtained, as measured by equation 4.31, if only n-butane rather than a proposed feed of n-butane and methane was used. Also, a reactor length of 25.0cm. as used for initial kinetic investigations was too long. A length of less than 16.0 cm. was not acceptable since the chosen designs would place all temperatures at the upper limit of temperatures which could be achieved in the fluidized bed. At this time the operating conditions to be selected for the final fluidized bed studies were now known. As a compromise a reactor length of 19.0 cm. was chosen.

To use equation 4.31 the determinant must be evaluated over the full range of control variables as indicated in Table 4.4. The temperature range was defined by the upper possible limit of operation in the fluidized bed. A flow much below 1.0 ml./sec. would come close to the limit of some of the model restraints for the packed bed and a flow greater than 2.7 ml./sec. produced an excessive pressure drop. A ratio lower than 3.0 could produce coking and a ratio greater than 6.0 produced little reaction. The reaction conditions generally chosen by the design were at high temperature, high flow and low ratio.

The maximization of the determinant in equation 4.31 could be achieved by a direct grid search but because of the high computer time expenditures involved, a Monte Carlo technique was employed (C9, B16, J3).

VARIABLE	RANGE	INTERVAL
Temperature (°F.)	485. - 525.	1.0
Flow (ml./sec.)	1.0 - 2.7	0.1
Ratio ($P^{o}_{H_2}/P^{o}_{C_4}$)	3.0 - 6.0	0.1

TABLE 4.4 RANGE OF INDEPENDENT VARIABLES FOR THE DESIGN OF EXPERIMENTS FOR PARAMETER ESTIMATION

A set of twelve "best" experiments to obtain the parameter estimates was determined. The initial $\underline{X}$ matrix was determined for the experimental trials reported in Table 4.2. The derivatives of each response with respect to the parameters were determined for each of the proposed trials chosen by the Monte Carlo search. The derivatives for each of these proposed trials were added, one at a time, to the $\underline{X}$ matrix and then the determinant of $\underline{X}^T \underline{\tilde{\Sigma}}^{-1} \underline{X}$ calculated. The operating conditions resulting in the maximum value of the determinant were selected as the next set of operating conditions to be added to the design and its derivatives added to the $\underline{X}$ matrix.
This procedure was repeated twelve times. The chosen operating conditions are shown in Table 4.5.

Unlike single response data, the data for a multiple response kinetic study with a series reaction can provide information about all the parameters even at 100% conversion of the primary reactant. Visual analysis of the expected responses suggested that this should be a reasonable design since many of the operating conditions selected were in the range where ethane readsorption would be occurring to an appreciable degree. Even though these conditions would result in no n-butane and very little propane in the reactor effluent the model would have to treat their reactions correctly since they affect not only when and how ethane is generated in the reactor but also the rate of consumption of hydrogen. If during the experiment, the chosen operating conditions did not produce the expected responses approximately the operating conditions were adjusted slightly to achieve

	°F.	ml./sec.	RATIO	EXPECTED RESPONSES		
				CONV.	S_2	S_3
a	488.	1.1	3.6	0.999	.300	.023
b	489.	1.5	3.2	1.000	.256	.001
c	496.	2.0	3.2	1.000	.120	.000
d	500.	2.4	3.3	1.000	.185	.000
e	516.	2.0	3.8	1.000	.061	.000
f	488.	2.1	3.2	0.851	.268	.348
g	485.	1.4	3.3	0.949	.308	.220
h	494.	2.3	3.1	1.000	.269	.003
i	490.	1.6	3.4	0.989	.314	.100
j	520.	1.0	6.0	1.000	.134	.001
k	486.	1.1	3.2	1.000	.114	.000
l	490.	1.7	3.1	1.000	.197	.000

TABLE 4.5 OPERATING CONDITIONS CHOSEN BY EXPERIMENTAL DESIGN FOR PARAMETER ESTIMATION

them. Since the initial parameter estimates were wrong, the predictions were wrong. The experiments were chosen to give the predicted responses.

4.5 EXPERIMENTAL RESULTS AND PARAMETER ESTIMATION

The experiments designed for parameter estimation as described in section 4.4 were performed. In addition, experiments at the same flow and feed composition but different temperatures were performed. These experiments were chosen when it was observed that some of the designed experiments exhibited a very severe temperature profile.

In addition, five sets of five replicated experiments were later performed in an attempt to obtain an estimate of the experimental error variance-covariance matrix. The total data for the packed bed studies are presented in Appendix I. Both the raw data and the analyzed results are listed.

Experiments 441 to 488 were performed to obtain an estimate of the experimental variance-covariance matrix. Four sets of five replicated experiments were performed. The five replicates were performed one after the other. Later analysis of these data showed that the experiments had not been randomized properly. Randomization of experiments was required since the catalyst activity changed slightly with operation conditons. Thus, if the catalyst activity were not known exactly for each experimental trial the residual after the kinetic parameters had been estimated would be larger than if the catalyst activity were known exactly. Since the "variance-covariance" experimental trials were performed serially there would be little or not change in the catalyst activity since the operating conditions

had not changed. Thus the estimated variance-covariance matrix only reflected the experimental error associated with replicated experiments at the same operating conditions. It could not be used as an independent estimate of the experimental error associated with replicated experiments performed at slightly different catalyst activities. Since sufficient experimental trials had been designed and performed for parameter estimation the alternate method of Box and Draper (B6) as given by equation 3.9 was used for parameter estimation. The consequences of not having an independent estimate of the variance-covariance matrix resulting from experimental error will be discussed in section 4.6

The results of the variance-covariance experiments were analyzed to ensure that all four of the hydrocarbon responses from the chromatograph were linearly independent. Box et al (B7) have indicated the problems which may arise when parameters are estimated from measured experimental responses which are not independent. Their recommended procedures relating to the eigen values-eigen vectors of the responses were employed and all four responses were found to be independent. The chromatograph was used as an absolute instrument and the responses were not normalized. Instead, a sample of the same constant volume, pressure and temperature was analyzed each time. Only four of the five components (excluding hydrogen) were measured in the analysis.

The formal procedure for choosing a transformation of the responses so as to obtain a constant error variance-covariance matrix over the entire response surface is presented by Box and Cox (B5). The three

forms of the response investigated for this study were:

1. (chromatographic area) x (attenuation)
2. chromatographic area
3. (chromatographic area) x $\sqrt{\text{attenuation}}$

Both the second and third forms of the experimental responses proved acceptable on the basis of a Bartlett test on the variance elements (K16). The third form was better than the second. It was reasoned that the magnitude of the variance-covariance matrix for the responses was related to both the area of the response peak and to a lesser degree to the amount of each component in the sample being analyzed. This was the form of the response used in parameter estimation.

The experiments used for parameter estimation are shown in Table 4.6. The temperature profiles are listed in Appendix I along with the parameter estimation program showing the exact form of the input data. Data 375 to 390 are from the experimental design. Some of the data points obtained using the designed operating conditions were omitted because they were beyond the range of the model and/or exhibited excessive temperature profiles or reactor runaway. It is not uncommon when using experimental design techniques early in a study that some of the chosen experiments cannot be used for parameter estimation, since extreme conditions are often chosen. It is often quite difficult to know which experimental conditions may be too severe. Experiments 421 and 425 were performed at the end of the designed run at two different temperatures. Points 447 to 484 are from those designed to obtain an estimate of the experimental variance-covariance matrix

TABLE 4.6 EXPERIMENTS USED FOR PARAMETER ESTIMATION

RUN	$P_{C_4}^{o}$	$P_{H_2}^{o}$	ml./sec.	S_1	S_2	S_3	CONV
375	.268	.884	2.12	2.607	.245	.301	95.78
380	.265	.841	1.43	2.764	.248	.247	98.90
368	.287	.884	2.33	2.991	.253	.168	99.68
390	.252	.871	1.70	2.588	.263	.295	97.25
421	.152	1.007	2.24	2.218	.236	.437	80.86
425	.150	1.006	2.23	2.048	.223	.502	66.75
447	.215	.918	2.39	2.284	.235	.415	89.76
458	.150	.964	2.06	2.148	.245	.454	89.13
466	.101	1.047	2.66	2.587	.307	.266	99.23
484	.177	.972	2.70	2.388	.252	.369	94.98
347	.212	.922	1.80	2.328	.241	.297	87.87
378	.208	.921	1.79	2.324	.258	.387	92.45
383	.207	.923	1.82	2.203	.231	.445	81.34
394	.200	.929	1.80	2.170	.228	.458	79.95
418	.207	.922	1.78	2.173	.231	.455	77.14
423	.209	.921	1.79	2.167	.224	.462	76.09
442	.156	.972	2.30	2.269	.243	.415	90.61
463	.153	.974	2.28	2.289	.262	.396	94.69
487	.154	.970	2.23	2.362	.264	.370	96.31

over the range of operating conditions investigated. The remaining points represent a few of the experiments for monitoring the catalyst activity throughout the study. Replicate experiments were performed at each operating condition. The second of the two replicates was always chosen for parameter estimation. The reactor and the reaction conditions were more stable and a larger chromatogram could be obtained from observing the first analysis and setting the appropriate attenuations. A compromise was made here with respect to statistical considerations since only one of the replicates could be included because of computer time limitations.

The parameters to be estimated are:

ΔE_B, n', K_{P1}, K_{P2}, ΔE_{P2}, n', K_{E2}, K_E, ΔE_E, n''

These parameters are estimated for a given value of k_B and catalyst activity. After the best estimates are determined, the catalyst activity which pre-multiplies the frequency factors for butane, propane and ethane is determined by equation 4.7. With the updated estimates of the catalyst activity the above parameters are estimated once more. This procedure is repeated until there is no further change in the parameter estimates. The frequency factor for butane is not included in this iterative cycle of parameter estimation because any change in the rate of reaction of butane is reflected in the catalyst activity and therefore a simultaneous search is not possible. If k_B were estimated each step, its estimated value and that of the catalyst activities would always change since there is an infinite set of these parameters that would satisfy the observed experimental results. It is the product of the two that is of interest. For this case, the process

of parameter estimation is an iterative procedure of first estimating a set of kinetic parameters and then independently estimating the catalyst activity at the experimental trials used to estimate the kinetic parameters.

Some of the kinetic parameters were transformed when used in the search routine. The transformations were:

ΔE searched = (ΔE actual) X 0.001

k searched = $\log_{10}$ (k actual)

n searched = n actual

This was only done to obtain numbers of a convenient magnitude to work with in the search routine.

It would be uneconomical to search for ten parameters simultaneously using a model of this complexity and the Rosenbrock search technique. More recent work at this university (W2) indicates that a simultaneous ten parameter search using the simplex search technique on a similar problem may be more efficient. In this case, however, the parameters were searched for in groups of two or three at a time using the Rosenbrock method. Parameters that were expected to be highly correlated were searched for simultaneously. The grouping of parameters generally used and the order in which they were searched were:

1. K_{P1}, K_{P2}
2. n', n"
3. K_E, K_{E2}, n"

After every other search cycle the activation energies were investigated. Although there is a strong correlation between the activation energies and

the corresponding frequency factors, the activation energies are very difficult to determine accurately. The use of the kinetic model was for prediction and the temperatures in both the fluidized and the packed bed reactors were within the same range. Thus, the increment of search for the activation energies was chosen to be 2.0 kcal./mole ^{o}R. and no finer grid was investigated.

Using the original parameter estimates from the initial study, eight search cycles as described above were performed. At that point it was discovered that the experimental variance-covariance matrix being used for weighting did not properly reflect the uncertainty in the catalyst. The method of Box and Draper (B5) was then employed to seek optimal parameter estimates. Three more search cycles were completed with very little change in the estimated parameters. On the third cycle, n and n' were the only two parameter estimates that were changing significantly from cycle to cycle. When they were over relaxed a large increase in the lack of fit resulted. The parameter estimates at this third stage (final estimates) as well as the three preceeding stages are shown in Table 4.7. Further searching (500 evaluations of objective function) failed to reduce |v|or change the parameter estimates.

Within each search cycle the parameters were searched for within their respective groups for fifteen to forty evaluations of the objectvie function. At the end of each of these searches, the cross correlation of the residuals was investigated. A correlation with the exit hydrogen mole fraction indicated that the exponents n, n' and n" were not estimated correctly. A correlation with temperature indicated that the activation energies were not estimated correctly. In this way the number of evaluations of the

Program	Thesis	Search	Initial	$(\underline{y}-\underline{\eta})^T \underline{\Sigma}^{-1} (\underline{y}-\underline{\eta})$	1st	2nd	3rd	over relaxed	FINAL ESTIMATES
A1	ΔE_B	X0.001	56.900	51.	51.				51.
A2	ΔE_{P1}	A3 + 10.	54.334	40.	40.				40.
A3	ΔE_{P2}	X0.001	37.579	30.	30.				30.
A4	ΔE_E	X0.001	16.853	16.	16.				16.
A5	k_B	FIXED	17.703	15.6604					15.6604
A6	K_{P1}	$\log_{10}$	16.133	10.6604	10.6283	10.6324	10.6322		10.6322
A7	K_{P2}	$\log_{10}$	14.973	12.1613	12.2223	12.2223	12.2229		12.2229
A8	K_E	$\log_{10}$	6.978	6.848	6.8153	6.8140	6.8140		6.8140
A9	n^E	n	-1.59	-2.004	-2.0505	-2.1074	2.1550	-2.348	-2.1550
A10	n'	n'	-2.47	-2.059	-2.0652	-2.0707	2.0753	-2.151	-2.0753
A11	ΔE_{E2}	A4 + 10.		26.	26.				26.
A12	K_{E2}	$\log_{10}$		4.453	4.5239	4.5208	4.5208		4.5208
A13	n^{E2}	n''		-2.153	-2.1881	2.1881	-2.2115		-2.2115
			$\lvert \underline{v} \rvert$	3.90	1.94	1.79	1.74	4.00	

PROGRAM - Parameter names used in computer program

THESIS - Parameter names used in thesis

SEARCH - Form of the parameter used for search

INITIAL - Parameter estimates from Orlickas (02)

$(\underline{y}-\underline{\eta})^T \underline{\Sigma}^{-1} (\underline{y}-\underline{\eta})$ - Parameter estimates using this weighting

1st, 2nd, 3rd - Parameter estimates from search cycles using Box and Draper weighting

Over Relaxed - n and n' were changed and the lack of fit measured

TABLE 4.7 KINETIC PARAMETER ESTIMATES

objective function, and thus computation time could be minimized by changing some of the parameter estimates before the next search. These correlations could be detected by constructing dot diagrams. These residuals were all completely random by the end of the first search cycle using the Box and Draper weighting method because of the good parameter values from the previous analysis.

This concluded the study for the estimation of the kinetic parameters. The final two sections of this chapter present a discussion of the model fit and of the confidence in the parameter estimates as well as the conclusions of this kinetic study. Some of the conclusions that can be made concerning recommended techniques for parameter estimation and experimental design only became apparent once the total study, including the final fluidized bed study, was completed. These will be fully discussed in the general summary at the end of the thesis since they apply generally to the simulation methodology being developed in this thesis.

4.6 MODEL AND PARAMETER CONFIDENCE

When modelling a physical system, two considerations arise:

(i) An evaluation of the uncertainty in the parameters given that the model predicts the physical phenomenon, and

(ii) An evaluation of the uncertainty of the mathematical model.

These will be discussed in turn.

EVALUATING THE UNCERTAINTY IN THE PARAMETERS

It is important not only to supply the best point estimates of the parameters in a given model but also to indicate the relative uncertainty in the parameters. By using either Bayesian or likelihood methods, as described in section 3.3, individual or joint confidence intervals can be determined for the parameters.

In light of the total objectives of this study which relate to modelling of the fluidized bed reactor and consequently the discrimination among the fluidized bed models, it was concluded that the degree of confidence in the estimated kinetic parameters from the packed bed study should not be evaluated by the classical methods. Indeed the general approach to the design of experiments for parameter estimation employed in this and many other similar studies is not correctly dealt with by some parameter estimation techniques. One generally accepted method in the design of packed bed experiments is to minimize the uncertainty in the estimates of the kinetic parameters. These parameters are then usually assumed to be perfectly known when incorporated into the model of the reactor of primary interest. Note, however, that the overall objective here is the modelling of the fluidized bed reactor and not the packed bed reactor which was used to obtain the kinetic parameters. Hence, it is important to ensure that all the uncertainty in any element incorporated into the fluidized bed model is expressed in terms of possible prediction error in that model. That is to say, the only importance connected with the degree of confidence in the kinetic parameter estimates is how this affects the predicting abilities of the various fluidized bed models.

EVALUATING THE UNCERTAINTY IN THE MODEL

Assuming that the model describing the gas flow in the packed bed reactor is accurate (these considerations are presented in section 4.3.1 and Appendix F) the total lack of fit from these experiments is the quantity of interest. This may arise from inaccuracies in the kinetic model and from the experimental error. Both of these lead to errors in the parameter estimates and are thereby transmitted to the fluidized bed model. It is of course essential that the experimental conditions of temperature and concentration investigated in the packed bed reactor are the same as those occurring in the fluidized bed. The estimate of the variance-covariance matrix assuming the model to be correct is given by:

$$\underset{\sim}{\hat{\Sigma}} = \frac{1}{n - \left(\frac{p}{r}\right)} \sum_{u=1}^{n} \left(\underline{y}_u - \underline{\eta}(\underline{\xi}_u, \underline{\theta})\right) \left(\underline{y}_u - \underline{\eta}(\underline{\xi}_u, \underline{\theta})\right)^T \qquad 4.32$$

where n is the total number of experimental trials used for parameter estimation, p is the number of parameters estimated, r is the number of responses per experiment and the subscript u refers to a specific experimental trial. It should be stated that the divisor of (n-p/r) is arguable. The number of degrees of freedom for such a multiple response problem is not clearly defined. For the multiple response case in which only r means are estimated the divisor is most certainly n-1. It can be implied that the divisor should be (n-r/r) since there are r responses and r means estimated. If this is the case, then with p parameters estimated and r responses, the divisor would be n-p/r.

The estimate $\underset{\sim}{\hat{\Sigma}}$, which is a measure of the uncertainty in the responses (chromatogram area) x $\sqrt{\text{attenuation}}$ for the packed bed studies is given

TABLE 4.8 MATRIX $\tilde{\Sigma}$ FOR PACKED BED REACTOR RESPONSES

C_2	C_2	C_3	C_1	C_4
C_2	25.82	2.084	16.92	-38.31
C_3	2.084	93.07	-64.76	0.2322
C_1	16.92	-64.76	299.1	-81.97
C_4	-38.31	0.2322	-81.97	159.4

in Table 4.8. By combining the matrix $\tilde{\Sigma}$ with the derivatives of the responses of the packed bed reactor model with respect to the estimated parameters:

$$V(\underline{\theta}) = \sum_{u=1}^{n} \left[\underline{X}_u^T \; \tilde{\Sigma}^{-1} \; \underline{X}_u \right]^{-1} \qquad 4.33$$

the covariance matrix of the estimated parameters can be expressed (Appendix G). This is the total uncertainty due to the kinetic model, the estimated parameters and the catalyst activity. It is necessary to reflect this entire uncertainty. The resultant ten-by-ten matrix for equation 4.33 was evaluated and is presented in Table 4.9. The transmission of these error estimates to the fluidized bed models can be examined by investigating the derivatives of the responses of both the packed bed model and the fluidized bed model with respect to the kinetic parameters. The estimated variance-covariance matrix of the predicted responses in the fluidized bed arising from uncertainty in the kinetic parameters as estimated from the packed bed experiments is:

$$\underline{x}_u^T \; (\underline{X}^T \; \underline{A}^{-1} \; \underline{X})^{-1} \; \underline{x}_u \qquad 4.34$$

where

$$\underline{x}_u = \frac{\partial \eta_j(\xi_u, \theta)}{\partial \theta i} \qquad 4.35$$

where $\eta_j(\xi_u, \underline{\theta})$ is the value of the j'th response predicted by the fluidized bed model for control variables ξ_u and $\underline{X}$ and $\underline{A}$ are as defined previously for the packed bed model. It can be seen that the variance-covariance matrix of the predicted responses in the fluidized bed model will be small if the elements of $\underline{A}$ and $\underline{x}_u$ are small or the elements of $\underline{X}$ are large

There are 66 degrees of freedom for the set of parameters estimated. The nineteen experiments had four independent responses each and ten

A1	A3	A4	A6	A7	A8	A9	A10	A12	A13
2.18E-3	1.82E-2	-2.96E-2	7.69E-3	7.72E-3	-1.20E-2	5.98E-3	-1.40E-3	-1.34E-2	-2.35E-3
1.82E-2	4.56E+0	-6.47E+0	1.89E+0	1.88E+0	-2.71E+0	5.55E-2	1.39E-2	-2.47E+0	-8.40E-1
-2.96E-2	-6.47E+0	9.95E+0	-2.67E+0	-2.67E+0	4.17E+0	-8.80E-2	-3.32E-2	3.82E+0	1.12E+0
7.69E-3	1.89E+0	-2.67E+0	7.87E-1	7.76E-1	-1.12E+0	2.43E-2	-3.59E-3	-1.02E+0	-3.56E-1
7.72E-3	1.88E+0	-2.67E+0	7.76E-1	7.80E-1	-1.12E+0	2.27E-2	1.07E-2	-1.03E+0	-3.41E-1
-1.20E-2	-2.71E+0	4.17E+0	-1.12E+0	-1.12E+0	1.75E+0	-3.34E-2	-1.35E-2	1.59E+0	5.24E-1
5.98E-3	5.55E-2	-8.80E-2	2.43E-2	2.27E-2	-3.34E-2	1.77E-2	-5.49E-3	-3.70E-2	-1.04E-2
-1.40E-3	1.39E-2	-3.32E-2	-3.59E-3	1.07E-2	-1.35E-2	-5.49E-3	1.86E-2	-2.03E-2	9.13E-3
-1.34E-2	-2.47E+0	3.82E+0	-1.02E+0	-1.03E+0	1.59E+0	-3.70E-2	-2.03E-2	1.55E+0	3.42E-1
-2.35E-3	-8.40E-1	1.22E+0	-3.56E-1	-3.41E-1	5.24E-1	-1.04E-2	9.13E-3	3.42E-1	3.46E-1

TABLE 4.9 TRANSMISSION OF LACK OF FIT FROM KINETIC EXPERIMENTS TO ESTIMATED PARAMETERS

parameters were estimated. The estimation of the catalyst activity for each trial was determined independently using a preceeding and following data point. These data were not used for the estimation of the kinetic parameters.

The model fit can be judged by comparing the residuals (observed minus predicted responses) to an estimate of the experimental variance-covariance matrix. No independent estimate of the experimental variance-covariance matrix was available since the "variance-covariance" experiments had not been properly randomized to reflect the changing catalyst activity over the total experimental period. These experiments only reflected the error due to experimental observation. However, the purpose of the packed bed study was to obtain a set of parameter estimates for a specific model, the fluidized bed model. Thus the effect of the total lack of fit for the packed bed modelling rather than how this lack of fit compares to the data employed to estimate the parameters is the quantity of importance. Equation 4.34 can be used to transmit the lack of fit from the packed bed reactor, $\underset{\sim}{\Sigma}$, to the fluidized bed models.

4.7 DISCUSSION OF PACKED BED STUDIES

The overall goal of this study was the discrimination among models that described an actual fluidized bed reactor and to investigate and evaluate the necessary procedures to attain that goal. In order to produce a model of the reactor, the kinetics, as well as the flow of the reactants must be described. The required kinetic parameters were estimated independently of the fluidized bed reactor data since the estimation of the kinetic parameters using the fluidized bed models would have required excessive computer time. Also the flow of reactants through the packed bed reactor could be described accurately without the estimation of flow parameters.

It is very important to "start simple". Both the kinetics of the reaction and the flow within the fluidized bed reactor must be described. There is no advantage gained by developing a very sophisticated kinetic model if the limiting factor for describing the fluidized bed is the description of the reactant flow. The overall goal of the project must always be kept in perspective. The sequential investigation of both the kinetics and the flow description of reactants within the fluidized bed is an effective technique to achieve the final goal efficiently. Thus, it is important to "start simple". The least accurate component of the fluidized bed model can be improved only once all the components of the model have been assembled and that least accurate component identified.

In the search for the best parameter estimates, the correlation matrix of the estimated kinetic parameters can be employed to identify the most efficient grouping of parameters. The correlation matrix can be constructed from:

$$\left[\sum_{u=1}^{n} \underline{x}_u^T \, \tilde{\underline{\Sigma}}^{-1} \underline{x}_u \right]^{-1} \qquad 4.36$$

This p x p matrix is divided row and column by the square root of the diagonal elements. The matrix $\tilde{\underline{\Sigma}}$ as defined by equation 4.32 can be calculated at any time throughout the parameter estimation process. It is realized of course that this estimate of $\underline{\Sigma}$ is predicated on the assumption that the model is perfect. The final value of the correlation matrix of the estimated kinetic parameters for this study is presented in Table 4.10. Visual analysis indicated the high degree of correlation among parameters A3, A4, A6, A7 and A8. This indicates that some combination of these parameters should be grouped together for simultaneous searches for the parameters.

The correlation among the propane and ethane parameter estimates is not desirable. Usually a correlation value of 0.20 is considered acceptable. This correlation is due to two factors: the form of the kinetic model and the uncertainty of the estimates of the catalyst activity for the experimental conditions. One method of correcting this situation might be a more sophisticated model for the catalyst activity and further experimental studies to determine it.

A study of the form of the proposed kinetic model indicates that these parameters would be expected to be highly correlated. The fact that the mechanism is basically serial suggests a method of uncoupling this interaction. Any uncertainty in the description of the reaction rate for n-butane is transmitted through the system. Thus the possibility of independently estimating the rates of adsorption by using propane or ethane feeds to the reactor could be considered. In such a study the rate of adsorption and the rate of desorption-to-reaction would have to be estimated. Then, the ratio of these two rates, unaffected by the larger paraffins, could be determined. Then fixing this ratio in the total scheme for the hydrogenolysis of n-butane, the absolute magnitude of the two could be estimated. This may be the only method of uncoupling the correlations that occur. The final decision as to this extension of the program must be made in light of the necessity to provide a better description of the kinetics for the final fluidized bed studies. However at this stage the validity of the estimates of the kinetic parameters is acceptable. The estimated activation energies are consistent with those published from studies on pure n-butane, propane and ethane. Also the

	A1	A3	A4	A6	A7	A8	A9	A10	A12	A13
A1	1.00	.18	-.20	.19	.19	-.20	.96	-.22	-.23	-.09
A3	.18	1.00	-.96	.99	-.99	-.96	.20	-.05	-.93	-.67
A4	-.20	-.96	1.00	-.96	-.96	-.99	-.21	-.08	.97	.66
A6	.19	.99	-.96	1.00	.99	-.96	.21	-.03	-.92	-.68
A7	.19	-.99	-.96	.99	1.00	-.96	.19	.09	-.93	-.66
A8	-.20	-.96	-.99	-.96	-.96	1.00	-.20	-.07	.97	.67
A9	.96	.20	-.21	.21	.19	-.20	1.00	-.30	-.22	-.13
A10	-.22	-.05	-.08	-.03	.09	-.07	-.30	1.00	-.12	.11
A12	-.23	-.93	.97	-.92	-.93	.97	-.22	-.12	1.00	.47
A13	-.09	-.67	.66	-.68	-.66	.67	-.13	.11	.47	1.00

TABLE 4.10 FINAL CORRELATION MATRIX FOR ESTIMATED KINETIC PARAMETERS FROM PACKED BED STUDY

exponents of hydrogen in the reaction rate expressions are negative and of the right order of magnitude. Finally the reaction rate constants estimated are all positive.

5.0 INITIAL MODELLING OF FLUIDIZED BED REACTOR

This chapter reports the work and conclusions from the initial phase of modelling for the fluidized bed reactor. The final work is presented in Chapter 6. These two chapters are separated since there were significant conclusions drawn from this initial phase. In addition, there was a substantial change in the formulation of the fluidized bed models, the methods of treating the data and the basic kinetic model. Further experimental work was necessary to improve the kinetic model before the final analysis of the fluidized bed could be completed.

A pilot-plant scale fluidized bed reactor was chosen for this study for a number of reasons. The experience gained from chemical plant simulation at McMaster University in the Department of Chemical Engineering (C7, S8) has indicated that the models for chemical reactors were often the limiting factors in achieving the objectives of any given study. That is to say, the knowledge of the reactor and ability to model it with sufficient accuracy often limited the number and quality of the answers that could be provided for the questions posed for the simulation of the total plant. This has been the prime motivation for the present study: to investigate procedures which would allow the use of plant and other data to provide a meaningful model for a large scale reactor.

Undoubtedly, many of the problems inherent in noisy plant data, which complicate the analysis and modelling of large-scale industrial reactors, would be encountered in describing the performance of a pilot-plant unit. A fluidized bed reactor was chosen since the flow within it, which must be

described for a mechanistic model, was very uncertain and should provide a good test for any procedures and methodology developed. Moreover, there were a number of models reported in the literature for this type of reactor.

Our experience in the simulation of chemical plants indicates that the models, once developed, are often required for extrapolation outside the range of variables for which they were developed. In this case, mechanistic models, as opposed to purely empirical models obtained from an empirical regression analysis, are expected to provide better estimates of reactor performance. Although some arguments can be made against this statement, the mechanistic route was followed here. For such a model, a mechanistic description of both the chemical kinetics and the fluid mechanics must be developed.

For this study the investigation of the reaction kinetics was performed independently of the fluidized bed reactor. These kinetic parameters were then used to describe the reaction in the fluidized bed. The description of the flow behaviour required parameters which were not known accurately a priori; these were estimated using the conversion and selectivity data from the pilot-scale reactor. The justification for not attempting both these estimates from the fluidized bed data alone can be seen by observing Figure 5.1. This plot was constructed using the relatively simple model proposed by Orcutt et al (01) in which the emulsion is assumed to be perfectly mixed. It is possible with this model to choose a particular first order rate constant k_v and then find a fluid mechanical parameter, X, which will yield almost any conversion. This plot demonstrates that a wide range of these two parameters can be chosen for any specific conversion.

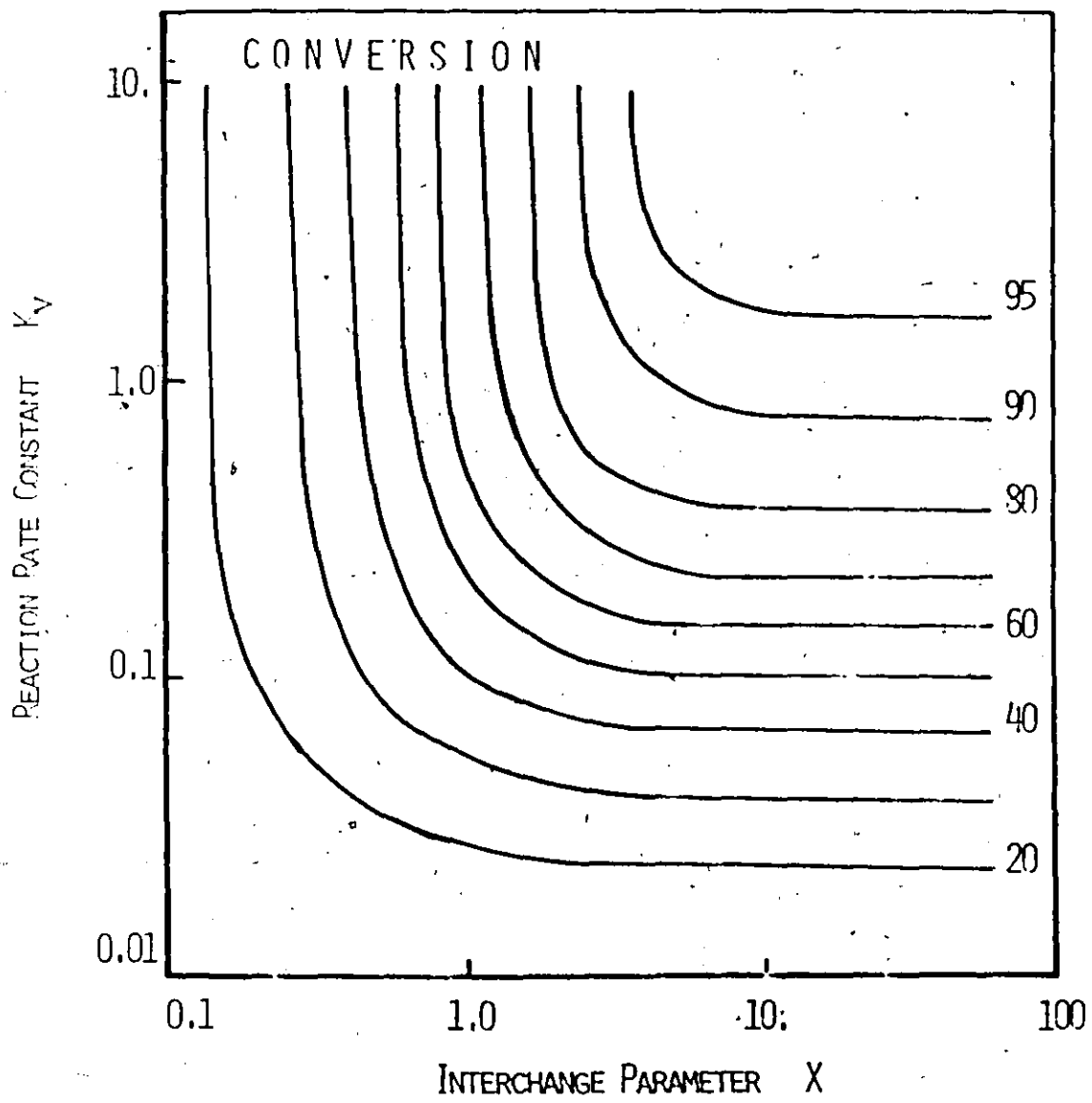


FIGURE 5.1 CONVERSION OF N-BUTANE FOR COMBINATIONS OF THE INTERCHANGE PARAMETER FOR ORCUTT'S PERFECTLY MIXED EMULSION MODEL AND THE REACTION RATE OF N-BUTANE

The choice of model does not affect this conclusion since they all exhibit the same behaviour.

Another important point emerges from this plot. Note the extremely low sensitivity of the interchange value at low values of k_v and low measured conversions. Indeed, in some situations any value within two orders of magnitude would predict a reasonable conversion! On the other hand if the interchange parameter in the model is very large under all operating conditions of interest, then a large error can be tolerated in its estimated value without significantly effecting the predicted conversion. In this case, the accuracy of the model is determined entirely by the error in estimating the reaction rate parameters. At the same time, it is important to note that if an interchange parameter is to be determined from a fluidized bed reactor, then the chemical reaction rate constant must be fairly large to ensure that the error in its estimated value will not produce a large error in the estimated value of the interchange factor. Moreover, any fluid mechanical model will only be put to a severe test in those regions where fluid mechanisms determine the conversion, that is at high reaction rates. Many investigators have not recognized these points in the past.

Thus, for this study it was decided to develop the total kinetic model independently from the fluidized bed data. The model, which is far more complex than the simple example presented here to predict only conversion was developed employing a packed bed reactor. In this system, the flow behaviour of reactants can be fairly accurately described and the kinetic rate parameters can be determined from the chemical analysis of the products.

This chapter includes the description of the fluidized bed reactor which was designed and constructed for this study. The two phase reactor model which is the basis of all the models used in this study is described. The bubble parameters which are common to all the models are summarized. The basic differences among the specific reactor models are indicated. The designs for the initial experiments and the results obtained are presented. The two simplest reactor models were investigated using these data. Both provided reasonable predictions of the reactor data once the appropriate parameters were estimated. From these studies a number of conclusions were drawn. These summarize the information obtained from this initial investigation and delineate the weaknesses in the models. These shortcomings had to be overcome before any discrimination studies could be performed among the various fluidized bed models.

5.1. REACTOR DETAILS

It was necessary to design and construct a fluidized bed reactor for this study. The details of its design, operating characteristics and limitations are described below. It was made large and complex so that it would respond, as much as possible, in the same way as a large industrial unit. When operating, it was observed to exhibit many of the same operating characteristics observed in much larger fluidized beds.

The diameter of the reactor was to be as large as possible. Previous studies reported in the literature with four inch or smaller diameter reactors were strongly criticized for the possibility of significant wall effects and slugging. A diameter of eight inches represents a compromise since a reactor any larger would be too costly to operate. During operation at the higher

flowrates studied, one large hydrogen cylinder (ca. 220 s.c.f.m.) was consumed each hour.

The hydrogenolysis of n-butane was chosen as the reaction. It is sufficiently complex containing both series and parallel reactions and provides multiple response data. This reaction occurs significantly around 480°F., is strongly exothermic and was known to exhibit very high activation energies.

A schematic diagram of the reactor system is shown in Figure 5.2. A photograph of the system, before it was insulated, is shown in Figure 5.3. The description of the apparatus is presented in three sections: feed-preparation, reactor and heating systems. The component equipment is identified by the numbers on Figure 5.2.

5.1.1 FEED PREPARATION

The feed gases are supplied from high pressure cylinders (1). Certified nitrogen is used for purging the system of oxygen and if necessary for emergency shut-down. The n-butane feed is C.P. grade (better than 99.5% purity, Matheson of Canada Ltd.). Warm water was sprayed onto the cylinder to provide the heat of vaporization and maintain a suitably high pressure in the n-butane cylinder. Three hydrogen cylinders (Canadian Liquid Air 99.99% purity) are connected to a common manifold and supply a minimum of three hours operation. A single reserve cylinder, connected in parallel with the other three supplies hydrogen when the main cylinders are being replaced. Check valves (2) are installed on all feed lines to prevent back flow of gases. The hydrogen and n-butane flow controls are mounted on the

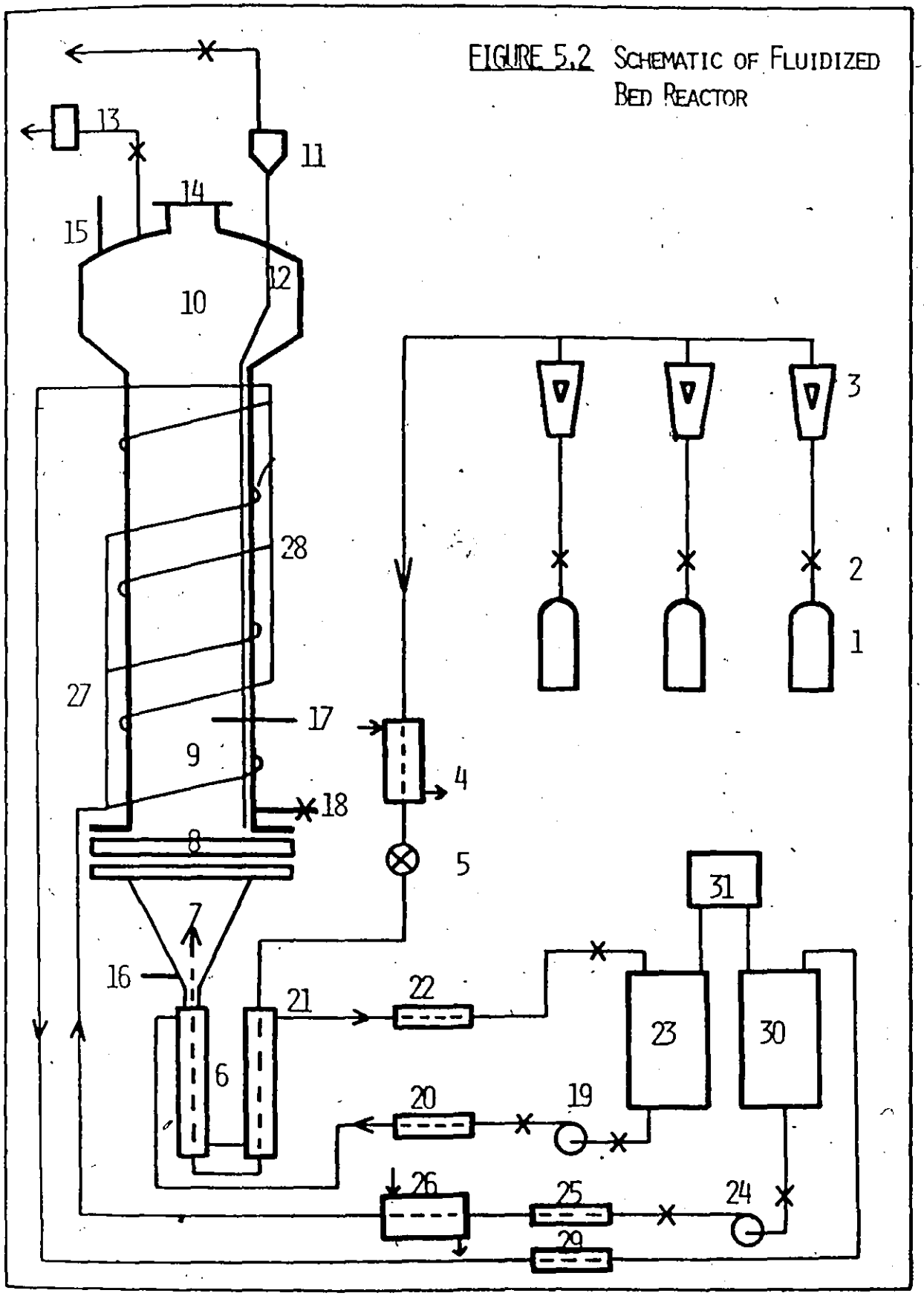
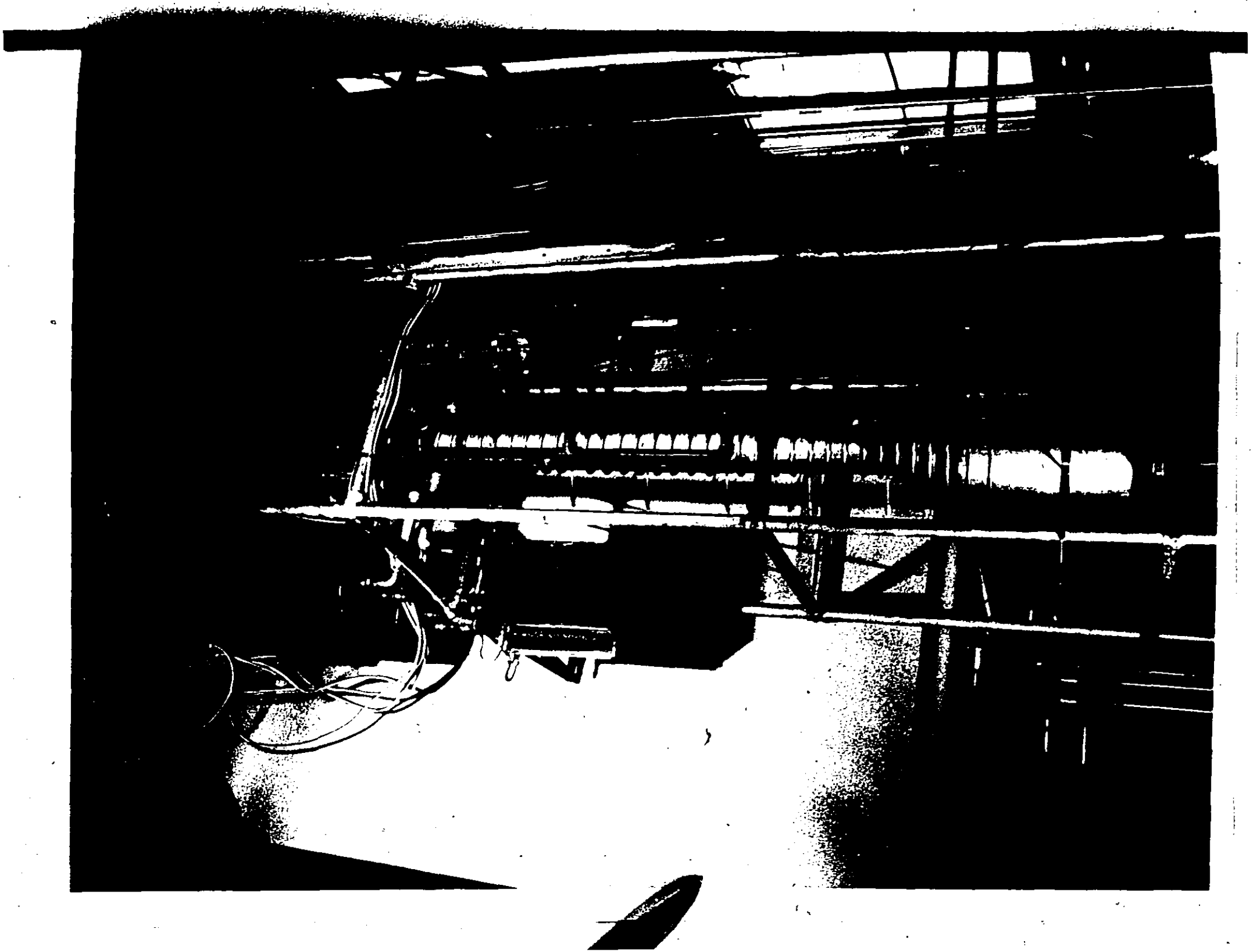


FIGURE 5.2 SCHEMATIC OF FLUIDIZED BED REACTOR

FIGURE 5.3 FLUIDIZED BED REACTOR



main control board. Rotameters are used to measure the gas flows (hydrogen, Fisher Porter FP-1/2-21-G-10/80; n-butane, Brooks BR-1/2-25G10; nitrogen Fisher Porter Ratiosight 1-AR5-593). The nitrogen rotameter is used only for flow indication. Both the hydrogen and the n-butane rotameters contain two specially designed floats so as to cover the flow ranges required. The calibration curves are given in Appendix A.

The feed gas is first heated with 100. p.s.i.g. steam in a brass shell-and-tube heat exchanger (4) (American Standard 200-8 BCF, single pass, 1.2 sq. ft.). A backpressure of 40 p.s.i.g. is maintained on the rotameters to prevent the floats from bouncing at low flows. The valve (5) (Research Controls Ltd., 1/2 in. stainless steel, air actuated, trim E) is pneumatic and is controlled by a Honeywell controller (Honeywell model PP972 1035, 0 to 15 p.s.i.g.). The feed gas is heated to the reactor temperature in two carbon steel heat exchangers (6) by circulating oil (American Standard 201-6 EP, single pass, 2. sq. ft.).

5.1.2 REACTOR

The reactor is constructed of 16 gauge type 316 stainless steel and mild steel plate. The bottom cone (7) is 8. in. at the top and is welded into a 12. in. square flange of 1/4 in. plate. The cone is packed with 3/4 in. stainless steel packing rings to disperse the gas flow across the column cross-section. The distributor plate (8) is a 12. in. square by 1/2 in. thick mild steel plate drilled with 230 holes of 0.055 in. diameter on a central 8.0 in. diameter circle. A sheet of 200 mesh stainless steel screening is bolted to the bottom of the plate to prevent solids from falling through. The reactor barrel was 7.986 in. I.D. and only 1/16 in.

off round at the worst point. The reacting section is 6.0 ft. high and is topped with a disengaging section (10) 2 ft. long by 18. in. in diameter. The bottom of the reactor was welded through a 12. in. square by 1/2 in. thick flange from which the total reactor system is fixed into the support frame of 2. in. pipe and Kee clamps as shown in Figure 5.3. The dome on top of the disengaging section was made of 12. gauge mild steel because of cost considerations. The exit gas flows through a cyclone (11) (Wright Austin, 1 1-1/4 TIS 8). Entrained catalyst is returned to the bottom of the bed in a 3/4 in. stainless steel dip leg (12). A 1. in. line leads to a pressure release valve (13) set at 5 p.s.i.g. A double pipe heat exchanger cooled with water is located between the reactor and the release valve to protect the valve seat. A 6. in. flanged port (14) is used for charging catalyst and visual observation of bubbles when using nitrogen gas. Pressure taps (15) and (16) are used to monitor the bed pressure drop on a manometer (Miriam 30 in. S.G. 1.04). The temperature in the reactor is measured by chromel-alumel thermocouples (17) at the feed and the distributor plate as well as at 6. in., 1. ft., 2. ft., 3. ft., and 4. ft. up the reactor. The thermocouples were 12. in. long and could be moved into the reactor through teflon ferrules in Swagelok fittings. The calibration data for the thermocouples are given in Appendix B. The catalyst can be removed from the reactor through a drain plug (18). The gas samples are taken at the cyclone exit. The reactor gas is exhausted through a large exhaust fan with measured capacity of 45,000 S.C.F.M. and powered by an explosion proof motor. At the maximum reactor flow the hydrogen content of the mixture of air and hydrogen is 140 times less than the lower explosive limit assuming

perfect mixing.

5.1.3 HEATING-COOLING SYSTEM

Two circulating oil systems are employed to control temperatures; one system controls the reactor and the other heats the feed gas. The circulating fluid is Sun 21 Heat Transfer Oil (Sun Oil Company) and can safely be used in a closed system with a cooled expansion head to 600.°F. Some thermal breakdown occurs but the residue does not foul the pipes. The pumps used in both systems (19) and (24) replaced initial pumps in which the seals could not withstand 580°F. for any period of time. The pumps were supplied by Sihi Pumps Ltd. (model ZLLE 4017/ISSQ, 5. USGPM at 15. ft. for 1/2 HP and 1200 RPM with cooled stuffing box for 600. to 700.°F). A triac control circuit (G3) was used to adjust the power to some of the heaters.

The first oil circulation system supplied heat to the heat exchangers (6) and heated the outside of the bottom cone (7). The pump vibrations were damped by two armored flexible couplings (20) and (22). The 10 gal. oil heating tank was constructed from 14 gauge mild steel and contained three 1500 watt immersion heaters supplied by Canadian Chromalox and controlled by three triac circuits.

The second oil circulation system was used to control the reactor temperature. Again the pump vibrations were damped by two armored flexible couplings (25) and (29). Heat was supplied by three 1500 watt immersion heaters controlled by triac circuits and two 2000 watt immersion heaters with on-off control. All these heating elements were contained in the second 10 gal. oil heating tank (30). The oil could be cooled in a heat exchanger (26) (American Standard 200-8, single pass, stainless steel, 1.2 sq. ft.).

The cooling fluid was 100 p.s.i.g. air and was vented through a simple two pipe muffler to reduce noise. The circulating oil was fed to a manifold of 1. in. pipe (27) on the side of the reactor which can be seen in Figure 5.3. Three lines of 1/2 in. type 316 stainless steel tubing were fitted to the manifold. These lines were wound on 2. in. centers up the reactor for 2. ft. sections of the reactor and emptied into an exhaust manifold (28) and returned to the oil heating tank (30). Both oil tanks were connected to an oil expansion tank containing water cooling coils. These lines contained only a 1/4 in. opening to reduce the natural circulation of oil between the cold expansion tank and the hot oil tanks.

5.1.4 OPERATING CHARACTERISTICS

A detailed set of operating instructions for start-up, catalyst conditioning and operation are given in Appendix E. This section of the thesis describes the operating characteristics and responses of the reactor for the hydrogenolysis of n-butane over the 10.% nickel on silica gel catalyst.

The reactor is manually controlled by adjusting the flow control valves on the hydrogen or n-butane, and adjusting the coolant temperature on the reactor walls via the oil heaters and the air heat exchanger. The feed gas temperature is also controlled by adjusting the heat input to this circulating system.

Because the reaction is exothermic and the activation energies are very high, it is very difficult to set the operating conditions (temperature, flow and ratio) at predetermined valves. The main control is exercised through the circulating coolant oil to remove the heat of reaction for a

given set of operating conditions and must be carefully monitored. A digital volt meter on which 0.025 mv. is approximately 1F.° was employed. Any consistent temperature change can immediately be detected by sampling on this sensitive instrument every second. Under general operating conditions the oil is about 40.°F. cooler than the bed of reaction catalyst. For very extreme conditions, the temperature difference may approach 80.°F. If the reactor temperature begins to increase above the desired temperature when the feed mixture is correct, more cooling is required. Since the response of the oil system to the air cooling is quite slow, the hydrogen flow is increased and/or the n-butane flow is decreased while a new coolant temperature is established. It is important however, to ensure that the reaction temperature does not fall more than a few degrees below the desired temperature since the cooling may be so severe that the reaction rate (and hence the heat generation rate) may be insufficient to satisfy the heat transfer rate. The reaction is then quenched and the coolant and the reactor temperature must be increased to initiate the reaction and the whole procedure started again.

5.1.5 REACTOR TEMPERATURE PROFILES

One of the best known advantages of a fluidized bed reactor is temperature uniformity due to the motion of the catalyst particles with the ensuing high heat transfer rate at any heat transfer surface in the bed. Insufficient mixing for good heat transfer and axial mixing occurred for flowrates below about five times minimum fluidization velocity. This was evidenced by large temperature gradients near the distributor plate and temperature excursions of as much as 15 to 20°F. at some of the

thermocouples. At flowrates in excess of ten times minimum fluidization velocity these temperature gradients did not occur.

A temperature traverse across the reactor at 6 in. above the distributor plate was carried out at fairly extreme reaction conditions (500°F., ratio = 6.5, flowrate = ten times minimum fluidization). This traverse indicated a maximum temperature variation of 1.5°C. over the central 7-1/2 in. core of the 8 in. diameter reactor. A similar temperature variation was observed in the axial direction from the distributor plate to the top of the bed as long as the feed gas was heated to near reaction temperature.

5.2 FLUIDIZED BED REACTOR MODELS

Despite the abundance of different reported fluidized reactor models there is only one basic model: the two phase model in which bubbles are assumed to rise through a fluid-like bed of solids. Although this is a mechanistic model, it is doubtful that the authors of the various models would claim that they describe anything more than an approximation of the truth.

The differences in the model descriptions can be resolved into three different parts:

(i) the make-up and size of the flow and the mixing behaviour of the bubble, cloud and wake regions

(ii) the flow of solids and gas in the emulsion phase

(iii) the interchange between the bubble and emulsion gas and the a priori prediction of its magnitude.

There are a large number of combinations of assumptions that can be made relating to the fluid mechanical phenomena but it is not the purpose

of this study to add to this already large number of so-called unique two-phase models. Rather, the object of the study was to simulate a specific fluidized bed reactor and to discriminate among the models chosen to describe it. Although some people have suggested that fluidized bed reactors can be modelled with sufficient accuracy, a priori predictions are generally not very good.

This study involves:

1. employing some form of the two-phase model and
2. estimating some model parameter(s) for each specific case.

These two basic statements summarize the approach taken throughout this study. The first statement implies that this study will make use of some of the large volume of work already done on fluidized bed reactors. This would be the logical first approach followed by any engineer in modelling process equipment. There is little to be gained in developing a new model unless the old have been proven to be inadequate and/or new insights or descriptions of the basic phenomena have come to light. Secondly, some parameters specific to the reactor of interest may be estimated using data from the operating reactor.

Given this basic approach and reaction kinetic parameters from a separate study, the questions to be resolved are:

(i) which of the two-phase models best predicts the product distribution in the reactor effluent, and

(ii) which parameter(s) in these two-phase models should be estimated using plant operating data.

To consider the second question, it is best to estimate as few parameters

as possible. Also the parameter(s) to be estimated should be those about which there is most uncertainty and which are the most difficult to estimate independently and accurately. For a large scale reactor operating within a plant the number of tests that can be performed on it may be very few. Indeed, the only data that may be possible to obtain may be that obtained under normal operating conditions.

For the purpose of this study the basic differences in the fluidized bed studies are grouped into three main categories. They are shown in Table 5.1. The first category of the basic assumptions includes: the makeup of the bubble phase, the flow pattern in the emulsion and the use of a constant size or growing bubble. These are the general minor variations in the basic two-phase models that have been suggested by various modellers. The question of interchange is placed in the third category. The second category of unknown parameters that can be estimated independently with reasonable accuracy includes: initial bubble size, bubble growth, maximum bubble size, bubble rise velocity, bubble shape, cloud thickness, wake fraction, emulsion voidage and bed expansion. Of these parameters perhaps the most important and the most difficult to describe accurately is the bubble size and growth. Some might argue that this should be the estimated parameter and the interchange should be included in the second category based on one or more of the four basic interchange mechanisms which include bubble circulation, diffusion, coalescence - breakup and wake and cloud shedding. However, considerable information is available on the variation of bubble size with height. These observations have been made in non-reacting systems using capacitance probes, X-rays and visual observations

TABLE 5.1 CLASSIFICATION OF ASSUMPTIONS AND PARAMETERS IN TWO-PHASE MODELS

I BASIC ASSUMPTIONS AND METHODS OF SOLUTION

II UNKNOWN PARAMETERS THAT CAN BE ESTIMATED INDEPENDENTLY

III MORE UNCERTAIN PARAMETERS

of bursting bubbles at the top of the bed. Since the description of the interchange phenomena occurring between the bubble and the emulsion is the least well known and hence uncertain, the overall interchange was chosen as the single physical parameter to be estimated in each model from the chemical concentration data for the experimental system.

The models of Orcutt et al, Kato and Wen and Partridge and Rowe are investigated. Initially the Kunii and Levenspiel model was also included; unfortunately, this model required a prohibitively high amount of computer time and so had to be abandonned. The basic assumptions concerning the makeup of the bubble phase, the flow patterns in the emulsion, the use of a constant size or a growing bubble and the method of solution used in this study (the type I assumptions of Table 5.1) are the same as those proposed by the authors of the individual models. The same relationships were used in all the fluidized bed models to describe the type II model parameters. A separate interchange parameter based on the Kato and Wen analysis was estimated for each model. The calculation of the parameters common to all the models is presented in Section 5.2.1. The formulation of the fluidized bed models used in this study is presented in Section 5.2.2 through 5.2.4.

5.2.1 CALCULATION OF PARAMETERS COMMON TO ALL MODELS

To ensure consistency among the basic models used to describe the reactor, certain parameters were the same for all the models. The estimation or measurement of these parameters is indicated in the following:

(a) INITIAL BUBBLE SIZE

The initial bubble size from a perforated plate can be calculated

if the hole spacing n_o cm^{-2} is known.

$$d_o = \frac{6(U-U_{mf})}{n_o \Pi}^{0.4} \quad g^{-0.2} \qquad 5.1$$

(b) BUBBLE SIZE AND GROWTH

The correlation as suggested by Kato and Wen (equation 2.16) is used to predict the bubble diameter at any height in the reactor. The

$$d_b = 1.4 \quad (\rho_p \, d_p) \, \left(\frac{U}{U_{mf}}\right) h + d_o \qquad 2.16$$

effective particle density was determined using mercury and the average particle diameter was determined from sieve analysis (Appendix D). The mean bubble size was the average over the total height of the bed. It must be noted that the correlation is a strong function of particle diameter. When used for non-spherical particles some caution should be used.

(c) MAXIMUM BUBBLE SIZE

The accurate prediction of the maximum bubble size is very difficult. A plexiglas plate was clamped over the viewing port at the top of the reactor and the bed fluidized with nitrogen. Observation of the bursting bubbles indicated that the eruptions were of the order of about half the reactor diameter of 20. cm. From these experiments, it was postulated that the reactor was not slugging for the range of flows investigated. The observed eruptions were not at the center of the column and there were three or four distinctly different locations for subsequent bursting bubbles. Also there did not appear to be any gross rising and falling of the interface at the top of the bed. Subsequent closer observation of the bubble behaviour in a second plexiglas column of the exact same size and with the same distributor confirmed these observations. A maximum bubble size of 10. cm. was estimated.

This is to say that it appeared to be larger than 9. cm. and less than 11. cm.

There is considerable evidence from X-ray studies and two-dimensional bed photographs that some expansion of the bubble occurs just before exiting from the bed. However, since the theory of Harrison (H9) suggests a maximum bubble diameter greater than the reactor diameter, the visual observation of the erupting bubble was used.

(d) BUBBLE RISE VELOCITY

The bubble rise velocity is predicted by equation 2.17:

$$U_{br} = 0.711 \ (g \ d_b)^{1/2} \qquad 2.17$$

(e) BUBBLE SHAPE

The bubble was assumed to be spherical and of diameter as determined by equation 2.16. The bubble is surrounded by a spherical cloud of thickness determined by equation 2.18.

(f) CLOUD THICKNESS

For the models which included the cloud with the bubble phase, the cloud thickness was calculated from the Davidson model:

$$\frac{r_c}{r_b} = \left[\frac{U_{br} + 2 \ (U_{mf}/\epsilon_{mf})}{U_{br} - (U_{mf}/\epsilon_{mf})} \right]^{1/3} \qquad 2.18$$

(g) WAKE FRACTION

For the models which included the wake fraction with the cloud 0.25 of the bubble volume was assumed to be occupied by the wake.

(h) EMULSION VOIDAGE

It is essential to have an accurate measure of the emulsion voidage since the kinetic parameters were determined in a packed bed reactor of

different voidage. The voidage in the packed bed reactor which was packed and settled using a vibrator was 0.449, whereas that of the emulsion of the fluidized bed at incipient fluidization was determined to be 0.557. The voidage throughout the emulsion phase of the bubbling bed was assumed to be the voidage at incipient fluidization. Thus, the kinetic rate equations must be adjusted by:

$$(1.0 - 0.557)/(1.0 - 0.449)$$

The method for the determination of the voidages by mercury density and expansion to incipient fluidization is presented in Appendix D.

BED EXPANSION

The bed expansion from the freely settled state (as opposed to the vibrated and packed state used in the packed bed reactor) to minimum fluidization was determined in a separate column of silica gel and was found to be 4.3%. The expansion due to bubbles can be determined from:

$$\frac{L - L_{mf}}{L} = \frac{U - U_{mf}}{0.711\ (g\ d_b)^{1/2}} \qquad 2.22$$

This expression follows directly from assumptions relating to the volumetric flowrate in the emulsion and the bubble rise velocity.

BUBBLE-TO-EMULSION INTERCHANGE

The interchange or volumetric flow from the bubble to the emulsion was estimated for each individual model using the exit reactor concentrations. This interchange was described by:

$$K = \frac{cm^3 \text{ interchanged}}{cm^3 \text{ of bubble - sec.}} = \theta^* \times \frac{11}{d_b} \qquad 5.2$$

where d_b is the bubble diameter in centimeters and θ^* is the parameter to

be estimated. The effects of coalescence, breakup and wake shedding as well as the effects of gas circulation within the bubble and diffusion, are assumed to be included in this parameter.

SUMMARY

The description of the bed and bubble characteristics presented here are incorporated along with the kinetic equations describing the reaction rates into the fluidized bed models used in this study. These models with their various basic assumptions now can be compared using the same set of descriptions for their common parameters. The mathematical development of the flow equations for these models and the methods of solution are outlined in the following three sections of the thesis:

5.2.2 MODELS OF ORCUTT ET AL. (01)

The two models of Orcutt, Davidson and Pigford as originally presented are summarized in section 2.3.2 and in Table 2.2. Orcutt et al. proposed two ways to describe the flow of reactants in the emulsion. One was that all the emulsion gas was perfectly mixed and the other was that it was in plug flow. The basic assumptions of both these models according to classification I of Table 5.1 are: spherical bubbles of constant size containing no solids and all gas in excess of that required to provide the minimum fluidization velocity in the emulsion phase flows through the reactor as bubbles in plug flow.

PERFECT MIXING IN THE EMULSION (ORCMIX)

The model used in this study was named ORCMIX. A mass balance

for any component in the bubble gives:

$$Q\,(P_e - P_b) = U_{br} V_b \frac{dP_b}{dy} \qquad 5.3$$

Integrating equation 5.3 over the bed height H gives the partial pressure of any component at the exit in the bubble as:

$$P_b = P_e + (P_o - P_e)\exp(-X) \qquad 5.4$$

where $$X = QH/U_{br}V_b \qquad 5.5$$

and Q is the interchange or transfer rate of any component which results from diffusion and bulk flow of fluid into and out of the bubble. The subscripts e, b and o refer to the emulsion, bubble and feed respectively. From a total mass balance on the emulsion as a mixed tank:

Net Flow in From Bubbles	+	Net Flow in From Feed	=	Rate of Disappearance Due to Reaction

$$(P_o - P_e)\,NV_bU_{br}\,(1-\exp(-X)) + (P_o - P_e)U_{mf} = r_v HRT(1-NV) \qquad 5.6$$

where N = number of bubbles per unit volume

u_{mf} = minimum fluidization velocity (cm. /sec.)

r_v = rate of disappearance (moles/sec. $cm.^3$)

Using the notation of Orcutt and substituting

$$\beta = 1 - U_{mf}/U_{br}$$

$$= \frac{U_{bm}}{RTH}\,(1 - \beta\,\exp(-X))$$

equation 5.6 for the emulsion becomes:

$$(P_o - P_e)\gamma = r_v \qquad 5.7$$

The five rate expressions for each of the components are substituted into equation 5.7 resulting in five equations plus equation 5.4 to be solved. A solution is obtained by choosing the correct partial pressure of hydrogen

in the emulsion phase. Once a partial pressure of hydrogen is assumed all of the six equations can be calculated directly. The calculated hydrogen pressure is compared to the estimated or guessed value. After two hydrogen concentrations have been guessed and a corresponding calculated value obtained, a Regula Falsi convergence technique can be used to obtain the correct value of the hydrogen partial pressure.

The total computation is very rapid since no integration techniques are needed.

PLUG FLOW IN THE EMULSION (ORCPLG)

The model used in this study was named ORCPLG. From a mass balance on the bubble phase over a differential height of the reactor Δy :

$$(U - U_{mf})\ A\Delta P_b = QNA\ \Delta y\ (P_e - P_b) \qquad 5.8$$

where $U - U_{mf} = NV_bU_{br}$

and U is the superficial velocity for the total feed. Taking limits as $\Delta y \to 0$ and as before defining:

$$X = QH/U_{br}V_b \qquad 5.5$$

$$\frac{dP_b}{dy} = \frac{X}{H}(P_e - P_b) \qquad 5.9$$

In the emulsion phase at any height:

$$(U-U_{mf})\frac{dP_b}{dy} + U_{mf}\frac{dP_e}{dy} = RTr_v \qquad 5.10$$

where again r_v is the rate of disappearance.

Substituting equation 5.9 into 5.10

$$\frac{dP_e}{dy} = \left(\frac{X}{H}\right)(P_b - P_e)\left(\frac{U-U_{mf}}{U_{mf}}\right) - \frac{RTr_v}{U_{mf}} \qquad 5.11$$

For each of the five components there exists two differential equations

5.9 and 5.11 to be solved. They describe the partial pressures of each component at any height up the reactor. Since both the emulsion and bubble flow are upward from the distributor, the problem is an initial value one. A fourth order Runge Kutta integration routine is used. The error of integration is calculated and the step size specified so that the error on the partial pressure between each integration step is controlled between 10^{-6} and 10^{-8}.

The models of Orcutt et al. are two of the simplest available. The assumptions of no solids in the bubbles and of no growth of the bubbles may limit the accuracy of the model predictions. However, the calculation time for the perfectly mixed model is about twenty times faster than any of the other models because of these two assumptions.

5.2.3 MODELS OF KATO AND WEN (K3)

The basic model of Kato and Wen along with two modified versions of it were included in this study. The two modified versions investigated the effect of including the wake perfectly mixed with the bubble and also the effect of modelling the emulsion flow of gas as a perfectly mixed tank. The basic assumptions of the original model according to classification I of Table 5.1 are: spherical bubbles with spherical clouds, growing bubbles, no flow of feed into the emulsion, solution of the mass balance differential equations by assumed zones (integration steps) equal in height to the bubble diameters and perfect mixing within each emulsion zone but no axial transfer between these zones. The partitioning of the bed into zones for the purpose of solving the reactor equations is a most unique feature of the original Kato and Wen model.

BASIC KATO AND WEN MODEL (KATWEN(0)

The model used in this study was named KATWEN(0). A mass balance on the bubble phase for component i in any zone up the bed gives:

$$(F_i)_{n-1} = KV'_b \ (P_{bi} - P_{ei}) + RTV'_c \ r_i + (Su_{br}P_{bi})_n \qquad 5.12$$

where S = cross sectional area of the bubble phase

U_{br} = superficial velocity of the bubble phase

K = interchange ($cm.^3/cm.^3$ - sec.)

$(F_i)_{n-1} = Su_{br} \ (P_{bi})_{n-1}$ from the stage below (known)

V'_b = volume of the bubble phase in the zone

V'_c = volume of the cloud phase in the zone

A mass balance on the emulsion phase for component i within each zone with no axial flow gives:

$$KV'_b \ (P_{bi} - P_{ei}) = RTV'_c r_i + 0 - 0 \qquad 5.13$$

The five equations for the rates of reaction are substituted into equations 5.12 and 5.13. These equations are then solved for P_{bi} and then P_{ei}. Given the flow from the zone below, the partial pressures of hydrogen must be guessed for both the bubble and the emulsion phase. Then the partial pressures can be calculated. The solution for each zone converges very quickly.

KATO AND WEN WITH WAKE IN BUBBLE (KATWEN(1))

The model used in this study is named KATWEN(1). The only difference from the model KATWEN(0) is in the calculation of the cloud volume V'_c. In this model the cloud volume is increased by an amount equal to 25 percent of the bubble. This involves the changing of two cards from the KATWEN(0)

program.

KATO AND WEN WITH ENTIRE EMULSION PERFECTLY MIXED (KWMIX)

The model used in this study is named KWMIX. The equation for the bubble phase for this model is equation 5.12 without the wake included with the bubble. The equation for the emulsion phase is different since the other two models are developed using the net interchange of a component between the bubble and the emulsion. The mass balance equation for the mixed volume with reaction for component i is:

$$(A-S)U_{mf}P_i^\circ + \sum_{j=1}^{k} (KV_bP_{bi})_j = (A-S)U_{mf} + \sum_{j=1}^{k} (KV_b)_j \; P_{ei} + RTr_iV_e \qquad 5.14$$

where (A-S) is the cross sectional area for the emulsion, V_e is the total emulsion volume and P_i° is the partial pressure of component i in the feed to the reactor. The second term on the left hand side is the sum of the total flow of component i from each of the k zones in the bubble phase.

A solution of this model is obtained by first assuming the emulsion partial pressures as calculated using the ORCMIX model which executes very rapidly. Knowing the approximate emulsion partial pressures, the composition of the bubble phase can be calculated up the reactor. Now, given the total input to the emulsion from the bubbles and from the feed, the emulsion partial pressures can be calculated from equation 5.14. Then the bubble and emulsion partial pressures are alternately calculated until the change in the partial pressure of hydrogen in the emulsion is less than 10^{-4} between subsequent iterations. Only three or four cycles are required and the solution converges rapidly since the ORCMIX model provides very good starting values.

5.2.4 MODEL OF PARTRIDGE AND ROWE (P3, P4) (PARROW)

The model used in this study is named PARROW. The basic assumptions for this model in accordance with classification I of Table 5.1 are: spherical bubbles with spherical clouds, growing bubbles, gas in the emulsion flows upwards in plug flow at the minimum fluidization velocity and all the remaining feed gas flows through the reactor in plug flow as bubbles. The bubble mechanics are described as indicated in Section 5.2.1.

The mechanics of calculating the bubble properties in the original Partridge and Rowe model are significantly different from those employed here. They made use of data from a two-dimensional bed to determine a bubble size distribution. The validity of this technique and the subsequent conversion to the three-dimensional case is questionable.

For this study, the equations for the Partridge and Rowe model are the same as those for the ORCPLG model except that the bubble size changes up the reactor and the bubble phase includes a reaction term. The resulting ten coupled differential equations form an initial value problem since the flow of both phases is upwards from the distributor.

5.3 INITIAL EXPERIMENTS AND MODEL FITTING

The results and the analysis of the initial two sets of experiments are presented in this section. The model of Orcutt et al. with perfect mixing in the emulsion phase (ORCMIX) was used for most of this initial analysis since it was by far the least expensive in computational time. Limited studies using the Kato and Wen model KATWEN(0) indicated that the residual fit for this model on the basis of a weighed least square estimate was about half that for the ORCMIX model.

Shortcomings of the apparatus were found during preliminary tests of the reactor, the heating systems and the feed gas system. The range of operating conditions over which reaction would occur and the reactor could be controlled were investigated. A reasonable conversion of n-butane occurred above 470°F. At temperatures above 530°F. the seals on the circulating oil pumps failed after about 20 hours. An air cooled heat exchanger was added to the oil circulating system; without it in the reactor could not be controlled and temperature runaway occurred. Below a flowrate of about ten times the minimum fluidization velocity the reactor could not be controlled and hot spots occurred. It was postulated that below that flow there was not sufficient movement of the catalyst to remove the heat of reaction through contact with the reactor walls.

The combination of conditions for the experimental design is shown in Table 5.2. Experiments were performed at two levels each of temperature, ratio and flow. A centre point or standard condition experiment was performed at the temperature, ratio and flow conditions of: 485°F, 5.3 and 10 U/U_{mf} respectively. Two samples were taken at each operating condition and a pair of center point experiments were performed between each of the sixteen experiments indicated in Table 5.2. The results of these and all the other experiments performed along with the data and the data analysis computer programs are presented in Appendix J. For these initial experiments the feed ratios were determined from the chromatographic analysis rather than from the rotameter readings due to an initial error in the calibration of the n-butane rotameter. For subsequent experiments the material balance as determined from the rotameters and the chromatographic analysis agreed within four percent.

TEMPERATURE (°F)	470.	500.
RATIO (H_2/C_4H_{10})	3.3	7.3
FLOW (U/U_{mf})	10.	15.

TABLE 5.2 NOMINAL OPERATING CONDITIONS FOR INITIAL FLUIDIZED BED EXPERIMENTS 1-34

Two subsequent sets of experiments were performed with the same depth of catalyst bed:

i) Experiments 35 to 46 were designed to determine if the catalyst activity, which remained constant over the first set of experiments would be the same when the catalyst was conditioned in the same way four months later. The observed conversion and selectivities at the same center point operating conditions were identical to those obtained previously. Several experimental trials were performed using first propane and then ethane instead of n-butane in the feed. The failure of a pump seal did not allow all the planned experiments to be completed.

ii) Experiments 48 to 86 were designed to investigate a wider range of control variables (temperature, flow rate and feed ratio). Two of the three control variables were set at the mid-point values (485°F., U/U_{mf} = 10 and $P^{\circ}_{H2}/P^{\circ}_{C4}$ = 5.3) and the third one varied. In this way, temperatures of 440, 455, 515, 530 and 550, ratios of 2.5 and 11.0 and a flow of 22 times the minimum fluidization velocity were investigated. The experiments at high temperature were performed to test the fluidized bed models at very high reaction rates.

COMPARISON OF FIXED AND FLUIDIZED EXPERIMENTAL RESULTS

Some conclusions can be drawn by comparing the experimental data from the packed bed and from the fluidized bed reactors. Figure 5.4 shows plots of the integral selectivities against the resultant conversion of n-butane. The selectivity of methane increases to its maximum value of four and the ethane and propane selectivities decrease toward their minima of zero as the conversion of butane increases to 100%. The scatter in these

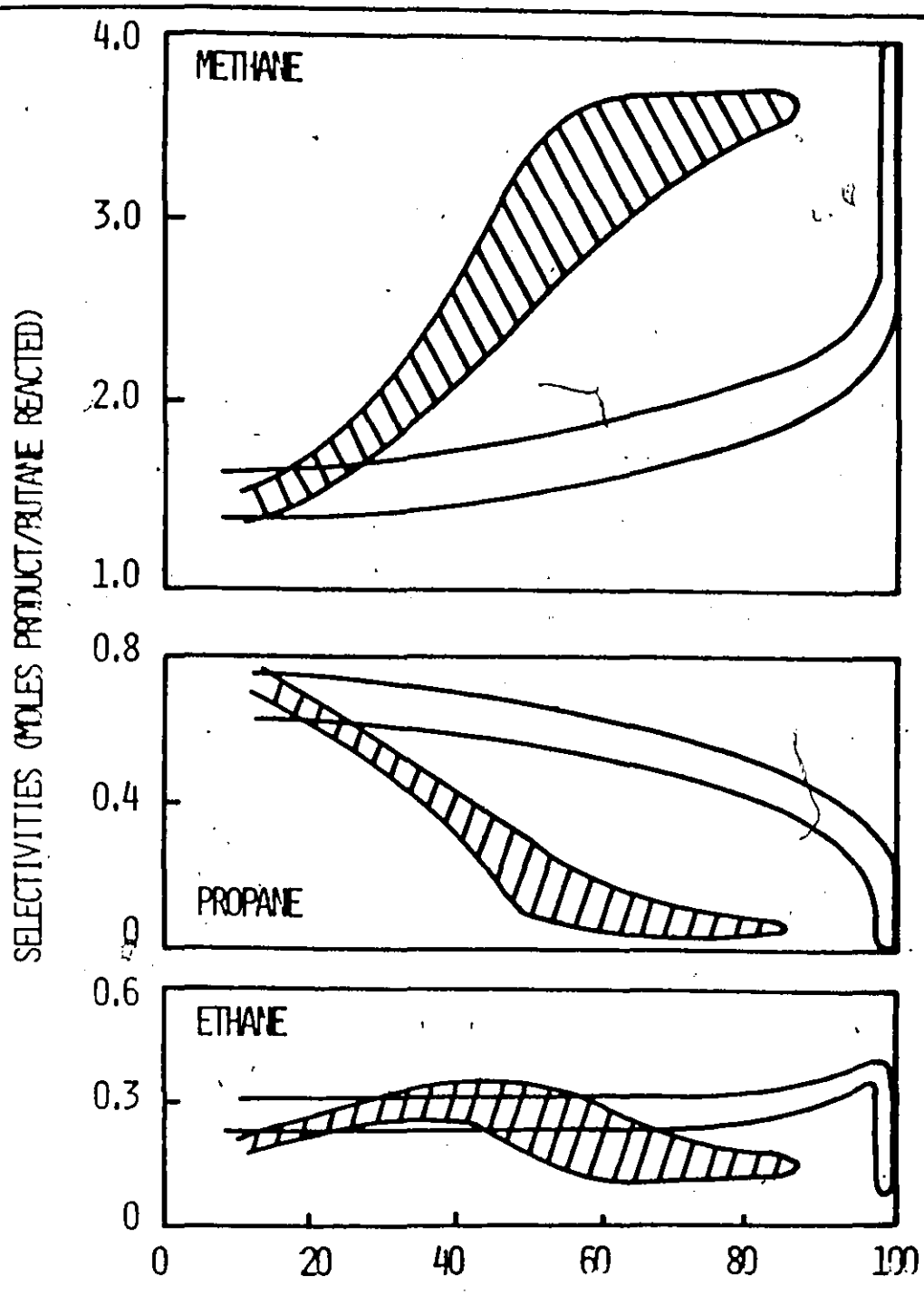


FIGURE 5.4 PACKED BED AND FLUIDIZED BED SELECTIVITIES
(ZONE INDICATING FLUIDIZED BED DATA ▨)

plots is due mainly to the wide range of temperature and feed ratios used in obtaining the data; the scatter occurs as expected from the kinetic model. The observed scatter is wider for the fluidized bed mainly because the fluidized bed was operated over a wider range of temperature and ratio (by almost a factor of two).

It is to be noted that for the fluidized bed data, the selectivity of methane is usually greater and the selectivities of ethane and propane are usually smaller than the corresponding selectivities observed in the packed bed. The selectivities approach each other at low conversions where presumably differences in composition between the two phase in the fluidized bed become small (interchange rate high relative to the reaction rate) and hence the two reactors exhibit essentially the same behaviour. At low hydrogen-to-butane molar feed ratios, the hydrogen inhibits the reaction much less and higher rates and conversions are observed. This is a region where interchange significantly influences the conversion attained.

For overall conversions greater than 40% in the fluidized bed, the selectivities observed for the fluidized bed runs correspond to selectivities in the packed bed at essentially total conversion of butane. Moreover, at high reaction rates the selectivities are most probably determined by the local extent of reaction. This suggests that the conversion of butane in the emulsion phase, where most of the reaction takes place, is quite high and hence the relatively low overall conversion is due to the bypassing effect of the bubbles. It follows that the reaction kinetics if they are to be applied to a fluidized bed reactor must be accurate in the region of high conversions of the primary

reactant (in this case, butane).

The selectivites of methane, ethane and propane are independent of the rate of butane reaction. The selectivities are however strongly dependent on the local extent of reaction in the sense that extent of reaction determines the local gas phase composition and hence the surface composition of absorbed species on the catalyst. The rate of butane reaction is strongly correlated with gas interchange rate as shown in Figure 5.1. Selectivities will, of course, also be determined by the gas interchange rate because this phenomenon affects gas composition in the emulsion phase. Our experience suggests, however, that when the ratio of rate of reaction to rate of gas interchange is high, the selectivity will be determined primarily by the local extent of reaction.

PREDICTION OF FLUIDIZED BED SELECTIVITIES AND CONVERSION

To determine how closely the reactor could be modelled and to detect any major weakness in the two-phase modelling concept the ORCMIX (Orcutt's bubbling bed model assuming perfect mixing in the emulsion) model was used. This model was chosen for its simplicity and short computing time requirements. The interchange parameter which in the Orcutt model is given by

$$\frac{(q + k_G S_h)\ L}{U_{br} V_b} \qquad 5.15$$

accounts for the gas interchange between bubble and emulsion phases. Here it was not estimated from equation 5.15. A value was estimated for each operating condition such that the sum of squares of the difference between the predicted and observed conversion and selectivities was a minimum leaving two degrees of freedom per trial. The sum of the relative errors between

the predicted and the observed values of the conversion and the selectivities of propane and ethane was used as the objective function. The selectivity of methane is not an algebraically independent response and so was not included in the weighting. The kinetic parameters used were those from the initial packed bed study and are shown in the first column of Table 4.7. A constant catalyst activity of 3.65 as indicated from packed bed studies was assumed to describe the activity of the catalyst in the fluidized bed. Hence, the interchange parameter was the only adjustable parameter in the reactor model. The variation of this reactor interchange parameter showed no direct correlation with flow but some with temperature. Its most probably value was in the range of 1.0 to 1.5. Some of these interchange factors were as low as 0.6 while others were as high as 30. No real significance can be attached to some of these values for the reasons suggested in Section 5.4.

The calculated selectivities are shown along with the envelopes covering the experimental data in Figure 5.5. The propane selectivities are predicted fairly well. Above about 25% butane conversion, however, the ethane selectivity is predicted too high and was worst for the low ratio runs. Since methane is not an independent component, predicting the ethane selectivity too high results in the methane selectivity being predicted too low. A few conditions were tested using the ORCPLG and the KATWEN (0) models and the same trends were observed.

This result is not surprising since the kinetic model was known to break down at low hydrogen-to-butane ratios and high conversions.

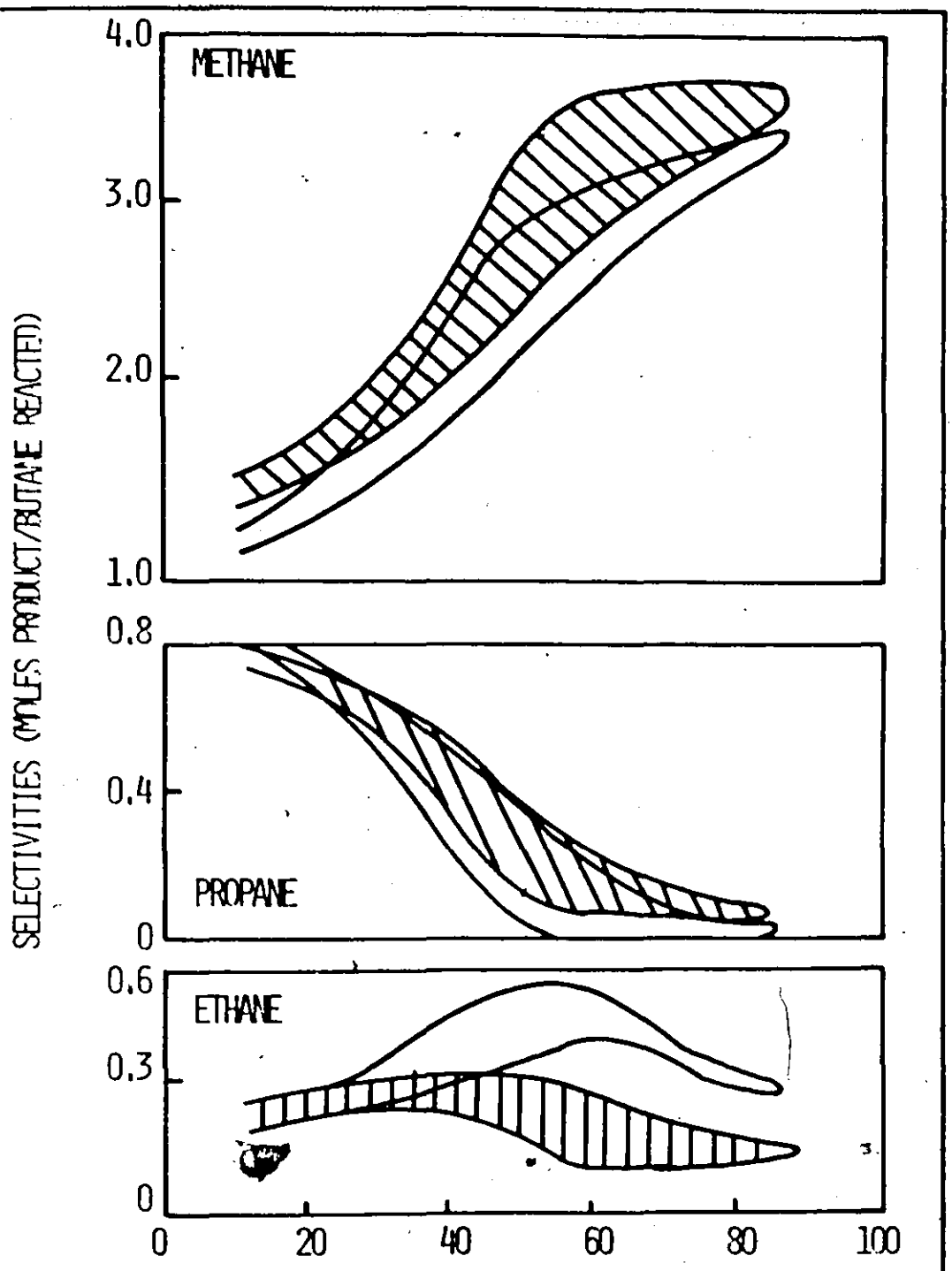


FIGURE 5.5 PREDICTED FLUIDIZED BED SELECTIVITIES WITH ORIGINAL KINETICS.
(ZONE INDICATING FLUIDIZED BED DATA ▨)

The selectivities observed for a wide range of conversions in the fluidized bed are in the exact range of selectivities observed for the packed bed reactor at 100% conversion. This suggests that even at moderate overall conversions in the fluidized bed reactor there is a very high conversion occurring in the emulsion phase. This means that any kinetic model must be quite accurate in its predictions at high conversions.

ONE KINETIC PARAMETER ADJUSTED

The predictions of the selectivities were poor and deviated systematically as the observed conversion in the fluidized bed increased. The hypothesis to be tested was that the predicted selectivities were poor because:

(i) the conversions of butane and propane are high where reaction occurs in the bed and

(ii) the inability of the kinetic model to predict the ethane behaviour at these high conversions is the prime reason for the breakdown of the overall reactor model.

To do this, the kinetic parameter relating the ratio of reaction rate of ethane to its desorption rate was adjusted empirically to account for the lack of readsorption of ethane. That is, increasing this ratio has the same overall effect as readsorbing ethane on the catalyst; the desorption rate thus becomes a net rate. This is not entirely correct since the other kinetic parameters were determined on the basis that readsorption was negligible. This parameter was found in the following way: the interchange parameters which were determined in the first fit of experimental and predicted data were used here; this new kinetic

parameter was estimated to yield the minimum sum of squares fit of the calculated and observed mole fractions of ethane in the exit stream of all runs.

The new predictions of selectivities are shown on Figure 5.6. The trends are now predicted extremely well. Both the methane and propane selectivities improve because of the interaction among hydrocarbon components and with hydrogen concentration. The accuracy of the predictions is more easily visualized on Figure 5.7 where the observed responses are plotted against the predicted ones. There is however, a significant correlation of the selectivity residuals with conversion.

TEST OF FLUID MECHANIC MODEL

Most of the initial modelling of the fluidized bed was carried out using the Orcutt perfectly mixed model, ORCMIX. The computing time requirements were low and a complete investigation using all six models was not warranted since it was demonstrated in the packed bed experiments and the fluidized bed experiments that the kinetic model was deficient in its treatment of the ethane adsorption-desorption phenomena. However, the predictions of the ORCMIX model were compared to those of the Kato and Wen (KATWEN(0)) model. The original kinetic parameters were used and again an interchange parameter was estimated for each run. The observed versus the predicted conversions are shown for both models in Figure 5.8. Much of the correlation of residuals is removed by the Kato and Wen model. The sum of squares of residuals for the Kato and Wen model is half that for the Orcutt perfectly mixed model.

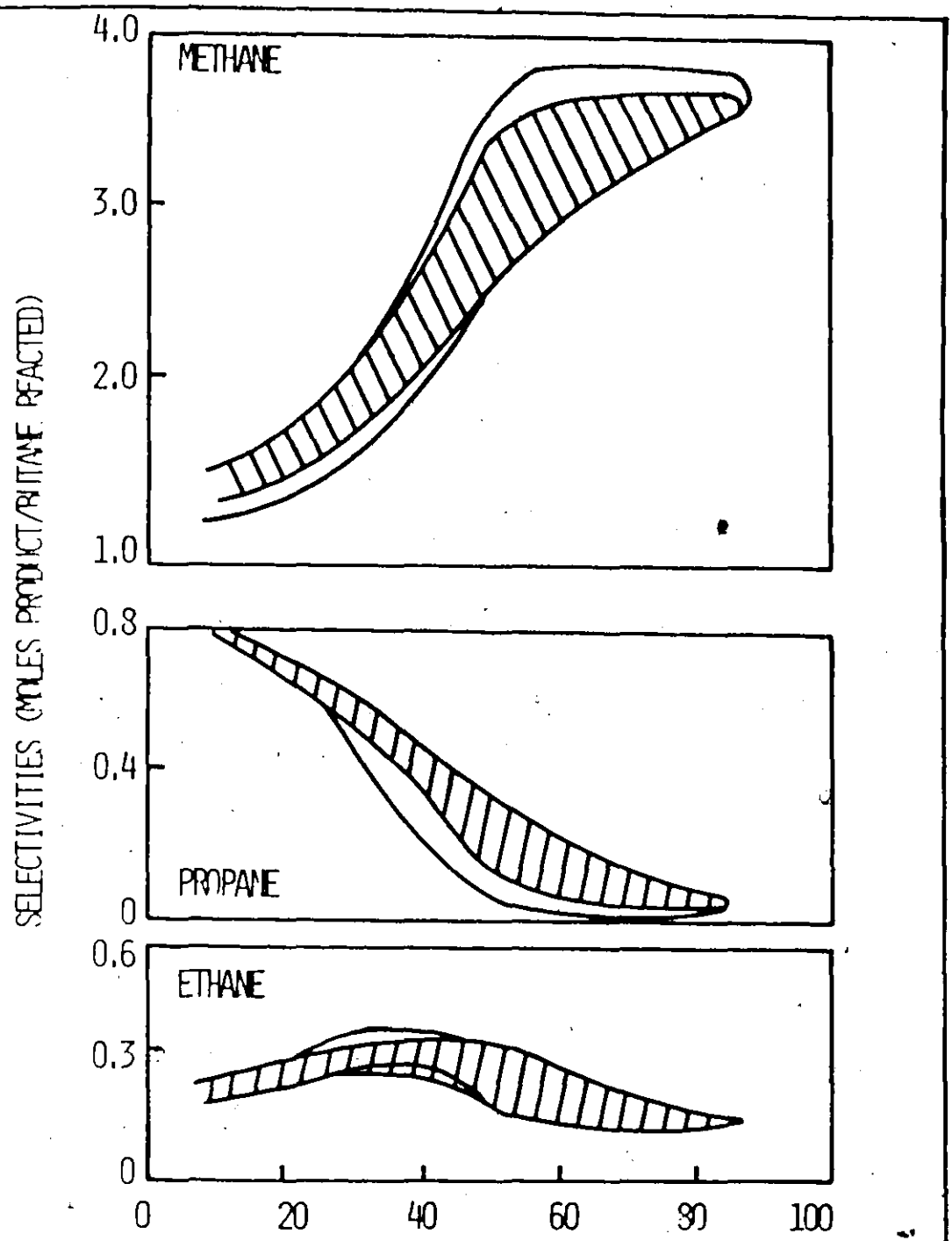


FIGURE 5.6 PREDICTED FLUIDIZED BED SELECTIVITIES WITH CORRECTED KINETICS (ZONE INDICATING FLUIDIZED BED DATA ▨)

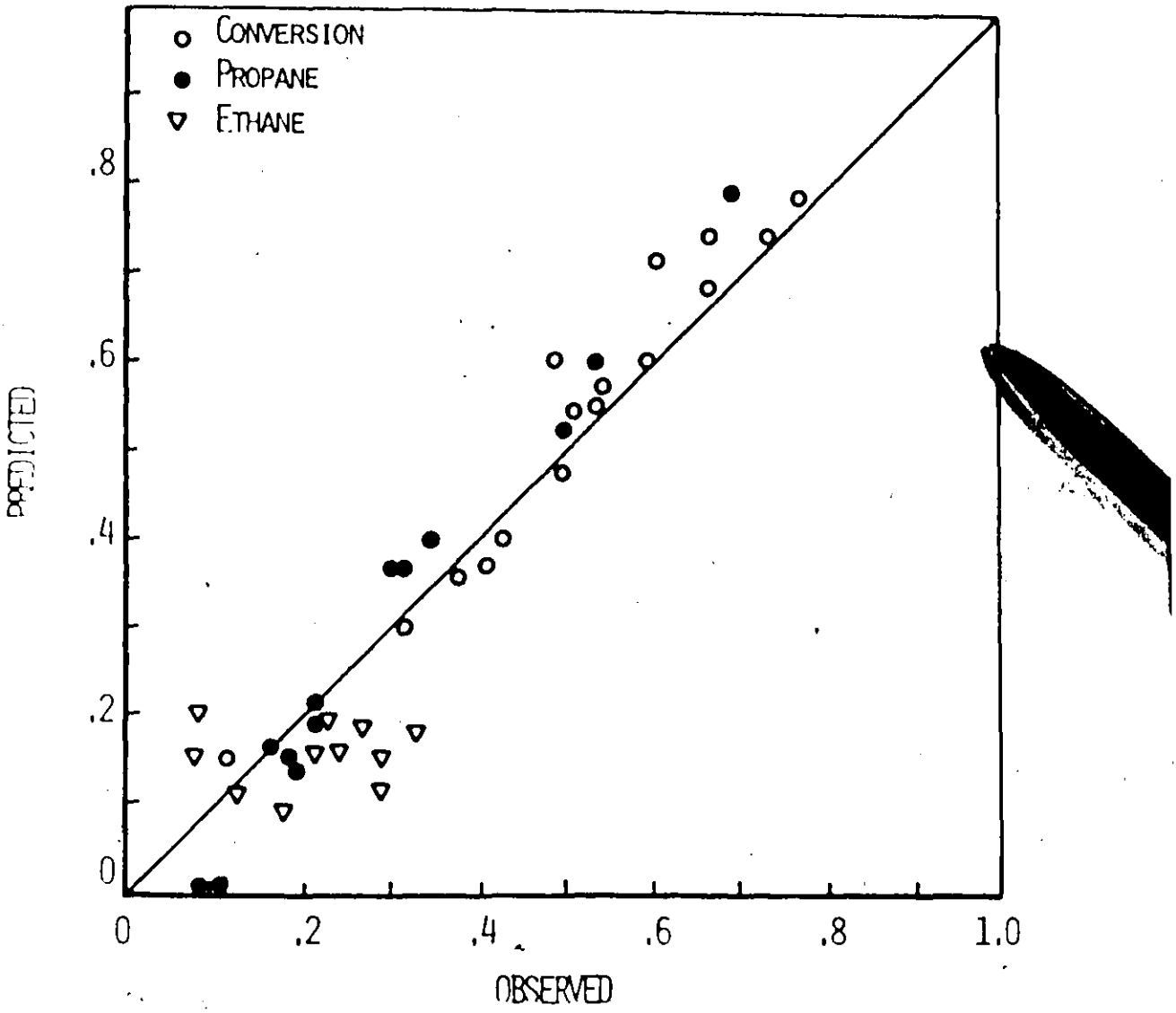


FIGURE 5.7 ACCURACY OF PREDICTIONS OF FLUIDIZED BED DATA FOR ORCUTT PERFECTLY MIXED MODEL AND ADJUSTED KINETICS

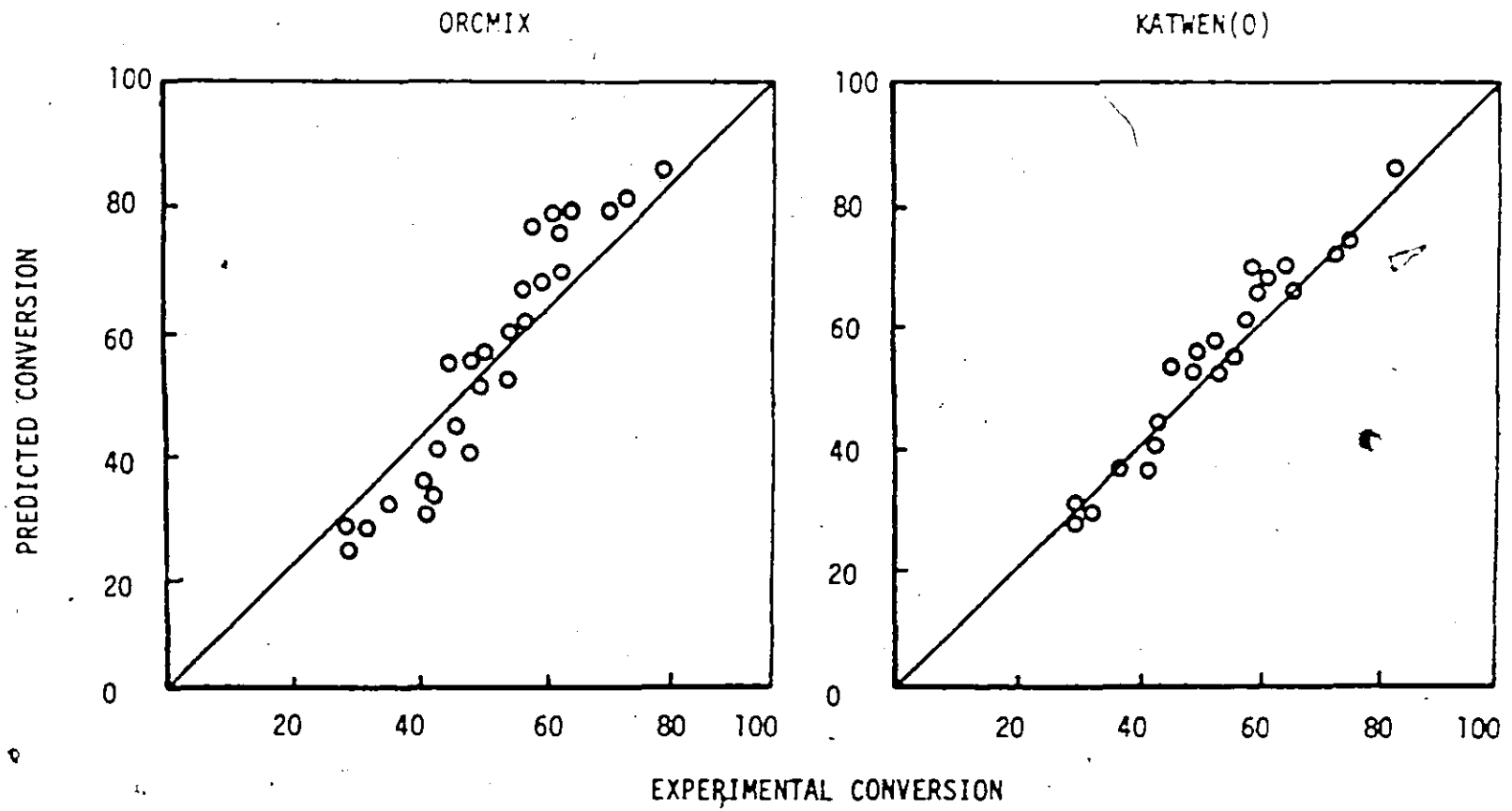


FIGURE 5.8 PREDICTED AND EXPERIMENTAL CONVERSION FOR ORCUTT PERFECTLY MISEC AND KATO AND WEN MODELS USING UNADJUSTED KINETICS

5.4 SUMMARY OF INITIAL FLUIDIZED BED STUDY

An evaluation of the initial phase of the study can only be made by first considering the goals of the study. They are to first produce simulation models of an existing fluidized bed and then to discriminate among the available models and to choose the best one. In developing the simulation models, the kinetics of the reaction are determined independently of the fluidized bed. Then, using these kinetics, the fluidized bed is modelled by estimating a parameter which describes the flow within the reactor.

A satisfactory model for a fluidized bed chemical reactor for inclusion within a process simulation has been achieved through use of:

(a) a simple model to describe the fluid mechanical behaviour within the reactor,

(b) kinetic constants evaluated from experiments performed on a bench-scale integral fixed-bed reactor (01), and

(c) conversion and selectivity data obtained from reactor experiments.

This model predicts conversion and selectivities of all components with fair accuracy over a wide range of feed flowrates, hydrogen-to-butane feed ratios and temperatures. A single parameter which could be related to the fluid mechanical behaviour could be estimated from the reactor experiments. Moreover, the chemical kinetic model could be modified through use of the same experiments to partially account for inadequacies in the original kinetic model based on the fixed bed experiments. The structure of this mechanistic model provided an insight into the actual modification required.

No attempt was made to discard any of the fluidized bed models at this stage, since a number of refinements and modifications needed to be made to all the models. The discarding of some of the models would not reduce the computation time necessary to affect the modifications. The changes that had to be made before discrimination was attempted were:

(i) The kinetic model must include the readsorption of ethane onto the catalyst and must be tested at very high conversions.

(ii) A better model is needed to describe the gas interchange between the emulsion and bubble phases.

(iii) The effect of the uncertainty in the kinetic parameters on the predicting ability of the fluidized bed models must be investigated.

The importance of multiple response data including selectivities as well as conversion becomes very evident. It must be emphasized that selectivity information, unlike only conversion information (as used entirely in most previous studies reported in the literature) gives more information about the conditions of the local areas where reaction actually occurs. That is, from conversion data alone, local rates of reaction or conversion cannot be inferred without an almost perfect knowledge of gas interchange between bubble and emulsion. This is because, in a fluidized bed model, the rate of reaction and the interchange parameter are strongly correlated so that a single conversion may be obtained from a wide variety of rates and interchange parameters. This also means that unless one has a high level of confidence in the chemical reaction model and the kinetic parameters at the local conversion or extent of reaction, correlation between an estimated

interchange value and the actual physical interchange value would be fortuitous.

In the situation where the rate of reaction is large compared to the rate of interchange between the bubble and the emulsion, the emulsion will be almost depleted of reactants. It thus becomes necessary to investigate the kinetics over all conversions and particularly at the high conversions that will occur throughout the emulsion phase of the fluidized bed. Thus in the study of fluidized bed reactors, the study of gas interchange and bubble mechanics may not be sufficient. For a fast reaction it is also necessary and equally important that the reaction rate be investigated under conditions that will exist in the cloud, wake and emulsion. If this is not done, any physical interpretation of interchange parameters would be unreasonable.

The performances of the various two-phase models are evaluated and compared in Chapter 6. Once the kinetic and interchange models are improved, model discrimination can be attempted.

6.0 FINAL FLUIDIZED BED STUDIES

In Chapter 5, the predicting ability of the fluidized bed models was evaluated using the initial set of parameters for the reaction kinetics. The results indicated that further experimental work was necessary to modify the kinetic model and to estimate the required parameters at higher conversions. This refinement of the kinetic model and the design of the required experiments is described in Chapter 4. The discrimination studies among the fluidized bed models with the improved kinetic model are reported in this Chapter.

6.1 MODEL EVALUATION WITH IMPROVED KINETICS AND INTERCHANGE

The six fluidized bed models were evaluated using the existing experimental data. Two parameters were estimated in each model (the interchange parameter θ^* in equation 5.2 and the catalyst activity in equations 4.8, 4.16 and 4.23) by maximizing the likelihood function for these two parameters, that is:

$$L(\theta^*, \frac{k}{k_o}) \sim p(\underline{y}/\underline{\eta},\ \theta^*, \frac{k}{k_o}) = \frac{1}{(2\pi)^{N/2}|\underline{\Sigma}|^{n/2}} \exp\left\{-\tfrac{1}{2} \sum_{u=1}^{n} (\underline{y}_u - \underline{\eta}_u)^T\ \underline{\Sigma}^{-1}\ (\underline{y}_u - \underline{\eta}_u)\right\} \quad 6.1$$

To do this the objective function:

$$\sum_{u=1}^{n} (\underline{y}_u - \underline{\eta}_u)^T\ \underline{\Sigma}^{-1}\ (\underline{y}_u - \underline{\eta}_u) \quad 6.2$$

was minimized with respect to θ^* and k/k_o. The Rosenbrock algorithm (R4) was used to search for the parameters. $\underline{\Sigma}$ is the variance-covariance matrix for the fluidized bed experiments.

EXPERIMENTAL VARIANCE COVARIANCE MATRIX

An estimate of the experimental error was needed for the three independent experimental responses. They were: the selectivity of methane, the selectivity of propane and the quantity unity minus conversion. During

the first set of 1-86 experiments, there were 29 independent trials at the mid-point or center-point operating conditions. Since these trials were also randomized, they were used to provide an estimate of the experimental variance-covariance matrix. These experiments had been included in the initial trials to monitor the catalyst activity or any other phenomena that would have affected the experimental responses other than the three control variables. The variance-covariance matrix evaluated from these mid-point experiments is shown in Table 6.1. No transformation of the variables was necessary for the fluidized bed experiments.

With 29 experiments there are a large number of degrees of freedom for $\tilde{\Sigma}$. Thus $\tilde{\Sigma}$ should be a good estimate of Σ and could be used for weighting in parameter estimation.

PARAMETER ESTIMATION

The 32 experiments used for parameter estimation are listed in Appendix J. These data represent the second of the two analyses which were obtained at each experimental condition. The second was chosen because the reactor operation had stabilized for a longer period and the attenuations on the chromatograph could be properly chosen for each response. The trials in this series employing propane or ethane feeds were not included because the kinetics were not tested for these feeds and the reaction rate was low at the operating conditions investigated. As presented in section 5.0 and shown in Figure 5.1, experimental

	S1	S3	1-CONV.
S1	1.4115×10^{-3}	-2.1312×10^{-4}	-1.1692×10^{-4}
S3	-2.1312×10^{-4}	6.8623×10^{-5}	4.3709×10^{-5}
1-CONV	-1.1692×10^{-4}	4.3709×10^{-5}	1.4982×10^{-4}

TABLE 6.1 VARIANCE-COVARIANCE MATRIX DUE TO EXPERIMENTAL ERROR FOR THE FLUIDIZED BED

trials at low reaction rates may not be reliable for estimating the interchange that is occurring.

The results of estimating both the catalyst activity and the interchange parameter for each model using the 32 trials are shown in Table 6.2. The time reported is the time in seconds required for the evaluation of each model at one catalyst activity and one interchange parameter for all of the 32 trials. Note that there is a wide range of execution times for the various models employed. The large computer time for the Partridge and Rowe and the Orcutt plug flow models arises because of the integration and error evaluating routines and hence makes them less desirable as models for optimization studies. Indeed, the cost of computer time for these models with the complex kinetics included was considered too great to include them in any further part of this study.

With the exception of the Kato and Wen model KATWEN (1) which includes the wake with the bubble, the parameters estimated for the basic six models are quite similar. The estimated values of the catalyst activity range from 1.42 to 1.65 for the various models. The interchange parameter ranges from 0.371 to 0.436. In fact, much of this range is due to the KWMIX model with a higher estimate of the catalyst activity and a corresponding lower estimate of the interchange parameter. There is obviously a fairly large correlation between the interchange parameter and the catalyst activity but this correlation was not investigated.

MODEL DISCRIMINATION BY THE MAXIMUM LIKELIHOOD METHOD

The likelihood values in Table 6.2 are scaled by an arbitrary constant. The absolute value of the reported likelihood is of no direct interest, rather

MODEL	CATALYST ACTIVITY	0*	k * L	TIME
DRCMIX	1.42	0.426	1.9×10^{-95}	1
DRCPLG	1.45	0.422	2.0×10^{-85}	110
PARROW	1.53	0.436	5.0×10^{154}	320
KATWEN (0)	1.58	0.430	6.4×10^{174}	36
KATWEN (1)	1.37	0.218	$< 10^{-200}$	39
KWMIX	1.65	0.371	1.1×10^{156}	25
KATWEN (0) D_B = CONSTANT	1.68	0.374	2.2×10^{165}	
KATWEN (0) V_C = 0.0	1.74	0.429	3.6×10^{-102}	

TABLE 6.2 ESTIMATED CATALYST ACTIVITY, INTERCHANGE PARAMETER FOR FLUIDIZED BED EXPERIMENTS 1-86 AND MODEL LIKELIHOODS

the ratios of those values can be examined to assess relative goodness of fit from one model to another. A ratio of likelihoods of 100 denotes strong preference for one model over another; a ratio of 10 usually indicates a real difference.

The first six entries in Table 6.2 are for the models as presented in section 5.2. On the basis of the likelihood ratios, the basic Kato and Wen model proves to be by far the best to describe the operation of the fluidized bed reactor. The Kato and Wen formulation with a completely mixed emulsion appears to be next best but is definitely inferior. Surprisingly, this mixed emulsion model is only marginally more acceptable than the Partridge and Rowe model which is based on plug flow of the gas in the emulsion phase. The Orcutt et al. models are very poor relative to those already mentioned. The model with the worst performance is the basic Kato and Wen model with the wake and associated catalyst particles included with the bubble. The experimental trials at very high reaction rates are most responsible for the poor performance of this model. The high reaction rates and the amount of catalyst in contact with n-butane in the bubble resulted in predicted conversions that were far higher than those observed. Even reducing the wake fraction to 10 % which is well below the accepted range of 20% to 35% made little improvement in the performance of the model.

MODEL SENSITIVITY TO ASSUMPTIONS

In order to investigate whether the assumption of a constant bubble size or the assumption of no cloud included with the bubble was the major cause of the poor performance of the models of Orcutt et al., two additional

tests were performed. The basic Kato and Wen model KATWEN(o), was modified to closely behave as the ORCMIX model except for the method of solution so as to investigate these assumptions one at a time. The results of these tests are shown in Table 6.2. For the experimental trials performed, the assumption of a constant bubble size does not appear to be as restrictive as the assumption of no catalyst in the phase representing the cloud and the bubble.

The sensitivity of a number of the bubble properties was investigated at this time. The KATWEN(o) model was chosen for the study since it had performed best in predicting the reactor selectivities and conversion. The catalyst activity and the interchange parameter were not estimated again. The values of these parameters as reported in Table 6.2 were used. The various parameters investigated were each increased 5% one at a time. The results are shown in Table 6.3. One observation to be made from these data is the greater change in the likelihood effected by the 5% increase in the interchange than by a corresponding change in any of the other parameters. It is noted that by increasing the volume of the cloud a slightly larger likelihood results.

Table 6.2 summarizes the evaluation of the relative performance of the various models in predicting the experimental data obtained during the initial reactor trials. All these trials were at one depth of catalyst bed and had not been designed specifically to discriminate among the various models. In order to evaluate the models for a different bed depth, experiments were designed for the purpose of discriminating among the models at a lower bed depth. These experiments and the design techniques employed to choose the operating temperatures, feed ratios and

PARAMETER INVESTIGATED	k L
KATWEN (0) FROM TABLE 6.2	1.0
1.05 x cloud volume	5.5
1.05 x bubble rise velocity	2.5×10^{-2}
1.05 x bed height	4.7×10^{-6}
1.05 x 0* (interchange)	1.6×10^{-8}
1.05 x catalyst activity	1.2×10^{-5}

TABLE 6.3 INVESTIGATION OF FIVE PERCENT CHANGE IN SEVERAL PARAMETERS IN THE KATWEN (0) MODEL

flowrates are presented in section 6.2

6.2 EXPERIMENTAL DESIGN FOR MODEL DISCRIMINATION

A summary of some of the possible techniques employed for the design of experiments for model discrimination is presented in section 3.4.2. In some of the simpler criteria operating conditions are selected so that the predicted responses of the models being entertained will be most different. However, the precision of the predictions under the models being entertained may be greater for some operating conditions than others. This latter effect along with differences in predicted responses are incorporated into the design criterion proposed by Box and Hill (B12, H7). However, the Box and Hill criterion was not employed. This method required the evaluation of the terms referring to the error in prediction for the models. In this particular case, the major contribution to the prediction error is not as indicated by Box and Hill but is that resulting from uncertainties due to the kinetic parameters. To include this effect would require a large expenditure of computer time since derivatives would have to be evaluated at each possible operating condition.

A modified criterion was employed to determine the separation among the model responses for a particular operating condition. The original formulation by Roth (R7) was for the single response case. This can be modified to cover the multiple response situation as shown in equation 3.22.

$$z'(\underline{\xi}) = \sum_{i=1}^{m} \sum_{\substack{j=1 \\ j \neq i}}^{m} \{P(i,n-1) + P(j,n-1)\} \{(\underline{\eta}_i - \underline{\eta}_j)^T \tilde{\underline{\Sigma}}^{-1} (\underline{\eta}_i - \underline{\eta}_j)\} \qquad 6.3$$

where subscripts i and j refer to each of the models. Note that the quadratic form within the curved brackets is multiplied by the sum of the current Bayesian probability of each model which is determined after (n-1) trials.

From the results of initial investigations of the models as presented in Table 6.2, three models were far more likely than the others. Because of excessive computational requirements the PARROW model was not included. For experimental design for model discrimination between two models the prior probability of each model does not affect the choice of operating conditions for the discrimination function employed.

If a block of experiments is to be performed, the standard design techniques will choose the same or very nearly the same set of operating conditions to be repeated. This, of course, is to be expected since there is usually one condition that will be better than the rest for the purpose of discriination. However, in additon to obtaining good discrimination among a number of models, the engineer evaluating them should make some attempt to test the models over the total range of operating conditions expecially if the conditions are different from any investigated to date. There may be operating conditions far from those that provide the best possible discrimination however, that still provide good discrimination. By including these experiments in a block of experiments, the total separation achieved among the models may be slightly less, but the performance of the models can be evaluated over a wide range of control variables. A number of trials at one condition may be no better than a point estimate. In keeping with this philosophy, a bed height different from that of all the previous trials was used. Since no additional catalyst

was available, the bed height was reduced from 77 cm. to 47.6 cm.

The first vector of operating conditions selected was the one that produced the greatest difference between the two models as defined by equation 6.3. The second and subsequent operating conditions are selected by maximizing the expression given by equation 6.4:

$$\left[Z'(\underline{\xi}_k)\right]^b \times \left[\sum_{i=1}^{n'} \sqrt{\left(\sum_{j=1}^{3} (\xi_{jk} - \xi_{ji})^2\right)}\right] \quad \begin{matrix} k = 1,400 \\ i = 1, n' \end{matrix} \qquad 6.4$$

where $Z'(\underline{\xi}_k)$ is the measure of the difference between the models for the k'th possible set of control variables $\underline{\xi}_k$ as defined in equation 6.3. The subscript j refers to each of the three control variables. The second term in equation 6.4 represents the sum of the distances in control variable space between the k'th possible set of control variables and each of the control variables for the n' conditions already selected to be included in the design. The exponent b is used to scale the relative magnitudes of the two terms in equation 6.4. Its value can be set depending on the range of values of $Z'(\underline{\xi})$ over the control variable space and how much weighting is required on the second term in equation 6.4. For this study, a value of 0.20 was chosen to ensure a wide range of operating conditions since the range of $Z'(\underline{\xi})$ was quite large.

The experiments that were chosen were selected from a possible set of 400. This total set of possible experiments was generated using a Monte Carlo technique to choose temperatures, flows and feed ratios uniformly and randomly distributed over the ranges shown in Table 6.4. With 400 operating conditions selected the probability of excluding the best 1% of the operating conditions is:

$$p = (1-0.01)^{400} = 0.018$$

CONTROL VARIABLE	RANGE	INCREMENT
TEMPERATURE (°F)	470. - 510.	1.0
FLOW (C.F.M.)	6.0 - 12.0	0.2
RATIO (HYDROGEN/n-BUTANE)	4.0 - 6.5	0.1

TABLE 6.4 RANGE OF CONTROL VARIABLES FOR EXPERIMENTAL DESIGN FOR DISCRIMINATION BETWEEN FLUIDIZED BED MODELS

It was recognized that the Monte Carlo technique might not be the most efficient method of selecting the very best condition for one trial. However, it was chosen so that a very large number of operating conditions within the total range of conditions would be investigated. This is important since the criterion for evaluating the design also included a term which weights the spread in the sets of control variables as measured by the distance in control variable space among the control variables.

The best 13 experimental trials to perform, as selected from the 400 are listed in Table 6.5 in decreasing order according to the criterion of equation 6.4. The value of $Z'(\underline{\xi})$ for each of the operating conditions as well as the expected responses for both modles are presented. These data are for a bed depth of 47.6 cm. which was the measured depth of catalyst in the reactor. The best estimates of catalyst activity and interchange for each separate model, as listed in Table 6.2, were used to calculate the model responses.

Several observations can be made concerning the operating conditions selected. The greatest separation between the models large ($Z'(\underline{\xi})$) occurs at high temperature and low ratio (high reaction rate) and at intermediate values of flow. The modified Kato and Wen model with the perfectly mixed emulsion predicts higher conversions and methane selectivities but lower propane selectivities.

Since the catalyst activity did not change during the earlier experiments, a standard experiment was not performed after each experiment with a new operating condition, as was done in the earlier set. Rather, the second

	FLOW c.f.m.	TEMP. °F.	RATIO	k Z' (ξ)	S1		S3		CONVERSION	
					1*	2**	1	2	1	2
1	9.4	509.	4.1	3088.	3.54	3.72	0.082	0.035	0.561	0.613
2	6.0	470.	4.0	68.	2.75	2.61	0.275	0.298	0.606	0.584
3	11.6	510.	4.3	1864	3.46	3.62	0.094	0.051	0.599	0.651
4	6.6	507	4.1	2450	3.57	3.74	0.078	0.033	0.480	0.529
5	10.8	507.	4.0	2255	3.55	3.72	0.082	0.037	0.589	0.638
6	6.2	510.	5.6	248	3.31	3.41	0.120	0.088	0.481	0.520
7	10.4	508.	4.0	2826	3.56	3.74	0.080	0.034	0.579	0.631
8	7.0	505.	4.3	1583	3.49	3.66	0.090	0.045	0.508	0.547
9	12.0	507	4.5	576.	3.36	3.48	0.112	0.075	0.614	0.658
10	6.0	500.	4.2	668.	3.48	3.64	0.093	0.051	0.472	0.503
11	11.6	502.	4.0	795.	3.49	3.64	0.091	0.051	0.612	0.651
12	6.2	509.	6.4	56.	3.20	3.28	0.142	0.117	0.494	0.526
13	8.6	505.	4.0	2061.	3.56	3.74	0.079	0.034	0.551	0.595

* MODEL 1: KATWEN (0), KATO AND WEN MODEL

** MODEL 2: KWMIX, KATO AND WEN MODEL WITH PERFECTLY MIXED EMULSION

k is an arbitrary constant for scaling

TABLE 6.5 OPERATING CONDITIONS SELECTED FROM EXPERIMENTAL DESIGN FOR MODEL DISCRIMINATION

trial, as indicated in Table 6.5 was repeated at the end of the block of experiments to check that the catalyst activity had not changed. This trial is at a low temperature and thus a low reaction rate, a condition where the experimental responses are the most sensitive to changes in catalyst activity.

Great care was taken in setting the control variables at the exact values selected by the experimental design. The potentiometer used for these experiments had been sent to the manufacturer for calibration. At the end of these experiments, all the instruments that had been used were re-checked. It was discovered that there had been a large error made in the factory calibration of the potentiometer and as a result the temperatures that had been very carefully set for the experimental trials were about 13.°F. lower than the desired settings. The experimental design program was run again with a 13.°F. lower temperature range from which to choose the experimental temperatures. The same experimental conditions, except for the lower temperatures, were chosen. Now the corresponding values of $k\,Z'.(\underline{\xi})$ indicating the difference between the predictions of the two models was about eight times lower at these lower temperatures.

The conversions and selectivities of the two low temperature experiments 106, 107, 125 and 126, two samples were taken in each case, were the same. Thus, it was assumed that the catalyst activity was constant for experiments 101 to 126.

The catalyst activity and interchange parameters were estimated for the ORCMIX, KATWEN (0), KATWEN (1) and KWMIX models. The models PARROW and ORCPLG were not included.

The estimated catalyst activity and interchange parameter for each model, and the maximum value of the likelihood function, scaled by an arbitrary

constant, are shown in Table 6.6. By comparing the likelihood values of the various models, it is seen that for the data obtained at the lower bed height, the models that treat the emulsion as being perfectly mixed, ORCMIX and KWMIX, are now the most likely models. The KATWEN (1) model, as for the previous trials, is the least likely of the models used to fit the data. Including the wake solids perfectly mixed with the gas in the bubble does not result in a satisfactory model even at the lower reaction rates (lower temperatures) of these trials. The KATWEN (0) model with the stagnant zones in the emulsion does not provide as good a fit of the data as do the two models that assume a perfectly mixed emulsion phase. It would be expected that the two models PARROW and ORCPLG would, like the KATWEN (0) model, not fit these data as well as the models with perfect mixing in the emulsion phase.

There is not as great a difference between the likelihood values for experiments 101 to 126 as there was for the first set of experiments. One reason is that these likelihoods are calculated using only eleven experimental trials and not thirty-two. Also, lower bed heights and lower operating temperatures result in less discrimination between a model assuming a concentration gradient in the emulsion and those models with a perfectly mixed emulsion.

The estimated catalyst activities for all the models are less than those for the corresponding models for the preceeding trials. This may be due, wholly or in part, to the fact that the catalyst was conditioned 13.°F. lower than for all the previous trials due to the faulty potentiometer. However, the fact that the settled bed height was almost half of the height

MODEL	CATALYST ACTIVITY	θ*	k'*L
ORCMIX	0.963	0.398	2.11×10^{113}
KATWEN (0)	1.054	0.492	2.64×10^{78}
KATWEN (1)	0.980	0.250	6.12×10^{-63}
KWMIX	1.118	0.453	1.56×10^{110}

TABLE 6.6 ESTIMATED CATALYST ACTIVITY AND INTERCHANGE PARAMETER FOR FLUIDIZED BED EXPERIMENTS 101-126

of the previous trial may explain the difference in estimated catalyst activity. If the fluidized bed models do not properly account for the change in the depth of the catalyst bed, the estimated values of the catalyst activity could be expected to differ at different bed depths even if the catalyst activity were constant.

From the ratios of the likelihood values reported in Table 6.6, it can be seen that the ORCMIX and the KWMIX models are far better than the others. In addition, the ratio of the likelihood values for these two models is greater than 10^3 which was be taken as a very significant difference.

6.3 MODEL DISCRIMINATION INCLUDING THE EFFECT OF UNCERTAINTY IN ESTIMATED PARAMETERS

The likelihood values for the fluidized bed models shown in Table 6.2 and 6.6 are calculated assuming that the only errors in $\underline{w}$ the vector of observed-minus-predicted responses are due to experimental error. The vector $\underline{w}$ is assumed to be $\underline{N}(\underline{0}, \underline{A})$ where $\underline{0}$ is a 3n x 1 null vector since each of the n experimental trials produce three independent responses. The matrix $\underline{A}$ is a 3n x 3n matrix and is composed of n variance-covariance matrices $\underline{\Sigma}$ along the diagonal with all other elements zero. $\underline{\hat{\Sigma}}$ is estimated from the replicated centre-point experiments and reflects the error in experimental measurement. The effect of uncertainty in any of the parameters in these models has not been included in the calculation of the likelihoods.

Reilly (R5) in illustrating a method of model discrimination by Bayes' theorem shows one method of integrating out the nuisance parameters that are

in the models. Following that method, but for the case of multiple response experimental trials, the vector $\underline{\theta}$ of all the parameters in the fluidized bed model is $N(\underline{\theta}_o, \underline{U})$. $\underline{\theta}_o$ is the prior estimate of the parameters and $\underline{U}$ is their covariance matrix, in this case 12 x 12 since there are 10 kinetic and 2 fluidized bed parameters. The first 10 x 10 portion is the covariance matrix of the kinetic parameters $V(\underline{\theta})$ as given in Table 4.9. The eleventh and twelfth diagonal elements are the prior estimates of variance of the catalyst activity and interchange parameter respectively.

Consider the model:

$$\underline{y}_u = \left[f_i(\underline{\theta}, \underline{\xi}_u)\right] + \underline{\varepsilon}_u \qquad i = 1,2, \ldots r \qquad 6.6$$

where $\underline{y}_u$ is the vector of observed experimental responses for the u'th experiment and $\underline{\varepsilon}_u$ is the vector of experimental errors for the u'th experiment. The vector $\underline{\varepsilon}_u$ is assumed to be $N(\underline{O},\underline{\Sigma})$ where $\underline{O}$ is an r x 1 null vector and $\underline{\Sigma}$ is the r x r variance-covariance matrix. The vector $\underline{\xi}_u$ is the control variables for the u'th experiment and $\underline{\theta}$ is the vector of all parameters for the model $\underline{f}$. The quantity in square brakets is the i'th element of the r x 1 vector.

The model can be approximately linearized with respect to $\underline{\theta}$ as follows (B12):

$$\underline{w}_u = \underline{X}_u(\underline{\theta} - \underline{\theta}_o) + \underline{\varepsilon} \qquad 6.7$$

where the i'th element of $\underline{y}_u$ is

$$y_i = f_i(\underline{\theta}_o, \underline{\xi}_u) \qquad 6.8$$

$\underline{\varepsilon}$ is a vector of errors

and

$$\underset{rxp}{\underline{X}_u} = \left[\frac{\partial f_i(\underline{\theta}, \underline{\xi}_u)}{\partial \theta_j}\right]_{\underline{\theta} = \underline{\theta}_o} \qquad 6.9$$

for all the kinetic and fluidized bed parameters. Then taking expectations and covariances on the linearized model (with respect to variation in both $\underline{\theta}$ and $\underline{\varepsilon}$) the distribution of $\underline{w}_u$ is multivariate normal with expectation $\underline{0}$ and covariance matrix $\underline{X}_u \underline{U} \underline{X}_u^T + \underline{\Sigma}$. This now reflects the total uncertainty in $\underline{w}_u$ arising from uncertainties in $\underline{\theta}$ and from the experimental error.

Let $\underline{w}$ be the rnxl vector of observed minus predicted responses for all n experimental trials. Then Df ($\underline{w}$/M) the unconditional density function of $\underline{w}$ given model M is:

$$Df(\underline{w}/M) = \frac{\exp\{-\frac{1}{2} \sum_{u=1}^{n} \{ \underline{w}_u^T (\underline{X}_u \underline{U} \underline{X}_u^T + \underline{\Sigma})^{-1} \underline{w}_u \} \}}{(2\pi)^{nr/2} \left| \sum_{u=1}^{n} (\underline{X}_u \underline{U} \underline{X}_u^T + \underline{\Sigma}) \right|^{n/2}} \qquad 6.10$$

This density function can be determined for each of the models at the best estimate values of the parameters $\underline{\theta}$ and the relative magnitudes compared for the purpose of model discrimination.

A computational problem occurs when the vector $\underline{w}$ is large. In the case of the first set of experimental trials, there were 32 experiments each with 3 responses used to estimate the catalyst activity and the interchange parameter. To use equation 6.10 the determinant and inverse of a 96 x 96 matrix would have to be evaluated. It can be shown (Appendix H) that equation 6.10 can also be written:

$$Df(\underline{w}/M) = \frac{\exp\left\{-\frac{1}{2}\left\{\underline{w}^T\underline{A}^{-1}\underline{w} - \underline{w}^T\underline{A}^{-1}\underline{X}\left(\underline{X}^T\underline{A}^{-1}\underline{X} + \underline{U}^{-1}\right)^{-1}\underline{X}^T\underline{A}^{-1}\underline{w}\right\}\right\}}{(2\pi)^{nr/2}\left|\underline{U}\right|^{n/2}\left|\underline{\Sigma}\right|^{n/2}\left|\sum_{u=1}^{n}\left(\underline{X}_u^T\underline{\Sigma}^{-1}\underline{X}_u + \underline{U}^{-1}\right)\right|^{n/2}} \qquad 6.12$$

where $\underline{X}$ is a rnxp matrix of all n $\underline{X}_u$ matricies and $\underline{A}$ is a rnxrn matrix with n $\underline{\Sigma}$ matricies along the diagonal and all other elements zero. Now the quantity $\sum_{u=1}^{n}(\underline{X}_u^T\underline{\Sigma}^{-1}\underline{X}_u + \underline{U}^{-1})$ is of dimensions p x p where p is the number of nuisance parameters to be integrated out. The determinant of the rn x rn matrix $\underline{A}$ can easily be evaluated since there are n identical rxr matrices along the diagonal and all other elements are zero.

$\underline{U}$ is a 12 x 12 matrix since there are 10 kinetic and 2 fluidized bed nuisance parameters to be integrated out. The eleventh and twelfth diagonal elements are the prior estimates of the variance of the catalyst activity and of the interchange parameter respectively. Since the knowledge of the kinetic parameters in no way influenced the opinions held about the catalyst activity and the interchange parameter, the covariance among these parameters was set at zero. To estimate an a priori variance for the catalyst activity for experiments 1-86, it was expected that the catalyst activity would be greater than 0.6 and less than 1.8. Half this range is 0.6 and thus 0.36 was employed as the variance estimate. Similarly for the interchange factor, for a maximum expected range of 0.2 to 1.2, a variance estimate of 0.25 was obtained. For the second set of experiments, the assumed range was arbitrarily chosen as 0.25 of that for the first set since there was now less uncertainty in these parameters. It must be emphasized that in these cases the maximum uncertainty or ignorance in these parameters is being expressed.

The posterior probabilities for the models ORCMIX, KWMIX and KATWEN(O) are shown in Table 6.7. The ORCPLG and PARROW models were not included in

MODEL	POSTERIOR PROBABILITIES	
	Bed Height=47cm.	Bed Height=77cm.
ORCMIX	.0137	$<<.3 \times 10^{-222}$
KWMIX	.9856	$.7 \times 10^{-205}$
KATWEN (0)	.0007	1

TABLE 6.7 POSTERIOR PROBABILITIES FOR VARIOUS FLUIDIZED BED MODELS FOR ALL EXPERIMENTS PERFORMED

this final study because of the excessive computer time required. For comparison the maximum likelihoods for these models assuming the kinetic parameters to be perfectly known are shown in Tables 6.2 and 6.6. Note that as previously found for the deeper bed, the best model is again the original Kato and Wen model, but now the Kato and Wen mixed emulsion model is favoured over the others for the shallow bed contrary to the results using the maximum likelihood criterion.

For experiments 1-86 with the deeper catalyst bed (height-to-diameter ratio of approximately four), the KATWEN(0) model is far better. The other two models describe all the gas in the emulsion as being perfectly mixed while the KATWEN(0) model assumes that the gas in the emulsion phase is in stagnant zones with no axial mixing between zones. However, for experiments 101-126, with the shallow catalyst bed (height-to-diameter ratio of approximately two), there is far less difference between the models. In fact, now the two models assuming the emulsion gas to be perfectly mixed, appear to be the more likely models. It was expected that the degree of discrimination would be less for the second set of experiments for several reasons. There are only 11 instead of 32 data points included in the analysis. Also, the discrimination among the models is lower at lower bed depths and is lower at the lower temperatures at which these experiments were performed.

In this discrimination process, each model was linearized by a Taylor's series linearization about the preliminary estimated values for the chemical kinetic parameters and the final fitted values for the fluid mechanical parameter. This of course leads to two types of error. One results from the fact that the linearization itself is intrinsically an approximation and the other is an error in that the linearization would be better if better parameter estimates had been chosen for the point at which to linearize.

6.4 MODEL EVALUATION

The evaluation of a model resolves itself into two parts:

(i) testing whether the residuals are correlated with any of the independent variables, and

(ii) comparing the error in predictions with the error arising from experimental measurements.

Each of these are discussed in turn.

6.4.1 ANALYSIS OF RESIDUALS

A. Deep Bed Experiments

The observed and the predicted responses for the KATWEN (0) model at the best parameter estimates are shown in Figure 6.1. The mid-point experiments can be identified by the group of points at: S1 equal 2.8, S3 equal 0.22 and 1-X equal 0.48. The residuals of all the three responses are randomly scattered about zero (the 45° line) although the predicted propane responses at the mid-point experiments are slightly higher than the corresponding observed values.

Figures 6.2, 6.3 and 6.4 show the residuals plotted against flowrate, temperature and rates, respectively. Again, it is noted that the residuals scatter uniformly about zero, indicating no correlation with the independent variable. The model is therefore satisfactory from this viewpoint.

B. Shallow Bed Experiments

Figure 6.5 shows the observed and predicted responses for the KWMIX model at the shallow bed experiments. The points are randomly scattered about the 45° line indicating no correlation. The residuals are plotted against the three independent variables in Figure 6.6. Again, there is no

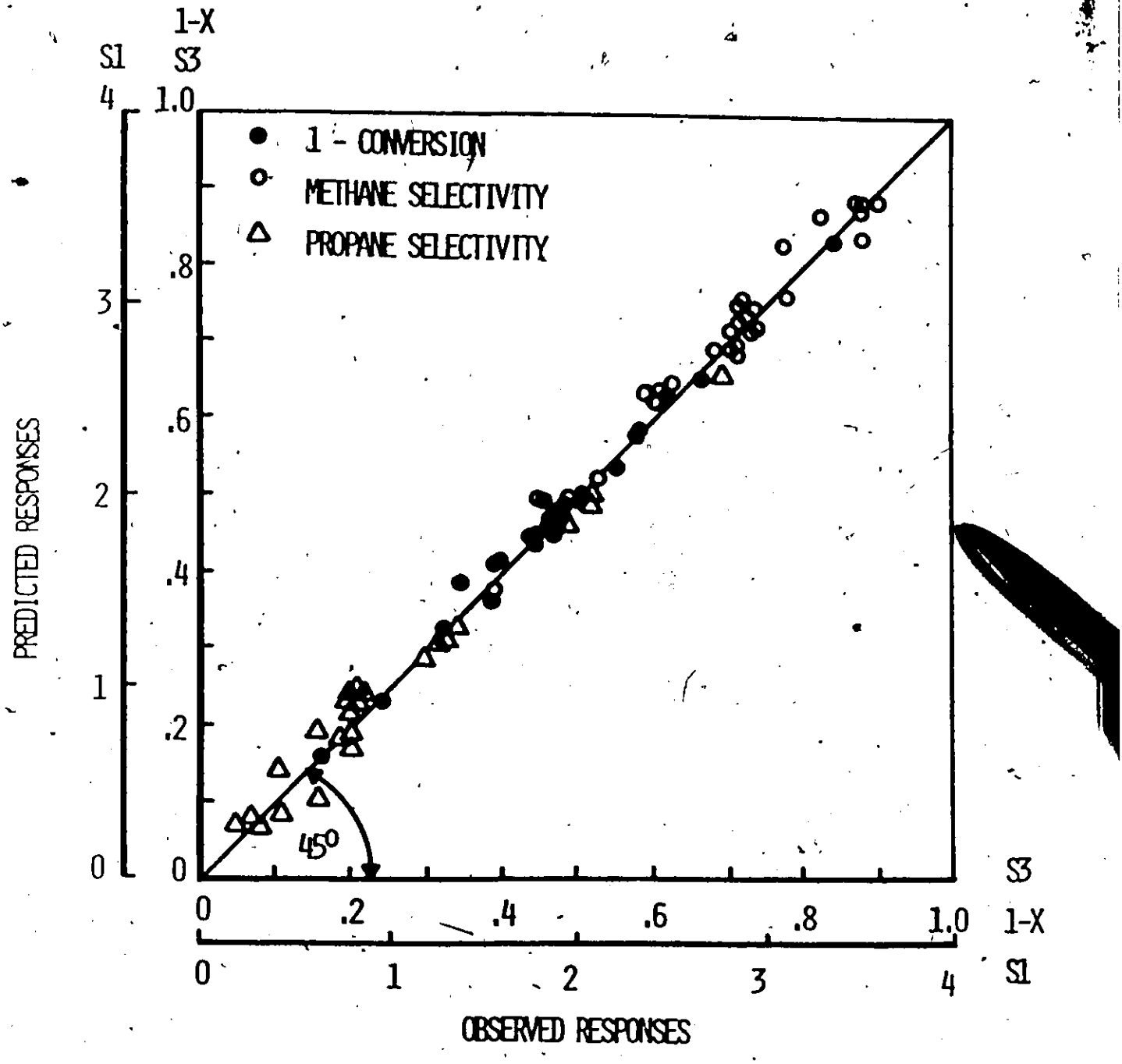


FIGURE 6.1 OBSERVED AND PREDICTED RESPONSES FOR KATHEN(0) MODEL (EXPERIMENTS 1 - 86.

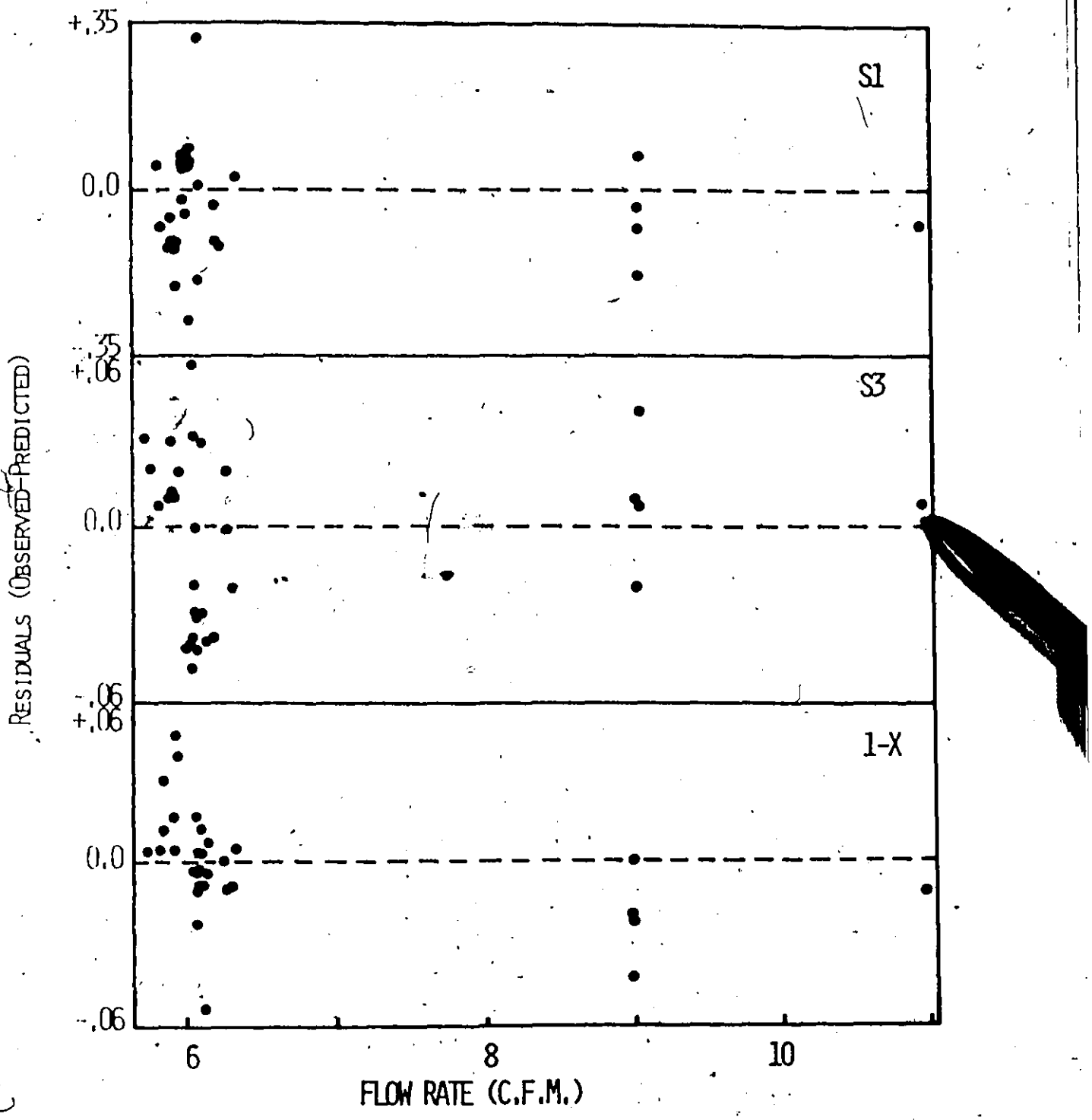


FIGURE 6.2 RESIDUALS FOR KATHEN (0) MODEL AND EXPERIMENTS 1-86 VS. FLOWRATE

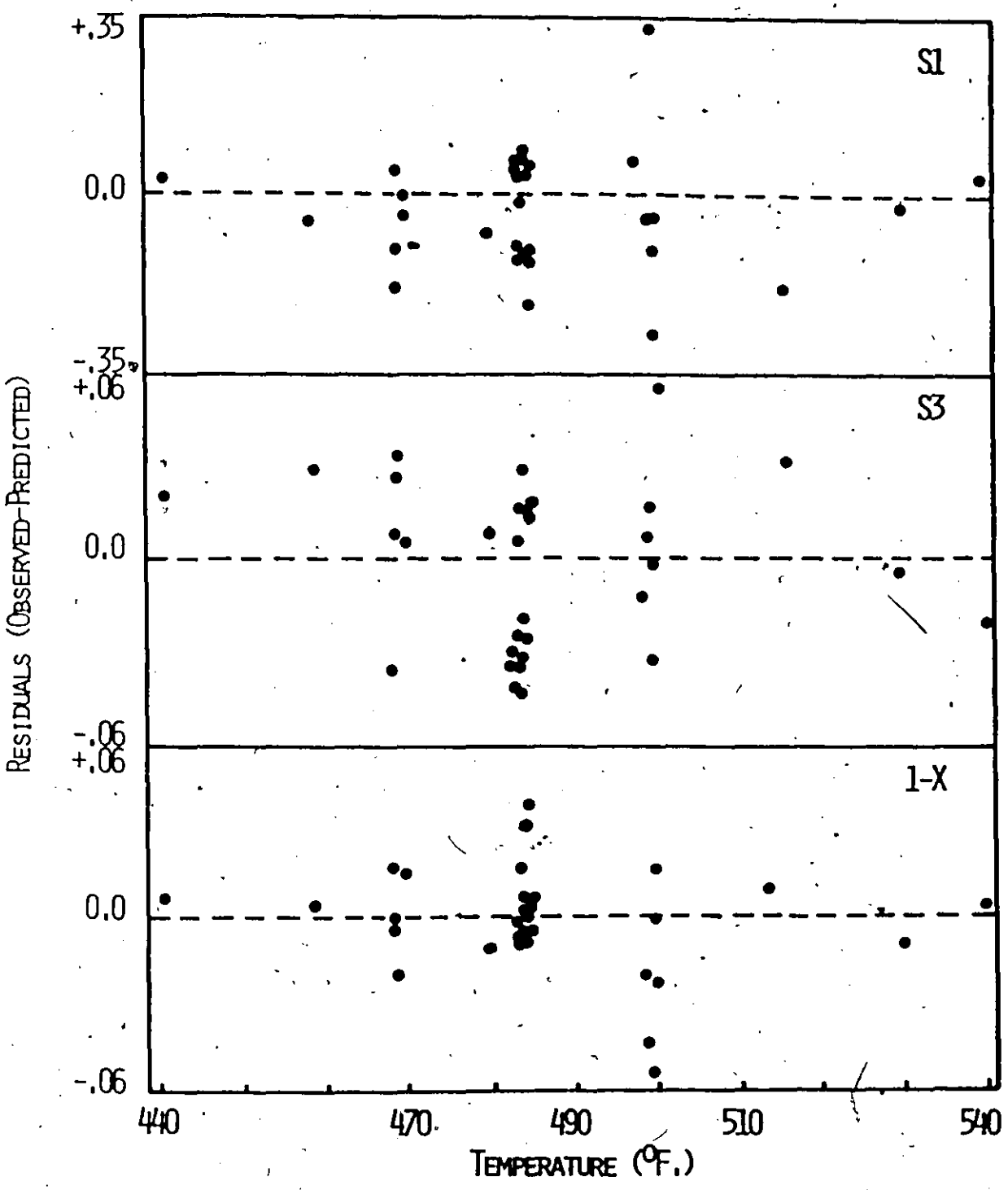


FIGURE 6.3 RESIDUALS FOR KATWEN (0) MODEL AND EXPERIMENTS 1-86 VS. TEMPERATURE

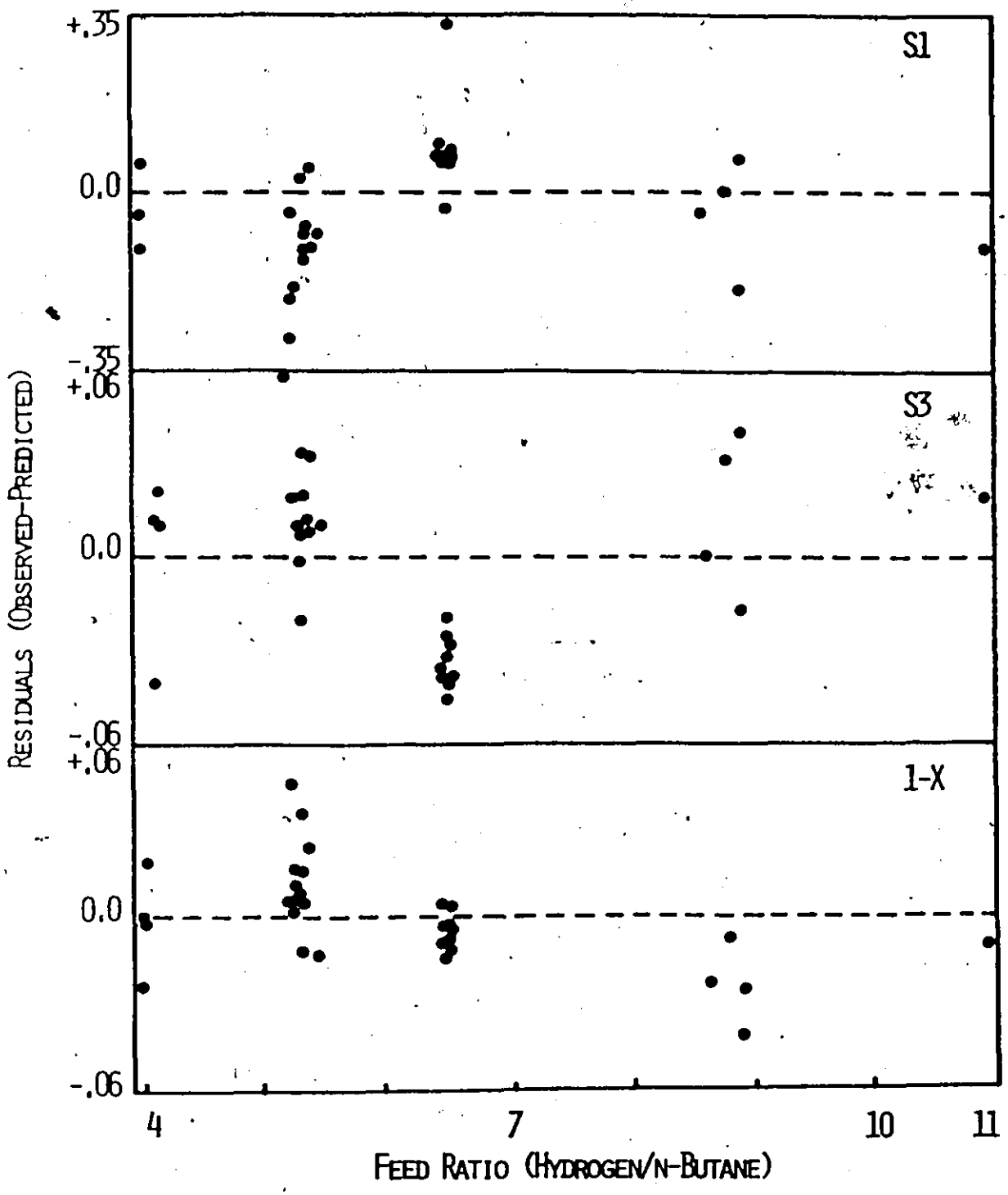


FIGURE 6.4 RESIDUALS FOR KATHEN (0) MODEL AND EXPERIMENTS 1-86 VS. FEED RATIO

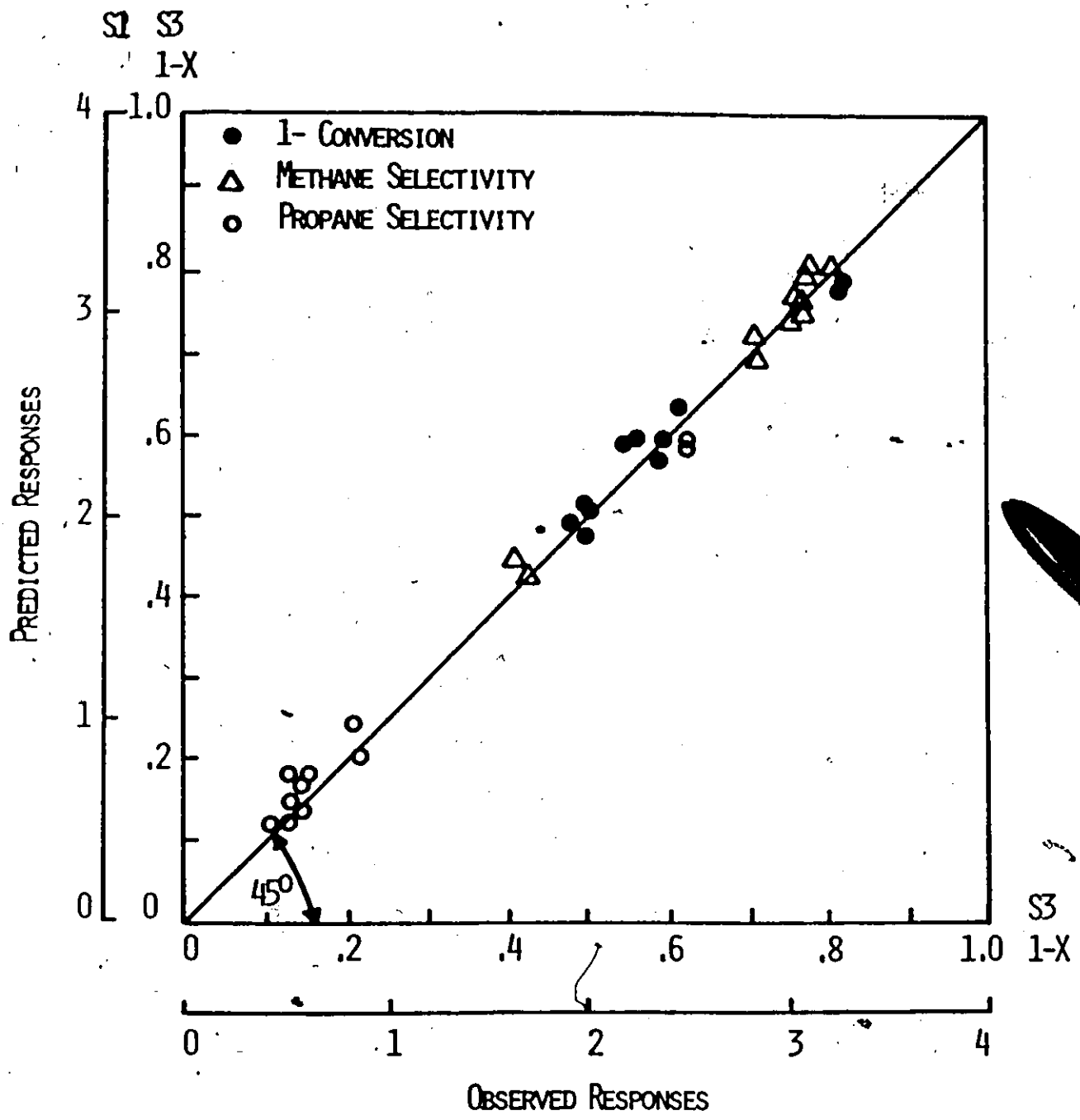


Figure 6.5 Observed and Predicted Responses for KWMIX Model (Experiments 101-126)

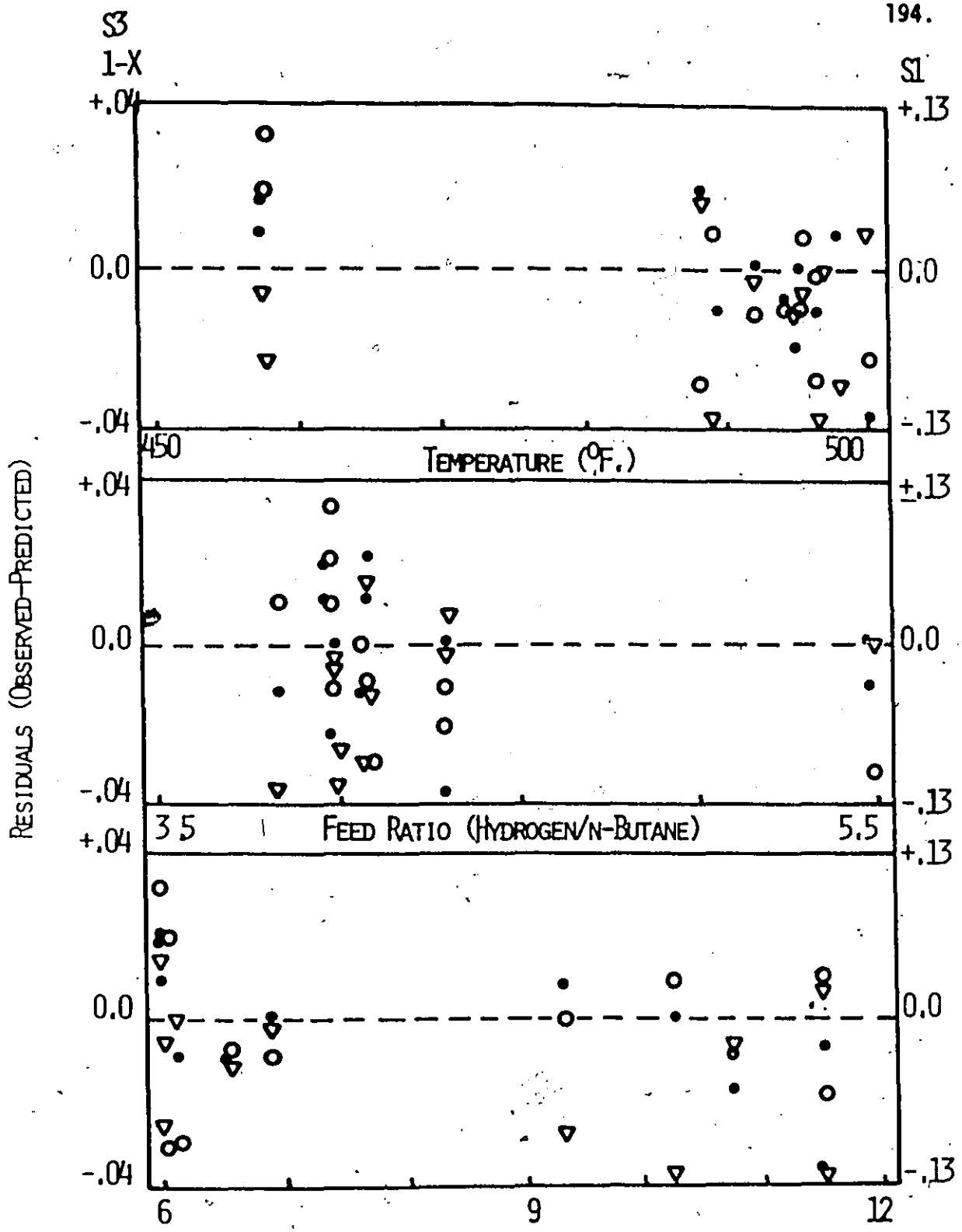


FIGURE 6.6 RESIDUALS FOR KWMIX MODEL AND EXPERIMENTS 101-126
(• 1-X, ▽ S1, ○ S3)

correlation indicating that this model is satisfactory with respect to randomization of the residuals.

6.4.2 COMPARISON OF MODEL FIT WITH EXPERIMENTAL AND PREDICTION ERRORS

For the case of an experimental system with one measured response per experimental trial, the experimenter can assess the lack of fit of a model by comparing the difference between the observed and the predicted responses with an independent estimate of the experimental error. In the case of experiments with more than one response per trial, covariances must also be considered. If there is uncertainty in the model predictions other than due to the experimental error involved in measuring the responses of the trials, the analysis of the lack of fit of the model is further complicated. When the prediction errors in the model also depend on the operating conditions for an individual trial (non-linear model), the experimenter may be forced to compare the lack of fit to the prediction error at each condition to assess the performance of a model.

In this case, a simple approach was taken and the three responses were considered separately. This was done by examining the elements on the principal diagonal of the estimated variance-covariance matrix describing experimental error from the 29 replicated center-point experiments performed on the deep bed at different times over the whole experimental period. This variance-covariance matrix is shown in Table 6.8. These were compared with the estimates of the same variance obtained from the residuals of the fitting of the model. The residual sum of squares divided by the degrees of freedom $(n-2)$ for the deep bed experiments are 1.6×10^{-2}, 9.7×10^{-4}, and 4.8×10^{-4} for the responses S_1, S_3 and $(1-X)$, respectively. Performing an F-test on these values relative to the diagonal elements in Table 6.8 at the appropriate degrees of freedom for each indicates that the model is inadequate. For the

experiments at the lower bed depth, the residual sum of squares divided by the degrees of freedom for the KWMIX model are 4.90×10^{-3}, 3.97×10^{-3} and 3.00×10^{-4} for the responses S_1, S_2 and (1-X) respectively. Again, performing an F-test on these values relative to the diagonal elements in Table 6.8 indicates that the model is inadequate. It must be emphasized that the model tested here is that of the form described and includes kinetic parameter values estimated from the fixed bed work. Also this F-test is very sensitive to departure from normality of the error distribution but in this case it is believed that the normality assumption should be reasonably good.

Of interest here also, but not directly related to the test of goodness of fit of the model, is the error in predictions from the model produced by errors in the estimates of the kinetic parameters. The variance-covariance matrix of this error is evaluated approximately at an experimental condition $\underline{\xi}$ through a linearization procedure as:

$$\underline{x}^T \; \underline{V}(\underline{\theta})^{-1} \; \underline{x} \qquad 6.12$$

where

$$\underline{x} = \left[\frac{\partial \eta_j (\underline{\xi}, \underline{\theta})}{\partial \theta_i}\right]_{\underline{\theta} = \underline{\theta}} \qquad 6.13$$

where $\underline{\eta}$ are the predicted responses for a fluidized bed model, $\underline{\theta}$ are the best estimates of the ten kinetic parameters from the packed bed experiments and $\underline{V}(\underline{\theta})$ is the variance-covariance matrix for these parameters which can be extimated from the packed bed experiments. Here the fluid bed response derivatives are evaluated at the center-point experimental conditions using the Kato and Wen model and using the variances of the parameters as determined from the packed bed experimental program. This matrix is shown

$$\text{Var}\begin{bmatrix} S_1 \\ S_2 \\ 1-x \end{bmatrix} = \begin{bmatrix} 1.41 \times 10^{-3} & -2.13 \times 10^{-4} & -1.17 \times 10^{-4} \\ -2.13 \times 10^{-4} & 6.86 \times 10^{-5} & 4.37 \times 10^{-5} \\ -1.17 \times 10^{-4} & 4.37 \times 10^{-5} & 1.50 \times 10^{-4} \end{bmatrix}$$

TABLE 6.8 VARIANCE-COVARIANCE MATRIX FOR EXPERIMENTAL ERROR

$$\text{Var}\begin{bmatrix} S_1 \\ S_3 \\ (1-X) \end{bmatrix} = \begin{bmatrix} 1.61 \times 10^{-1} & 6.94 \times 10^{-3} & -2.82 \times 10^{-3} \\ 6.94 \times 10^{-3} & 1.16 \times 10^{-1} & 1.54 \times 10^{-3} \\ -2.82 \times 10^{-3} & 1.54 \times 10^{-3} & 9.77 \times 10^{-5} \end{bmatrix}$$

TABLE 6.9 VARIANCE-COVARIANCE MATRIX FOR THE PREDICTIONS DUE TO ERRORS IN KINETIC PARAMETERS (KATWEN (0) MODEL)

in Table 6.9. The lack of fit of the model as determined by the F-test may be at least partly the result of the propagation of errors in the kinetic parameters into the fluidized bed model as is illustrated in Tables 6.8 and 6.9. Therefore, it is not possible at this stage to say the fluidized bed fluid mechanical model is inadequate without performing more experiments to determine the kinetic parameters more precisely. Moreover, some of the error in the kinetic parameters may arise because of the inadequacy of the packed bed model. Thus, the packed bed model would have to be evaluated by determining the measurement error variance-covariance matrix through replicating those experiments and carrying suitable tests of fit analogous to the F-test used above. Alternatively, all the kinetic and fluid mechanical parameters can be evaluated from the fluid bed responses employing Bayes' Theorem to utilize the prior information from the packed bed experiments.

Of course, no mathematical model provides a perfect representation of reality and the best model here has been tested by comparison against rather good experimental data. This is a severe test and its failure does not necessarily imply that the model is not useful in practice. However, because of the failure of the model to fit the data some caution must be exercised in interpreting the parameter estimates obtained. Our experiments suggest that the best model found in this investigation should be satisfactory for plant simulation and reactor optimization studies. This is demonstrated by observing the randomness of the residuals as shown in Figures 6.2, 6.3, 6.4 and 6.6 and the relatively small error between the predictions and the observed values. The model at least responds in the correct way.

7.0 RESUME AND FINDINGS

This study encompassed a wide spectrum of topics involving experimental work on fundamental physical and chemical phenomena, modelling and statistical analysis. For this reason, a summary is included to gather the various topics together. The conclusions and contributions to knowledge are presented in sections 7.4 and 7.5 respectively.

This study was undertaken to investigate and to evaluate a strategy for developing a steady state model for an industrial reactor. Such models can be used by themselves or incorporated into a full scale model of a chemical plant such as in a MACSIM, PACER or similar executive routine (C7). A secondary or subsidiary objective may be stated as follows: it is expected that by carrying out well designed experiments on industrial reactors and analyzing the results of such experiments to ascertain the basic physical and chemical phenomena occurring, then a better understanding of the principles of scale-up in design will be achieved. These design principles would be the generalization accruing from the many simulation experiences.

Developing a model of a large scale industrial reactor that will answer the questions asked of the simulation in which it is to be employed can be a difficult task. The problem is further complicated by the inherently noisy or error filled data that is usually obtained from a large operating reactor. Also, the reaction occurring may be complex and the flow of reactants and products within the reactor may be complicated to describe.

In order to model such a reactor, statistical techniques for the design and analysis of the experiments and the experimental results must be employed. Experiments for the estimation of the required parameters and the discrimination

among possible models can be designed so as to minimize the harm done by experimental error. These errors are always present and greatly reduce the precision of the model selected to describe the reactor. At all times, the experimenter or model builder must be aware of the degree of precision that the model possesses in predicting the responses of the reactor being studied.

A pilot plant reactor was modelled. The hydrogenolysis of n-butane over nickel-on-silica gel was carried out in a fluidized bed reactor. Not only was the conversion of n-butane predicted but also the selectivities of propane, ethane and methane, the three products of the reaction, were described by the model. This is a complex reaction in a reactor of uncertain flow patterns.

A mechanistic rather than an empirical model was selected to describe the kinetics and the reactor. Since models are often employed to predict at conditions outside those at which their parameters have been estimated, it was believed that mechanistic models would be more suitable to investigate in this study.

There are several possible schemes that can be used to estimate the required kinetic and reactor flow parameters. The kinetics could be estimated in a separate reactor or from the results of fluidized bed experiments. The reactor flow parameters could be estimated in a separate reactor, the reactor of interest at non-reacting conditions or during reaction. Also, all the parameters could be estimated at once from the results of fluidized bed experiments. The latter method was rejected to avoid the excessive computer time that would be required. The kinetic parameters were estimated from separate bench-scale experiments in a packed bed reactor

where the flow of reactants should be more accurately described than in a fluidized bed reactor. The reactor flow parameter was estimated from fluidized bed reactor experiments where not only the conversion but also the selectivities could supply information for its estimation.

This summary is presented in two parts. In section 7.1, those details applying specifically to the experimental work and the fluidized bed models and modelling are presented. In section 7.2, the general techniques for developing simulation models are discussed.

7.1 MODELLING OF FLUIDIZED BED AND MODEL DISCRIMINATION

The models evaluated in this study were all two-phase models. The first phase, the bubbles of gas, flows through the bed of catalyst particles which constitutes the second phase. In order to estimate the interchange of gas between the bubbles and the emulsion, it is necessary to conduct experiments at high reaction rates where the performance of the reactor is limited by gas interchange rather than by reaction. With the hydrogenolysis of n-butane and the experimental conditions which could be employed in the reactor system, as designed and operated in this investigation, these high reaction rates could be obtained. The use of a complex reaction involving series and parallel reactions with high activation energies is a real challenge and a severe test for any proposed model.

Parameters within these models must be estimated from experimental data and then experiments designed to allow discrimination among the models to allow the selection of the best one for the purposes at hand. In estimating these parameters, the following philosophy was followed:

1) Estimate the kinetic parameters in a separate experimental system so as to have a large amount of tractable data applicable to their estimation.

2) Estimate the parameter(s) describing the least known phenomena in the fluidized bed models and to use existing correlations and bubble mechanics models where possible.

3) Employ the concept of total experimental redesign to improve the parameter estimates that limited the precision and accuracy.

As suggested by the first statement, the required kinetic parameters were estimated independently from the fluidized bed reactor. The estimates of the parameters in the fluidized bed are dependent on the point estimates of the kinetic parameters obtained from the packed bed experiments. These point estimates, however, were obtained cheaply while to have obtained them from fluidized bed data would have been a tedious and extremely expensive operation. Based at least on judgment it appears that the experimental errors in the bench-scale packed bed were considerally smaller than those experienced in the pilot-scale fluidized bed.

Now that this has been done it is obvious that a Bayesian approach should be taken in which bench-scale data are analyzed to produce posterior distributions for the kinetic parameters. Then this would be applied as prior distribution for the analysis of the pilot-scale data to obtain a posterior distribution for all parameters combining all the data from both experimental systems. This is the obvious next step in the program.

The second point in the modelling philosophy explains why the interchange of gas between the bubble and the emulsion phase was chosen as the parameter to be estimated for the fluidized bed models. Of all the models for phenomena associated with the bubble mechanics in a fluidized bed, this is the least certain.

The forms of the models used in this study were modified versions of those proposed by their authors. The major model considerations such as the nature of the flow in the emulsion phase, the method of solution, the use of a constant size or growing bubble and the inclusion or exclusion of catalyst particles in the bubble phase were retained. The various authors proposed different methods of describing bubble-associated parameters. In this study, these parameters were described in the same manner for all models employing existing literature data and recommendations. The interchange of gases between the bubble and the emulsion was estimated for each model. The interchange model that was used assumed that the amount of gas interchanged was proportional to the inverse of the bubble diameter.

The third part of the modelling philosophy was to use an iterative technique here referred to as total experimental redesign. The importance of "starting simple" when developing a simulation model is well known. A simulation study is undertaken to answer specific questions about a process to a certain degree of accuracy and precision. An initial model and its associated parameter estimates may be sufficient to answer the questions about the process; if not, the model must be made more sophisticated or the parameter estimates determined more precisely and accurately. The operating conditions or control variables must be chosen using the appropriate experimental design techniques. As equally important, the experimental apparatus, the analytical tools and apparatus as well as the form of the model to be employed should be redesigned if necessary. The possibility of these limiting the effectiveness of the model in answering the questions for the simulation must not be overlooked.

First-stage or preliminary models were developed to describe the kinetics of the reaction and the fluidized bed reactor. The kinetic model was then incorporated into the reactor model, the required reactor parameters estimated and the ability of the model to predict the conversion and selectivities of the experimental reactor was assessed.

It was observed that the selectivities of propane, ethane and methane in the fluidized bed at conversions greater than about 40% were similar to those in the packed bed reactor near 100% conversion. The relatively low overall conversion is due to the bypassing effect of the bubbles. It follows that the reaction kinetics if they are to be applied to a fluidized bed reactor must be accurate in the region of high conversion of the primary reactant.

The model used during the initial investigation of the fluidized bed reactor was the Orcutt model (O1) assuming perfect mixing in the emulsion phase. This was the simplest of the models and required the least computer time. An interchange parameter was estimated for each experimental trial such that the sum of squares of the difference between the predicted and the observed conversion and selectivities were a minimum. This left two degrees of freedom per experimental trial since the conversion and two of the three selectivities were independent responses.

The conversion and the selectivity of propane were predicted quite well but the predicted ethane selectivity was too high, especially at high reaction rates. The other fluidized bed models exhibited the same behaviour. This was due to the absence of an ethane readsorption term in the kinetic model. The kinetic parameter relating the ratio of reaction

rate of ethane to its desorption was adjusted to minimize the sum of the squares of the observed minus the predicted ethane selectivities. The overall effect of increasing this ratio is the same as including the readsorption of ethane onto the catalyst. The resultant improvement in the predicted selectivities of ethane and methane indicated the gains to be made by improving the kinetic model through further experimentation in the packed bed reactor.

Further experiments were performed in the packed bed reactor and the kinetic model and parameter estimates improved. The reactor, the reactor model and the method of gas analysis were all modified to improve the precision and accuracy of the parameter estimation procedure. The operating variables (temperature, feed rate and hydrogen to n-butane feed ratio) within a specified range were chosen so as to maximize $\underset{\sim}{X}^T \underset{\sim}{A}^{-1} \underset{\sim}{X}$ and hence minimize the uncertainty in the parameter estimates due to experimental error.

The method of Box and Draper (B6) was used to weight the responses for parameter estimation since the experimentally determined variance-covariance matrix did not properly reflect the effect of uncertainty in the catalyst activity. The variance-covariance matrix of the parameters was estimated.

The fluidized bed reactor models were assessed once the improved kinetic model and the necessary parameters were available. A separate interchange parameter and catalyst activity were estimated for each of the reactor models in fitting all the experimental trials. The Kato and Wen

model provided the best fit of the experimental data. The Partridge and Rowe model and a modified version of the Kato and Wen model assuming perfect mixing in the emulsion phase provided the next best fit. The two Orcutt models were far less suitable but were not as inadequate as was a model which included the catalyst in the bubble wake completely mixed with the gas in the bubble phase.

Experiments were designed to provide discrimination between the Kato and Wen model and the modified version of it. Because of the large requirement of computer time, the Partridge and Rowe model was excluded from the design criterion. The design criterion for selecting the operating conditions (temperature, flowrate and hydrogen-to-n-butane feed ratio) was chosen not only to provide as large a difference between the model responses at the same operating conditions as possible, but also to provide as large a difference as possible between the chosen operating conditions. This set of experiments was performed at half the catalyst bed depth of the previous experiments.

The posterior probabilities of the various models at both bed heights were calculated. In doing so, the effect of uncertainty in the so-called nuisance parameters, the ten kinetic parameters as well as the catalyst activity and the interchange parameter, was integrated out. For the experiments with the deep catalyst bed and for the models considered, the KATWEN (0) model had a posterior probability of unity while that of the ORCMIX, KATWEN (1) and KWMIX were each less than 10^{-200}. At the shallow catalyst bed depth, the posterior probabilities of the models with the emulsion phase perfectly mixed were greater than that of the KATWEN (0)

model. The KWMIX model had a posterior probability of 0.986.

The fact that different fluid mechanical models were found to be best for the two bed heights suggests that the available descriptions may not account for all the important phenomena occurring. For example, a description of the bubble coalescence and break-up, the effect of solids movements on gas flow in the bed, and phenomena occurring near the distributor plate are not included. More adequate descriptions of these may be required before a universal model can be achieved.

7.2 THE EFFECT OF ERRORS AND THE USE OF STATISTICAL TECHNIQUES

Experimental errors exist. It is the task of the experimenter to estimate and minimize the uncertainty they will cause in the parameter estimates in the model predictions that are made and in the conclusions that are drawn. This can be accomplished by improving the equipment and experimental techniques employed (reduce the magnitude of these errors) and/or by choosing the best available operating conditions at which to perform experiments (reduce the effect of these errors on the experiments to be performed). Both of these methods are equally important and can only be exploited to the maximum benefit if the structure of the errors that exist is known.

It is equally important that the experimenter know how much precision is required for the models that are being developed. It can be very costly to develop a model of greater precision than required to do the job, or to answer the questions a project or study was initiated to study. The conclusions and suggested methodology for obtaining steady-state models for existing chemical reactors in operating processes are summarized.

UNCERTAINTY IN MODEL PREDICTIONS FROM PARAMETERS ASSUMED TO BE KNOWN

It has been and continues to be common practice in the chemical industry when modelling large industrial reactors to estimate the required kinetic parameters in a laboratory-scale reactor. These kinetics are then incorporated into a reactor model. It is not common practice to estimate the necessary reactor parameters from experimental data obtained from the reactor under operating conditions. In this study, this was done. The parameters were chosen so as to minimize $\underline{W}$ the vector of differences between the observed responses and the model predictions. It must be realized that each element of $\underline{W}$ is subject to uncertainty from two separate sources: one from the reactor experiments and the other from the kinetic parameters, or any other parameters, in the reactor model used to generate the predicted responses.

The effect of uncertainty in model predictions can be removed for the case of model discrimination. In evaluating the likelihood function, the kinetic parameters are assumed to be perfectly known; hence an error in its magnitude arises because of the error in these parameters. These errors may be transformed by the model into the likelihood function in different ways, thus leading to erroneous ratios. A discrimination criterion was developed which removed the effect of this uncertainty by obtaining a posterior probability of the models which had the parameter uncertainty removed. This problem was demonstrated in this program since the latter criterion indicated a different "best" model than the likelihood criterion.

ESTIMATING PARAMETERS IN ONE SYSTEM FOR USE IN ANOTHER SYSTEM OR MODEL

The kinetic parameters that were estimated in the packed bed reactor were for use in the fluidized bed reactor model. The precision of these parameters is only of importance inasmuch as they affect the precision of the fluidized reactor model. As summarized above, the vector $\underline{W}$ contains uncertainty resulting from both the experimental error and the model predictions. A proposed design technique for estimating parameters in one system for use in another is presented in Appendix K. This method minimizes the uncertainty of the prediction error in the second system rather than the uncertainty of the parameter estimates from the first system. When tested for this study, different operating conditions were selected.

In estimating parameters in one system for use in another model, a second very important fact must be recognized. The estimated parameters may provide a good prediction in the model for which they were estimated, but if the model is in error a compensating error will be introduced into the parameter estimates. Then, when these estimates are employed in another model, the error in this model's prediction would be greater than that implied by the variance of these parameters. This would be a systematic error. Thus, when parameters are to be estimated using a system and model other than the one in which they are to be used, caution must be exercised. This model must accurately account for the phenomena that are occurring.

EXPERIMENTAL DESIGN FOR MODEL DISCRIMINATION

To discriminate among models, operating conditions are selected so that the responses of the various models will be as different as possible at identical operating conditions. The desired experiment is performed and the likelihood of each model is determined. Since the vector $\underline{W}$ (observed minus

predicted responses) has variance due to experimental error as well as model prediction error, both these factors must be considered in the choice of an operating condition. As shown in this study, there could be considerable error or uncertainty in parameter estimates obtained in one system and then incorporated into the model of the process to be studied.

There is a further consideration that should be included when designing experiments for model discrimination when there is still considerable uncertainty in the performances of the various models. If more than one experiment is to be designed, conventional techniques would select all the operating conditions at, or very nearly at, the same settings. There is usually one operating condition that would provide the best discrimination. However, there may be a number of other very different operating conditions that would provide almost as good discrimination. These are of great value if the accuracy of the model predictions have not been well tested over the entire control variable space. Such experiments, while providing only slightly less discrimination power, provide far more information about the various models over the entire control variable surface to be considered.

A Monte Carlo technique was used to generate a number of possible sets of operating conditions for this study. Because of the computer time involved only the experimental error and not the model prediction error was used to determine the discrimination power of each of these operating conditions. The set of control variables providing the maximum discrimination was selected to be performed in the first experiment. The remaining operating conditions were selected according to the criterion:

$$\text{MAX} \left[(\Delta x) \ (\Delta y)^b \right]$$

The term Δy is the discrimination provided by the i'th vector of operating conditions and Δx is the sum of the distances in control variable space of these operating conditions from those already selected to be included in the block of experiments to be performed. The exponent b (0.2 in this case) can be chosen so as to increase or decrease the importance of either term.

ESTIMATION OF PARAMETERS IN INDEPENDENT SYSTEMS

It may be necessary to estimate a large number of parameters for use in a reactor model. This can be an expensive procedure if the reactor model requires extensive computer time and/or the required experimental trials themselves are expensive to perform. Furthermore it may be very difficult to obtain precise estimates of some of the parameters from trials performed on a large reactor. As shown in this study, under certain operating conditions, there may be a very wide range of reaction rates and interchange that will produce the same conversion. Thus there may be considerable reason not to estimate all the required parameters using the large reactor. In this case the kinetic parameters were estimated from packed bed reactor trials. Then using these parameters the interchange parameter was estimated from fluidized bed reactor trials. Of course, the effect of uncertainty in the kinetic parameters affecting the precision of the interchange parameter so estimated must be realized.

ITERATIVE CYCLE OF TOTAL EXPERIMENTAL REDISIGN

A model is developed to answer questions to a certain degree of accuracy and precision. It is important to start simple. It is costly to develop a model that is more sophisticated than needed for the questions to be answered.

Once a model is available its adequacy can be evaluated. If it is not sufficient, parameters may have to be re-estimated or additional phenomena included in the model. Further experimentation will be necessary. Operating conditions should be chosen using the experimental design techniques already discussed. Equally as important, it may also be necessary to redesign the experimental apparatus, the analytical tools and apparatus and the form of the model. These aspects of the total experimental program can introduce either systematic or random errors that may make it impossible to answer the questions for which the simulation or modelling was initiated. Thus, in designing an experimental program attention must be paid not only to selection of operating conditions, but also to the precision and accuracy of the experimental procedures; moreover, the model must include the effect of the phenomena of major importance that are occurring.

7.3 RECOMMENDATIONS FOR FURTHER WORK

The kinetic parameters should be re-evaluated in an attempt to reduce the uncertainty in the predictions of the fluidized bed models. Using the existing fluidized bed data and Bayes' Theorem, the prior parameter estimates from the packed bed experiments can be updated. The residual sum of squares of the responses divided by the degrees of freedom can be compared to the diagonal elements of the variance-covariance matrix due to experimental error. If these residuals are still too large as determined by an appropriate test, further experimentation in the packed bed reactor should be initiated.

The performance of both the reactor model and the estimated value of the interchange factor could be assessed using propane feed to the reactor and propane kinetics in the models.

A fluidized bed reactor model with two separate horizontal zones in the emulsion phase should be investigated. As shown in this study, a shallow bed is best modelled with a perfectly mixed emulsion and a deep bed is better modelled assuming plug flow in the emulsion. The bottom of the catalyst bed where there are a large number of small bubbles and violent mixing may well behave as a well mixed region. Higher in the bed where there are fewer and larger bubbles the emulsion phase is more likely to have an axial concentration profile.

Fluidized bed models requiring less computer time should be investigated. These should include models such as those proposed by Van Deemter (V1, V2) where the results of pulse testing are employed to characterize the gas mixing and residence time. Also, the performance of simple regression models should be evaluated.

There are a number of bubble parameters that could be investigated further and the updated information included in the models employed in this study. These include: the maximum size of bubbles, the relationship between bubble size and height up the reactor, the phenomena occurring at the distributor plate, the gas interchange due to break-up and coalescence and the effect of the movement of solids on the gas flow in the emulsion. More information on these topics would be very valuable to the field of fluidization engineering.

The proposed design techniques outlined for the estimation of parameters in one system for use in another should be investigated further.

7.4 SUMMARY AND CONCLUSIONS

An experimental study involving the determination of kinetic parameters in a rather complicated reaction has indicated the value of statistical procedures in experimental design and analysis. Procedures for designing experiments in a fluidized bed reactor for discrimination and model testing have been developed and evaluated.

A mathematical model (K7) was adapted to describe the hydrogenolysis of n-butane. It was shown that for such models to be useful when incorporated in a fluidized bed model, they must describe the reaction over all conversions and particularly at the high conversions of the primary reactant that will occur in the emulsion phase.

Selectivity information, unlike only conversion information (as used entirely in most previous studies reported in the literature) gives more information about the conditions of the local areas where reaction actually occurs. That is, from conversion data alone, local rates of reaction or conversion cannot be inferred without an almost perfect knowledge of gas interchange between bubble and emulsion. For a fast reaction, it is also necessary and equally important that the reaction rate be investigated under conditions that will exist in the cloud, wake and emulsion. If this is not done, any physical interpretation of interchange parameters would be unreasonable.

The maximum likelihood criterion was used to discriminate among the fluid mechanical models for a fluidized bed because of its relatively small computer time requirements and its ease of application. Although this criterion

could be used to establish those models which were vastly superior, incorrect conclusions may result if the models exhibit different sensitivities to errors in predetermined parameters. A Bayesian method which integrates out this effect has been derived and its successful use has been demonstrated.

The problem of weighting the responses, when estimating parameters by the maximum likelihood method, in situations where there is appreciable error in these predetermined parameters has been delineated.

In the present reaction/reactor system, further experimentation is suggested in which the packed bed reactor model is tested for adequacy and more and perhaps better experiments are performed to reduce the errors in those parameters which lead to large errors in the prediction of the propane and methane selectivities.

This study has indicated that the present mechanistic models to describe the fluid mechanical behaviour in a fluidized bed do not describe all of the important effects. This is suggested by the observation that the model which was found to be best for the deep bed was found to be inferior to another for the shallower bed. The different descriptions of the emulsion phase for deep and shallow beds suggest that the overall gross behaviour of these beds is different. This difference may reflect the relative importance with these beds of those phenomena occurring near the distributor plate, the bubble coalescence and break-up, solids flow, with the accompanying gas flow resulting from the rising bubbles, etc. Only when these phenomena are better understood will this difference in gross behaviour be explained.

Within the limitations of the assumed behaviour and prior information, the interchange factors determined from these experiments are about 0.43 to 0.45 times the values recommended by Kato and Wen's correlation.

Notwithstanding the inadequacies indicated above, the fluidized bed reactor model which arises out of this study, based on the Kato and Wen formulation, is quite satisfactory for simulation and optimization studies. Therefore, the statistical techniques and experimental procedures used in this study are recommended for developing such models.

7.5 CONTRIBUTIONS TO KNOWLEDGE

Because of the nature of this research program, the contributions to knowledge are best summarized according to the various areas that have been investigated. These are indicated in turn.

1. Chemical Kinetics

A kinetic model for the hydrogenolysis of n-butane on a catalyst, comprised on 10% nickel on silica gel, has been formulated on the basis of a proposed mechanism involving adsorption, desorption and reaction of activated hydrocarbon molecules on the catalyst surface. The kinetic constants, namely preexponential factors, activation energies and exponents of reactants, have been evaluated from integral packed bed experiments. This model allows the conversion of butane and the selectivities of all reaction products to be predicted with good accuracy over the full range of butane conversions, including those at 100% conversion.

2. Phenomena Occurring in Fluidized Bed Reactors

A pilot-scale fluidized bed reactor has been designed, constructed and operated with the n-butane hydrogenolysis reaction. Conversion and selectivity data of high accuracy have been obtained in this reactor at two bed heights under reaction conditions where fluid mechanical phenomena are controlling. Moreover, the experimental system together with the physical and chemical properties of the catalyst have been well characterized. These data, along with the kinetic description of the reaction, will be useful for further testing of any new fluidized bed models that may be proposed in the future.

Interchange parameters to describe the interchange of gas between the emulsion and bubble phases in current models for fluidized bed reactors have been determined. These factors indicate that the interchange in a fully fluidized reactor, operating at fairly high u/u_{mf} flow ratios, is approximately one-half that determined by other investigators in single bubble experiments.

This investigation has indicated that the model proposed by Kato and Wen (K3) is the best of the two-phase mechanistic models tested. Furthermore, the results of this investigation strongly suggest that the bubble wake should not be included with the bubble phase. This further suggests that the sophisticated model proposed by Kunii and Levenspiel, which includes the wake with the bubble phase, would be inferior to the Kato and Wen model.

The fact that different models are required for the mixing patterns in the emulsion phase at two different bed heights suggests that the current models do not account for all of the primary phenomena occurring in a fluidized bed.

3. Statistics

Statistical methods have been successfully applied to the design and analysis of experiments from which a relatively large number of model parameters had to be estimated. The shortcomings of these methods have been delineated.

A criterion for designing experiments for both model discrimination and model testing has been proposed and successfully applied.

The inadequacies of the model discrimination criterion employing maximum likelihood ratios have been delineated in its application to situations where there are errors in the parameters.

A new criterion for model discrimination which is independent of parameter uncertainty has been developed and successfully tested.

A method for designing experiments in one apparatus for estimating parameters which will be used in modelling the behaviour in another apparatus has been suggested.

4. Simulation Methodology

The classical approach in chemical reaction engineering in which kinetic parameters are estimated in a bench-scale apparatus and then used in design and simulation of large scale reactors with different fluid mechanical behaviour, has been evaluated in this case study. Some of the problems arising out of the uncertainty in the parameters have been delineated for the first time.

A strategy for steady-state modelling of industrial reactors has been suggested and critically tested. It has been shown that this methodology can lead to reactor models of sufficient accuracy for most simulation purposes.

8.0 REFERENCES

A1 Anderson, J.R., Baker, B.G., Proc. Roy. Soc. (London), A 271, 402 (1963).

A2 Anderson, T.W., An Introduction to Multivariate Statistical Analysis, Wiley (1958).

A3 Atkinson, A.C., Hunter, W.G., Technometrics, 10, 271 (1968).

B1 Bird, R.B., Stewart, W.E., Lightfoot, E.N., Transport Phenomena, p. 546, John Wiley and Sons, New York (1960).

B2 Bond, G.C., Catalysis by Metals, p. 396, Academic Press, New York (1962).

B3 Beek, J., Adv. in Eng. Chem., 59 (2), 18 (1967).

B4 Baird, M.H.I., Davidson, J.F., C.E.S., 17, 87 (1962).

B5 Box, G.E.P., Cox, D.R., J. Roy. Stat. Soc. J., Series B, 26, 211 (1964).

B6 Box, G.E.P., Draper, N.R., Biometrika, 52, 355 (1965).

B7 Box, G.E.P., Hunter, W.G., MacGregor, J.F., Erjavec, J., Technometrics, 15, No. 1, 33 (1973).

B8 Box, G.E.P., Hunter, W.G., Technometrics, 4, No. 3, 301 (1962).

B10 Barnard, G.A., Jenkins, G.M., Winston, C.G., J.R. Stat. Soc. (A) 125, 321 (1962).

B11 Box, G.E.P., Lucas, H.L., Biometrika, 46, 77 (1959).

B12 Box, G.E.P., Hill, W.J., Technometrics, 9, 57 (1967).

B13 Box, G.E.P., Hunter, W.G., Technometrics, 7, 23 (1965).

B14 Box, M.J., Technometrics, 12, 569 (1970).

B15 Box, M.J., Roy. Stat. Soc. J., Series B, 30, No. 2, 290 (1968).

B16 Brooks, S.H., A Discussion of Random Methods for Seeking Maxima, Operations Research, 6, pp 244-251 (1958).

C1 Carberry, J.J., Breton, R.H., A.I.Ch.E.J., 4, No. 3 367 (1958).

C2 Cimino, A., Boudart, M., Taylor, H.S., J. Phys. Chem., 58, 796 (1954).

C9 Cochran, W.G., Cox, G.M., Experimental Designs, Wiley, New York p 266 (1957).

C3 Clift, R., Grace, J.R., C.E.P. to be published.

C4 Clift, R., Grace, J.R., C.E.P. to be published.

C5 Chernoff, H., Ann. Math. Stat., 24, 586 (1953).

C6 Chiba, T., Kobayashi, H., C.E.S., 25, 1375 (1970).

C7 Crowe, C.M., et al., Chemical Plant Simulation, Prentice-Hall (1971).

C8 Carberry, J.J., Catalyst Reviews, 3(1), 61 (1969).

D1 Davidson, J.F., Harrison, D., Fluidized Particles, Cambridge University Press (1963).

D2 De Groot, J.H., Proceedings of the International Symposium on Fluidization, Netherlands University Press, 348-361 (1967).

D3 Drinkenburg, A.A.H. (editor), Proceedings of the International Symposium on Fluidization, Netherlands University Press (1967).

D4 Davidson, J.F., Paul, R.C., Smith, J.S., Duxbury, H.A., Trans. Inst. Chem. Engrs., 37, 323 (1959).

D5 Davidson, J.F., Trans. Inst. Chem. Engrs., 39, 230 (1961).

D6 Draper, N.R., Hunter, W.G., Biometrica, 54, 147 (1967).

D7 Drinkenburg, A.A.H., 4'th CHISA Congress, Prauge (1972).

D8 Draper, N.R., Smith, H., Applied Regression Analysis, p. 272, John Wiley and Sons Inc., New York (1966).

D9 Davies, O.L., The Design and Analysis of Industrial Experiments, p. 145, Oliver and Boyd, Publishers, London (1960).

D10 Draper, N.R., Hunter, W.G., Biometrika, 53, 525 (1966).

D11 Draper, N.R., Hunter, W.G., Biom., 54, 662 (1967).

D12 Davidson, J.F., Harrison, D., C.E.S., 21, 8, 731-737 (1966).

E1 Ettre, Leslie S., Zaltkis, A., Practice of Gas Chromatography, Wiley (1967).

E2 Ellis, J.E., Partridge, B.A., Lloyd, D.E., Comparison of the Predicted with Experimental Butadiene Yields for the Oxydehydrogenation of Butenes in a Gas - Fluidized Bed. Paper presented at Tripartite Chemical Engineering Conference, Montreal (1968).

F1 Froment, G.F., Analysis and Design of Fixed Bed Catalytic Reactors. A State of the Art Review, Symposium on Chemical Reaction Engineering, Washington, D.C., June 8, 1970.

F2 Froment, G.F., Ind. Eng. Chem., 59, No. 2, 18 (1967).

G1 Gilliland, F.R., Mason, E.A., Ind. Eng. Chem., 41, 6, 1191 (1949).

G2 Gomezplata, A., Shuster, W.W., A.I. Ch. E. Journal 6, 454 (1960).

G3 Galloway, J.H. Using the Triac for Control of AC Power, Application Note 200.35 3166, General Electric, Semiconductor Products Dept.

G4 Grace, J.R., Harrison, D., C.E.S., 24, 3, 497-508 (1969).

G5 Godard, K., Richardson, J.F., C.E.S., 24, 4, 663-670.

H1 Hougen, O.A., Watson, K.M., Ind. Eng. Chem., 35, No. 5, S29 (1943).

H2 Hlavacek, V., Ind. Eng. Chem., 62, No. 7, 8 (1970).

H3 Harrison, D., Leung, L.S., Trans. Inst. Chem. Engrs., 39, 409 (1961).

H4 Higbie, R., Trans. Am. Inst. Chem. Engrs., 31, 365 (1935).

H5 Himmelblau, D.M., Process Analysis by Statistical Methods, Wiley (1970).

H6 Hill, W.J., Hunter, W.G., Wichern, D.W., Technometrics, 10, 145 (1968).

H7 Hill, W.J. Statistical Techniques in Model Building, Ph.D. Thesis, University of Wisconsin (1966).

H8 Hargraves, J.H., Pyle, D.L., C.E.S., 27, 433 (1972).

H9 Harrison, D., Davidson, J.F., De Kock, J.W., Trans. Instn. Chem. Engrs., 37, 328 (1961).

H10 Hunter, W.G., Hill, W.J., Henson, T.L., Can. J. Chem. Eng., 47, 76 (1969).

H11 Hunter, W.G., Mezaki, R., Am. Inst. Chem. Eng. J., 10, No. 3, 315 (1964).

H12 Hill, W.J., Statistical Techniques for Model Building, Ph.D. Thesis, University of Wisconsin (1966).

H13 Hunter, W.G., Reiner, A.M., Technometrics, 7, No. 3, 307 (1965).

H14 Hill, W.J., Hunter, W.G., Wichern, D.W., Technometrics, 10, No. 1, 145 (1968).

H15 Hillyer, M.J., Roth, P.M., C.E.S., 27, 2, 187-198 (1972).

H16 Hoffman, T.W., Orlickas, A., C.J. Ch. E. Submitted for publication.

I1 Iwasaki, M., Furuoya, I., Sueyoshi, H, Shirasaki, T., and Echigoya, E., Chem. Eng. Japan, 29, 892 (1965).

I2 Ishii, T. and Osberg, G.L., A.I. Ch. E. Journal, 11, 279 (1965).

J1 Jackson, R., Trans. Inst. Chem. Engrs., 41, 13, 22 (1963).

J2 Jenkins, G.M., Watts, D.G., Spectral Analysis, Holden Day (1968).

K1 Kunii, D., Levenspiel, O., Ind. Eng. Chem. Fundamentals, 7, No. 3, 446 (1968).

K2 Kunii, D., Levenspiel, O., Ind. Eng. Chem. Des. and Development, 7, No. 4, 481 (1968).

K3 Kato, K., Wen, C.Y., Chem. Eng. Sci., 24, 1351 (1969).

K4 Krieth, F., Principles of Heat Transfer, p. 596, International Textbook Company, Scranton Penn. (1966).

K5 Kemball, C., Taylor, H.S., J. Am. Chem. Soc., 70, 345 (1948).

K6 Kikucki, E., Morita, Y., Hydrogenolysis of n-Pentane on Nickel Catalyst, Personal Communication to A.J. Orlickas, Department of Applied Chemical, School of Science and Engineering, Waseda University, 4-170 Nishi-Okubo, Shinjuku-Ku, Tokyo, Japan (1970).

K7 Kempling, J.C., Hydrogenolysis of Some Small Hydrocarbons over Supported Ruthenium, Ph.D. Thesis, Chem. Eng., Dept. McMaster University (1971).

K8 Kato, K., Imafuku, K., and Kubota, H., Chem. Eng. Japan, 31, 10, 967 (1967).

K9 Kobayashi, H., Arai, F. and Sunagawa, T., Chem. Eng. Japan, 31, 239 (1967).

K10 Kato, K., Ph.D. Thesis, Tokyo Institute of Technology (1967).

J3 Johri,H.P., Approaches to Optimality in Sizing Plants Under Seasonal Demand, Ph.D. Thesis, U. of Waterloo (1973).

K11 Kobayashi, H., Arai, F., Isawa, S., Sunagawa, T., and Miya, K., Chem. Eng. Japan, 30, 656 (1966).

K12 Kobayashi, H., Arai, F., Tanaka, T., Sakaguchi, Y., Sagawa, N., Sunagawa, T., Shiba, T., and Takahashi, K., The 6th Reaction Engineering Symposium (Japan) , 13 (1966).

K13 Kobayashi, H., Arai, F. and Shiba, T., Chem. Eng. Japan, 29, 858 (1965).

K14 Kunii, D., Yoshida, K., Hiraki, I., Proc. Intern. Symp. on Fluidization, Netherlands University Press (1967).

K15 Krishnaiah, P.R. (editor), Multivariate Analysis, Academic Press (1966).

K16 Kenney, J.F., Keeping, E.S., Mathematics of Statistics I, D. Van Nostrand Co., Toronto (1960).

K17 Kiefer,J.C., Proc. Fourth Berkeley Symp., 1, 381 (1961).

K18 Kittrell, J.R., Hunter, W.G., Watson, C.C., A. I. Ch. En. J., 12, 5 (1966).

K19 Khinchin, A.Y., Mathematical Foundations of Information Theory, Dover (1957).

K20 Kittrell, J.R., Mezaki, R., Watson, C.C., Brit. Chem. Eng., 11, No. 1, 15 (1966).

K21 Kittrell, J.R., Mezaki, R., Brit. Chem. Eng., 11, No. 12, 1538 (1966).

K22 Kittrell, J.R., Hunter, W.G., Watson, C.C., Am. Inst. Chem. Eng. J., 11, No. 6, 1051 (1965).

K23 Kittrell, J.R., Mezaki, R., Watson,C.C., Ind. Eng. Chem. J., 57 No. 12, 18 (1965).

L1 Levenspiel, O., Kunii, D., Fluidization Engineering, John Wiley and Sons Inc. (1969).

L2 Leva, M., Fluidization, McGraw-Hill (1959).

L3 Lockett, M.J. and Harrison, D., p. 257 Proceedings of International Symp. on Fluidization, Netherlands University Press, Amsterdam (1967).

L4 Latham, R., Hamilton, C., Potter, O.E., Brit. Chem. Eng., 13, No. 5, 666 (1968).

L5 Leung, L.S., Sandford, I.C., Mak, F.K., C.E.S., 25, 1, 220-221 (1970).

M1 Morikawa, K., Benedict, W.S., Taylor, H.S., J. Am. Chem. Soc., 58, 1795 (1936).

M2 Morikawa, K., Trenner, N.R., Taylor, H.S., J. Am. Chem. Soc., 59, 1103 (1937).

M3 Murray, J.D., J. Fluid Mech., 21, 465 (1965); 22, 57 (1965).

M4 Muchi, I., Mamuro, T., and Sasaki, K., Chem. Eng. Japan, 25, 747 (1961).

M5 Massimilla, L. and Johnstone, H.F., Chem. Eng. Sci., 16, 105 (1961).

M6 May, W.G., Chem. Eng. Prog., 55, No. 12, 49 (1959).

M7 Mireur, J.P., Bischoff, K.B., Am. Inst. Chem. Eng., 13, No. 5, 839 (1967).

M8 Murray, J.D., National Science Foundation Grant GP2226, Report No. 1, Harvard University, October, (1963).

N1 Nicklin, D.J., C.E.S., 17, 693 (1963).

O1 Orcutt, J.C., Davidson, J.E. and Pigford, R.L., Chem. Eng. Prog. Symp. Series, 58, 38, 1 (1962).

O2 Orlickas, A.J., Kinetic Study of the Hydrogenolysis of n-Butane on Nickel Catalyst, M. Eng. Thesis, Chem. Eng. Dept., McMaster University (1970).

O3 Othmer, D.F., Fluidization, Reinhold (1965).

O4 Orcutt, J.C., Carpenter, B.H., C.E.S., 26, 1049 (1971).

P1 Perry, R.H., Chilton, C.H., Kirkpatrick, S.D., Chemical Engineers' Handbook, p. 14-22, p. 3-196, McGraw-Hill Book Co., New York, Fourth edition (1963).

P2 Petersen, E.E., Chemical Reaction Analysis, Prentice Hall Inc. (1965).

P3 Partridge, B.A. and Rowe, P.N., Trans. Inst. Chem. Engrs, 44, T349 - T357 (1966).

P9 Plackett, R.L., Biometrika, 34, 311 (1947).

P4 Partridge, B.A. and Rowe, P.N., Trans. Inst. Chem. Engrs. 44, T335 - T348 (1966).

P5 Partridge, B.A. and Rowe, P.N., Trans. Inst. Chem. Engrs. 43, T157 - T175 (1965).

P6 Pierce, J., Symbols, Signals and Noise, Hutchison (1962).

P7 Parratt, L.G., Probability and Experimental Errors in Science, Wiley and Sons Inc., New York (1961).

P8 Pyle, D.L., Harrison, D., C.E.S., 22, 4, 531-535 (1967).

R1 Rowe, P.N., Chem. Engr. Progr. Sym. Series, 58, 42 (1962).

R2 Reuter, H., Chem. Ing. Tech., 35, 98, 219 (1963).

R3 Rosenbrock, H.H., Comp. J., 3, No. 3, 175 (1960).

R4 Rosenbrock, H.H., Storey, C., Computational Techniques for Chemical Engineers, Pergamon Press, New York (1966).

R5 Reilly, P.M., Can. J. Chem. Eng., 48, 168, April (1970).

R6 Reilly, P.M. Personal Communication, University of Waterloo, Waterloo, Ontario, Canada.

R7 Roth, P.M., Design of Experiments for Discrimination Among Rival Models, Ph.D. Thesis, Princeton University (1965).

R8 Rowe, P.N., Partridge, B.A., Lyall, E., Chem. Eng. Sci., 19, 973 (1964).

R9 Rowe, P.N., Matsuno, R., C.E.S., 26, 6, 923-935 (1971).

R10 Rowe, P.N., Evans, T.J., Middleton, J.C., C.E.S., 26, 11, 1943-1948 (1971).

S1 Smith, J.M., Van Ness, H.C., Introduction to Chemical Engineering Thermodynamics, ch. 5, McGraw-Hill Book Co., second edition (1959).

S2 Satterfield, C.N., Sherwood, T.K., The Role of Diffusion In Catalysis, p. 31, Addison-Wesley Publishing Co. Inc., London (1963).

S3 Shepard, F.E., J. Catalysis, 14, 148 (1969).

S4 Schuit, G.C.A., Van Reijen, L.L., Adv. in Catalysis, 10, 242 (1958).

S5 Sinfelt, J.H., Catalysis Reviews, 3(2), 175 (1969).

S6 Shen, C.Y. and Johnstone, H.F., A.I.Ch.E. Journal, 1, 349 (1955).

S7 Shannon, C.E., Bell System Tech. J., 27, 379 and 623 (1948).

S8 Shaw, I.S.D., An Appraisal of the MACSIM Simulation Routine in its Application to an Alkylation Plant, M. Eng. Thesis, McMaster University (1969).

T1 Taylor, W.F., Yates, D.J.C., Sinfelt, J.H., J. Phys. Chem., 68, No. 10, 2962 (1965).

T2 Taylor, W.F., Sinfelt, J.H., Yates, D.K.C., J. Phys. Chem. 69, No. 11, 3857 (1965).

T3 Tajbl, D.G., Can. J. Chem. Eng., 47, 154 (1969).

T4 Toli, R., Matsuno, R., Proc. Intern. Symp on Fluidization, Netherlands University Press (1967).

T5 Toei, R., Matsuno, R., Miyakawa, H., Nishiya, K. and Komagawa, Y., Chem. Eng. Japan, 32, 565 (1968).

T6 Turner, J.C.R., C.E.S., 21, 10, 971-974 (1966).

T7 Tigrel, A.Z., Pyle, D.L., C.E.S. 26, 1, 133-145 (1971).

V1 Van Deemter, J.J., Chem. Eng. Sci., 13, No. 3, 143 (1961).

V2 Van Deemter, J.J., Proceedings of the International Symposium on Fluidization, 322, Eindhoven (1969).

W1 Winter, D.H., Symposium on Fundamental and Applied Fluidization I, A.I.Ch.E. 51st National Meeting.

W2 Wainwright, M.S., Personal Communication, Ph.D. Student, Dept. Chem. Eng., McMaster University (1972).

W3 Wheeler, A., Catalysis, P. H. Emmett (editor) Reinhold, New York, Vol. 2 (1955).

Y1 Yates, D.J.C., Taylor, W.F., Sinfelt, J.H., J. Am. Chem. Soc., 86, 2996 (1964).

Yates, D.J.C., Sinfelt, J.H., J. Catalysis, 8, 348 (1967).

Yates, J.G., Rowe, P.N., Whang, S.T., C.E.S., 25, 1387 (1970).

Zenz, F.A., Othmer, D.F., Fluidization and Fluid-Particle Systems, Reinhold (1960).

APPENDIX A

GAS FLOW METER CALIBRATION FOR PACKED BED AND FLUIDIZED BED

The hydrogen and the n-butane feeds to both reactors were metered separately. Capillary flow meters were used for the low flows to the packed bed while rotameters were used for the fluidized bed. All the flow meters were calibrated before and after each set of experimental trials. In the case of the packed bed, the calibrations were checked throughout the run. Gas flow through the reactor was maintained using an auxillary hydrogen supply.

PACKED BED REACTOR

A constant pressure of 11.90 in. of mercury was maintained on the capillary flow meters with a back pressure valve. Thus, any change in the reactor pressure drop would not affect the calibrations. Both flow meters were calibrated using a soap bubble flow meter. The hydrogen capillary was 28. in. of 1/2 mm. I.D. glass tubing. The pressure differential was measured on a vertical manometer filled with 1.04 S.G. manometer oil. The n-butane capillary was 6.2 in. of 0.010 in. I.D. stainless steel hypodermic tubing. The pressure differential was measured on 6. in. vertical equivalent mercury manometer inclined at 10.°. It was necessary to use mercury since Meriam fluid dissolved n-butane and changed density. The calibration curves did not change over the three months they were used although they were constantly rechecked. The calibration curves are shown in Figures A.1 and A.2.

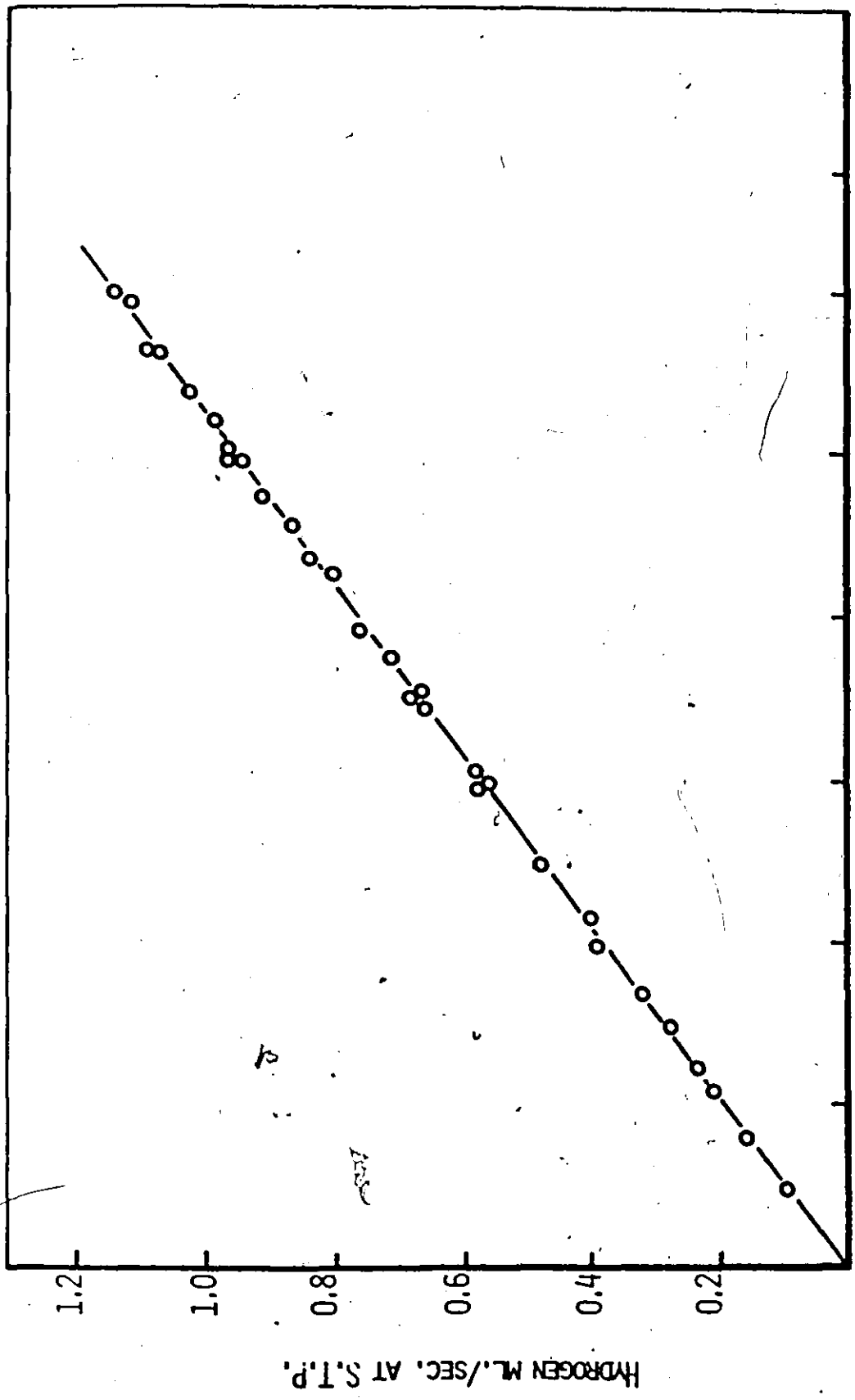


FIGURE A.1 HYDROGEN FLOW CALIBRATION FOR PACKED BED REACTOR

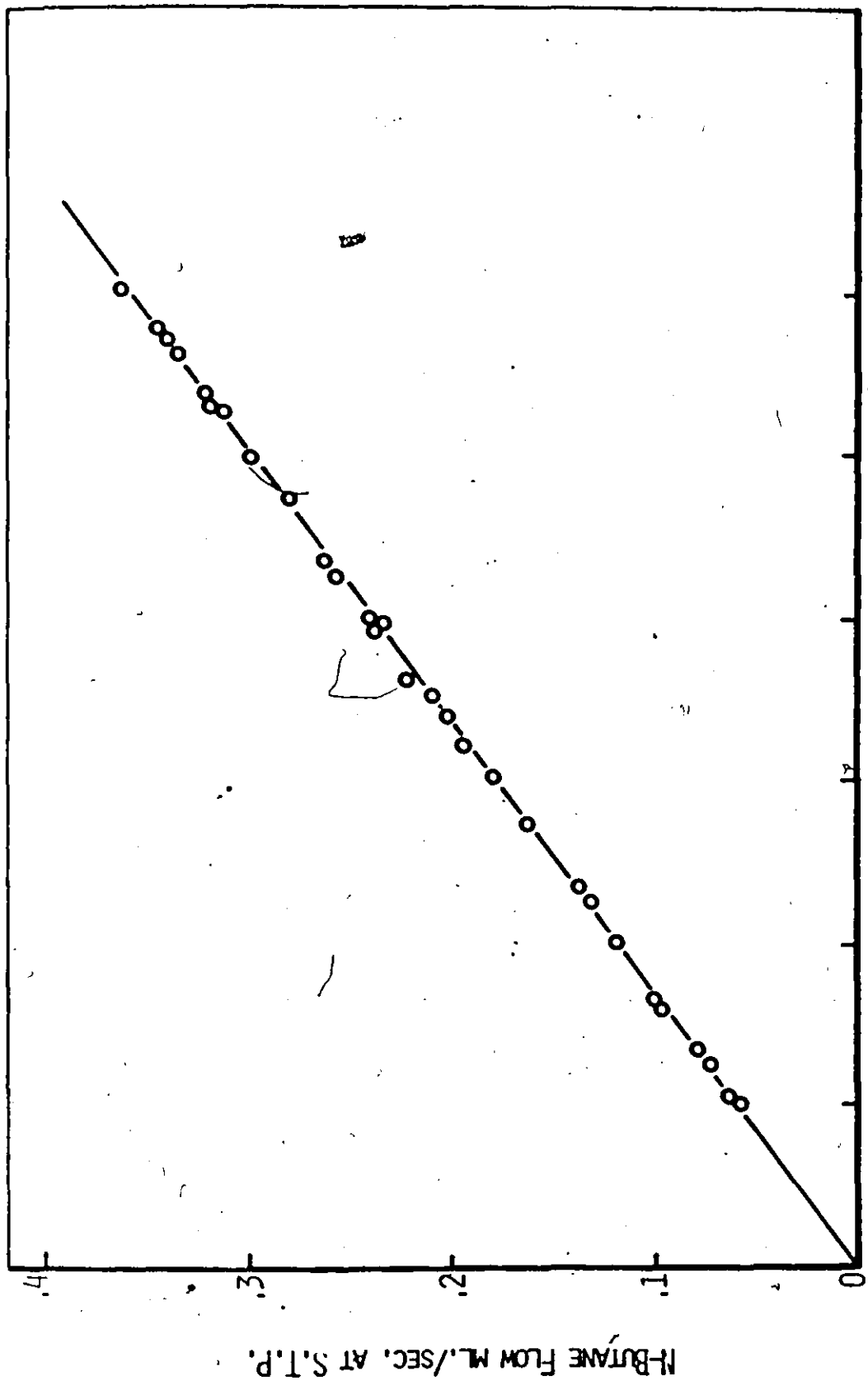


FIGURE A.2 N-Butane Flow Calibration for Packed Red Reactor

FLUIDIZED BED REACTOR

The total volumetric flows to the fluidized bed reactor ranged from 2.0 to 6.0 S.C.F.M. Floats were designed and made for commercially available rotameter tubes (Brooks Instrument Company) to cover the exact flow range required. The rotameters were calibrated at a pressure of 4.0 P.S.I.G. This back pressure was necessary to eliminate rotameter "bounce". The n-butane rotameter was calibrated using a wet test meter (Precision Scientific Company). The hydrogen rotameter was calibrated up to 1.3 S.C.F.M. using the wet test meter and hydrogen. For higher flows, precision orifice nozzles and nitrogen (for safety) were used. When readings were converted to equivalent hydrogen flows, no discrepancy in calibration was noted between the two methods. The calibration curves are shown in Figures A.3 and A.3.

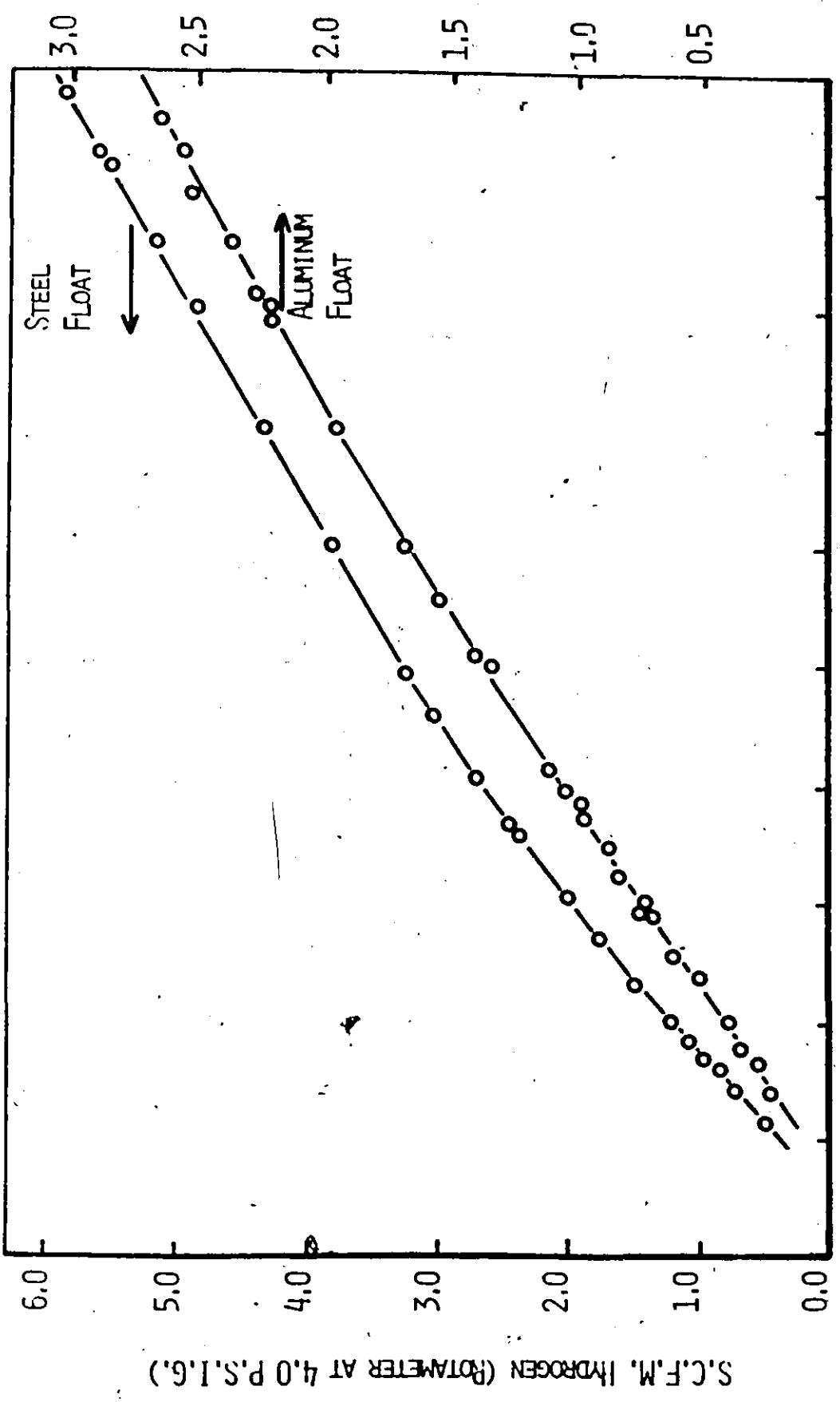


FIGURE A.3 HYDROGEN FLOW CALIBRATION FOR FLUIDIZED BED

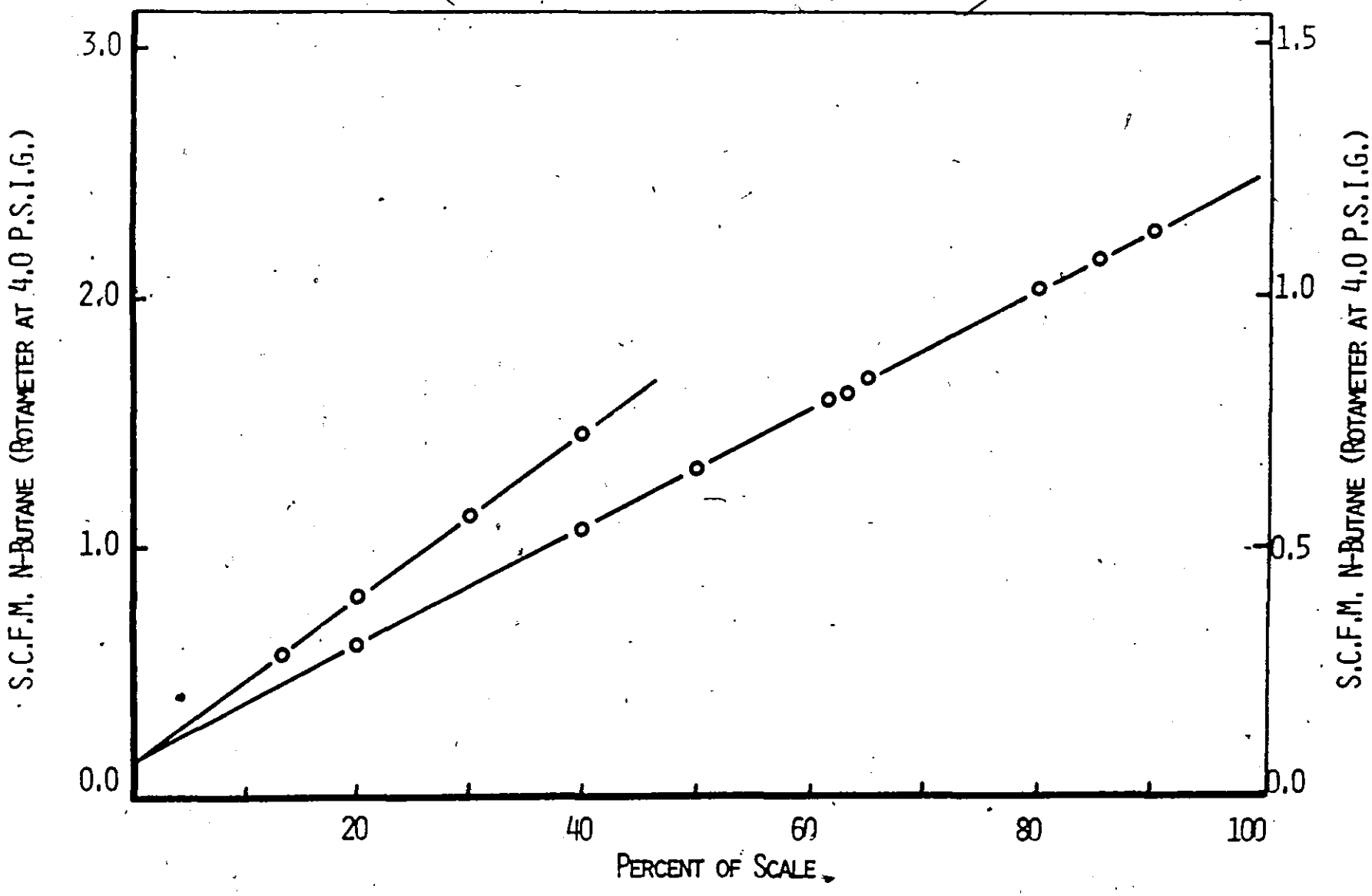


FIGURE A.4 N-Butane Flow Calibration for Fluidized Bed

APPENDIX B

THERMOCOUPLE CALIBRATION

Some variation in the e.m.f. temperature calibration is expected among thermocouples from the same batch of wire and even a greater variation is expected between thermocouples from different batches of wire. Thermocouples should be calibrated. It is very critical in this study because of the high activation energies of the reactions. Also, because the kinetic parameters are estimated in one reactor and are then used to describe a second reactor containing different thermocouples, a thermocouple error could be very serious.

Ceramo thermocouples from Thermo Electric of Canada Ltd. were used. All thermocouples were chromed-alumel with a 316 stainless steel sheath and were filled with magnesium oxide insulation. The packed bed thermocouples had a 1/16 in. sheath with 30 AWG wires and the fluidized bed and the standard thermocouples had a 1/8 in. sheath with 24 AWG wires.

One thermocouple was calibrated using the freezing point of a tin sample (U.S. National Bureau of Standards Sample 42 with freezing point of 231.88°C $\pm$ 0.01 on 1948 International Temperature Scale). The standard thermocouple read low by 0.034 $\pm$ 0.004 mv. as measured with a digital volt meter (FLUKE MODEL 8300A). The packed bed reactor was emptied of catalyst and filled with molten salt and placed in the reactor salt bath. The standard thermocouple was inserted into the reactor beside each thermocouple for calibration. The thermocouples from the fluidized bed were tied together

with the standard thermocouple and placed in a small muffle furnace to be calibrated. Table B.1 indicates the results of the calibrations. The correction factors must be subtracted from the experimentally recorded millivolt readings before the temperatures can be calculated from the standard conversion tables

THERMOCOUPLE LOCATION		CORRELATION (mV) SUBTRACT FROM READING
	FLUIDIZED BED	
No. 1	ON DISTRIBUTOR PLATE	0.054
No. 2	6. in. UP REACTOR	0.038
No. 3	1. ft. UP REACTOR	0.025
No. 4	2. ft UP REACTOR	0.004
No. 6	3. ft. UP REACTOR	0.024
No. 5	4. ft. UP REACTOR	0.041
No. 9	REACTOR FEED GAS	0.073
	PACKED BED	
No. 1	REACTOR FEED GAS	0.000
No. 2	1.0 cm. FROM TOP	0.073
No. 8	3.6 cm. FROM TOP	0.111
No. 3	6.2 cm. FROM TOP	0.054
No. 4	11.4 cm. FROM TOP	0.080
No. 5	11.4 cm. FROM TOP	0.069
No. 6	16.5 cm. FROM TOP	0.074

TABLE B.1 Thermocouple Calibration Corrections

APPENDIX C

CHROMATOGRAPHIC ANALYSIS AND CALIBRATION

A gas analysis technique should be designed to provide the required accuracy in the minimum time. It was important to minimize the analysis time since at least two samples were taken at each operating condition with the fluidized bed and it was often difficult to maintain steady operation for an extended period of time.

Four different chromatographic analysis were evaluated. The first technique described was used for the initial packed bed (02) and fluidized bed experiments. It was redesigned to provide increased accuracy and decreased analysis time. The calibration method and the preparation of synthetic samples, as described in the following section, were used for all four analytical methods.

CALIBRATION PROCEDURE

Mixtures of methane, ethane, propane, n-butane and hydrogen were prepared in a 2 ft. by 6 in. diameter sample bottle. A mercury manometer was used to measure the pressure in the bottle as each pure gas was added. The order in which the gases were added was randomized from sample to sample. The sample bottle was filled and evacuated three times with the first gas to be added. The filling lines to the sample bottle were also filled and evacuated three times as the next pure gas was added. The partial pressure of each component was calculated knowing the mercury manometer readings and the final total pressure in the sample bottle.

CHROMATOGRAPHIC ANALYSIS

A Varian Aerograph model 90-P chromatograph and a Sargent model DSRG recorder with disc integrator were used for all the analysis. Samples were introduced into the chromatograph using an on-line Varian Aerograph plunger-type gas sample valve with a 1.0 ml. sample loop. A thermal conductivity detector was used.

METHOD 1

Two columns in series at room temperature with a helium carrier gas flowrate of 35 ml./min. were used to effect a separation. The first column was 24. ft. of 1/4 in. O.D. copper tube packed with 20.0% dimethyl-sulfolane on 80 /100 mesh P acid washed chromasorb. Three peaks were obtained: a combined hydrogen-methane-ethane peak, a propane peak and a n-butane peak. The products from this first separation were passed through one side of the detector cell and then held up in a 40. ft. delay column of 1/4 in. O.D. copper tubing until all the sample had passed through the detector. The second column was 3. ft. of 1/4 in. O.D. copper tubing packed with 60 /80 mesh 5A modecular sieves. This column had a semi-infinite retention time for ethane, propane and n-butane and effected the separation of hydrogen and methane. These two gases were passed through the other side of the detector cell. The ethane response was determined by subtracting the sum of the separated hydrogen peak and methane peak from the original combined hydrogen-methane-ethane peak.

This method of analysis was used to obtain initial estimates of the kinetic parameters (02). The analysis time of 18. minutes was exessive for use with the fluidized bed reactor. Also, a study of the errors involved

in the chromatographic analysis (02) indicated that for a high conversion of n-butane, the error in estimating the ethane response would be of the same order of magnitude as the response itself. Since further parameter estimation required packed bed reactor data at very high conversions, a new method of analysis was required.

METHOD 2

This method of analysis involved a separate hydrogen analysis and a second hydrocarbon analysis using a hydrogen carrier gas. Two sample valves in series at the reactor exit were used to obtain the gas samples. By first determining the percent hydrogen in the sample, and then by determining the relative amounts of the four hydrocarbons, the composition of the reactor effluent could be calculated.

The hydrocarbons were analyzed in the gas chromatograph using a hydrogen carrier gas. Thus, no hydrogen peak appeared. Two columns in series were used with a carried gas flow of 83. ml./min. The first column was 9. ft. of 1/4 O.D. copper tube packed with 40 /60 mesh Porapak S at 140.^{o}C. The four hydrocarbons were completely separated and were passed through one side of the detector cell. Because the first peak, methane, was very narrow and not very useful for quantitative analysis, a second column was used. The gas from the detector cell was held up in 14. ft. of 1/4 in. O.D. copper tubing until the third gas, propane, had passed through the detector. The second column was 1. ft. of 1/4 in. O.D. copper tubing packed with 60 /80 mesh 5A molecular seive at 0^{o}C. This column had a semi-infinite retention time for ethane, propane and butane. The methane from this column was passed through the other side of the detector cell before the butane was

eluted from the first column.

The hydrogen was analyzed volumetrically. A 10. ml. sample was introduced into a 2. ft. by 1/4 in. o.o. copper tube packed with 40./60. mesh activated charcoal at room temperature. A carrier gas flow of 30. ml./min. of carbon monoxide was used. This column separated hydrogen and methane and had a semi-infinite retention time for ethane, propane and butane. The gas from the column was bubbled into a saturated solution of potassium hydroxide which completely reacted with the carbon monoxide carrier gas to form non-gaseous products. The hydrogen was collected in a calibrated tube above the bubbler and its volume recorded.

This method of analysis did not provide an accurate enough determination of hydrogen. However, it was noted that if the carrier gas flow, the detector block temperature and the filament current were held constant, the sample composition could be directly and accurately calculated from the hydrocarbon responses from the chromatograph. The third method of analysis involved the calibration of the detector cell response with a known amount of nitrogen.

METHOD 3

The same sample valve and sample loop at constant temperature and at atmospheric pressure was used for: calibrating with known gas mixtures, analyzing the reactor effluent, and calibrating the detector cell with nitrogen. At a constant filament current, carrier gas flow and detector block temperature (E1), the response from a standard amount of nitrogen (from the gas sample valve) could be used to calibrate the detector cell at any time:

$$\begin{pmatrix}\text{Mole fraction of}\\ \text{hydrocarbon in}\\ \text{gas sample}\end{pmatrix} = \begin{pmatrix}\text{peak area of}\\ \text{hydrocarbon}\\ \text{from gas sample}\end{pmatrix} \times \begin{pmatrix}\text{mole fraction per}\\ \text{peak area from}\\ \text{calibration}\end{pmatrix} \times \begin{pmatrix}\text{nitrogen peak area}\\ \text{from calibration}\\ \hline \text{nitrogen peak area}\\ \text{at time of gas sample}\end{pmatrix}.$$

The same Paropak S column as in method 2 was used for the hydrocarbon separation. This method of analysis proved to be accurate. The nitrogen responses were constant within experimental error. It was decided to use a pure butane sample to calibrate the detector cell. This was the method of analysis for the final packed bed and fluidized bed studies.

METHOD 4

The specifications for the chromatographic analysis of the reactor effluent containing methane, ethane, propane, n-butane and hydrogen are listed in table C.1.

The four hydrocarbons are separated on column 1 and pass into one side of the detector cell. The first peak, methane, is too narrow for quantitative analysis and so the gases then pass through the delay column 2 and into column 3. This column has a semi-infinite retention time for ethane, propane and n-butane. The methane from column 3 passes through the other side of the detector cell before the butane and after the propane is released from column 1. The analysis is complete in less than 5 minutes from the time of sample injection.

Repeated determination of the n-butane response from pure n-butane samples and n-butane calibration mixtures gave an average total butane response of 8,498. and a standard deviation of 1.6% based on 27 samples obtained during calibration and before and after all packed bed and

COLUMNS 1)	9. ft. by 1/4 in. in O.D. copper tubing packed with 40 /60 Poropak S at 140.°C.
2)	14. ft. by 1/4 in. O.D. copper tubing delay column.
3)	1. ft. by 1/4 in. O.D. copper tubing packed with 60 /80 5A molecular seive at 0.°C.
DETECTOR	thermal conductivity cell 165.°C 220. ma. filament current
CARRIER GAS	hydrogen at 83. ml/min.

TABLE C.1 - Specifications for Chromatographic Separation and Analysis of Product Gases

fluidized bed experiments. The relative responses for the four hydrocarbons are:

methane	1.020	σ = 2.0%
ethane	1.483	σ = 1.2%
propane	1.839	σ = 1.1%
butane	2.131	σ = 1.6%

The mole fraction of each component can then be calculated:

$$x_i = \frac{\text{(Area i) x (Attenuation)}}{8498.} \times \frac{\text{relative response n-butane}}{\text{relative response i}}$$

This method of analysis provides four independent responses for each chromatographic analysis. The same sample loop must be used for the calibration procedure and the analysis. The sample loop must also be at one constant temperature and at constant pressure (atmospheric).

APPENDIX D

CATALYST PREPARATION AND CHARACTERIZATION

PREPARATION

Thirty liters of 10.% nickel on silica gel catalyst was produced. The silica gel support was Davidson grade 81 silica gel with a reported size range of 70 to 297 microns (this material was donated by Davidson Chemicals). Fisher certified N-62 nickelous nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) was used to provide the nickel.

The silica gel was dried at 180.°C. Each litre of dried support weighed 430. gm. and required 315. ml. of solution containing 220. gm. of nickelous nitrate to just fill the pores. The nickel solution was added to the dried support stirring constantly. The resultant green material was placed on type 316 stainless steel trays to a depth of 1. in. The trays were put in airtight type 316 stainless steel boxes equipped with inlet and outlet lines for air. The boxes were placed in electric muffle furnaces and constantly purged with air. The temperature was raised to 300°F. and held for 1-1/2 hours. The temperature was then held at 450°F. for 1-1/2 hours and then at 690°F. for eight hours. The exit air, along with the poisonous nitrogen oxides were bubbled into a packed column filled with 1 normal NaOH solution.

The resulting grayish solid was placed in the fluidized bed reactor. It was reduced with hydrogen for eight hours at 550°F. Taylor, Yates and Sinfelt (T1) observed extensive reduction of their 10.% nickel on silica gel

catalyst when reduced to 482°F. To ensure complete reduction the catalyst used in their study was reduced at 700°F. The maximum reduction temperature for this study was limited to 550°F by the closed oil heating system for the fluidized bed.

CHARACTERIZATION

The silica gel support was sharp and jagged and appeared to have been produced by crushing. The particle density was determined. Also the voidage in the packed and in the fluidized bed was measured. Two determinations of the particle size distribution were made. A sieve analysis was done. Also, a measurement of particle size from magnified catalyst photographs was performed.

The density of a catalyst particle is 0.957 gm./cc. The volume of a 10. cc. sample bulb was determined using mercury. The bulb was filled with catalyst and then slowly heated to 200°C. in a vacuum and the weight of the catalyst recorded. Mercury was introduced into the evacuated tube and filled only the voids between the particles.

From the above method it was also determined that the voidage was 0.449. The catalyst in the sample bulb was vibrated to pack it. When filling the pack bed reactor with catalyst, it was vibrated in the same way.

The bulk density of the dry catalyst is 0.528 gm./cc. This was determined by filling a graduated cylinder with catalyst and heating it for four hours at 200°C to remove water.

The voidage of the fluidized bed at the minimum fluidization velocity is 0.557. This was determined by filling a 3. ft. by 1. in. diameter glass

tube with dry catalyst and vibrating it to obtain the same packing of particles as in the packed voidage determination. The height of the catalyst bed was recorded and then the bed was fluidized at the minimum fluidization velocity and the height recorded.

Photographs were taken of 522 catalyst particles and 435 silica gel support particles. The photographs were taken through a 6. power microscope with the particles on a glass slide with a 1.mm. scale etched on it. Enlarged positive prints were made and the particle size distribution based on the equivalent circle diameter was determined using a Zeiss Particle Size Analyzer (model TGZ3). The results are shown in Figure D.1. Because the particles are non-spherical, this analysis can only be used to indicate the particle size distribution and to show that some attrition has taken place in the fluidized bed.

A sieve analysis of the catalyst indicated a mean particle size of 162. microns. The results of the seive analysis are shown in Table D.1. The number of particles in any size range is proportional to the mass of the particles collected, divided by the average size cubed.

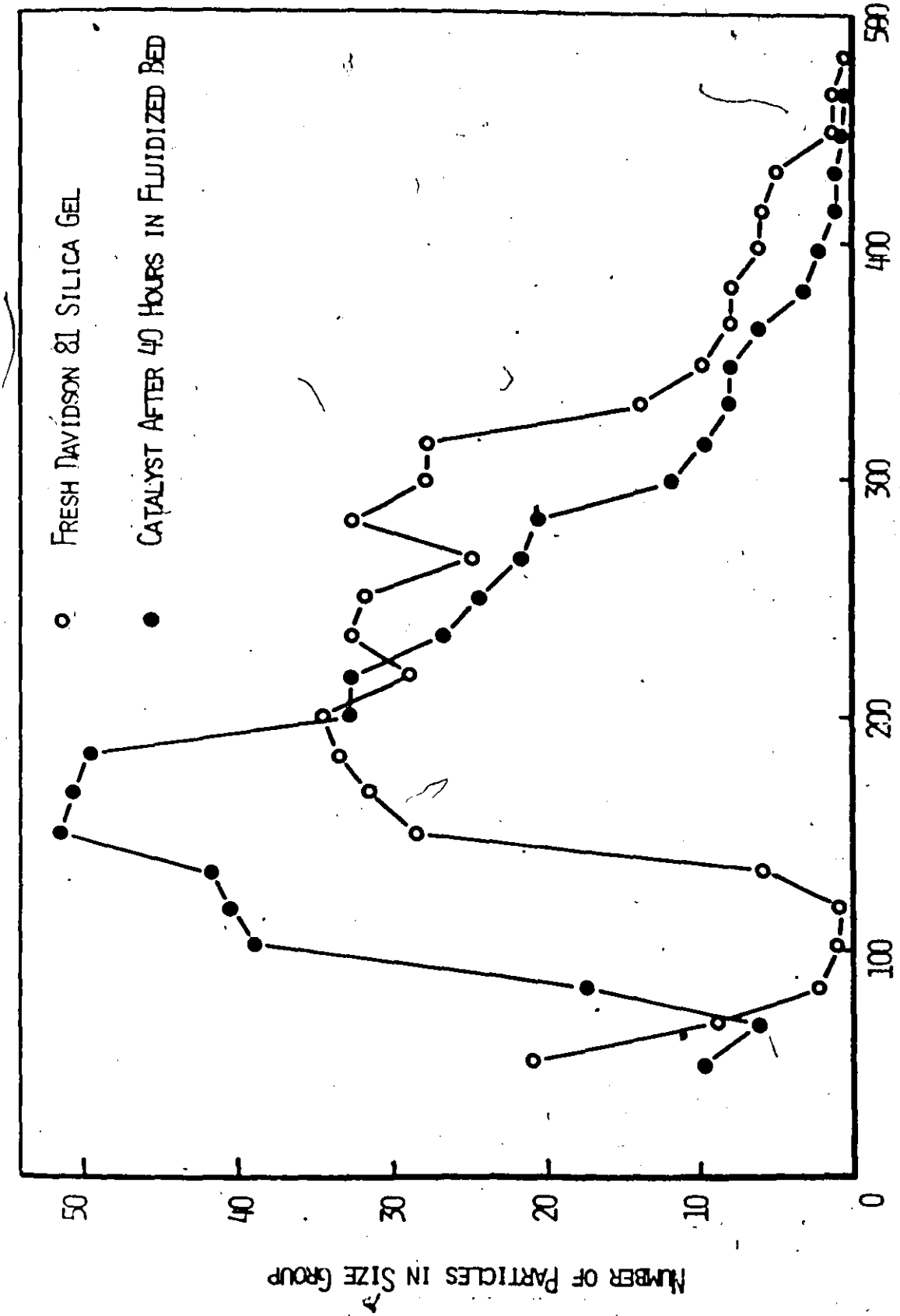


FIGURE 11 Particle Size Distribution Base on Equivalent Area Circles

FRACTION	MESH SIZE (microns)	grams collected (G_i)	average size (D_i)	$G_i/(D_i)^3 \times 10^8$	Percent
on 40	420	0.0	---	---	---
on 50	297	1.477	359.	3.	0.02
on 70	210	156.150	253.	964.	5.00
on 100	149	144.969	180.	2,487.	12.89
on 140	105	73.662	127.	3,611	18.71
on 170	88	24.456	96.5	2,726	14.13
on 200	74	17.045	81.0	3,210	16.64
on 270	53	5.332	63.5	2,083.	10.80
on 325	44	3.263	48.5	2,860.	14.83
on 400	37	0.309	40.5	465.	2.41
through 400		0.378	35.	882.	4.57
				19,291	100.00

TABLE D.1 Sieve Analysis of Catalyst after Forty Hours in Fluidized Bed

APPENDIX E

FLUIDIZED BED REACTOR OPERATION AND START UP

Because of the use of large quantities of hydrogen, the high temperature and the mechanical complexity and size of the apparatus, a detailed check of the reactor is necessary to ensure safe operation. This check will also reduce the chance of mechanical breakdown. This section contains instructions for pre-experimental check out, catalyst conditioning, and reactor operation.

PRELIMINARY CHECK OF HEAT EXCHANGER OIL SYSTEM

- open all three valves in the oil system
- ensure expansion oil tank is filled to 5. in. when cold
- turn heaters on to 40.% for 2 hrs
- turn off heaters
- turn on pump
- turn on heaters to full power
- turn on expansion oil tank cooling water
- remove insulation from pump to check for oil leak
- heat to 400°F.
- turn off heaters and pump
- repair oil leaks and insulate pump

PRELIMINARY CHECK OF CIRCULATING OIL SYSTEM

- open both valves in circulating system

- ensure expansion oil tank is filled to 5. in.
- turn the three adjustable heaters to 40.% for 2 hrs.
- turn off heaters since there is a large amperage surge when starting pump
- turn on pump stuffing box cooling water
- turn on pump
- turn on all heaters to full power (5 switches)
- turn on expansion oil tank cooling water
- remove all oil from pan below pump
- place drip tray under stuffing box
- remove insulation from pump to check for oil leaks
- heat to 350°F
- turn off heaters, pump and cooling water
- repair oil leaks and insulate pump

LEAK TEST FEED SECTION

- remove pipe nipple from back-pressure control valve and seal with a plug (the valve does not provide a perfect seal)
- pressurize with nitrogen to 15. P.S.I.G.
- if pressure drops more than 0.4 P.S.I. in 1. hr. check for leaks, especially:
  - steam heat exchanger
  - rotameter tube seals
  - all dart unions

CALIBRATE FEED ROTAMETERS

- remove plug from control valve that had been inserted for leak listing and connect to wet test meter venting to dump fan
- turn heating water on for n-butane tank
- set n-butane rotameter and adjust control valve for 4.0 P.S.I.G. on rotameter
- remove wet test meter and connect line to large orifice drum
- connect nitrogen cylinder to hydrogen feed system
- set hydrogen rotameter and adjust control valve for 4.0 P.S.I.G. on rotameter
- convert calibration to hydrogen flow

LEAK TEST REACTOR

- remove insulation from around top flange, distributor plate, and feed heat exchangers
- cap both exit lines from reactor (valves leak slightly)
- ensure all thermocouple wells and the catalyst drain line are sealed
- open feed back pressure valve full
- pressurize to 10. P.S.I.G. with nitrogen
- if pressure drops more than 0.2 P.S.I. in 90. min. search for leaks especially:
  - feed heat exchanges
  - top flange
  - distributor plate
  - thermocouple wells
  - thermocouples

- catalyst drain line
- gas sample line for chromatograph

- insulate
- remove caps from exit lines

CATALYST CONDITIONING (morning before experimental trials)

- open reactor exit
- purge reactor and feed system with nitrogen . .
- purge feed system with butane
- purge feed system with hydrogen
- heat circulating oil to about 580°F. (see instructions for circulating oil system check)
- heat the heat exchanger oil to about 500°F (see instructions for heat exchanger oil system check)
- hold catalyst at 550. ± 5.°F for 5-1/2 hrs. with sufficient hydrogen flowing through reactor to maintain a pressure drop of 10. in. of water across the bed
- shut down all pumps and heaters

LEAVE CATALYST OVERNIGHT (for experimental trials next day)

- leave the six adjustable heaters on at 40.%
- leave reactor exit line open
- adjust hydrogen flow to obtain 3. in. of water pressure drop across reactor.

REACTOR OPERATION

The reaction is highly exothermic and constant attention is required to maintain steady operation for five to ten minutes before sampling. The key to steady operation is to control and monitor the exit temperature of the circulating oil which is 20 to 40°F. below the reactor temperature. This oil temperature can be increased by increasing the n-butane flow (heat of reaction) or by turning on the electrical heaters. It can be decreased by increasing the hydrogen flow (decreasing the reaction) or by cooling the circulation oil in the air cooled heat exchanger. The oil temperature must be monitored constantly with a digital volt meter so that a temperature drift can be detected immediately.

The experimental flow and temperature conditions are set as follows:

1. choose an exit circulating oil temperature.
2. obtain this temperature using approximately the desired experimental flows.
3. set the hydrogen and n-butane flows at the desired conditions.

If the reactor temperature is not the desired temperature and stable, or the circulating oil temperature is not stable repeat the above steps until the desired operating conditions are achieved and they remain stable for three to five minutes. This procedure may have to be repeated five or six times to obtain the required stable operating conditions.

Because of the operating characteristics of the reactor, several details must be remembered. Below a feed ratio of 3. coking of the catalyst can occur. Because of the high heat of reaction and high activation energies, temperature runaway can occur. This can be halted by reducing the butane

flow, and by increasing the hydrogen flow which will cool the catalyst particles on the reactor walls. If the reaction extinguishes (catalyst too cold), it can only be restarted by heating the catalyst using the circulating oil. Once the reaction is started the oil must again be cooled. This operation requires about an hour.

APPENDIX F

PACKED BED REACTOR CALCULATIONS

HEAT OF REACTION (S1)

For severe reaction conditions the following reaction could result:

$$4C_4H_{10} + 9H_2 \rightarrow 11CH_4 + C_2H_6 + C_3H_8$$

Reaction	$\Delta H^\circ_{25^\circ C}$ Cal./gm. mole of butane
$C_4 \rightarrow 4C_1$	41400.
$C_4 \rightarrow 2C_2$	10322.
$C_4 \rightarrow C_3 + C_1$	13560.

By Hess' law of constant heat sumation, the standard heat of reaction at 25°C is 30,305 cal./gm. mole of butane reacted. At 260°C the heat of reaction is 31,300 cal./gm. mole of butane reacted.

PARTICLE REYNOLDS NUMBER

Feed flowrate = 1.5 ml./sec. (constant through reactor)

Reactor cross-section = 0.386 $cm.^2$

Superficial velocity = 3.85 cm./sec.

Molar flowrate = $\frac{PV}{RT} = \frac{1.0 \times 1.5}{82.06 \times 550.} = 3.32 \times 10^{-5}$ gm./moles/sec.

Average molecular weight assuming 5:1 hydrogen to butane molar ratio = $\frac{(1. \times 5.) + (58. \times 1.)}{6.} = 10.5$ gm./gm.-mole

Superficial mass velocity = G

$$= \frac{3.32 \times 10^{-5} \times 10.5}{0.386}$$

$= 9.02 \times 10^{-4}$ gm./sec.-cm.^{2}

Mean particle diameter = 0.0162 cm.

Gas viscosity = 1.1×10^{-4} poise (Pl)

Reynolds Number = $\frac{G\, d_p}{\mu} = 0.13$

AVERAGE MASS FLUX FROM PARTICLES

Assume severe reaction conditions of 260.°C, partial pressure of butane of 0.3 atm. and partial pressure of hydrogen of 0.5 atm and catalyst activity of 1.4.

$$r_{c_4} = 1.4 \times 10^{15.6604} \times \exp(-51000./1.99 \times 533.) \times 0.3^{+1} \times 0.5^{-2.348}$$

$$= 8.40 \times 10^{-6} \times 0.3 \times 5.09$$

$$= 1.28 \times 10^{-5} \text{ gm.moles/sec. - cm.}^3 \text{ of reactor}$$

Reactor voidage = 0.449

$$\frac{\text{Surface area of particles}}{\text{Volume of reactor}} = \frac{6. \times (1. - 0.449)}{d_p} = 204. \text{ cm.}^2/\text{cm.}^3$$

$$\text{Mass flux} = \frac{r_{c_4}}{204}$$

$$N = 6.27 \times 10^{-8} \text{ gm.moles/sec. - cm.}^2$$

AVERAGE HEAT FLUX FROM PARTICLES

Using previously calculated mass flux and heat of reaction:

Heat Flux $Q = N\Delta H$

$$= 6.27 \times 10^{-8} \times 31{,}300.$$

$$Q = 1.96 \times 10^{-3} \text{ cal./sec. - cm.}^2$$

J_d AND J_h VALUES FOR MASS AND HEAT TRANSFER

From the j_d and j_h correlations of Satternfield and Sherwood (S2) for a Reynolds number of 0.13:

$$j_d \approx j_h \approx 40$$

DRIVING FORCE FOR MASS TRANSFER

$$\text{Density } \rho = \frac{P}{RT} \times \text{Average Molecular Weight} = \frac{1}{82.06 \times 533.} \times 10.5$$

$$= 2.40 \times 10^{-4} \text{ gm./cm.}^3$$

$$\text{Diffusivity } D \approx 0.3 \text{ cm.}^2/\text{sec.} \quad \text{(P1)}$$

$$\text{Schmidt number } Sc = \frac{\mu}{\rho D} = \frac{0.00011}{0.00024 \times 0.3}$$

$$= 1.53$$

The mass transfer coefficient, k_g, is calculated using the j_d factor.

$$k_g = \frac{j_d \quad G}{P \times (Sc)^{1/3} \times (\text{AVERAGE MOLECULAR WEIGHT})}$$

$$= \frac{40. \times 9.02 \times 10^{-4}}{1.0 \times (1.53)^{1/3}} \times 10.5$$

$$= 0.0030 \text{ gm. moles/sec. - cm.}^2\text{-atm.}$$

The driving force required to bring the reactants to the catalyst surface must be:

$$\Delta P = \frac{N}{k_g} = \frac{6.27 \times 10^{-8}}{0.0030}$$

$$= 2.1 \times 10^{-5} \text{ atm.}$$

Therefore, there is no mass transfer limitation on the catalyst surface.

DRIVING FORCE FOR HEAT TRANSFER

Average heat capacity of reaction gases at 260°C (S1)

C_p = 14. cal./gm. mole - C°

Average thermal conductivity of reaction gases at 260°C (K4)

k = 0.00206 cal./sec. - cm. - C°

Prandtl number $Pr = C_p u/k$

$$= \frac{14. \times 0.00011}{0.00206}$$

$$= 0.75$$

Heat transfer coefficient

$$k = \frac{j_h \times G \times C_p}{(Pr)^{1/3}}$$

= 0.58 cal./sec. - cm.^{2} - C°

Driving force to remove generated heat

$$\Delta T = \frac{Q}{h} = \frac{0.00196}{0.58}$$

= 0.0034 C°

Therefore, there is essentially no temperature difference between the catalyst particle and the gas flowing past it.

PORE DIFFUSION LIMITATION

A reaction is not limited by pore diffusion if the effectiveness factor, η, is essentially unity. As the Thisle modulus, ϕ, approaches zero, the factor approaches unity.

$$\phi = L \sqrt{\frac{k_v}{D}}$$

For spherical catalyst pellets (S2)

L = radius /3.

= 0.0081/3.

= 0.0027 cm.

The first order reaction rate based on the bulk volume of the catalyst particle k_v can be calculated (previous calculation at extreme conditions).

$$r_B = (8.40 \times 10^{-6}) \times P_{C_4} \times P_{H_2}^{2.348}$$

for P_{H_2} = 0.5 atm.

$$r_B = (4.27 \times 10^{-5}) \times R \times T \times C_{C_4} = 1.87\ C_{C_4}$$

$$k_v = \frac{1.87}{(1-\epsilon)} = \frac{1.87}{(1-0.449)}$$

= 3.40 per sec.

The effective diffusion coefficient D is difficult to estimate. An order of magnitude estimate would be 0.1 $cm.^2/sec$. For the lowest possible case, that is involving Knudsen diffusion, the coefficient would be of the order of 0.0001 $cm.^2/sec$. ((S2) cumene gas at 147°C. on silica alumina cracking catalyst). Taking this case:

$$\text{Thiele modulas} = 0.0027 \sqrt{\frac{3.40}{0.001}}$$

= 0.16

For a Thiele modulus of this magnitude (B1) the effectiveness factor is essentially unity. Hence, the reaction is not limited by pore diffusion.

AXIAL DIFFUSION TERM IN MODEL

From Peterson (P2) for steady state including the axial component in a packed bed reactor:

$$E_{DA}\left(\frac{d^2c}{dz^2}\right) - \bar{u}\left(\frac{dc}{dz}\right) - k_v c = 0$$

where C = concentration of reactant gm. mole/cm.^{3}

z = length along the reactor

k_v = first order rate constant

E_{DA} = eddy diffusivity cm.^{2}/sec.

in dimensionless form

$$\alpha^2\left(\frac{d^2\psi}{d\tau^2}\right) - \left(\frac{d\psi}{d\tau}\right) - \psi = 0$$

where $\alpha^2 = \frac{k_v E_{DA}}{\bar{U}^2}$ $\quad \tau = \frac{kZ}{\bar{U}}$ $\quad \psi = \frac{C}{C_o}$

For an order of magnitude estimate of the eddy diffusivity, Carberry (C1) suggests that for Reynolds numbers less than 1.0 the molecular diffusivity can be used. Therefore, using a pseudo first order rate constant and the minimum flow rate of 1.8 ml./sec.

$$\bar{U} = \frac{1.8}{0.386} = 4.66 \text{ cm./sec.}$$

The maximum α^2 is

$$\frac{1.87 \times 0.3}{(4.66)^2}$$

$$= 0.026$$

Figure F.1 shows the reactor concentration profiles for the most severe condition used as predicted from the plug flow model. The curvature of the concentration profiles as predicted by the model is very small. Therefore,

$$0.026\ \frac{d^2\psi}{dZ^2} << \frac{d\psi}{dZ}$$

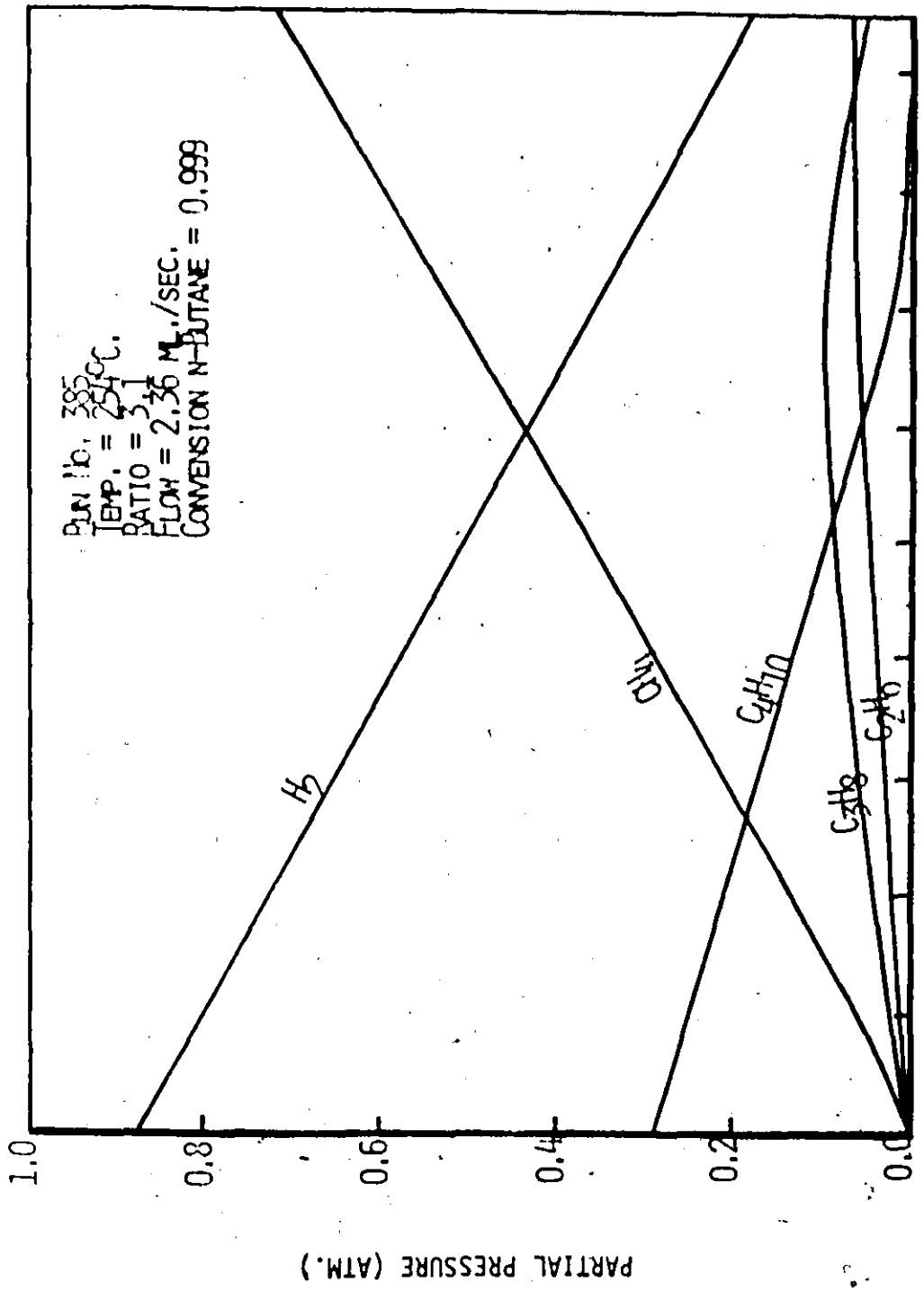


FIGURE E.4 CONCENTRATION PROFILE FOR MOST SEVERE CONDITIONS USED FOR PARAMETER ESTIMATION

This means that the axial diffusion term is negligible when compared to the convection term.

SAMPLE CALCULATION

The calculations will be based on the most extreme conditions used for parameter estimation. This is run 385 as shown in Figure F.1.

Taking ΔZ = 1. cm. (much larger than used in model)

Z = 10. cm.

then for the packed bed reactor equation

$$0.3 \frac{d^2P}{dZ^2} - 4.66 \frac{dP}{dZ} = 1.87P$$

$$\frac{\Delta P}{\Delta Z} = 0.020$$

$$\frac{\Delta^2 P}{\Delta Z^2} \approx 0.001$$

for this case P is 0.08, therefore

reaction term = 0.08 x 1.87 = 0.15

first derivative term = 4.66 x 0.020 = 0.09

second derivative term = 0.3 x 0.001 = 0.0003

Hence, axial diffusion is not important.

APPENDIX G

VARIANCE-COVARIANCE MATRIX OF ESTIMATED PARAMETERS

There are two ways of estimating $V(\underline{y})$ the variance-covariance matrix of the observations. One is to perform replicated experiments. The other is to use the $\underline{v}$ matrix of Box and Draper (B6):

$$\underline{v} = \sum_{u=1}^{n} \left[\underline{y}_u - \underline{\eta}_u\ (\underline{\xi}_u, \underline{\theta})\right] \left[\underline{y}_u - \underline{\eta}_u\ (\underline{\xi}_u, \underline{\theta})\right]^T \qquad G.1$$

where n is the number of experiments performed and $\underline{\xi}_u$ is the vector of control variables for the u'th experiment. This method assumes that the model $\underline{\eta}$ is adequate. For the purposes of using $V(\underline{y})$ to estimate the variance-covariance matrix of the estimated parameters $V(\underline{\theta})$ the second method was employed.

If the vector $\underline{\theta}$ which minimizes the determinant of $\underline{v}$ is substituted into the definition of $\underline{v}$ in equation G.1, then:

$$\frac{1}{n - \left(\frac{p}{r}\right)} \left[\underline{v}\right] \qquad G.2$$

is an estimate of $V(\underline{y}_u)$ for any experimental trial u. n is the number of experiments performed and r is the number of responses per experiment used to estimate the p parameters in $\underline{\theta}$. Now defining one single vector of all the responses:

$$\underset{nr \times 1}{\underline{Y}} = \begin{bmatrix} \underline{y}_1 \\ \underline{y}_2 \\ \vdots \\ \underline{y}_n \end{bmatrix} \qquad G.3$$

Then $V(\underline{y})$ becomes

$$\underset{nr \times nr}{V(\underline{y})} = \begin{bmatrix} \underline{\Sigma} & \underline{0} & \underline{0} & \cdots & \underline{0} \\ \underline{0} & \underline{\Sigma} & \underline{0} & \cdots & \underline{0} \\ \underline{0} & \underline{0} & \underline{\Sigma} & \cdots & \underline{0} \\ \vdots & \vdots & \vdots & & \vdots \\ \underline{0} & \underline{0} & \underline{0} & & \underline{\Sigma} \end{bmatrix} \qquad \text{G.3}$$

where

$$\underset{r \times r}{\underline{\Sigma}} = V(\underline{y}_u) \qquad u = 1, 2, \ldots n \qquad \text{G.5}$$

and n is the number of experimental trials. Null matricies $\underline{0}$ arise since the successive observation vectors are uncorrelated with each other.

Also let $\underset{nr \times p}{\underline{X}} = \begin{bmatrix} \underline{X}_1 \\ \underline{X}_2 \\ \vdots \\ \underline{X}_n \end{bmatrix}$ for all n experiments. G.6

where $\underset{r \times p}{\underline{X}_u} = \left[\frac{\partial \underline{n} \; (\underline{\xi}_u, \underline{\theta})}{\partial \underline{\theta}} \right]_{\theta = \hat{\theta}}$ G.7

and the subscript u refers to the u'th experimental trial.

Then the estimated variance-covariance matrix of the estimated parameters is:

$$V(\hat{\theta}) = \frac{1}{n-p} \left(\underline{X}^T \, \underline{V}(y)^{-1} \, \underline{X} \right)^{-1} = \frac{1}{n-p} \left[\sum_{u=1}^{n} \underline{X}_u^T \, \underline{\Sigma}^{-1} \underline{X}_u \right]^{-1} \qquad \text{G.8}$$

APPENDIX H

DERIVATION OF Df (w/M)

The effect of uncertainty in model (nuisance) parameters can be integrated out before attempting to discriminate among a number of models employed to describe a physical phenomenon. The unconditonal density functional Df (w/M) is:

$$Df(\underline{w}/M) = \frac{\exp\{-\frac{1}{2}\sum_{u=1}^{n}\{\underline{w}_u^T(\underline{X}_u\underline{U}\underline{X}_u^T+\underline{\Sigma})^{-1}\underline{w}_u\}\}}{(2\pi)^{nr/2}\left|\sum_{u=1}^{n}(\underline{X}_u\underline{U}\underline{X}_u^T+\underline{\Sigma})\right|^{n/2}} \qquad 6.10$$

where $\underline{w}$ is the vector of observed minus predicted responses for all n trials given model M. Equation 6.10 can also be written:

$$Df(\underline{w}/M) = \frac{\exp\{-\frac{1}{2}\{\underline{w}^T\underline{A}^{-1}\underline{w} - \underline{w}^T\underline{A}^{-1}\underline{X}(\underline{X}^T\underline{A}^{-1}\underline{X}+\underline{U}^{-1})^{-1}\underline{X}^T\underline{A}^{-1}\underline{w}\}\}}{(2\pi)^{nr/2}\left|\underline{U}\right|^{n/2}\left|\underline{\Sigma}\right|^{n/2}\left|\sum_{u=1}^{n}(\underline{X}_u^T\underline{\Sigma}^{-1}\underline{X}_u+\underline{U}^{-1})\right|^{n/2}} \qquad 6.12$$

Proof of Equivalence of Equations 6.10 and 6.12 (R.6)

Equation 6.10 can be rewritten:

$$Df(\underline{w}/M) = \frac{\exp\{-\frac{1}{2}\underline{w}^T(\underline{X}\underline{U}\underline{X}^T+\underline{A})^{-1}\underline{w}\}}{(2\pi)^{nr/2}\left|\underline{X}\underline{U}\underline{X}^T+\underline{A}\right|^{\frac{1}{2}}} \qquad (H.1)$$

and equation 6.12 can be rewritten:

$$Df(\underline{w}/M) = \frac{\exp\{-\frac{1}{2}\left[\underline{w}^T\underline{A}^{-1}\underline{w} - \underline{w}^T\underline{A}^{-1}\underline{X}(\underline{X}^T\underline{A}^{-1}\underline{X}+\underline{U}^{-1})^{-1}\underline{X}^T\underline{A}^{-1}\underline{w}\right]\}}{(2\pi)^{nr/2}\left|\underline{U}\right|^{\frac{1}{2}}\left|\underline{A}\right|^{\frac{1}{2}}\left|\underline{X}^T\underline{A}^{-1}\underline{X}+\underline{U}^{-1}\right|^{\frac{1}{2}}} \qquad (H.2)$$

where $\underline{X}$ is the nr x p matrix of all $\underline{X}_u$ for all trials and $\underline{A}$ is nr x nr matrix of n $\underline{\Sigma}$ matricies along the diagonal and all other elements zero.

1. The Matrix of the Quadratic Form in the Exponent

It can be shown by direct multiplication that:

$$(\underline{XUX}^T + \underline{A})^{-1} = \underline{A}^{-1} - \underline{A}^{-1}\underline{X}(\underline{X}^T\underline{A}^{-1}\underline{X} + \underline{U}^{-1})^{-1}\ \underline{X}^T\underline{A}^{-1} \qquad (H.3)$$

2. The Determinants

Consider the partitioned matrix

$$\underline{B} = \left[\begin{array}{cc} \underline{U}^{-1} & -\underline{X}^T \\ \hline \underline{X} & \underline{A} \end{array}\right] \qquad (H.4)$$

It can be established by direct multiplication that the inverse of $\underline{B}$, if it exists, is

$$\underline{B}^{-1} = \begin{bmatrix} \underline{U} - \underline{UX}^T\ (\underline{XUX}^T + \underline{A})^{-1}\ \underline{XU} & \underline{UX}^T\ (\underline{XUX}^T + \underline{A})^{-1} \\ -(\underline{XUX}^T + \underline{A})^{-1}\ \underline{XU} & (\underline{XUX}^T + \underline{A})^{-1} \end{bmatrix} \qquad (H.5)$$

In the cases in which we are interested all the sub-matrices of $\underline{B}^{-1}$ exist and therefore in these cases $\underline{B}$ is non-singular.

By the use of the following identity which can be verified by direct multiplication:

$$\underline{U} - \underline{UX}^T\ (\underline{XUX}^T + \underline{A})^{-1}\ \underline{XU} = (\underline{X}^T\underline{A}^{-1}\underline{X} + \underline{U}^{-1})^{-1} \qquad (H.6)$$

(H.5) can be rewritten as:

$$\underline{B}^{-1} = \begin{bmatrix} \underline{X}^T\underline{A}^{-1}\ \underline{X}\ \ \underline{U}^{-1})^{-1} & \underline{UX}^T(\underline{XUX}^T\ \ \underline{A})^{-1} \\ -(\underline{XUX}^T\ \ \underline{A})^{-1}\ \underline{XU} & (\underline{XUX}^T\ \ \underline{A})^{-1} \end{bmatrix} \qquad (H.7)$$

Applying Jacobi's theorem to equations (H.4) and (H.7) one obtains:

$$\left|(\underline{X}^T\underline{A}^{-1}\underline{X} + \underline{U}^{-1})^{-1}\right| = \left|\underline{A}\right|\left|\underline{B}\right|^{-1} \qquad (H.8)$$

and by the same theorem applied again:

$$\left|(\underline{XUX}^T + \underline{A})^{-1}\right| = \left|\underline{U}^{-1}\right|\left|\underline{B}\right|^{-1} \qquad (H.9)$$

It follows then, by eliminating $|\underline{B}|$ from (H.8) and (H.9) and rearranging, that

$$\left|\underline{XUX}^T + \underline{A}\right| = \left|\underline{U}\right|\left|\underline{A}\right|\left|\underline{X}^T\underline{A}^{-1}\underline{X}\ \ \underline{U}^{-1}\right| \qquad (H.10)$$

3. Equivalence of Equations (H.1) and (H.2)

When equations (H.3) and (H.10) are substituted into equation (H.1), equation (H.2) results.

RUN	P C4	P H2	FLOW	S1	S2	S3	CONV
260	.176	.919	1.57	2.256	.233	.426	67.53
261	.172	.924	1.58	2.260	.225	.430	67.53
262	.176	.922	1.60	2.256	.245	.418	71.16
264	.209	.886	1.47	3.021	.242	.165	99.25
265	.212	.883	1.47	3.151	.229	.130	99.74
266	.186	.909	1.52	2.331	.239	.397	78.81
267	.186	.910	1.53	2.292	.240	.409	76.74
268	.373	.714	1.31	3.559	.150	.047	100.00
269	.379	.710	1.32	3.653	.136	.025	100.00
271	.182	.915	1.57	2.077	.218	.496	47.40
272	.178	.919	1.57	2.071	.222	.495	47.73
273	.169	.927	1.56	2.471	.253	.341	92.52
274	.168	.929	1.55	2.143	.229	.466	71.18
275	.245	.852	1.55	2.201	.223	.451	72.33
276	.184	.904	1.38	2.204	.232	.444	76.12
277	.259	.829	1.38	2.245	.228	.433	76.79
279	.222	.865	1.26	3.150	.229	.130	99.68
281	.218	.866	1.25	2.937	.245	.191	99.27
282	.171	.928	1.60	2.048	.230	.497	64.23
285	.204	.890	1.45	2.347	.234	.395	84.49
286	.205	.889	1.44	2.433	.231	.368	85.27
287	.205	.888	1.43	2.402	.241	.372	86.94
288	.205	.888	1.44	2.471	.238	.351	88.68
289	.205	.889	1.43	2.485	.242	.344	90.16
290	.207	.887	1.42	2.570	.235	.320	92.18
291	.201	.892	1.48	2.457	.243	.353	88.05
292	.201	.892	1.49	2.440	.244	.357	87.98
293	.201	.893	1.47	2.456	.234	.358	87.95
294	.201	.893	1.47	2.392	.244	.373	87.39
295	.187	.885	1.00	3.600	.188	.008	100.00
296	.187	.884	1.01	3.652	.171	.002	100.00
297	.199	.894	1.44	2.314	.229	.410	81.13
298	.199	.895	1.43	2.289	.238	.411	81.46
299	.226	.867	1.38	3.501	.195	.037	100.00
300	.225	.868	1.38	3.442	.209	.046	100.00
301	.196	.898	1.41	2.231	.233	.435	74.43
302	.194	.898	1.42	2.183	.233	.450	73.88
304	.230	.859	1.33	3.132	.218	.144	99.64
305	.198	.894	1.46	2.149	.223	.468	68.97
306	.199	.894	1.46	2.234	.216	.445	70.65
310	.245	.894	1.46	3.547	.211	.010	100.00
312	.258	.940	2.20	2.973	.263	.167	99.64
313	.258	.941	2.19	2.936	.270	.175	99.50
314	.259	.940	2.18	2.949	.267	.172	99.64
316	.249	.885	1.44	3.435	.228	.036	100.00
317	.249	.884	1.44	3.452	.221	.035	100.00
318	.246	.948	2.20	2.594	.241	.308	93.90
319	.248	.946	2.20	2.596	.240	.308	93.64
321	.242	.885	1.50	2.594	.243	.307	93.55
322	.240	.886	1.51	2.518	.251	.327	92.72
324	.227	.901	1.63	2.613	.253	.294	96.18
325	.228	.902	1.63	2.570	.245	.313	95.06
326	.213	.917	1.64	2.527	.245	.328	92.93
327	.209	.921	1.60	2.460	.255	.344	92.45
329	.210	.926	1.67	3.132	.264	.114	100.00

330	.205	.933	1.67	3.166	.266	.101	100.00
331	.232	.896	1.60	2.669	.247	.279	97.25
332	.231	.898	1.58	2.678	.251	.273	96.87
333	.215	.914	1.82	2.227	.235	.434	80.80
334	.214	.918	1.80	2.223	.234	.436	81.04
336	.250	.834	1.12	3.699	.151	0.000	100.00
337	.247	.841	1.12	3.566	.205	.008	100.00
338	.244	.844	1.11	3.512	.221	.015	100.00
339	.210	.919	1.78	2.223	.231	.438	82.17
340	.204	.925	1.77	2.183	.237	.448	81.05
341	.275	.844	1.56	3.436	.218	.043	100.00
342	.267	.851	1.55	3.336	.252	.053	100.00
343	.212	.918	1.78	2.258	.236	.423	83.78
344	.216	.915	1.80	2.303	.228	.414	85.15
345	.278	.876	2.02	3.476	.212	.034	100.00
346	.275	.878	2.02	3.434	.219	.043	100.00
347	.212	.922	1.80	2.328	.241	.397	87.87
348	.211	.921	1.79	2.343	.229	.400	87.81
350	.283	.898	2.40	3.327	.232	.070	100.00
351	.278	.903	2.39	3.233	.246	.092	100.00
352	.210	.921	1.78	2.225	.242	.431	84.84
353	.206	.925	1.77	2.236	.235	.432	83.53
354	.209	.923	1.78	2.263	.234	.423	83.11
355	.250	.880	2.01	4.000	0.000	0.000	100.00
356	.250	.880	2.00	4.000	0.000	0.000	100.00
357	.256	.907	2.00	3.996	.002	0.000	100.00
358	.255	.907	1.99	3.993	.003	0.000	100.00
359	.255	.908	1.99	3.982	.009	0.000	100.00
360	.255	.908	1.99	3.983	.008	0.000	100.00
361	.214	.931	1.76	3.667	.147	.013	100.00
362	.215	.930	1.77	3.679	.146	.009	100.00
364	.212	.915	1.78	2.128	.220	.477	56.98
365	.207	.919	1.77	2.091	.218	.491	55.71
366	.209	.917	1.78	2.088	.217	.493	57.14
367	.208	.918	1.77	2.075	.218	.496	56.96
369	.208	.922	1.81	2.371	.245	.380	92.23
370	.207	.923	1.81	2.350	.248	.385	91.57
371	.206	.925	1.80	2.364	.241	.385	95.63
372	.206	.923	1.80	2.324	.248	.393	91.94
373	.205	.924	1.77	2.351	.247	.385	92.22
374	.275	.880	2.13	2.691	.247	.272	97.12
375	.268	.884	2.12	2.607	.245	.301	95.78
376	.265	.887	2.11	2.532	.245	.326	94.66
377	.208	.922	1.79	2.357	.253	.379	92.54
378	.208	.921	1.79	2.324	.258	.387	92.45
380	.265	.841	1.43	2.764	.248	.247	98.90
381	.263	.842	1.43	2.728	.255	.254	98.65
382	.208	.921	1.82	2.184	.235	.449	80.17
383	.207	.923	1.82	2.203	.231	.445	81.34
385	.287	.883	2.36	3.098	.241	.140	99.86
386	.287	.884	2.33	2.991	.253	.168	99.68
387	.285	.886	2.34	2.960	.259	.174	99.53
388	.205	.922	1.78	2.214	.230	.442	83.59
389	.202	.925	1.78	2.178	.237	.449	82.42
390	.252	.871	1.70	2.588	.263	.295	97.25
391	.260	.864	1.68	2.668	.252	.276	97.76
392	.216	.913	1.81	2.154	.232	.460	80.16

393	.200	.929	1.81	2.197	.234	.445	80.03
394	.200	.929	1.80	2.170	.228	.458	79.95
396	.270	.819	1.13	3.557	.189	.022	100.00
397	.268	.821	1.13	3.549	.188	.025	100.00
398	.204	.925	1.81	2.045	.209	.512	55.23
399	.208	.921	1.82	2.036	.220	.508	57.04
400	.206	.923	1.82	2.014	.217	.518	57.25
401	.205	.919	1.80	1.869	.190	.583	17.85
402	.208	.919	1.78	1.879	.194	.578	18.72
403	.208	.918	1.79	1.847	.189	.592	19.52
404	.209	.917	1.79	1.873	.188	.584	22.70
405	.207	.919	1.79	1.910	.181	.576	23.16
407	.203	.930	1.84	2.291	.249	.403	90.69
408	.206	.927	1.82	2.345	.252	.384	92.60
409	.210	.922	1.81	2.386	.250	.371	93.66
410	.204	.929	1.81	2.359	.249	.381	92.32
411	.201	.931	1.80	2.360	.247	.382	92.31
412	.203	.928	1.82	2.183	.220	.459	74.53
413	.207	.925	1.82	2.168	.222	.463	74.37
414	.207	.925	1.83	2.158	.228	.462	74.76
415	.151	1.003	2.25	1.970	.199	.544	53.46
416	.150	1.004	2.24	1.921	.208	.554	52.82
417	.210	.920	1.79	2.185	.239	.446	78.89
418	.207	.922	1.78	2.173	.231	.455	77.14
419	.206	.923	1.78	2.158	.230	.461	76.77
420	.152	1.007	2.24	2.216	.240	.435	80.94
421	.152	1.007	2.24	2.218	.236	.437	80.86
422	.210	.919	1.80	2.174	.236	.452	77.13
423	.209	.921	1.79	2.167	.224	.462	76.09
424	.154	1.003	2.24	2.052	.225	.499	67.61
425	.150	1.006	2.23	2.048	.223	.502	66.75
426	.204	.926	1.78	2.146	.229	.465	76.07
427	.201	.928	1.78	2.103	.228	.481	74.15
428	.277	.879	2.15	2.480	.254	.338	90.51
429	.282	.875	2.16	2.609	.252	.296	94.24
430	.208	.923	1.80	2.105	.232	.477	76.16
431	.203	.927	1.79	2.135	.228	.470	74.27
434	.209	.914	1.84	2.740	.262	.245	99.13
435	.210	.913	1.79	2.774	.274	.226	99.28
436	.212	.911	1.86	2.706	.254	.262	98.25
437	.206	.898	1.81	2.861	.274	.197	99.88
438	.205	.899	1.80	2.839	.277	.202	99.88
439	.198	.907	1.82	2.803	.276	.215	99.75
440	.245	.866	1.92	3.553	.212	.007	100.00
441	.155	.971	2.31	2.269	.251	.410	89.29
442	.156	.972	2.30	2.269	.243	.415	90.61
443	.156	.972	2.30	2.220	.246	.429	90.67
444	.215	.918	2.37	2.320	.241	.399	90.74
445	.215	.918	2.37	2.296	.236	.410	90.57
446	.215	.918	2.37	2.284	.236	.414	90.01
447	.215	.918	2.39	2.284	.235	.415	89.76
448	.214	.919	2.37	2.265	.239	.419	89.34
449	.215	.918	2.38	2.266	.237	.420	89.40
450	.215	.918	2.37	2.300	.241	.406	89.38
451	.154	.972	2.29	2.201	.246	.436	87.91
452	.154	.972	2.30	2.176	.240	.448	87.80
453	.151	.963	2.06	2.168	.234	.455	87.75

454	.151	.963	2.06	2.148	.178	.499	86.95
456	.151	.963	2.06	2.135	.247	.457	88.24
457	.150	.964	2.06	2.118	.247	.463	88.24
458	.150	.964	2.06	2.148	.245	.454	89.13
459	.150	.964	2.05	2.123	.244	.463	89.21
460	.150	.964	2.05	2.142	.240	.459	89.13
461	.150	.964	2.05	2.136	.246	.458	89.43
462	.153	.974	2.27	2.343	.254	.383	94.72
463	.153	.974	2.28	2.289	.262	.396	94.69
464	.101	1.047	2.66	2.638	.297	.256	99.47
465	.101	1.046	2.67	2.589	.304	.268	99.38
466	.101	1.047	2.66	2.587	.307	.266	99.23
467	.101	1.047	2.66	2.606	.300	.265	99.44
468	.101	1.047	2.66	2.635	.285	.265	99.48
469	.100	1.047	2.65	2.644	.297	.254	99.50
470	.100	1.048	2.66	2.622	.302	.258	99.81
471	.155	.977	2.25	2.834	.389	.129	100.00
473	.152	.975	2.24	2.426	.282	.336	98.00
474	.152	.975	2.24	2.435	.279	.336	98.18
475	.153	.971	2.27	2.344	.236	.395	90.27
476	.149	.974	2.26	2.314	.238	.404	91.18
477	.148	.977	2.26	2.337	.242	.393	92.21
479	.178	.971	2.71	2.356	.254	.378	94.58
480	.177	.972	2.70	2.362	.258	.374	94.33
481	.177	.972	2.70	2.367	.258	.373	94.80
483	.177	.972	2.70	2.388	.255	.367	95.22
484	.177	.972	2.70	2.388	.252	.369	94.98
485	.176	.973	2.69	2.383	.258	.367	95.17
486	.154	.969	2.23	2.405	.260	.358	96.57
487	.154	.970	2.23	2.362	.264	.370	96.31
488	.151	.973	2.22	2.415	.261	.354	96.81
489	.150	1.003	2.59	3.737	.113	.012	100.00
490	.150	1.004	2.58	3.745	.112	.010	100.00
491	.150	1.003	2.59	3.761	.107	.009	100.00
492	.149	1.003	2.59	3.763	.106	.009	100.00
493	.150	1.003	2.59	3.764	.105	.009	100.00
494	.149	1.003	2.59	3.758	.107	.009	100.00
495	.149	.972	2.24	2.412	.275	.346	97.64
496	.147	.975	2.24	2.384	.266	.361	97.31
498	.144	.978	2.24	2.406	.262	.357	96.58

RUN	FEED	1.0CM	3.6CM	6.2CM	11.4CM	11.4CM	16.5CM
260	250.76	253.10	252.29	252.68	253.07	253.27	252.97
261	250.88	253.19	252.44	252.83	253.10	253.41	253.12
262	251.20	253.46	252.80	253.19	253.24	253.70	253.48
264	252.90	255.48	255.11	255.31	255.43	255.99	255.70
265	252.97	255.50	255.23	255.40	255.50	256.09	255.79
266	250.81	253.07	252.46	252.80	252.97	253.31	253.07
267	250.76	253.10	252.49	252.83	252.97	253.31	253.12
268	253.27	256.64	256.04	255.79	255.65	256.01	255.31
269	253.51	257.20	256.40	256.23	255.94	256.52	255.75
271	251.44	253.95	252.97	253.34	253.46	253.68	253.48
272	251.44	253.90	252.95	253.31	253.58	253.73	253.41
273	246.41	251.25	249.98	250.23	250.32	250.76	250.86
274	0.00	247.62	246.31	246.63	247.19	247.43	247.41
275	0.00	247.70	246.41	246.73	247.26	247.53	247.48
276	0.00	248.69	247.79	248.14	248.43	248.74	248.84
277	0.00	248.74	247.82	248.18	248.35	248.77	248.91
279	246.34	250.37	249.96	250.25	250.49	251.22	250.83
281	246.26	250.27	249.81	250.18	250.32	251.00	250.59
282	0.00	248.35	247.62	248.14	248.48	248.84	248.43
285	0.00	249.16	247.92	248.38	248.84	249.45	248.96
286	0.00	249.11	247.92	248.38	248.86	249.55	249.08
287	0.00	249.08	247.82	248.33	248.86	249.55	249.08
288	0.00	249.08	247.84	248.26	248.96	249.62	249.18
289	0.00	248.96	247.77	248.23	248.91	249.69	249.23
290	0.00	248.79	247.70	248.14	248.84	249.55	249.23
291	0.00	248.67	247.65	248.06	248.57	249.35	249.08
292	0.00	248.62	247.82	248.33	248.65	256.74	256.43
293	0.00	248.62	248.06	248.57	248.77	249.55	249.16
294	0.00	248.60	248.09	248.62	248.77	249.55	249.11
295	0.00	256.57	256.67	256.99	256.45	257.33	256.47
296	0.00	256.72	256.77	257.13	256.52	257.37	256.50
297	0.00	248.45	247.94	248.48	248.67	249.30	248.79
298	0.00	248.65	248.14	248.69	248.89	249.50	249.06
299	0.00	251.88	251.90	252.27	252.32	253.44	252.90
300	0.00	251.93	251.98	252.37	252.41	253.46	252.90
301	0.00	255.26	247.89	248.52	248.82	249.38	248.89
302	0.00	248.60	247.70	248.31	248.74	249.30	248.84
304	0.00	250.93	250.64	250.96	251.32	251.49	250.74
305	0.00	248.48	247.84	248.48	248.62	249.25	248.74
306	0.00	248.65	248.06	248.62	248.82	249.40	248.99
310	247.43	255.75	253.97	254.34	254.09	254.77	253.80
312	247.07	255.11	253.48	254.02	254.02	254.89	254.41
313	247.07	254.99	253.46	253.97	254.02	254.89	254.38
314	247.07	254.87	253.41	253.92	253.95	254.82	254.38
316	245.85	254.14	253.29	253.92	253.82	254.72	254.09
317	245.97	254.19	253.46	254.02	253.92	254.80	254.14
318	245.61	253.85	252.92	253.65	253.68	254.34	254.09
319	245.36	253.65	252.78	253.48	253.58	254.89	253.90
321	249.86	255.43	254.09	254.46	254.31	254.99	254.92
322	249.93	255.43	254.09	254.46	254.26	254.97	254.87
324	246.94	252.68	251.10	251.86	252.90	253.07	252.15
325	246.90	252.24	252.15	251.78	252.63	252.95	252.00
326	247.19	252.68	251.66	252.39	253.46	252.95	252.29
327	247.43	252.73	251.66	252.46	253.58	253.00	252.39
329	253.63	259.66	258.37	258.78	259.47	259.22	258.27

330	254.55	260.85	259.56	259.98	260.19	259.95	259.25
331	247.07	253.05	251.61	252.37	253.41	253.05	252.32
332	247.14	253.10	251.78	252.49	253.41	253.05	252.37
333	250.23	250.40	251.42	250.91	250.47	251.03	250.66
334	250.23	250.32	251.34	250.86	250.44	250.93	250.57
336	250.98	251.47	253.63	252.83	251.47	251.86	251.05
337	250.13	250.59	252.44	251.73	250.69	251.05	250.25
338	250.13	250.62	252.34	251.61	250.69	251.00	250.20
339	249.89	250.20	251.10	250.64	250.25	250.86	250.54
340	249.72	250.06	250.88	250.42	250.13	250.66	250.32
341	250.03	250.30	252.27	251.59	250.86	252.17	251.32
342	249.98	250.15	252.07	251.42	250.76	251.93	251.22
343	249.89	249.96	251.15	250.66	250.27	250.91	250.74
344	249.79	249.93	251.08	250.62	250.10	250.81	250.69
345	253.44	253.95	256.69	255.58	253.99	255.99	254.99
346	253.46	253.95	256.69	255.53	253.90	255.72	254.94
347	250.27	250.57	251.66	251.10	250.18	250.91	251.37
348	250.23	250.71	251.54	250.96	250.13	250.83	251.30
350	255.62	256.16	259.08	257.71	256.60	258.18	256.89
351	255.62	256.11	259.03	257.69	256.67	258.18	256.86
352	250.32	250.32	251.49	251.03	250.74	251.17	250.98
353	250.18	250.30	251.25	250.81	250.62	251.03	250.79
354	249.84	250.08	250.93	250.49	250.57	251.00	250.79
355	267.37	270.80	267.46	267.22	266.88	267.08	266.98
356	265.25	268.97	265.47	265.18	264.84	265.08	264.91
357	263.77	267.44	264.06	263.89	263.31	263.53	263.40
358	262.46	266.10	262.80	262.33	262.02	262.21	262.09
359	260.44	263.91	260.83	260.32	259.93	260.15	260.02
360	260.46	263.89	260.85	260.34	259.90	260.15	260.02
361	250.79	251.90	252.58	251.00	250.42	250.71	250.44
362	250.74	251.83	252.58	250.91	250.37	250.66	250.37
364	250.52	250.52	251.20	250.86	250.62	250.98	251.20
365	250.37	250.32	251.05	250.69	250.54	250.88	250.98
366	250.20	250.25	250.86	250.52	250.37	250.81	250.81
367	250.23	250.30	250.88	250.54	250.42	250.76	250.79
369	250.03	250.93	251.42	250.74	250.35	250.96	250.52
370	249.93	250.83	251.32	250.69	250.23	250.81	250.42
371	250.06	250.98	251.51	250.86	250.42	251.00	250.64
372	250.06	250.88	251.49	250.83	250.37	251.00	250.54
373	250.06	250.93	251.49	250.86	250.40	250.96	250.57
374	249.45	250.86	251.76	250.81	250.27	251.32	250.88
375	249.33	250.74	251.59	250.69	250.25	251.20	250.74
376	249.25	250.64	251.37	250.49	250.08	251.05	250.64
377	250.18	251.00	251.64	250.98	250.54	251.17	250.71
378	250.23	251.05	251.64	250.98	250.52	251.13	250.76
380	247.02	248.01	248.79	248.06	247.60	248.65	247.41
381	246.99	248.01	248.74	248.04	247.62	248.62	247.50
382	249.86	250.69	251.13	250.49	250.23	250.83	250.01
383	250.03	250.76	251.25	250.69	250.37	250.98	250.20
385	252.32	254.46	255.75	254.41	253.53	255.06	253.07
386	252.39	254.53	255.79	0.00	253.51	255.11	253.22
387	252.41	254.53	255.82	254.46	253.58	255.09	252.92
388	250.13	251.05	251.42	250.83	250.47	251.05	250.35
389	250.13	251.00	251.42	250.86	250.52	251.05	250.35
390	249.01	250.32	251.00	250.27	249.76	250.76	249.62
391	248.91	250.20	250.86	250.13	249.62	250.57	249.40
392	249.93	250.91	251.25	250.81	250.47	251.00	250.37

393	250.03	252.44	251.32	250.76	250.49	251.00	250.37
394	250.15	251.05	251.32	250.83	250.52	251.05	250.40
396	250.57	252.97	254.77	252.73	250.66	250.81	250.57
397	250.59	252.92	254.65	252.71	250.66	250.83	250.57
398	250.91	251.86	252.20	251.66	250.96	251.10	250.81
399	250.96	251.90	252.24	251.73	250.96	251.08	250.91
400	251.00	251.95	252.27	251.78	251.00	251.13	250.93
401	250.66	250.74	251.00	250.88	250.66	250.79	250.62
402	250.71	251.10	251.08	250.93	250.66	250.83	250.66
403	250.76	250.86	251.17	250.98	250.76	250.93	250.79
404	250.83	251.15	250.96	250.88	250.42	250.83	250.74
405	250.81	251.17	250.93	250.79	250.25	250.79	250.79
407	249.79	251.34	251.66	250.86	250.20	250.74	250.69
408	250.03	251.54	252.00	251.17	250.40	250.98	250.91
409	249.93	251.51	251.90	251.13	250.32	250.88	250.91
410	249.98	251.59	251.88	0.00	250.35	250.86	250.96
411	249.98	251.76	251.86	251.13	250.49	250.86	251.08
412	250.91	251.93	252.56	251.88	250.74	251.00	251.05
413	250.76	251.81	252.39	251.78	250.62	250.88	250.86
414	250.74	251.81	252.44	251.76	250.54	250.81	250.83
415	251.68	252.24	252.61	252.22	251.44	251.68	251.71
416	251.37	252.17	252.56	252.17	251.39	251.64	251.64
417	250.91	252.03	252.58	251.90	250.66	250.93	250.91
418	250.81	251.88	252.46	251.86	250.64	250.91	250.98
419	250.81	251.90	252.49	251.86	250.69	250.98	250.96
420	257.01	258.27	258.61	257.86	256.79	257.01	256.99
421	257.06	258.27	258.64	257.91	256.79	257.06	257.08
422	250.64	251.76	252.20	251.54	250.59	250.86	250.69
423	250.49	251.59	251.98	251.39	250.42	250.76	250.57
424	254.12	255.16	255.38	254.87	254.14	254.36	254.24
425	253.99	255.02	255.23	254.75	254.09	254.31	254.19
426	250.27	251.56	251.90	251.27	250.52	250.76	250.54
427	250.23	251.47	251.71	251.15	250.37	250.62	250.44
428	250.66	252.80	253.61	252.61	250.88	251.44	251.00
429	250.66	253.05	253.92	252.88	250.96	251.05	251.17
430	250.49	251.66	252.00	251.42	250.59	250.86	250.66
431	250.44	251.59	251.86	251.27	250.44	250.76	250.59
434	252.90	253.95	254.14	253.85	252.92	253.36	253.34
435	252.97	254.09	254.29	253.97	253.10	253.51	253.41
436	253.27	253.73	254.56	254.53	253.34	253.80	253.75
437	250.96	252.44	253.17	252.32	251.42	251.68	251.30
438	250.96	252.39	253.12	252.32	251.34	251.66	251.30
439	251.05	252.56	253.02	252.32	251.51	251.81	251.39
440	251.37	254.29	255.23	253.87	251.83	252.12	251.59
441	251.56	252.58	252.54	252.34	251.93	252.20	251.90
442	251.64	252.68	252.61	252.41	252.03	252.29	252.00
443	251.66	252.80	252.63	252.51	252.07	252.37	252.00
444	248.82	250.18	250.08	250.01	249.40	249.84	249.47
445	248.84	250.25	250.06	249.98	249.38	249.79	249.52
446	248.82	250.15	250.03	249.89	249.33	249.74	249.47
447	248.84	250.20	250.03	249.93	249.38	249.84	249.55
448	248.84	250.13	250.08	249.93	249.40	249.81	249.52
449	248.94	250.23	250.10	249.96	249.42	249.86	249.62
450	248.96	250.32	250.20	250.08	249.52	249.93	249.64
451	251.34	252.51	252.22	252.12	251.73	252.07	251.73
452	251.32	252.51	252.17	252.10	251.76	251.98	251.76
453	249.25	250.37	250.01	249.84	249.59	249.86	249.52

454	249.23	250.27	250.03	249.79	249.55	249.86	249.52
456	249.25	247.89	250.08	249.81	249.62	249.86	249.52
457	249.25	250.32	250.08	249.81	249.59	249.86	249.52
458	249.28	250.37	250.18	249.86	249.64	249.93	249.57
459	249.33	250.44	250.20	249.93	249.67	249.93	249.59
460	249.28	250.40	250.15	249.84	249.64	249.86	249.52
461	249.28	250.32	250.13	249.81	249.62	249.89	249.52
462	252.17	253.63	253.36	252.85	252.54	252.83	252.44
463	252.12	253.56	253.29	252.78	252.51	252.83	252.44
464	260.15	262.16	261.48	260.71	260.41	260.66	260.29
465	260.15	262.16	261.48	260.68	260.41	260.63	260.29
466	260.15	262.16	261.51	260.66	260.39	260.61	260.29
467	260.17	262.19	261.43	260.71	260.41	260.66	260.29
468	260.15	262.19	261.53	260.68	260.41	260.63	260.34
469	260.15	262.24	261.53	260.68	260.44	260.61	260.29
470	260.15	262.16	261.53	260.68	260.41	260.61	260.29
471	252.41	255.11	253.17	252.68	252.54	252.75	252.44
473	252.24	253.95	253.80	253.10	252.58	252.90	252.56
474	252.32	253.97	253.82	253.10	252.63	252.90	252.56
475	252.88	253.14	254.16	253.58	252.97	253.29	253.10
476	252.95	253.22	254.38	253.70	253.05	253.36	253.17
477	252.95	253.24	254.48	253.75	253.10	253.36	253.17
479	252.90	253.24	255.11	254.07	253.10	253.48	253.24
480	252.90	253.36	255.11	254.12	253.14	253.51	253.27
481	252.90	253.36	255.14	254.14	253.17	253.53	253.31
483	252.92	253.44	255.09	254.21	253.17	253.53	253.36
484	252.90	253.36	255.04	254.14	253.14	253.48	253.29
485	252.85	253.39	254.94	254.12	253.10	253.48	253.31
486	252.71	253.17	254.21	253.68	252.88	253.14	252.95
487	252.71	253.19	254.14	253.68	252.85	253.14	252.92
488	252.73	253.17	254.09	253.68	252.83	253.14	252.92
489	259.34	260.78	259.51	259.22	259.10	259.22	259.17
490	259.42	260.71	259.49	259.20	259.08	259.20	259.20
491	259.47	260.66	259.49	259.27	259.12	259.27	259.22
492	259.44	260.66	259.49	259.32	259.12	259.27	259.20
493	259.47	260.66	259.49	259.32	259.17	259.27	259.25
494	259.47	260.63	259.44	259.32	259.17	259.27	259.25
495	252.78	253.53	254.09	253.61	252.90	253.14	253.00
496	252.75	253.41	254.04	253.56	252.83	253.07	252.97
498	252.54	253.17	253.68	253.19	252.56	252.83	252.68

IAN S.

```
ORD.
UN(S)
ETINDF.
EDUCE.
GO.
      6400 END OF RECORD
     PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
    1CH)
     SHAW  DEC    1971 DATA ANALYSIS FOR PACKED BED REACTOR

     DIMENSION RUN(230),FH2(230),FC4(230),TFLOW(230),T(230,8),TATM(230)
     DIMENSION A(230,4),NATEN(230,4),TREAC(230)
     DIMENSION TDIF(230),PFEED(230),CALIB(4),NTEMP(230)
     DIMENSION RFEED(230),TREACC(230),CORECT(8),DIF4(230)
     DIMENSION CINC4(230),CINH2(230)
     DATA CALIB /1.483, 1.839, 1.000, 2.131/
     READ(5,996) NRUNS
     READ(5,999) CORECT

     DO 60 I=1,NRUNS
     READ(5,995) RUN(I),FH2(I),FC4(I),DPREAC,DP,TATM(I),TIME,TFLOW(I)
     WRITE(6,995) RUN(I),FH2(I),FC4(I),DPREAC,DP,TATM(I),TIME,TFLOW(I)
     PFEED(I) = (29.92+DPREAC)/29.92
     TFLOW(I) = TFLOW(I)/TIME
     READ(5,998) RUM,((A(I,J),NATEN(I,J)),J=1,4)
     WRITE(6,998) RUM,((A(I,J),NATEN(I,J)),J=1,4)
     IF(RUM.NE.RUN(I))    STOP
     DO 40 J=1,4
  40 A(I,J) = A(I,J)*NATEN(I,J)/CALIB(J)
     READ(5,990) RUM,NTEMP(I),(T(I,J),J=1,8)
     WRITE(6,990) RUM,NTEMP(I),(T(I,J),J=1,8)
     IF(RUM.NE.RUN(I))    STOP
     WRITE(6,997)
  60 CONTINUE

     DO 100 I=1,NRUNS
     DO 80 J=1,8
     TT = T(I,J) - CORECT(J)
     T(I,J) = 480.00 - (10.110-TT)*(20.00/0.457)
  80 IF(T(I,J).LT.50.0)  T(I,J) = 0.0
     TREAC(I) = 0.0
     DO 85 J=2,8
  85 TREAC(I) = TREAC(I) + T(I,J)
     DIV = NTEMP(I)
     TREAC(I) = TREAC(I)/DIV
     TREACC(I) = (TREAC(I)-32.0)*(5.0/9.0)
     TDIF(I) = 0.0
     DO 87 J=1,8
     IF(T(I,J).EQ.0.0)  GO TO 87
     T(I,J) = T(I,J) - TREAC(I)
     IF(ABS(T(I,J)).GT.ABS(TDIF(I)).AND.J.NE.1)  TDIF(I) = T(I,J)
  87 CONTINUE
 100 CONTINUE

     WRITE(6,992)
     DO 120 I=1,NRUNS
```

```
      ADJUST = (460.0+TREAC(I))/(460.0+TATM(I))
      FLOW = ADJUST*(FH2(I)+FC4(I))
      FEEDH2 = FH2(I)/(FH2(I)+FC4(I))
      FEEDC4 = FC4(I)/(FH2(I)+FC4(I))
      CINC4(I) = FEEDC4*PFEED(I)
      CINH2(I) = FEEDH2*PFEED(I)
      RFEED(I) = CINH2(I)/CINC4(I)
      TFLOW(I) = TFLOW(I)*ADJUST
      DFLOW = TFLOW(I) - FLOW
      C4 = (A(I,1)*0.5+A(I,2)*0.75+A(I,3)*0.25+A(I,4))*(CALIB(4)/8498.)
      C44 = CINC4(I)/(CINC4(I)+CINH2(I))
      DIF4(I) = C4 - C44
      WRITE(6,994) RUN(I),FLOW,TFLOW(I),DFLOW,C4,C44,DIF4(I),
     1 (T(I,J),J=1,8),TDIF(I),TREAC(I)
      DIF4(I) = DIF4(I)/C44
  120 CONTINUE

      WRITE(6,992)
      DO 280 I=1,NRUNS
      REAC = A(I,1)*0.50 + A(I,2)*0.75 + A(I,3)*0.25
      S1 = A(I,3)/REAC
      S2 = A(I,1)/REAC
      S3 = A(I,2)/REAC
      Z1 = REAC + A(I,4)
      CONV = 100.0*REAC/Z1
      WRITE(6,993) RUN(I),S1,S2,S3,CONV,RFEED(I),TREAC(I),TFLOW(I),
     1     TDIF(I),TREACC(I),DIF4(I)
      TOTAL = 0.0
      DO 250 J=1,4
      A(I,J) = A(I,J)*CALIB(J)/NATEN(I,J)
  250 TOTAL = TOTAL + A(I,J)
      WRITE(7,989) RUN(I),((A(I,J),NATEN(I,J)),J=1,4),TOTAL,CINC4(I),
     1  CINH2(I),TFLOW(I)
      DO 260 J=1,8
      IF(T(I,J).EQ.0.0)  GO TO 260
      T(I,J) = ((TREAC(I)+T(I,J))-32.0)*(5.0/9.0)
  260 CONTINUE
      WRITE(7,991) RUN(I),(T(I,J),J=1,8)
  280 CONTINUE

      STOP
  989 FORMAT(F4.0,4(F6.1,I2,1X),F6.1,2F7.4,F6.3)
  990 FORMAT(F5.0,I2,1X,8F9.3)
  991 FORMAT(F4.0,1X,8F7.2)
  992 FORMAT(1H1)
  993 FORMAT(1X,F4.0,2X,F6.2,2F6.3,F7.2,3X,F8.3,F8.2,F6.2,F6.2,F8.2,F10.
     12)
  994 FORMAT(1X,F4.0,2X,2F6.2,F7.3,4X,3F6.3,2X,8F7.2,2F8.2)
  995 FORMAT(F6.0,4X,2F10.4,2F10.2,F10.1,2F10.2)
  996 FORMAT(I5)
  997 FORMAT(/)
  998 FORMAT(F6.0,4X,4(F7.1,I2,1X,),F10.2)
  999 FORMAT(8F10.3)
      END
        6400 END OF RECORD
146
      0.044      0.146      0.061      0.067      0.063      0.044      0.044
```

.7430	.1425	2.85	-0.00	84.0	33.20	30.00	
24.1 8	54.7 8	157.4 8	71.5 8				
10.222	10.327	10.396	10.327	10.349	10.353	10.322	10.335
.7510	.1395	2.87	-0.00	84.0	33.10	30.00	
22.7 8	53.9 8	153.9 8	69.8 8				
10.227	10.331	10.402	10.333	10.350	10.359	10.328	10.340
.7590	.1445	2.93	-0.00	84.0	32.70	30.00	
26.8 8	56.8 8	166.7 8	63.8 8				
10.240	10.342	10.417	10.348	10.356	10.371	10.343	10.352
.6600	.1555	2.84	-0.00	84.0	35.80	30.00	
21.016	35.5 8	176.816	15.0 1				
10.310	10.425	10.512	10.435	10.446	10.465	10.434	10.434
.6600	.1585	2.83	-0.00	84.0	35.60	30.00	
20.916	29.5 8	194.016	5.5 1				
10.313	10.426	10.517	10.439	10.449	10.469	10.438	10.437
.7150	.1465	2.85	-0.00	84.0	34.30	30.00	
29.1 8	60.0 8	191.6 8	47.1 8				
10.224	10.326	10.403	10.332	10.345	10.355	10.326	10.339
.7170	.1465	2.86	-0.00	84.0	34.10	30.00	
29.0 8	61.3 8	186.7 8	52.6 8				
10.222	10.327	10.404	10.333	10.345	10.355	10.328	10.340
.4730	.2475	2.61	-0.00	84.0	40.10	30.00	
27.8 8	43.0 2	111.132	0.0 1				
10.325	10.473	10.550	10.455	10.455	10.466	10.418	10.422
.4750	.2535	2.64	-0.00	84.0	39.70	30.00	
25.1 8	22.8 2	113.632	0.0 1				
10.335	10.496	10.565	10.473	10.467	10.487	10.436	10.440
.7280	.1445	2.90	-0.00	84.0	33.30	30.00	
15.7 8	44.3 8	100.9 8	114.9 8				
10.250	10.362	10.424	10.354	10.365	10.370	10.343	10.350
.7460	.1445	2.90	-0.00	84.0	33.30	30.00	
15.9 8	44.0 8	100.1 8	112.8 8				
10.250	10.360	10.423	10.353	10.370	10.372	10.340	10.350
.7360	.1345	2.90	-0.00	84.0	33.30	30.00	
36.4 8	61.0 8	120.116	33.5 4				
10.043	10.251	10.301	10.226	10.236	10.250	10.235	10.221
.7340	.1325	2.90	-0.00	84.0	33.30	30.00	
25.2 8	63.6 8	79.516	64.0 8				
-0.000	10.102	10.150	10.078	10.107	10.113	10.093	10.082
.7340	.2115	2.90	-0.00	84.0	33.30	30.00	
25.3 8	63.3 8	168.0 8	124.5 4				
-0.000	10.105	10.154	10.082	10.110	10.117	10.095	10.092
.6420	.1305	2.62	-0.00	84.0	37.40	30.00	
26.5 8	62.8 8	169.6 8	102.9 4				
-0.000	10.146	10.211	10.140	10.158	10.167	10.152	10.142
.6420	.2005	2.62	-0.00	84.0	37.60	30.00	
26.6 8	62.6 8	176.5 8	101.3 4				
-0.000	10.148	10.212	10.142	10.155	10.168	10.155	10.146
.5450	.1395	2.60	-0.00	84.0	48.30	35.00	
21.716	61.3 4	100.632	7.0 1				
10.040	10.215	10.300	10.231	10.243	10.269	10.234	10.233
.5420	.1365	2.50	-0.00	84.0	48.60	35.00	
21.716	41.9 8	175.316	15.0 1				
10.037	10.211	10.294	10.224	10.236	10.260	10.224	10.230
.7340	.1355	2.98	-0.00	84.0	43.20	40.00	
21.8 8	58.5 8	131.0 8	151.8 4				
-0.000	10.132	10.204	10.140	10.160	10.171	10.135	10.148

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    .6300      .1445      2.82      -0.00      84.0      35.80      30.00
  16.416     68.7 8    111.016    148.0 2
-0.000    10.165   10.216   10.150   10.175   10.196   10.157   10.159
    .6280      .1445      2.80      -0.00      84.0      35.90      30.00
  16.916     33.516    120.316     72.8 4
-0.000    10.163   10.216   10.150   10.176   10.200   10.162   10.157
    .6260      .1445      2.80      -0.00      84.0      60.40      50.00
  17.716     33.816    118.816     63.3 4
-0.000    10.162   10.212   10.148   10.176   10.200   10.162   10.158
    .6250      .1445      2.80      -0.00      84.0      36.10      30.00
  18.516     33.816    129.416     57.0 4
-0.000    10.162   10.213   10.145   10.180   10.203   10.166   10.160
    .6220      .1435      2.80      -0.00      84.0      42.20      35.00
  19.016     33.516    131.616     49.3 4
-0.000    10.157   10.210   10.144   10.178   10.206   10.168   10.159
    .6160      .1435      2.81      -0.00      84.0      36.40      30.00
  19.516     33.016    144.016     40.5 4
-0.000    10.150   10.207   10.140   10.175   10.200   10.168   10.157
    .6360      .1435      2.80      -0.00      84.0      35.10      30.00
  18.916     34.116    129.116     60.8 4
-0.000    10.145   10.205   10.137   10.164   10.192   10.162   10.153
    .6360      .1435      2.80      -0.00      84.0      46.80      40.00
  19.416     35.216    130.716     62.4 4
-0.000    10.143   10.212   10.148   10.167   10.496   10.464   10.460
    .6390      .1435      2.80      -0.00      84.0      35.20      30.00
  18.916     35.816    133.516     63.5 4
-0.000    10.143   10.222   10.158   10.172   10.200   10.165   10.170
    .6370      .1435      2.82      -0.00      84.0      35.20      30.00
  19.116     36.216    126.216     64.9 4
-0.000    10.142   10.223   10.160   10.172   10.200   10.163   10.167
    .4430      .0935      2.15      -0.00      84.0      43.90      25.00
  29.7 8      6.3 2     95.932      0.0 1
-0.000    10.470   10.576   10.504   10.488   10.520   10.466   10.467
    .4420      .0935      2.13      -0.00      84.0      51.90      30.00
  27.7 8      2.0 2    100.032      0.0 1
-0.000    10.476   10.580   10.510   10.491   10.522   10.467   10.475
    .6350      .1415      2.80      -0.00      84.0      36.00      30.00
  15.816     35.116    107.816     92.4 4
-0.000    10.136   10.217   10.154   10.168   10.190   10.150   10.160
    .6360      .1415      2.80      -0.00      84.0      36.30      30.00
  16.416     35.116    106.216     90.0 4
-0.000    10.144   10.225   10.163   10.177   10.198   10.161   10.168
    .5820      .1515      2.76      -0.00      84.0      37.90      30.00
  18.916     35.2 2    114.632      0.0 1
-0.000    10.277   10.380   10.310   10.318   10.360   10.319   10.312
    .5840      .1515      2.78      -0.00      84.0      37.80      30.00
  19.316     42.5 2    107.132      0.0 1
-0.000    10.279   10.383   10.314   10.322   10.361   10.319   10.310
    .6490      .1415      2.80      -0.00      84.0      36.90      30.00
  13.316     30.816     86.016    112.9 4
-0.000    10.416   10.215   10.156   10.174   10.193   10.154   10.159
    .6500      .1405      2.77      -0.00      84.0      36.60      30.00
  13.116     31.316     82.616    114.0 4
-0.000    10.142   10.207   10.147   10.171   10.190   10.152   10.158
    .5510      .1475      2.68      -0.00      84.0      45.70      35.00
  22.116     36.3 8    107.232      8.5 1
-0.000    10.238   10.328   10.256   10.277   10.280   10.230   -0.000
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    .6510      .1445       2.71       -0.00        84.0      41.40      35.00
  13.216     34.416     85.816     153.1 4
-0.000    10.137    10.213    10.154    10.166    10.188    10.148    10.144
    .6490      .1445       2.79       -0.00        84.0      35.40      30.00
  26.3 8     67.2 8     91.816     145.5 4
-0.000    10.144    10.222    10.160    10.174    10.194    10.158    10.153
    .6590      .1805       4.14       -0.00        84.0      48.00      40.00
  17.616      8.4 2     99.632       0.0 1
10.085    10.436    10.465    10.395    10.391    10.415    10.356    10.377
   1.0160      .2785       5.92       -0.00        84.0      39.70      50.00
  21.716     34.3 8     82.832       3.0 1
10.070    10.410    10.445    10.382    10.388    10.420    10.381    10.396
   1.0150      .2785       5.97       -0.00        84.0      39.80      50.00
  22.216     35.7 8     81.532       9.6 1
10.070    10.405    10.444    10.380    10.388    10.420    10.380    10.393
   1.0120      .2785       5.96       -0.00        84.0      40.10      50.00
  22.316     35.7 8     83.032       9.0 1
10.070    10.400    10.442    10.378    10.385    10.417    10.380    10.390
    .6520      .1835       4.00       -0.00        84.0      60.40      50.00
  19.416     30.8 2     98.732       0.0 1
10.020    10.370    10.437    10.378    10.380    10.413    10.368    10.375
    .6530      .1835       3.98       -0.00        84.0      60.60      50.00
  19.616     31.2 2    103.432       0.0 1
10.025    10.372    10.444    10.382    10.384    10.416    10.370    10.382
   1.0200      .2645       5.80       -0.00        84.0      39.60      50.00
  19.016     60.2 8     68.932     117.6 1
10.010    10.358    10.422    10.367    10.374    10.397    10.368    10.400
   1.0190      .2675       5.80       -0.00        84.0      39.70      50.00
  18.916     60.0 8     68.832      61.4 2
10.000    10.350    10.416    10.360    10.370    10.395    10.360    10.390
    .6830      .1865       3.78       -0.00        84.0      46.50      40.00
  18.816     29.516    135.516      61.4 2
10.185    10.423    10.470    10.400    10.400    10.424    10.402    10.410
    .6840      .1855       3.79       -0.00        84.0      46.30      40.00
  18.416     29.716    124.516      66.2 2
10.188    10.423    10.470    10.400    10.398    10.423    10.400    10.410
    .7620      .1925       3.83       -0.00        84.0      53.50      50.00
  20.016     28.816     69.732      36.1 2
10.065    10.310    10.347    10.293    10.342    10.345    10.288    10.310
    .7620      .1925       3.90       -0.00        84.0      53.30      50.00
  19.116     30.316     67.632      46.6 2
10.063    10.292    10.390    10.290    10.331    10.340    10.282    10.310
    .7740      .1795       3.87       -0.00        84.0      37.20      35.00
  17.716     29.416     61.632      63.2 2
10.075    10.310    10.370    10.315    10.365    10.340    10.294    10.320
    .7810      .1775       3.90       -0.00        84.0      48.90      45.00
  17.516     29.316     57.032      64.5 2
10.085    10.312    10.370    10.318    10.370    10.342    10.298    10.322
    .7820      .1775       4.07       -0.00        84.0      52.70      50.00
  19.516     41.6 4     78.032       0.0 1
10.340    10.597    10.646    10.578    10.612    10.598    10.540    10.563
    .7900      .1735       4.12       -0.00        84.0      52.80      50.00
  20.016     37.7 4     80.432       0.0 1
10.378    10.646    10.695    10.627    10.642    10.628    10.580    10.600
    .7320      .1895       3.81       -0.00        84.0      43.50      40.00
  20.516     28.816     74.832      27.0 2
10.070    10.325    10.368    10.314    10.363    10.344    10.295    10.324
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    .7360       .1895        3.86       -0.00        84.0       55.00       50.00
  20.416      27.616      73.532      30.2 2
10.073    10.327    10.375    10.319    10.363    10.344    10.297    10.325
    .8562       .2013        3.87       -0.00        84.0       38.10       40.00
  28.3 8      64.9 8      90.516      82.3 4
10.200    10.216    10.360    10.254    10.242    10.261    10.227    -0.000
    .8535       .1987        3.93       -0.00        84.0       38.50       40.00
  28.2 8      65.2 8      90.316      81.0 4
10.200    10.213    10.357    10.252    10.241    10.257    10.223    -0.000
    .5050.      .1515        2.53       -0.00        84.0       46.50       30.00
  13.216       0.0 1     109.232       0.0 1
10.231    10.260    10.451    10.333    10.283    10.295    10.243    -0.000
    .5050       .1485        2.63       -0.00        84.0       54.40       35.00
  17.916       6.9 2     105.032       0.0 1
10.196    10.224    10.402    10.288    10.251    10.262    10.210    -0.000
    .5040       .1455        2.61       -0.00        84.0       47.00       30.00
  19.216      13.0 2     102.832       0.0 1
10.196    10.225    10.398    10.283    10.251    10.260    10.208    -0.000
    .8562       .1955        3.86       -0.00        84.0       48.60       50.00
  13.816      32.416      89.416      74.4 4
10.186    10.208    10.347    10.243    10.233    10.254    10.222    -0.000
    .8562       .1892        3.86       -0.00        84.0       48.90       50.00
  13.516      31.616      83.816      76.5 4
10.179    10.202    10.338    10.234    10.228    10.246    10.213    -0.000
    .6870       .2235        3.56       -0.00        84.0       44.60       40.00
  20.816      20.3 4      55.364       0.0 1
10.192    10.212    10.395    10.282    10.258    10.308    10.254    -0.000
    .6870       .2155        3.53       -0.00        84.0       44.80       40.00
  22.916      48.2 2     102.232       0.0 1
10.190    10.206    10.387    10.275    10.254    10.298    10.250    -0.000
    .8506       .1961        3.88       -0.00        84.0       48.60       50.00
  14.616      32.416      94.016      68.7 4
10.186    10.198    10.349    10.244    10.234    10.256    10.230    -0.000
    .8533       .2012        3.92       -0.00        84.0       48.20       50.00
  14.516      32.616      98.716      63.7 4
10.182    10.197    10.346    10.242    10.227    10.252    10.228    -0.000
    .9030       .2865        4.60       -0.00        84.0       43.20       50.00
  20.016      31.6 2      55.464       0.0 1
10.332    10.362    10.577    10.446    10.387    10.465    10.405    -0.000
    .9040       .2835        4.60       -0.00        84.0       43.20       50.00
  20.616      40.0 2      54.564       0.0 1
10.333    10.362    10.577    10.444    10.383    10.454    10.403    -0.000
    .8543       .1961        3.99       -0.00        84.0       48.20       50.00
  15.616      31.816     101.516      51.3 4
10.202    10.223    10.370    10.262    10.230    10.256    10.256    -0.000
    .8543       .1961        3.96       -0.00        84.0       48.50       50.00
  14.716      31.816     101.416      51.2 4
10.200    10.229    10.365    10.256    10.228    10.253    10.253    -0.000
   1.0620       .3345        5.40       -0.00        84.0       36.60       50.00
  21.216      31.6 4     102.632       0.0 1
10.422    10.453    10.675    10.534    10.494    10.555    10.483    -0.000
   1.0620       .3265        5.39       -0.00        84.0       36.70       50.00
  22.416      41.4 4      99.232       0.0 1
10.422    10.451    10.673    10.533    10.497    10.555    10.482    -0.000
    .8581       .1957        3.93       -0.00        84.0       48.80       50.00
  14.816      32.716      91.916      62.9 4
10.204    10.213    10.363    10.259    10.253    10.267    10.240    -0.000
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    .8581      .1911       3.93      -0.00       84.0      49.00      50.00
  13.816     31.516     88.716     66.7 4
10.198   10.212   10.353   10.250   10.248   10.261   10.232   -0.000
    .8497      .1923       3.94      -0.00       84.0      38.90      40.00
  14.116     31.716     92.116     70.5 4
10.184   10.203   10.340   10.237   10.246   10.260   10.232   -0.000
    .8960      .2545       3.89      -0.00       84.0      44.50      50.00
   0.0 1      0.0 1     59.064      0.0 1
10.905   11.055   11.020   10.925   10.917   10.921   10.898   -0.000
    .8940      .2535       3.89      -0.00       84.0      44.50      50.00
   0.0 1      0.0 1     59.964      0.0 1
10.818   10.980   10.938   10.841   10.833   10.839   10.813   -0.000
    .8930      .2525       4.89      -0.00       84.0      44.50      50.00
    .7 4      0.0 1     58.564      0.0 1
10.757   10.917   10.880   10.788   10.770   10.775   10.751   -0.000
    .8970      .2525       4.87      -0.00       84.0      44.50      50.00
   1.2 4      0.0 1     60.164      0.0 1
10.703   10.862   10.828   10.724   10.717   10.721   10.697   -0.000
    .8980      .2525       4.87      -0.00       84.0      44.50      50.00
   3.1 4      0.0 1     59.364      0.0 1
10.620   10.772   10.747   10.641   10.631   10.636   10.612   -0.000
    .8980      .2525       4.87      -0.00       84.0      44.50      50.00
   5.8 2      0.0 1     58.164      0.0 1
10.621   10.771   10.748   10.642   10.630   10.636   10.612   -0.000
    .8507      .1955       4.32      -0.00       84.0      49.20      50.00
  11.016     1.216     92.532      0.0 1
10.223   10.278   10.408   10.258   10.240   10.248   10.218   -0.000
    .8497      .1961       4.32      -0.00       84.0      48.90      50.00
  10.916     3.5 4     92.332      0.0 1
10.221   10.275   10.408   10.254   10.238   10.246   10.215   -0.000
    .8423      .1948       3.79      -0.00       84.0      48.70      50.00
   9.116     24.516     59.416     89.8 8
10.212   10.221   10.351   10.252   10.248   10.259   10.249   -0.000
    .8403      .1892       3.76      -0.00       84.0      39.20      40.00
  17.2 8     48.0 8     55.616     90.1 8
10.206   10.213   10.345   10.245   10.245   10.255   10.240   -0.000
    .8394      .1911       3.76      -0.00       84.0      48.70      50.00
  17.5 8     49.4 8     56.916     87.1 8
10.199   10.210   10.337   10.238   10.238   10.252   10.233   -0.000
    .8394      .1898       3.77      -0.00       84.0      39.20      40.00
  17.4 8     49.1 8     55.816     86.6 8
10.200   10.212   10.338   10.239   10.240   10.250   10.232   -0.000
    .8590      .1937       3.88      -0.00       84.0      38.30      40.00
  16.216     31.116     52.832     32.0 4
10.192   10.238   10.360   10.247   10.237   10.258   10.221   -0.000
    .8600      .1931       3.89      -0.00       84.0      47.90      50.00
  16.216     31.216     51.832     34.6 4
10.188   10.234   10.356   10.245   10.232   10.252   10.217   -0.000
    .8600      .1911       3.90      -0.00       84.0      48.10      50.00
  15.616     30.916     51.632     17.0 4
10.193   10.240   10.364   10.252   10.240   10.260   10.226   -0.000
    .8524      .1905       3.87      -0.00       84.0      48.10      50.00
  16.216     31.816     51.132     65.7 2
10.193   10.236   10.363   10.251   10.238   10.260   10.222   -0.000
    .8459      .1873       3.84      -0.00       84.0      39.20      40.00
  15.916     30.716     51.032     62.4 2
10.193   10.238   10.363   10.252   10.239   10.258   10.223   -0.000
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    .9530      .2975       4.61      -0.00       84.0      40.80      50.00
  21.616     29.516     79.432     14.9 4
10.168   10.235   10.374   10.250   10.234   10.273   10.236   -0.000
    .9470      .2875       4.55      -0.00       84.0      32.70      40.00
  20.716     31.516     74.232     21.4 4
10.163   10.230   10.367   10.245   10.233   10.268   10.230   -0.000
    .9470      .2825       4.53      -0.00       84.0      32.90      40.00
  20.416     33.716     71.132     27.0 4
10.160   10.226   10.358   10.237   10.226   10.262   10.226   -0.000
    .8478      .1911       3.87      -0.00       84.0      48.50      50.00
  16.516     30.716     51.932     60.5 2
10.198   10.241   10.369   10.257   10.245   10.267   10.229   -0.000
    .8497      .1917       3.85      -0.00       84.0      38.70      40.00
  16.816     31.316     51.132     61.2 2
10.200   10.243   10.369   10.257   10.244   10.265   10.231   -0.000
    .6310      .1987       3.17      -0.00       84.0      48.30      40.00
  22.616     55.7 8     84.932     11.7 2
10.068   10.118   10.252   10.137   10.124   10.163   10.093   -0.000
    .6320      .1975       3.15      -0.00       84.0      48.20      40.00
  23.316     28.716     83.932     14.4 2
10.067   10.118   10.250   10.136   10.125   10.162   10.097   -0.000
    .8608      .1943       3.84      -0.00       84.0      47.70      50.00
  13.316     31.516     41.732     80.5 4
10.185   10.228   10.348   10.237   10.232   10.253   10.200   -0.000
    .8618      .1937       3.89      -0.00       84.0      44.80      47.00
  13.316     31.716     85.416     75.8 4
10.192   10.231   10.353   10.245   10.238   10.259   10.208   -0.000
   1.0290      .3345       5.10      -0.00       84.0      37.00      50.00
  22.716     16.316     98.232      3.0 1
10.286   10.383   10.538   10.398   10.368   10.427   10.326   -0.000
   1.0290      .3345       5.11      -0.00       84.0      37.40      50.00
  23.216     38.2 8     92.532      6.7 1
10.289   10.386   10.540   10.399   10.367   10.429   10.332   -0.000
   1.0300      .3315       5.11      -0.00       84.0      37.30      50.00
  23.516     39.3 8     90.732      9.8 1
10.290   10.386   10.541   10.400   10.370   10.428   10.320   -0.000
    .8487      .1887       3.81      -0.00       84.0      48.80      50.00
  13.516     32.216     87.716     66.3 4
10.196   10.243   10.360   10.251   10.242   10.262   10.214   -0.000
    .8497      .1854       3.81      -0.00       84.0      48.80      50.00
  13.416     31.516     83.016     69.3 4
10.196   10.241   10.360   10.252   10.244   10.262   10.214   -0.000
    .7440      .2155       3.67      -0.00       84.0      50.90      50.00
  21.716     30.216     72.032      6.7 8
10.150   10.213   10.343   10.228   10.213   10.250   10.184   -0.000
    .7430      .2235       3.69      -0.00       84.0      51.70      50.00
  21.616     29.416     77.232     11.3 4
10.146   10.208   10.337   10.222   10.207   10.242   10.175   -0.000
    .8000      .1892       3.85      -0.00       84.0      48.00      50.00
  13.116     32.216     81.916     80.2 4
10.188   10.237   10.353   10.250   10.242   10.260   10.215   -0.000
    .8627      .1861       3.86      -0.00       84.0      48.00      50.00
  24.9 8     29.316     78.716     76.2 4
10.192   10.300   10.356   10.248   10.243   10.260   10.215   -0.000
    .8627      .1853       3.86      -0.00       84.0      48.10      50.00
  25.1 8     31.316     80.616     79.4 4
10.197   10.243   10.356   10.251   10.244   10.262   10.216   -0.000
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    .4930      .1625      2.65      -0.00      84.0      61.30      40.00
  18.516     21.4 2     58.864      0.0 1
10.214   10.322   10.498   10.329   10.250   10.252   10.223   -0.000
    .4940      .1615      2.66      -0.00      84.0      61.40      40.00
  18.216     24.2 2     58.064      0.0 1
10.215   10.320   10.493   10.328   10.250   10.253   10.223   -0.000
    .8600      .1898      3.85      -0.00      84.0      48.00      50.00
   8.116     24.616     26.732     45.116
10.228   10.276   10.392   10.285   10.262   10.264   10.233   -0.000
    .8618      .1949      3.85      -0.00      84.0      38.10      40.00
   9.016     25.816     56.216     88.6 8
10.230   10.278   10.394   10.288   10.262   10.263   10.237   -0.000
    .8627      .1924      3.87      -0.00      84.0      47.60      50.00
  17.5 8     25.916     54.816     86.6 8
10.232   10.280   10.395   10.290   10.264   10.265   10.238   -0.000
    .8506      .1898      3.71      -0.00      84.0      48.20      50.00
   4.7 8     35.7 4     31.1 8     40.832
10.218   10.230   10.343   10.253   10.250   10.251   10.225   -0.000
    .8506      .1924      3.78      -0.00      84.0      48.70      50.00
   9.8 4     36.2 4     64.0 4     78.816
10.220   10.245   10.346   10.255   10.250   10.253   10.227   -0.000
    .8487      .1924      3.76      -0.00      84.0      48.50      50.00
  10.1 4     39.3 4     66.7 4     79.316
10.222   10.235   10.350   10.257   10.254   10.257   10.232   -0.000
    .8478      .1937      3.78      -0.00      84.0      38.70      40.00
  11.8 4     45.5 4     79.4 4     76.916
10.225   10.247   10.341   10.253   10.240   10.253   10.230   -0.000
    .8477      .1905      3.77      -0.00      84.0      48.40      50.00
  11.5 4     45.3 4     81.7 4     75.616
10.224   10.248   10.340   10.249   10.233   10.251   10.232   -0.000
    .8780      .1911      3.98      -0.00      84.0      47.20      50.00
  15.316     30.716     94.816     36.2 4
10.182   10.255   10.370   10.252   10.231   10.249   10.228   -0.000
    .8710      .1937      3.99      -0.00      84.0      47.70      50.00
  16.416     31.016     51.532     29.9 4
10.192   10.263   10.384   10.265   10.239   10.259   10.237   -0.000
    .8600      .1962      3.97      -0.00      84.0      48.00      50.00
  16.616     30.516     53.332     25.8 4
10.188   10.262   10.380   10.263   10.236   10.255   10.237   -0.000
    .8609      .1887      3.95      -0.00      84.0      48.00      50.00
  15.816     30.016     50.532     60.7 2
10.190   10.265   10.379   10.263   10.237   10.254   10.239   -0.000
    .8609      .1861      3.95      -0.00      84.0      48.20      50.00
  15.416     29.616     49.732     59.8 2
10.190   10.272   10.378   10.263   10.243   10.254   10.244   -0.000
    .8609      .1887      3.94      -0.00      84.0      47.80      50.00
  10.316     26.716     34.532     92.1 4
10.228   10.279   10.407   10.294   10.253   10.260   10.243   -0.000
    .8618      .1924      3.95      -0.00      84.0      47.70      50.00
  22.4 8     57.9 8     73.816    100.0 4
10.222   10.274   10.400   10.290   10.248   10.255   10.235   -0.000
    .8650      .1937      3.95      -0.00      84.0      47.50      50.00
  23.6 8     59.2 8     75.216    100.3 4
10.221   10.274   10.402   10.289   10.245   10.252   10.234   -0.000
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  10.3 8     17.416     34.316     32.316
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10.228    10.283    10.408    10.295    10.250    10.257    10.237    -0.000
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10.217    10.272    10.392    10.280    10.247    10.254    10.228    -0.000
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  23.2 8     29.716     75.816     93.7 4
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END OF RECORD

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15.616 33.616 51.132 79.0 2
10.135 10.210 10.304 10.216 10.197 10.210 10.180 -0.000
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15.516 33.716 50.532 83.7 2
10.134 10.206 10.303 10.212 10.195 10.208 10.178 -0.000
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15.416 33.416 49.132 88.2 2
10.135 10.205 10.305 10.214 10.198 10.211 10.180 -0.000
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15.316 33.716 49.432 88.1 2
10.139 10.209 10.306 10.215 10.199 10.213 10.184 -0.000
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15.516 32.416 49.932 87.9 2
10.140 10.213 10.310 10.220 10.203 10.216 10.185 -0.000
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23.2 8 51.0 8 70.016 74.6 2
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  23.1 8     53.0 8     34.132     66.0 2
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  22.8 8     53.6 8     34.032     66.0 2
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   1.0200      .1591      3.43      -0.00      75.0      43.00      50.00
  22.4 8     51.7 8     32.832     61.9 2
10.153  10.213  10.307  10.209  10.207  10.214  10.180  -0.000
   1.1340      .1787      3.80      -0.00      75.0      39.00      50.00
  24.9 8     46.5 8     77.416     31.4 2
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   1.1340      .1775      3.80      -0.00      75.0      38.80      50.00
  25.0 8     46.9 8     73.716     30.8 2
10.270  10.346  10.437  10.331  10.326  10.335  10.300  -0.000
   1.3730      .1325      4.43      -0.00      75.0      33.80      50.00
  10.516     22.4 8     15.764      4.3 1
10.600  10.700  10.774  10.657  10.651  10.657  10.623  -0.000
   1.3730      .1325      4.41      -0.00      75.0      33.70      50.00
  20.4 8     44.6 4     29.332      4.8 1
10.600  10.700  10.774  10.656  10.651  10.656  10.623  -0.000
   1.3730      .1321      4.41      -0.00      75.0      33.80      50.00
  20.7 8     44.504     29.432      6.0 1
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   1.3730      .1321      4.41      -0.00      75.0      33.80      50.00
  20.4 8     44.7 4     29.932      4.4 1
10.601  10.701  10.772  10.657  10.651  10.657  10.623  -0.000
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   1.3730      .1316      4.41      -0.00      75.0      33.90      50.00
  18.5 8     39.3 4     27.832      3.6 1
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   1.3730      .1316      4.43      -0.00      75.0      33.80      50.00
  20.4 8     43.3 4     29.932      1.5 1
10.600  10.700  10.776  10.656  10.651  10.655  10.623  -0.000
   1.1080      .1757      3.95      -0.00      75.0      39.30      50.00
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   1.1100      .1728      3.80      -0.00      75.0      3          50.00
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  15.4 8     32.4 8     50.516     36.0 2
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   1.1150      .1687       3.72       -0.00       75.0      39.30      50.00
  12.3 8     24.8 8     40.116     24.7 2
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   1.3030      .2378       4.46       -0.00       75.0      32.90      50.00
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  22.7 4     10.4 1     64.032      0.0 1
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   1.2750      .1905       4.56       -0.00       75.0      34.60      50.00
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10.572    10.638    10.692    10.598    10.598    10.600    10.579    -0.000
   1.2750      .1900       4.56       -0.00       75.0      34.60      50.00
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10.571    10.638    10.692    10.600    10.598    10.600    10.578    -0.000
   1.2740      .1900       4.56       -0.00       75.0      34.60      50.00
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10.572    10.638    10.692    10.600    10.600    10.600    10.580    -0.000
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   1.1120      .1700       3.62       -0.00       75.0      39.50      50.00
  24.2 8     37.8 8     35.832     24.5 1
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RUN(S)
SETINDF.
REDUCE.
LGO.
        6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     MAIN PROGRAM FOR PARAMETER ESTIMATION IN PACKED BED REACTOR
C     SHAW DEC 1971
C
      COMMON /BLK2/ MCYC,MAXK,MKAT,NSTEP,ALPHA,BETA,EPS(7),V(7,7),AFK(7)
      COMMON /BLK3/ NRUNS,RUN(25),AKIN(13),AREA(25,4),ATTEN(25,4),HIGH,
     1  CAREA(25,4),FIN(25,2),XACT(25),ARCC(25),T(25,8),H2SAVE(25)
      COMMON /BLK5/ SUMN,AKE(7),KM,SMIN
      COMMON/BLK11/ CN(5),A(13),RESULT(5),RCC,TPRFIL(8),FCALC(5),HTSTOP
C
      READ(5,500) KM,MCYC,MAXK,MKAT,NSTEP
      READ(5,501)(EPS(I),I=1,KM)
      READ(5,501)(AKE(I),I=1,KM)
      READ(5,501) ALPHA,BETA
      SMIN=1.0E10
      V(1,1) = 1.0
      V(1,2) = 0.0
      V(1,3) = 0.0
      V(2,1) = 0.0
      V(2,2) = 1.0
      V(2,3) = 0.0
      V(3,1) = 0.0
      V(3,2) = 0.0
      V(3,3) = 1.0
C     READ IN REACTOR DATA
      READ(5,502)NRUNS,NOCOMP,RAREA,HIGH
      GC=82.06
      DO20I=1,NRUNS
      READ(5,991) RUN(I),((AREA(I,J),ATTEN(I,J)),J=1,4),TAREA,
     1       FIN(I,1),FIN(I,2),F
      WRITE(6,991)RUN(I),((AREA(I,J),ATTEN(I,J)),J=1,4),TAREA,
     1       FIN(I,1),FIN(I,2),F
      READ(5,992) RUM,(T(I,J),J=1,8)
      WRITE(6,992)RUM,(T(I,J),J=1,8)
      IF(RUM.NE.RUN(I))  STOP
      WRITE(6,994)
      DO 15 J=1,8
      IF(T(I,J).EQ.0.0)  GO TO 15
      T(I,J) = T(I,J) + 273.13
   15 CONTINUE
      ARCC(I) = GC*RAREA/F
   20 CONTINUE
      DO 30 I=1,NRUNS
      READ(5,993) RUM,XACT(I)
      IF(RUM.NE.RUN(I))  STOP
      WRITE(6,993) RUM,XACT(I)
   30 ARCC(I) = ARCC(I)*XACT(I)
      AKIN(1) = 51.0
      AKIN(3) = 30.0
      AKIN(2) = AKIN(3) + 10.0
      AKIN(4) = 16.0
      AKIN(5) = 15.6604
      AKIN(6) = 0.0
```

```
      AKIN(7) = 0.0
      AKIN(8) = 0.0
      AKIN(9) = 2.348
      AKIN(10) = 2.151
      AKIN(11) = AKIN(4) + 10.0
      AKIN(12) = 4.5208
      AKIN(13) = 2.2115
      WRITE(6,201)(AKIN(I),I=1,13)
      A(1) = AKIN(1)*1.0E+3
      A(2)=AKIN(2)*1.0E+3
      A(3)=AKIN(3)*1.0E+3
      A(4) = AKIN(4)*1.0E+3
      A(5) = 10.0**AKIN(5)
      A(6)=10.**AKIN(6)
      A(7)=10.**AKIN(7)
      A(8) = 10.0**AKIN(8)
      A(9) = AKIN(9)
      A(10) = AKIN(10)
      A(11) = AKIN(11)*1.0E+3
      A(12) = 10.0**AKIN(12)
      A(13) = AKIN(13)
      CALL SEARCH
      DO 50 I=1,KM
   50 AKE(I) = AFK(I)
      CALL OBJECT
      DO 80 K=1,4
      DO 60 I=1,NRUNS
      Y = (AREA(I,K) - CAREA(I,K))*SQRT(ATTEN(I,K))
      X = T(I,4)
      II = 20 + I
   60 CALL PLOTPT(X,Y,II)
   80 CALL OUTPLT
      DO 100 K=1,4
      DO 90 I=1,NRUNS
      Y = (AREA(I,K) - CAREA(I,K))*SQRT(ATTEN(I,K))
      X = H2SAVE(I)
      II = 20 + I
   90 CALL PLOTPT(X,Y,II)
  100 CALL OUTPLT
      STOP
  201 FORMAT(//1X,8H AKIN =    ,8F15.3,/9X,7F15.3//)
  500 FORMAT(5I5)
  501 FORMAT(10F8.1)
  502 FORMAT(2I5,2F10.3)
  991 FORMAT(F4.0,4(F6.1,F2.0,1X,),F6.1,2F7.4,F6.3)
  992 FORMAT(F4.0,1X,8F7.2)
  993 FORMAT(F4.0,6X,F10.4)
  994 FORMAT(/)
      END
      SUBROUTINE OBJECT
      OBJECTIVE FUNCTION FOR PAR EST FOR PACKED BED REACTOR
      SHAW DEC 1971
      COMMON /BLK3/ NRUNS,RUN(25),AKIN(13),AREA(25,4),ATTEN(25,4),HIGH,
     1  CAREA(25,4),FIN(25,2),XACT(25),ARCC(25),T(25,8),H2SAVE(25)
      COMMON /BLK5/ SUMN,AKE(7),KM,SMIN
      COMMON/BLK11/ CN(5),A(13),RESULT(3),RCC,TPRFIL(8),FCALC(5),HTSTOP
      DIMENSION CVARIN(4,4),CALIB(4),SDIFF(4),DIFF(4)
```

```
      DIMENSION ERROR(4,25), ERRORT(25), VV(4,4)
      DATA CALIB / 1.483, 1.839, 1.040, 2.131 /
      DATA CVARIN / 2.4903, 2.0526, 0.5084, 3.9360, 2.0526, 3.0896,
     1      0.6753, 4.9400, 0.5084, 0.6753, 0.2087, 1.2457, 3.9360,
     2      4.9400, 1.2457, 8.8421 /

      A(6) = 10.0**AKE(1)
      A(7) = 10.0**AKE(2)
      A(8) = 10.0**AKE(3)
      DO 10 J=1,4
      DO 10 JJ=1,4
   10 VV(J,JJ) = 0.0
      HTSTOP = HIGH
      SUMSQ=0.0
      CALL SECOND(TIME)
      TIME1 = TIME
      DO 50 I=1,NRUNS
      CN(1) = 0.0
      CN(2) = 0.0
      CN(3) = 0.0
      CN(4) = FIN(I,1)
      CN(5) = FIN(I,2)
      RCC = ARCC(I)
      DO 25 J=1,8
   25 TPRFIL(J) = T(I,J)
      CALL REAC10
      H2SAVE(I) = FCALC(5)*100.0
      CAREA(I,1) = (FCALC(2)*8498.0*CALIB(1))/(CALIB(4)*ATTEN(I,1))
      CAREA(I,2) = (FCALC(3)*8498.0*CALIB(2))/(CALIB(4)*ATTEN(I,2))
      CAREA(I,3) = (FCALC(1)*8498.0*CALIB(3))/(CALIB(4)*ATTEN(I,3))
      CAREA(I,4) = (FCALC(4)*8498.0*CALIB(4))/(CALIB(4)*ATTEN(I,4))
      DO 38 J=1,4
   38 ERROR(J,I) = 0.0
      ERRORT(I) = 0.0
      DO 40 J=1,4
      AT = SQRT(ATTEN(I,J))
      DO 40 K=1,4
      ATT = SQRT(ATTEN(I,K))
      ERR =              (CAREA(I,J)*AT-AREA(I,J)*AT)*(CAREA(I,K)*ATT-
     1  AREA(I,K)*ATT)
      IF(J.EQ.K)  ERROR(J,I) = ERR
   40 VV(J,K) = VV(J,K) + ERR
   50 CONTINUE
      CALL DETER(VV,D,4)
      SUMSQ = D
      CALL SECON4(TIME)
      TIME2 = TIME
      TTIME = TIME2 - TIME1
      WRITE(6,998) SUMSQ,(AKE(K),K=1,KM)
      WRITE(6,997) TTIME
      IF(SUMSQ.GT.SMIN)  GO TO 90
      DO 55 J=1,4
   55 SDIFF(J) = 0.0
      DO 80 I=1,NRUNS
      DO 70 J=1,4
      DIFF(J) = (AREA(I,J) - CAREA(I,J))*SQRT(ATTEN(I,J))
   70 SDIFF(J) = SDIFF(J) + DIFF(J)
```

```
      WRITE(6,999) RUN(I),((AREA(I,J),CAREA(I,J)),J=1,4),(DIFF(J),J=1,4)
     1,(ATTEN(I,J),J=1,4),H2SAVE(I),ERRORT(I),(ERROR(J,I),J=1,4)
   80 CONTINUE
      DO 85 J=1,4
   85 SDIFF(J) = SDIFF(J)/NRUNS
      WRITE(6,995) (SDIFF(J),J=1,4)
      SMIN=SUMSQ
   90 SUMN=SUMSQ
      RETURN
  995 FORMAT(50X,4F5.1)
  997 FORMAT(F7.2)
  998 FORMAT(///34H OBJECTIVE FUNCTION AND PARAMETERS,L15.5,5X,4F12.6/)
  999 FORMAT(1X,F3.0,1X,4(2F5.1,1X),1X,4F5.1,1X,4F2.0,1X,F5.1,1X,5F7.0)
      END
      SUBROUTINE REAC10
C     PACKED BED REACTOR FOR PARAMETER ESTIMATION
C     TEMPERATURE DOWN THE REACTOR
C     VARIABLE PRESSURE INTEGRAL REACTOR
C     MODIFIED  SHAW  NOV 3 1971
C
      COMMON/BLK11/ CN(5),A(13),RESULT(3),RCC,TPRFIL(8),FCALC(5),HTSTOP
      DIMENSION C(5),C1(5),DC(5),C2(5),C3(5),C4(5)
      DIMENSION CN1(5),CDX(5),EPSL(5),CIN(5)
      DIMENSION TRMAX(5),TRMIN(5),HEIGHT(8)
      DATA TRMAX / 5*1.0E-6 /
      DATA TRMIN / 5*1.0E-8 /
      DATA HEIGHT / 0.0, 1.0, 3.6, 6.2, 11.4, 16.5, 19.0, 25. /
C
      PFEED = CN(4) + CN(5)
      DPDY = (PFEED-1.0)/HTSTOP
      FIX = 0.9
      Z5 = A(5)*RCC
      Z1 = -A(1)/1.99
      Z6 = RCC*A(6)
      Z2 = -A(2)/1.99
      Z12 = RCC*A(12)
      Z11 = -A(11)/1.99
      Z3 = -A(3)/1.99
      Z4 = -A(4)/1.99
      NK=0
      DY = 0.5
      NOCOMP = 5
      NEQ=NOCOMP
      IHALF=0
      JHALF=0
C
C
      DO 1000 IAN1=1,7
      Y=0.0
      HT = HEIGHT(IAN1+1) - HEIGHT(IAN1)
      DTDHT =(TPRFIL(IAN1+1)-TPRFIL(IAN1))/HT
      DO 1 I=1,NEQ
    1 CIN(I) = CN(I)
    3 DYSAVE = DY
      CHECK = Y + DY
      IF(CHECK.GT.HT)  DY = HT - Y
      CHECK = Y + DY
```

```
      HFLEFT = (HT-Y)*0.5
      IF(DY.GT.HFLEFT.AND.CHECK.NE.HT)  DY = HFLEFT
C     WRITE(6,995) DY,DYSAVE
      SUM = 0.0
      DO 4 I=1,NEQ
    4 SUM = SUM + CN(I)
      DO 5 I=1,NEQ
    5 CN(I) = (CN(I)/SUM)*(PFEED-DPDY*(HEIGHT(IAN1)+Y+DY*0.5))
   10 DO20 I=1,NEQ
   20 C(I)=CN(I)
      N=1
      TT = TPRFIL(IAN1) + DTDHT*Y
      GOTO400
   30 DO 40 I=1,NEQ
      C1(I)=DC(I)
   40 C(I)=CN(I)+C1(I)/2.0
      N=2
      TT = TT + DTDHT*DY*0.5
      GOTO400
   50 DO60 I=1,NEQ
      C2(I)=DC(I)
   60 C(I)=CN(I)+C2(I)/2.0
      N=3
      GOTO400
   70 DO80 I=1,NEQ
      C3(I)=DC(I)
   80 C(I)=CN(I)+C3(I)
      N=4
      TT = TT + DTDHT*DY*0.5
      GOTO400
C
C     AT THIS POINT 4 RUNG KUTTA STEPS HAVE BEEN FINISHED
   90 DO100 I=1,NEQ
      C4(I)=DC(I)
  100 CN1(I)=CN(I)+(C1(I)+2.0*C2(I)+2.0*C3(I)+C4(I))/6.0
      YTOTAL = HEIGHT(IAN1) + Y
      IF(NK-1) 110,130,150
  110 DY=DY/2.0
      NK=1
      DO120 I=1,NEQ
  120 CDX(I)=CN1(I)
      GOTO10
  130 DO140 I=1,NEQ
  140 CN(I)=CN1(I)
      Y=Y+DY
      NK=2
      GOTO10
  150 DO160 I=1,NEQ
  160 CN(I)=(16.0*CN1(I)-CDX(I))/15.0
C     WRITE(6,997) YTOTAL,Y,DY,CN1
      Y = Y - DY
      DY=DY*2.0
      NK=0
      Y=Y+DY
      DO180 I=1,NEQ
  180 EPSL(I)=(ABS(CDX(I)-CN1(I)))/15.0
      NCOUNT = 0
```

```
      DO 171 I=1,NEQ
      IF(EPSL(I).LT.TRMIN)  NCOUNT=NCOUNT+1
      IF(EPSL(I).LT.TRMAX)  GO TO 171
      GOTO209
  171 CONTINUE
      IF(ABS(Y-HT).LT.0.000001)  GO TO 490
  170 IHALF=0
      IF(NCOUNT.EQ.NEQ)  DY = DY*2.0
      GOTO230
C     STEP SIZE MUST BE HALVED
  209 DO 210 I=1,NEQ
  210 CN(I)=CIN(I)
      Y=Y-DY
      DY = DY/2.0
      IHALF=IHALF+1
      IF(IHALF.LT.10)  GO TO 3
      WRITE(6,321)
      GOTO500
  230 DO240 I=1,NEQ
  240 CIN(I)=CN(I)
C
C     THE CN AND CIN VALUES ARE THE FINAL ONES AT THE END OF A STAGE
      DO 245 I=1,3
      II = 5 - I
      IF(CN(II).GT.0.0001)  GO TO 3
  245 CN(II) = 0.0
      GO TO 1020
C
  400 DO 430 I=1,NEQ
  430 IF(C(I).LT.0.0)  GO TO 435
      GO TO 460
C     MUST HALF STEP SIZE BECAUSE OF NEGATIVE COMPONENTS
  435 DY=DY/2.0
      JHALF=JHALF+1
      IF(JHALF.LT.10)  GO TO 3
      WRITE(6,331)
      GOTO500
C
C     DIFFERENTIAL EQUATIONS
  460 JHALF=0
      CRB = TT*Z5*EXP(Z1/TT)
      CRP1 = TT*Z6*EXP(Z2/TT)
      CRE2 = TT*Z12*EXP(Z11/TT)
      CRP2 = 1.0/(1.0+A(7)*EXP(Z3/TT))
      CRE = 1.0/(1.0+A(8)*EXP(Z4/TT))
      DC(4) = -DY*CRB*C(4)/(C(5)**A(9))
      DC(3) = (-FIX*DC(4)-DY*CRP1*C(3)/(C(5)**A(10)))*CRP2
      DC(2) = (-(2.0-FIX)*DC(4)-DC(3)-DY*CRE2*C(2)/(C(5)**A(13)))*CRE
      DC(1) = -4.0*DC(4)-3.0*DC(3)-2.0*DC(2)
      DC(5) = 3.0*DC(4)+2.0*DC(3)+DC(2)
      GOTO(30,50,70,90),N

  490 HTCHEK = HEIGHT(IAN1) + Y
      IF(HTCHEK.EQ.HTSTOP)  GO TO 1020
      DY = DYSAVE
 1000 CONTINUE
 1020 CONTINUE
```

```
C
C     FINAL CALCULATIONS ---  PROBLEM IS SOLVED
C     FINAL VALUES ARE CN(I)
      ADD = 0.0
      DO 281 I=1,NOCOMP
  281 ADD = ADD + CN(I)
      DO290I=1,NOCOMP
  290 FCALC(I) = CN(I)/ADD
      REAC = 0.25*FCALC(1) + 0.5*FCALC(2) + 0.75*FCALC(3)
      RESULT(1) = REAC/(REAC+FCALC(4))
      RESULT(2) = FCALC(2)/REAC
      RESULT(3) = FCALC(3)/REAC
  500 CONTINUE
      RETURN
C
  321 FORMAT(  1X, 19HIHALF = 10   RETURN)
  331 FORMAT(  1X, 19HJHALF = 10   RETURN)
  995 FORMAT(1X,2F15.7,I10)
  997 FORMAT(1X,3F10.4,3X,5F10.6/)
      END
      SUBROUTINE DETER(A,D,N)
      DIMENSION A(144),L(12),M(12)
C     DETERMINANT PART OF MCMASTER PROGRAM MINV
C
C        DESCRIPTION OF PARAMETERS
C           A - INPUT MATRIX, DESTROYED IN COMPUTATION AND REPLACED BY
C               RESULTANT INVERSE.
C           N - ORDER OF MATRIX A
C           D - RESULTANT DETERMINANT
C           L - WORK VECTOR OF LENGTH N
C           M - WORK VECTOR OF LENGTH N
C
C        METHOD
C           THE STANDARD GAUSS-JORDAN METHOD IS USED. THE DETERMINANT
C           IS ALSO CALCULATED. A DETERMINANT OF ZERO INDICATES THAT
C           THE MATRIX IS SINGULAR.
C
C
C        SEARCH FOR LARGEST ELEMENT
C
      D=1.0
      NK=-N
      DO 80 K=1,N
      NK=NK+N
      L(K)=K
      M(K)=K
      KK=NK+K
      BIGA=A(KK)
      DO 20 J=K,N
      IZ=N*(J-1)
      DO 20 I=K,N
      IJ=IZ+I
   10 IF( ABS(BIGA)- ABS(A(IJ)) 15,20,20
   15 BIGA=A(IJ)
      L(K)=I
      M(K)=J
   20 CONTINUE
```

```
C
C        INTERCHANGE ROWS
C
      J=L(K)
      IF(J-K) 35,35,25
   25 KI=K-N
      DO 30 I=1,N
      KI=KI+N
      HOLD=-A(KI)
      JI=KI-K+J
      A(KI)=A(JI)
   30 A(JI) =HOLD
C
C        INTERCHANGE COLUMNS
C
   35 I=M(K)
      IF(I-K) 45,45,38
   38 JP=N*(I-1)
      DO 40 J=1,N
      JK=NK+J
      JI=JP+J
      HOLD=-A(JK)
      A(JK)=A(JI)
   40 A(JI) =HOL4
C
C        DIVIDE COLUMN BY MINUS PIVOT (VALUE OF PIVOT ELEMENT IS
C        CONTAINED IN BIGA)
C
   45 IF(BIGA) 48,46,48
   46 D=0.0
      RETURN
   48 DO 55 I=1,N
      IF(I-K) 50,55,50
   50 IK=NK+I
      A(IK)=A(IK)/(-BIGA)
   55 CONTINUE
C
C        REDUCE MATRIX
C
      DO 65 I=1,N
      IK=NK+I
      IJ=I-N
      DO 65 J=1,N
      IJ=IJ+N
      IF(I-K) 60,65,60
   60 IF(J-K) 62,65,62
   62 KJ=IJ-I+K
      A(IJ)=A(IK)*A(KJ)+A(IJ)
   65 CONTINUE
C
C        DIVIDE ROW BY PIVOT
      KJ=K-N
      DO 75 J=1,N
      KJ=KJ+N
      IF(J-K) 70,75,70
   70 A(KJ)=A(KJ)/BIGA
   75 CONTINUE
```

```
C        PRODUCT OF PIVOTS
C
      D=D*BIGA
C
C        REPLACE PIVOT BY RECIPROCAL
C
      A(KK)=1.0/BIGA
   80 CONTINUE
      RETURN
      END
      SUBROUTINE SEARCH
C     OPTIMIZATION BY ROSENBROCK METHOD
C    AJ= INDICATORS
C    AFK= OPTIMIZED VALUES FOR VARIABLES
C    AKE = VARIBLES
C    ALPHA =SCALE FACTOR FOR STEP SIZE WHEN STEP IS SUCCESSFUL
C    BETA =SCALE FACTOR FOR STEP SIZE WHEN STEP IS UNSUCCESSFUL
C    E = TEMPORARY STORAGE FOR STEP SIZE
C    EPS =STEP SIZE
C    KAT = NO OF TIMES OBJECT BEING CALLED
C    KK1  =NO OF STAGES
C    KM = NO OF VARIBLES
C    MCYC = NO OF SUCCESSIVE FAILURES ENCOUNTERED IN ALL DIRECTIONS
C    NSTEP =1, USE INITIAL STEP SIZE FOR EVERY NEW STAGE
C    NSTEP =2, USE STEP SIZE OF KTH STAGE FOR (K+1)TH STAGE
C    OBJECT = SUBROUTINE FOR OBJECTIVE FUNCTION SUMN
C    SUMO = STORAGE FOR MINIMUM SUMN
C    V =ORTHOGONAL UNIT VECTORS
C    V IS A UNIT MATRIX INITIALLY
C    THE PROGRAMME TERMINATES AFTER  MAXK STAGES
C            OR AFTER  OBJECT BEING CALLED MKAT TIMES
C            OR AFTER MCYC SUCCESSIVE FAILURES BEINNG ENCOUNTERED
C     BEFORE TERMINATION
C
C
      COMMON /BLK2/ MCYC,MAXK,MKAT,NSTEP,ALPHA,BETA,EPS(7),V(7,7),AFK(7)
      COMMON /BLK5/ SUMN,AKE(7),KM,SMIN
      COMMON /BLK6/ E(7),AJ(7),D(7),AL(7,7),BL(7,7),BLEN(7)
C
      KAT =1
      CALL OBJECT
      SUMO =SUMN
      DO 812 K=1,KM
      AFK(K) =AKE(K)
  812 CONTINUE
      KK1=1
      IF (NSTEP .EQ.1) GO TO 1000
      DO 350 I=1,KM
      E(I)  =EPS(I)
  350 CONTINUE
 1000 DO 250 I=1,KM
      AJ(I) =2.0
      IF (NSTEP .NE.1) GO TO 250
      E(I) =EPS(I)
  250 D(I) =0.0
      III=0
  397 III=III+1
```

```
C        PRODUCT OF PIVOTS
C
      D=D*BIGA
C
C        REPLACE PIVOT BY RECIPROCAL
C
      A(KK)=1.0/BIGA
   80 CONTINUE
      RETURN
      END
      SUBROUTINE SEARCH
C     OPTIMIZATION BY ROSENBROCK METHOD
C    AJ= INDICATORS
C    AFK= OPTIMIZED VALUES FOR VARIABLES
C    AKE = VARIBLES
C    ALPHA =SCALE FACTOR FOR STEP SIZE  WHEN STEP IS SUCCESSFUL
C    BETA =SCALE FACTOR FOR STEP SIZE WHEN STEP IS UNSUCCESSFUL
C    E = TEMPORARY STORAGE FOR STEP SIZE
C    EPS =STEP SIZE
C    KAT = NO OF TIMES OBJECT BEING CALLED
C    KK1  =NO OF STAGES
C    KM = NO OF VARIBLES
C    MCYC = NO OF SUCCESSIVE FAILURES ENCOUNTERED IN ALL DIRECTIONS
C    NSTEP =1, USE INITIAL STEP SIZE FOR EVERY NEW STAGE
C    NSTEP =2, USE STEP SIZE OF KTH STAGE FOR (K+1)TH STAGE
C    OBJECT = SUBROUTINE FOR OBJECTIVE FUNCTION SUMN
C    SUMO = STORAGE FOR MINIMUM SUMN
C    V =ORTHOGONAL UNIT VECTORS
C    V IS A UNIT MATRIX INITIALLY
C    THE PROGRAMME TERMINATES AFTER  MAXK STAGES
C          OR AFTER  OBJECT BEING CALLED MKAT TIMES
C          OR AFTER MCYC SUCCESSIVE FAILURES BEINNG ENCOUNTERED
C     BEFORE TERMINATION
C
C
      COMMON /BLK2/ MCYC,MAXK,MKAT,NSTEP,ALPHA,BETA,EPS(7),V(7,7),AFK(7)
      COMMON /BLK5/ SUMN,AKE(7),KM,SMIN
      COMMON /BLK6/ E(7),AJ(7),D(7),AL(7,7),BL(7,7),BLEN(7)
C
      KAT =1
      CALL OBJECT
      SUMO =SUMN
      DO 812 K=1,KM
      AFK(K) =AKE(K)
  812 CONTINUE
      KK1=1
      IF (NSTEP .EQ.1) GO TO 1000
      DO 350 I=1,KM
      E(I)  =EPS(I)
  350 CONTINUE
 1000 DO 250 I=1,KM
      AJ(I) =2.0
      IF (NSTEP .NE.1) GO TO 250
      E(I) =EPS(I)
  250 D(I) =0.0
      III=0
  397 III=III+1
```

```
258 I=1
259 DO 251 J=1,KM
251 AKE(J) =AKF(J) +E(I) *V(I,J)
    CALL OBJECT
C ***********************************************************************
C  PRINT HERE IF DESIRED NO OF TIMES OBJECTIVE FUNCTION BEING CALLED
C   (KAT), OBJECTIVE FUNCTION(SUMN), VARIBLES(AKE(I))
C ***********************************************************************
    KAT =KAT +1
    IF (KAT .EQ. MKAT ) GO TO 1002
    IF(SUMN.LT.SUMO) GOTO253
    DO 254 J=1,KM
254 AKE(J) =AKE(J) -E(I) *V(I,J)
    E(I) =-BETA*E(I)
    IF (AJ(I) .LT. 1.5) AJ(I) =0.0
    GO TO 255
253 D(I) =D(I) +E(I)
    E(I) =ALPHA *E(I)
    SUMO =SUMN
    DO 813 K=1,KM
813  AFK(K) =AKE(K)
    IF (AJ(I) .GT. 1.5) AJ(I) =1.0
255 DO 256 J=1,KM
    IF (AJ(J) .GT. 0.5) GO TO 299
256 CONTINUE
    GO TO 257
299 IF (I.EQ. KM) GO TO 399
    I=I+1
    GO TO 259
399 DO 398 J=1,KM
    IF (AJ(J) . LT.2. ) GO TO 258
398 CONTINUE
    IF (III.LT. MCYC ) GO TO 397
    GO TO 1001
257 CONTINUE
    IF(KM.EQ.1)  GO TO 1000
    DO 290 I=1,KM
    DO 290 J=1,KM
290 AL(I,J) =0.0
C
C   ORTHOGONALIZATION
C
    WRITE (6,280 ) KK1
    WRITE (6,281) SUMO,(AKE(I) ,I=1,KM)
    DO 260 I=1,KM
    KL=I
    DO 260 J=1,KM
    DO 261 K=KL,KM
261 AL(I,J) =D(K) *V(K,J)+AL(I,J)
260 BL (I,J)= AL(I,J)
    BLEN(I)=0.0
    DO 351 K=1,KM
    BLEN(I)= BLEN(I) +BL(I,K)*BL(I,K)
351 CONTINUE
    BLEN(I) =SQRT(BLEN(I))
    DO 352 J=1,KM
    V(I,J) =BL(I,J) /BLEN(I)
```

```
  352 CONTINUE
      DO 263 I=2,KM
      II=I-1
      DO 263 J=1,KM
      SUMAVV=0.0
      DO 264 KK=1,II
      SUMAV =0.0
      DO 262 K=1,KM
  262 SUMAV=SUMAV + AL(I,K)*V(KK,K)
  264 SUMAVV =SUMAV*V(KK,J) +SUMAVV
  263 BL(I,J) =AL(I,J) -SUMAVV
      DO 266 I=2, KM
      BLEN(I) =0.0
      DO 267 K=1,KM
  267 BLEN(I) =BLEN(I) +BL(I,K) *BL(I,K)
      BLEN(I) = SQRT(BLEN(I) )
      DO 266 J=1, KM
  266 V(I,J) =BL(I,J) / BLEN(I)
      DO 408 IJ1=1,KM
  408 WRITE(6,999) (V(IJ1,IJ2),IJ2=1,KM)
  999 FORMAT(1X,7E17.4)
      KK1 =KK1+1
      IF (KK1.EQ.MAXK ) GO TO 1001
      GO TO 1000
 1002 WRITE (6,910 ) KAT
 1001 WRITE (6, 1003) KK1, KAT ,III
      WRITE (6, 1004) SUMO
      WRITE (6, 1006) (AFK(I),I=1, KM)
      WRITE (6, 294)
      WRITE(6,815) (( V (I,J) ,J=1,KM),I=1,KM)
  150 FORMAT (8F10.5)
  152 FORMAT (1015)
  280 FORMAT(//3X, 12HNO OF STAGE=, 3X, I5/)
  281 FORMAT (10X,  18HSUMO AND VARIABLES,3X, 6E12.4/)
  294 FORMAT(/3X, 23HORTHOGONAL UNIT VECTORS/)
  815 FORMAT (3X,9E12.4/)
  905 FORMAT ( 8F10.5)
  910 FORMAT(//3X,25HPROGRAM HAS CALLED OBJECT,2X,I5, 2X,
     1 25HTIMES WITHOUT CONVERGANCE/)
 1003 FORMAT(/3X, 13HNO OF STAGES=,I5, 3X, 23HAND OBJECT BEING CALLED,
     1 I5, 3X, 5HTIMES,3X,26HNO OF SUCCESSIVE FAILURES=,I5/)
 1004 FORMAT(/3X, 7HOBJECT=, E15.5/)
 1006 FORMAT(/3X, 16HTHE VARIBLES ARE, 6E12.5/)
      RETURN
      END
        6400 END OF RECORD
    3    20    40     7     2
-3.404   -2.390  -3.576
12.6792 12.2399 6.8140
        0.5
   19     5  0.386     19.0
 375  20.716    31.516    74.232    21.4 4   149.0   .2683   .8838 2.122
 375  249.33 250.74 251.59 250.69 250.25 251.20 250.74    0.00
 38   22.616    55.7 8    84.932    11.7 2   175.9   .2649   .8411 1.429
 38   247.02 248.01 248.79 248.06 247.60 248.65 247.41    0.00
 386  23.216    38.2 8    92.532     6.7 1   160.6   .2872   .8836 2.335
 386  252.39 254.53 255.79 254.43 253.51 255.11 253.22    0.00
```

```
390  21.716   30.216   72.032    6.7 8  132.5  .2521  .8705 1.702
390  249.01 250.32 251.00 250.27 249.76 250.76 249.62   0.00
421  18.9 8   43.5 8   60.016  109.2 2  231.6  .1518 1.0073 2.235
421  257.06 258.27 258.64 257.91 256.79 257.06 257.08   0.00
425  14.6 8   40.7 8   90.3 8   93.6 4  239.2  .1498 1.0063 2.234
425  253.99 255.02 255.23 254.75 254.09 254.31 254.19   0.00
447  15.316   33.516   50.132   85.3 2  184.2  .2147  .9183 2.385
447  248.84 250.20 250.03 249.93 249.38 249.84 249.55   0.00
458  23.1 8   53.0 8   34.132   66.0 2  176.2  .1497  .9643 2.057
458  249.28 250.37 250.18 249.86 249.64 249.93 249.57   0.00
466  20.7 8   44.5 4   29.432    6.0 1  100.6  .1007 1.0467 2.659
466  260.15 262.16 261.51 260.66 260.39 260.61 260.29   0.00
484  27.6 8   50.2 8   44.132   66.5 1  188.4  .1771  .9720 2.703
484  252.90 253.36 255.04 254.14 253.14 253.48 253.29   0.00
347  15.616   31.816  101.516   51.3 4  200.2  .2116  .9218 1.800
347  250.27 250.57 251.66 251.10 250.18 250.91 251.37   0.00
378  16.816   31.316   51.132   61.2 2  160.4  .2078  .9209 1.793
378  250.23 251.05 251.64 250.98 250.52 251.13 250.76   0.00
383  13.316   31.716   85.416   75.8 4  206.2  .2074  .9226 1.819
383  250.03 250.76 251.25 250.69 250.37 250.98 250.20   0.00
394  25.1 8   31.316   80.616   79.4 4  216.4  .1996  .9294 1.803
394  250.15 251.05 251.32 250.83 250.52 251.05 250.40   0.00
418  24.3 8   29.616   76.916   44.7 8  175.5  .2066  .9221 1.783
418  250.81 251.88 252.46 251.86 250.64 250.91 250.98   0.00
423  23.2 8   29.716   75.816   93.7 4  222.4  .2086  .9208 1.789
423  250.49 251.59 251.98 251.39 250.42 250.76 250.57   0.00
442  24.0 8   50.7 8   75.416   58.7 2  208.8  .1561  .9719 2.303
442  251.64 252.68 252.61 252.41 252.03 252.29 252.00   0.00
463  25.0 8   46.9 8   73.716   30.8 2  176.4  .1525  .9745 2.282
463  252.12 253.56 253.29 252.78 252.51 252.83 252.44   0.00
487  26.6 8   46.2 8   40.132   44.3 1  157.2  .1536  .9701 2.226
487  252.71 253.19 254.14 253.68 252.85 253.14 252.92   0.00
375      2.003
389      1.706
396      1.589
390      1.598
421      1.563
425      1.376
447      2.727
458      3.018
466      3.573
484      3.167
347      1.736
378      1.995
383      1.562
394      1.592
418      1.349
423      1.370
442      2.843
463      3.192
487      3.212
         END OF FILE
```

```
HPHD,T77.                                                    IAN S.
RUN(S)
SETINDF.
REDUCF.
LGO.
      - 6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     MAIN PROGRAM FOR CALCULATING CATALYST ACTIVITY
C     SHAW DEC 1971
C
      COMMON /BLK3/ NRUNS,RUN(50),AKIN(13),AREA(50,4),ATTEN(50,4),HIGH,
     1  CAREA(50,4),          FIN(50,2),XACT(50),ARCC(50),T(50,8)
      COMMON/BLK11/ CN(5),A(13),RESULT(3),RCC,TPREIL(8),FCALC(5),HTSTOP
      DIMENSION CVARIN(4,4),CALIB(4),SDIFF(4),DIFF(4),H2SAVE(50)
      DIMENSION VV(4,4)
      DATA CALIB / 1.483, 1.839, 1.030, 2.131 /
      DATA CVARIN / 2.4903, 2.0526, 0.5084, 3.9360, 2.0526, 3.0896,
     1      0.6753, 4.9400, 0.5084, 0.6753, 0.2087, 1.2457, 3.9360,
     2      4.9400, 1.2457, 8.8421 /
C
C     READ IN REACTOR DATA
      READ(5,502)NRUNS,NOCOMP,RAREA,HIGH
      GC=82.06
      DO20I=1,NRUNS
      READ(5,991) RUN(I),((AREA(I,J),ATTEN(I,J)),J=1,4),TAREA,
     1      FIN(I,1),FIN(I,2),F
      WRITE(6,991)RUN(I),((AREA(I,J),ATTEN(I,J)),J=1,4),TAREA,
     1      FIN(I,1),FIN(I,2),F
      READ(5,992) RUM,(T(I,J),J=1,8)
      WRITE(6,992)RUM,(T(I,J),J=1,8)
      IF(RUM.NE.RUN(I))  STOP
      WRITE(6,994)
      DO 15 J=1,8
      IF(T(I,J).EQ.0.0)  GO TO 15
      T(I,J) = T(I,J) + 273.13
   15 CONTINUE
      ARCC(I) = GC*RAREA/F
   20 CONTINUE
      DO 30 I=1,NRUNS
      READ(5,993) RUM,XACT(I)
      WRITE(6,993) RUM,XACT(I)
      IF(RUM.NE.RUN(I))  STOP
   30 CONTINUE
      AKIN(1) = 51.
      AKIN(2) = 40.
      AKIN(3) = 30.
      AKIN(4) = 16.0
      AKIN(5) = 15.6604
      AKIN(6) = 10.6322
      AKIN(7) = 12.2229
      AKIN(8) = 6.8140
      AKIN(9) = 2.35
      AKIN(10) = 2.176
      AKIN(11) = 26.0
      AKIN(12) = 4.5208
      AKIN(13) = 2.2115
```

```
      WRITE(6,201)(AKIN(I),I=1,13)
      A(1) = AKIN(1)*1.0E+3
      A(2)=AKIN(2)*1.0E+3
      A(3)=AKIN(3)*1.0E+3
      A(4) = AKIN(4)*1.0E+3
      A(5) = 10.0**AKIN(5)
      A(6)=10.**AKIN(6)
      A(7)=10.**AKIN(7)
      A(8) = 10.0**AKIN(8)
      A(9) = AKIN(9)
      A(10) = AKIN(10)
      A(11) = AKIN(11)*1.0E+3
      A(12) = 10.0**AKIN(12)
      A(13) = AKIN(13)
C
C
      HTSTOP = HIGH
      DEL = 0.002
      DO 1200 I=1,NRUNS
      TIMES = XACT(I) - 6.0*DEL
      SMALL = 1.0E+10
      ISTEP = 0
      DO 25 J=1,8
   25 TPREIL(J) = T(I,J)
      DO 1100 IAN1 = 1,30
      CN(1) = 0.0
      CN(2) = 0.0
      CN(3) = 0.0
      CN(4) = FIN(I,1)
      CN(5) = FIN(I,2)
      TIMES = TIMES + DEL
      SUMSQ = 0.0
      RCC = ARCC(I)*TIMES
      CALL REAC10
      H2SAVE(I) = FCALC(5)*100.0
      CAREA(I,1) = (FCALC(2)*8498.0*CALIB(1))/(CALIB(4)*ATTEN(I,1))
      CAREA(I,2) = (FCALC(3)*8498.0*CALIB(2))/(CALIB(4)*ATTEN(I,2))
      CAREA(I,3) = (FCALC(1)*8498.0*CALIB(3))/(CALIB(4)*ATTEN(I,3))
      CAREA(I,4) = (FCALC(4)*8498.0*CALIB(4))/(CALIB(4)*ATTEN(I,4))
      DO 40 J=1,4
      AT = SQRT(ATTEN(I,J))
      DO 40 K=1,4
      ATT = SQRT(ATTEN(I,K))
      ERR = CVARIN(J,K)*(CAREA(I,J)*AT-AREA(I,J)*AT)*(CAREA(I,K)*ATT-
     1  AREA(I,K)*ATT)
   40 SUMSQ = SUMSQ + ERR
      WRITE(6,999) RUN(I),((AREA(I,J),CAREA(I,J),J=1,4),(ATTEN(I,J),J=1
     1,4),TIMES,H2SAVE(I),SUMSQ
      IF(ISTEP.EQ.2)  GO TO 1150
      IF(SUMSQ.GT.SMALL)  ISTEP = ISTEP + 1
      SMALL = SUMSQ
 1100 CONTINUE
 1150 CONTINUE
      WRITE(6,994)
 1200 CONTINUE
      STOP
  997 FORMAT(F7.2)
```

```
  998 FORMAT(///34H OBJECTIVE FUNCTION AND PARAMETERS,F12.2,5X,5F12.6/)
  999 FORMAT(1X,F4.0,2X,4(2F6.1,2X),4X,4F3.0,3X,F8.3,F8.2,F15.3)
  201 FORMAT(//1X,8H AKIN =     ,8F15.5,/9X,7F15.5//)
  502 FORMAT(2I5,2F10.3)
  991 FORMAT(F4.0,4(F6.1,F2.0,1X,),F6.1,2F7.4,F6.3)
  992 FORMAT(F4.0,1X,8F7.2)
  993 FORMAT(F4.0,6X,F10.4)
  994 FORMAT(/)
  987 FORMAT(1X,F5.0,F9.5,4F10.4,3(3X,2F6.3))
      END
        6400 END OF RECORD
        6400 END OF RECORD
   15    5  0.386   19,0
 348  14.716   31.816  101.416   51.2 4  199.1  .2114  .9210 1.788
 348  250.23 250.71 251.54 250.96 250.13 250.83 251.30   0.00
 373  15.916   30.716   51.032   62.4 2  160.0  .2045  .9238 1.770
 373  250.06 250.93 251.49 250.86 250.40 250.96 250.57   0.00
 373  16.516   30.716   51.932   60.5 2  159.6  .2077  .9216 1.789
 377  250.18 251.00 251.64 250.98 250.54 251.17 250.71   0.00
 382  13.316   31.516   41.732   80.5 4  167.0  .2078  .9206 1.817
 382  249.86 250.69 251.13 250.49 250.23 250.83 250.01   0.00
 388  13.516   32.216   87.716   66.3 4  199.7  .2051  .9223 1.777
 388  250.13 251.05 251.42 250.83 250.47 251.05 250.35   0.00
 393  24.9 8   29.316   78.716   76.2 4  209.1  .2003  .9287 1.807
 393  250.03 252.44 251.32 250.76 250.49 251.00 250.37   0.00
 419  24.3 8   60.3 8   76.816   91.8 4  253.2  .2057  .9233 1.779
 419  250.81 251.90 252.49 251.86 250.69 250.98 250.96   0.00
 422  25.5 8   30.316   79.316   92.2 4  227.3  .2103  .9194 1.799
 422  250.64 251.76 252.20 251.54 250.59 250.86 250.69   0.00
 427  22.6 8   29.616   70.416   99.5 4  222.1  .2011  .9279 1.779
 427  250.23 251.47 251.71 251.15 250.37 250.62 250.44   0.00
 443  23.7 8   51.3 8   72.116   57.0 2  204.1  .1564  .9722 2.303
 443  251.66 252.80 252.63 252.51 252.07 252.37 252.00   0.00
 451  23.2 8   51.0 8   70.016   74.6 2  218.8  .1545  .9715 2.290
 451  251.34 252.51 252.22 252.12 251.73 252.07 251.73   0.00
 462  24.9 8   46.5 8   77.416   31.4 2  180.2  .1534  .9736 2.270
 462  252.17 253.63 253.36 252.85 252.54 252.83 252.44   0.00
 473  27.9 8   41.2 8   40.432   11.6 2  121.1  .1518  .9752 2.242
 473  252.24 253.95 253.80 253.10 252.58 252.90 252.56   0.00
 475  18.5 8   38.4 8   31.032   48.6 2  136.5  .1526  .9710 2.272
 475  252.88 253.14 254.16 253.58 252.97 253.29 253.10   0.00
 486  26.5 8   45.2 8   82.516   20.8 2  175.0  .1544  .9689 2.232
 486  252.71 253.17 254.21 253.68 252.88 253.14 252.95   0.00
 348       1.734
 373       2.018
 377       1.995
 382       1.562
 388       1.599
 393       1.592
 419       1.350
 422       1.369
 427       1.377
 443       2.844
 451       2.669
 462       3.191
 473       3.755
 475       3.077
```

```
HPHD,T5000.                                                    IAN'S.
RUN(S,,,,,,6000)
SETINDF.
REDUCE.
LGO.
        6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     EXPTL DESIGN FOR ESTIMATION OF KINETIC PARAMETERS IN PACKED BED
C     SHAW JUNE 3 1971
C
      COMMON/BLK1/CN(5),AA(13),RESULT(3),RCC,RT,HT,FCALC(5)
      DIMENSION X(3,25,12),XPRIMX(12,12),RAND(320),BMAX(15),SIGMA(3,3)
      DIMENSION DELA(13),SAVE(3),STORE1(4,15),STORE2(3,12),STORE3(3,15)
      DIMENSION B(144),VARIND(4),IRAND(12)
      DATA AA /56.921, 54.264, 37.297, 16.496, 17.703, 16.267, 15.188,
     1 7.051, 1.965, 2.48, 46.516, 12.577, 2.007 /
      DATA DELA / .0002, .001, .001, .001, .005, .005, .005, .005,
     1 .02, .03, .006, .02, .03 /
      DATA SIGMA / 1.62008, 0.78373, 0.72106, 0.78373, 0.69449, 0.44963,
     1 0.72106, 0.44963, 0.87011 /
C
      DO 20 J=1,13
   20 DELA(J) = AA(J)*DELA(J)
      HT = 19.0
      AREA = 0.386
      CACTIV = 3.1
C
      READ(5,9996) NEXPTS,NDSIGN,NPICK,NPAR
      WRITE(6,9996) NEXPTS,NDSIGN,NPICK,NPAR
      READ(5,9998) IRAND
      DO 50 J=1,NEXPTS
      DO 40 I=1,3
      READ(5,9999) (X(I,J,K),K=1,12)
   40 WRITE(6,9999) (X(I,J,K),K=1,12)
   50 WRITE(6,9990)
      WRITE(6,9985)
C
C
      NSUM = NEXPTS
      DO 3000 M2=1,NDSIGN
      CALL FRANDN(RAND,320,IRAND(M2))
      NRAND = -1
      NSUM = NEXPTS + M2
      AMAX = 0.0
      NNPICK = NPICK
      DO 2000 M1=1,NNPICK
      NRAND = NRAND + 1
      MRAND = 4*NRAND
C     PICK INDEPENDANT VARIABLE
      VARIND(1) = 485. + INT(41.0*RAND(MRAND+1))
      VARIND(2) = 1.0 + 0.1*(INT(18.0*RAND(MRAND+2)))
C     VARIND(3) = 0.0 + INT(6.0*RAND(MRAND+3))
      VARIND(3) = 0.0
      VARIND(4) = 3.0 + 0.1*(INT(31.0*RAND(MRAND+4)))
      PRESS = 1.05
      RT = (VARIND(1)-32.0)*(5.0/9.0) + 273.1
```

```
      RCC = CACTIV*(82.06*RT*AREA)/VARIND(2)
      RT = RT*1.99
      SAVCN4 = (PRESS)/(VARIND(3)+VARIND(4)+1.0)
      SAVCN1 = VARIND(3)*SAVCN4
      SAVCN5 = VARIND(4)*SAVCN4
      CN(1) = SAVCN1
      CN(2) = 0.0
      CN(3) = 0.0
      CN(4) = SAVCN4
      CN(5) = SAVCN5
      CALL REAC5
C     WRITE(6,997) RESULT
      SAVE(1) = RESULT(1)
      SAVE(2) = RESULT(2)
      SAVE(3) = RESULT(3)
      DETERM = 0.0
      IF(SAVE(2).GT.0.03)  GO TO 250
      NNPICK = NNPICK + 1
      IF(NNPICK.GT.80)  NNPICK = 80
      GO TO 428
  250 DO 300 M3=1,13
      IF(M3.EQ.5)  GO TO 300
      N3 = M3
      IF(M3.GE.5) N3 = N3-1
      IF(N3.GT.NPAR)  GO TO 315
      CN(1) = SAVCN1
      CN(2) = 0.0
      CN(3) = 0.0
      CN(4) = SAVCN4
      CN(5) = SAVCN5
      SAVEA = AA(M3)
      AA(M3) = AA(M3) + DELA(M3)
      CALL REAC5
C     WRITE(6,997) RESULT
      X(1,NSUM,N3) = (RESULT(1)-SAVE(1))/(AA(M3)-SAVEA)
      X(2,NSUM,N3) = (RESULT(2)-SAVE(2))/(AA(M3)-SAVEA)
      X(3,NSUM,N3) = (RESULT(3)-SAVE(3))/(AA(M3)-SAVEA)
      AA(M3) = SAVEA
  300 CONTINUE
  315 CONTINUE
C     WRITE(6,9990)
C     DO 350 I=1,3
C     WRITE(6,9992) (X(I,NSUM,K),K=1,NPAR)
C 350 CONTINUE
      DO 380 L1=1,NPAR
      DO 380 L2=1,NPAR
  380 XPRIMX(L1,L2) = 0.0
      DO 420 L1=1,3
      DO 420 L2=1,3
      DO 400 L3=1,NPAR
      DO 400 L4=1,NPAR
      TERM = 0.0
      DO 390 L5=1,NSUM
  390 TERM = TERM + X(L1,L5,L3)*X(L2,L5,L4)
      TERM = TERM*SIGMA(L1,L2)
  400 XPRIMX(L3,L4) = XPRIMX(L3,L4) + TERM
  420 CONTINUE
```

```
C     WRITE(6,9990)
C     DO 410 I=1,NPAR
C     WRITE(6,9992) (XPRIMX(I,J),J=1,NPAR)
C 410 CONTINUE
C     WRITE(6,9990)
      K = 0
      DO 426 I=1,NPAR
      DO 426 J=1,NPAR
      K = K + 1
  426 B(K) = XPRIMX(J,I)
      CALL DETER(B,DETERM,NPAR)
  428 WRITE(6,9997) M2,M1,VARIND,SAVE,DETERM
C     WRITE(6,9985)
      IF(DETERM.LT.AMAX) GO TO 2000
      AMAX = DETERM
      STORE1(1,M2) = VARIND(1)
      STORE1(2,M2) = VARIND(2)
      STORE1(3,M2) = VARIND(3)
      STORE1(4,M2) = VARIND(4)
      DO 430 J=1,3
      DO 430 I=1,NPAR
  430 STORE2(J,I) = X(J,NSUM,I)
      DO 450 J=1,3
  450 STORE3(J,M2) = SAVE(J)
 2000 CONTINUE
      BMAX(M2) = AMAX
      DO 2050 J=1,3
      DO 2050 I=1,NPAR
 2050 X(J,NSUM,I) = STORE2(J,I)
      WRITE(7,9998) M2
      DO 2100 I=1,3
      WRITE(7,9999) (X(I,NSUM,J),J=1,12)
 2100 CONTINUE
      DO 2200 I=1,3
      WRITE(6,9992) (X(I,NSUM,K),K=1,NPAR)
 2200 CONTINUE
 3000 CONTINUE
      WRITE(6,9985)
      DO 3050 J=1,NDSIGN
      FLOW = STORE1(2,J)*(539.0/(STORE1(1,J)+460.0))*1.05
      C4 = FLOW/(STORE1(4,J)+1.0)
      H2 = FLOW - C4
      FLOW1 = 50.0/FLOW
      FLOW2 = 40.0/FLOW
      FLOW3 = 30.0/FLOW
      WRITE(6,9995) (STORE1(I,J),I=1,4),(STORE3(I,J),I=1,3),BMAX(J),
     1  FLOW,C4,H2,FLOW1,FLOW2,FLOW3
 3050 CONTINUE
      WRITE(6,9985)
      DO 3100 I=1,3
      DO 3105 J=1,NSUM
 3105 WRITE(6,9992) (X(I,J,K),K=1,NPAR)
 3100 WRITE(6,9994)
C
C
      STOP
  997 FORMAT(11X,3F10.6)
```

```
9985 FORMAT(1H1)
9990 FORMAT(/)
9992 FORMAT(12F11.3)
9993 FORMAT(2I4,F7.0,F6.2,2F5.1,3F7.3,E11.3)
9994 FORMAT(///)
9995 FORMAT(1X,4F7.2,3F8.3,E16.5,6F8.4)
9996 FORMAT(I5,3X, 34HEXPERIMENTS HAVE ALREADY BEEN DONE/   I5,3X, 30HE
    1XPERIMENTS ARE TO BE DESIGNED/   I5,3X, 59HPOSSIBLE POINTS WILL BE
    2 CHOSEN FOR EACH EXPT TO BE DESIGNED/   I5,3X, 25HPARAMETERS ARE CO
    3NSIDERED///)
9997 FORMAT( /2I4,1X,4F10.3,5X,3F10.3,5X,E18.6)
9998 FORMAT(16I5)
9999 FORMAT(4E20.5)
     END
     SUBROUTINE REAC5
C    PACKED BED REACTOR MODEL FOR EXPTL DESIGN FOR PAR ESTIMATION
C     AND FOR THE PARAMETER ESTIMATION STEP
C    CONSTANT PRESSURE INTEGRAL REACTOR
C    MODIFIED SHAW JUNE 1 1971
C
     COMMON/BLK1/CN(5),AA(13),RESULT(3),RCC,RT,HT,FCALC(5)
     DIMENSION A(13)
     DIMENSION C(5),C1(5),DC(5),C2(5),C3(5),C4(5)
     DIMENSION CN1(5),CDX(5),EPSL(5),CIN(5)
     DIMENSION TRMAX(5),TRMIN(5)
     DATA TRMAX / 5*1.0E-6 /
     DATA TRMIN / 5*1.0E-8 /
C
     A(1) = AA(1)*1000.0
     A(2) = AA(2)*1000.0
     A(3) = AA(3)*1000.0
     A(4) = AA(4)*1000.0
     A(5) = 10.0**AA(5)
     A(6) = 10.0**AA(6)
     A(7) = 10.0**AA(7)
     A(8) = 10.0**AA(8)
     A(9) = AA(9)
     A(10) = AA(10)
     A(11) = AA(11)*1000.0
     A(12) = 10.0**AA(12)
     A(13) = AA(13)
     FIX = 0.9
     CRB = RCC*A(5)*EXP(-A(1)/RT)
     CRP1 = RCC*A(6)*EXP(-A(2)/RT)
     CRE2 = RCC*A(12)*EXP(-A(11)/RT)
     CRP2 = 1.0/(1.0+A(7)*EXP(-A(3)/RT))
     CRE = 1.0/(1.0+A(8)*EXP(-A(4)/RT))
     KNEG=0
     KFIN=0
     NK=0
     Y=0.0
     DY=0.5
     NOCOMP = 5
     NEQ=NOCOMP
     IHALF=0
     JHALF=0
     NSWIT=0
```

```
      KRET=1
    9 CONTINUE
      DO5 I=1,NEQ
    5 CN(I)=CN(I)
C
C
   10 CONTINUE
      DO20 I=1,NEQ
   20 C(I)=CN(I)
      N=1
      GOTO400
   30 CONTINUE
      DO 40 I=1,NEQ
      C1(I)=DC(I)
   40 C(I)=CN(I)+C1(I)/2.0
      N=2
      GOTO400
   50 CONTINUE
      DO60 I=1,NEQ
      C2(I)=DC(I)
   60 C(I)=CN(I)+C2(I)/2.0
      N=3
      GOTO400
   70 CONTINUE
      DO80 I=1,NEQ
      C3(I)=DC(I)
   80 C(I)=CN(I)+C3(I)
      N=4
      GOTO400
C
   90 CONTINUE
C     AT THIS POINT 4 RUNG KUTTA STEPS HAVE BEEN FINISHED
      DO100 I=1,NEQ
      C4(I)=DC(I)
  100 CN1(I)=CN(I)+(C1(I)+2.0*C2(I)+2.0*C3(I)+C4(I))/6.0
      IF(NK-1) 110,130,150
  110 DY=DY/2.0
      NK=1
      DO120 I=1,NEQ
  120 CDX(I)=CN1(I)
      GOTO10
  130 DO140 I=1,NEQ
  140 CN(I)=CN1(I)
      Y=Y+DY
      KRET=2
  145 CONTINUE
      Y=Y-DY
      NK=2
      GOTO10
  150 CONTINUE
      DO160 I=1,NEQ
  160 CN(I)=(16.0*CN1(I)-CDX(I))/15.0
      DY=DY*2.0
      NK=0
      Y=Y+DY
      KRET=3
  164 CONTINUE
```

```
      IF(KFIN)165,165,280
  165 IF(Y-HT) 170,250,250
  170 DO180 I=1,NEQ
  180 EPSL(I)=(ABS(CDX(I)-CN1(I)))/15.0
      DO 171 I=1,NEQ
      IF(EPSL(I).LT.TRMIN)  NCOUNT=NCOUNT+1
      IF(EPSL(I).LT.TRMAX)  GO TO 171
      NCOUNT=0
      GOTO209
  171 CONTINUE
      IF(NCOUNT-NEQ)175,176,176
  175 NCOUNT=0
      IHALF=0
      GOTO230
  176 NCOUNT=0
      GOTO220
  209 CONTINUE
C     STEP SIZE MUST BE HALVED
      DO 210 I=1,NEQ
  210 CN(I)=CIN(I)
      Y=Y-DY
      DY=DY/2.0
      IHALF=IHALF+1
      IF(IHALF-10)310,320,320
  320 NSWIT=1
      WRITE(6,321)
      GOTO500
  310 CONTINUE
      GOTO10
  220 DY=DY*2.0
      IHALF=0
  230 DO240 I=1,NEQ
      CIN(I)=CN(I)
  240  CONTINUE
C
C     THE CN AND CIN VALUES ARE THE FINAL ONES AT THE END OF A STAGE
      IF(CN(4).GT.0.0001)  GO TO 10
      CN(4) = 0.0
      IF(CN(3).GT.0.0001)  GO TO 10
      CN(3) = 0.0
      IF(CN(2).GT.0.0001)  GO TO 10
      CN(2) = 0.0
      GOTO280
C
  250 CONTINUE
C     THIS IS THE LAST CALC. IT STOPS THE INT AT EXACTLY HT
      IF(KFIN) 260,260,280
  260 KFIN=1
      Y=Y+DY
      KRET=4
  265 CONTINUE
      DY=HT-Y
      DO 270 I=1,NEQ
  270 CN(I)=CIN(I)
      GOTO10

  400 CONTINUE
```

```
      DO430 I=1,NEQ
      IF(C(I))410,430,430
  410 CONTINUE
      KNEG=1
  430 CONTINUE
      IF(KNEG) 460,460,440
  440 DY=DY/2.0
      JHALF=JHALF+1
      IF(JHALF-10)330,340,340
  330 NSWIT=1
      WRITE(6,331)
      GOTO500
  340 CONTINUE
      KNEG=0
      GOTO10

  460 CONTINUE
      JHALF=0
      DIFFERENTIAL EQUATIONS
      DC(4) = -DY*CRB*C(4)/(C(5)**A(9))
      DC(3) = (-F1X*DC(4)-DY*CRP1*C(3)/(C(5)**A(10)))*CRP2
      DC(2) = (-(2.0-F1X)*DC(4)-DC(3)-DY*CRE2*C(2)/(C(5)**A(13)))*CRE
      DC(1) = -4.0*DC(4)-3.0*DC(3)-2.0*DC(2)
      DC(5) = 3.0*DC(4)+2.0*DC(3)+DC(2)
      GOTO(30,50,70,90),N


  280 CONTINUE
      FINAL CALCULATIONS --- PROBLEM IS SOLVED
      FINAL VALUES ARE CN(I)
      ADD = 0.0
      DO 281 I=1,NOCOMP
  281 ADD = ADD + CN(I)
      DO290I=1,NOCOMP
  290 FCALC(I) = CN(I)/ADD
      REAC = 0.25*FCALC(1) + 0.5*FCALC(2) + 0.75*FCALC(3).
      RESULT(1) = REAC/(REAC+FCALC(4))
      RESULT(2) = FCALC(2)/REAC
      RESULT(3) = FCALC(3)/REAC
  500 CONTINUE
      RETURN

  321 FORMAT(  1X, 19H1HALF = 10   RETURN)
  331 FORMAT(  1X, 19HJHALF = 10   RETURN)
  498 FORMAT(1X,F10.3,6F10.5,F10.3)
      END
        6400 END OF RECORD
 11    12    35    12
  8    10    12    14    16    18    21    23    25    27    29    30    32    34    36    38
-2.0679386537E-01   -1.8846271946E-02   -3.6826447595E-02   -2.0984753962E-02
 2.1161427656E-02    9.3553455942E-02    5.0501168880E-02    2.1753853384E-01
 3.9605808486E-03   -7.9280033592E-04    2.9158432227E-03    4.1812352065E-04
-2.5666492617E-02   -4.4955685846E-02   -4.0841062211E-02    1.3623426013E-01
 1.1909267511E-01    1.0183563416E-01   -3.2659887093E-01    1.1461480287E-02
 2.5500036239E-02    8.8522485809E-03   -3.2238093425E-02   -5.5734761747E-03
 1.2318408501E-01    1.2816309542E-01    1.2196037083E-01    1.2141533376E-02
-1.4004902250E-01   -3.0499671551E-01   -2.9369809504E-02   -3.9225988145E-02
```

-7.2202743557E-02	4.7538219307E-04	-1.7520846054E-03	-2.5353747864E-04
-6.0191794110E-02	-2.1439350573E-03	-3.1611001964E-03	-2.5577426809E-03
5.6473787748E-03	7.7625055293E-03	6.2143180299E-03	2.0518662023E-02
8.0944433870E-04	-1.7423331231E-04	6.4120800892E-04	7.4368979513E-05
-5.7647632078E-03	-2.7614630510E-02	-7.1411507481E-03	1.3769105673E-01
7.0936722396E-02	1.9532266595E-02	-3.3769542827E-01	1.4571481629E-03
1.2144241336E-02	1.8776948026E-02	-6.8263108366E-02	-9.1414559835E-03
6.4787508136E-02	1.1356141512E-01	4.3056870475E-02	8.9756049728E-03
-2.9336105089E-01	-1.1450736654E-01	-2.2027784466E-02	-1.5303975943E-02
-4.9260716770E-02	6.2949166294E-04	-2.3346564009E-03	-2.7067058299E-04
-3.9258272408E-01	-1.9915996225E-03	-1.0636886500E-02	-4.7623804562E-03
5.4262492418E-03	2.6503649852E-02	1.1478892644E-02	4.9047897881E-02
2.5886426150E-04	-9.2271188120E-05	3.4401843640E-04	1.3329245541E-05
-4.4602776862E-03	-1.7248976166E-02	-5.1626784191E-02	1.3515792647E-01
4.6648934507E-02	1.2835833139E-01	-3.2553933141E-01	1.9938263464E-04
2.6999127370E-03	4.2523925187E-03	-1.5785947524E-02	-7.3478827767E-04
1.7850872731E-02	5.2993153256E-02	1.6066407507E-01	1.0966506548E-03
-1.4333629677E-01	-3.9949566368E-01	-2.6461607477E-03	-7.5256451990E-04
-8.2711947934E-03	2.1933779489E-05	-8.1779929279E-05	-3.2002968730E-06
-4.9557307212E-01	-1.9211315054E-02	-3.6397023332E-02	-2.1040418512E-02
5.2124959740E-02	9.2317874782E-02	5.0655750832E-02	2.1264323372E-01
9.1585165263E-03	-8.2445935657E-04	3.0325536033E-03	4.3629088225E-04
-3.6289065139E-02	-4.5640816782E-02	-3.9417457505E-02	1.3715409799E-01
1.2078363036E-01	9.8251732603E-02	-3.2902892509E-01	1.1663550899E-02
2.5999314820E-02	9.3021755949E-03	-3.3868806608E-02	-5.8842105378E-03
1.2770241689E-01	1.3154215864E-01	1.1953014065E-01	1.2801986443E-02
-3.4872063507E-01	-2.9889274049E-01	-3.0989560687E-02	-4.0666429597E-02
-7.4389909092E-02	5.1986411567E-04	-1.9166315541E-03	-2.7821454891E-04
-3.8623591476E-01	-3.3803803190E-03	-1.3811196553E-02	-6.3628037742E-03
9.1006665170E-03	3.4966119800E-02	1.5182657926E-02	1.1050081327E-01
1.0084981534E-03	-1.2028490492E-04	4.4247294575E-04	3.9843466797E-05
-8.5856564745E-03	-2.4111618826E-02	-5.6880320500E-02	1.2224645935E-01
6.4360522191E-02	1.4250042985E-01	-2.9111834003E-01	1.5659255666E-03
8.1477899477E-03	3.6590932207E-03	-1.3405549143E-02	-1.3694144985E-03
2.5706676780E-02	6.2371348479E-02	1.4873853221E-01	1.8410281690E-03
-1.6650840277E-01	-3.7272310074E-01	-4.3974779711E-03	-4.6254254342E-03
-2.1038963419E-02	3.5997110593E-05	-1.3242641364E-04	-1.2012104235E-05
0.	0.	0.	0.
0.	0.	0.	0.
0.	0.	0.	0.
1.6597013429E-02	-1.1969281238E-03	8.5289266161E-03	9.9358131331E-02
-5.7255943300E-03	-2.2364119430E-02	-2.4681394850E-01	-5.9944382415E-03
1.2192885945E-03	6.1080758567E-02	-1.9952752497E-01	-5.1989809790E-04
1.8843325338E-02	6.6933328024E-02	-1.9337338308E-02	7.3511109844E-03
-1.2838058436E-01	4.9781008325E-02	-1.8045317984E-02	-7.2552975778E-03
-4.5326572314E-02	1.7820309395E-03	-6.0638584309E-03	-1.4067449476E-03
-2.6012367920E-01	-7.3647513882E-03	-1.1891350568E-02	-7.6435655609E-03
1.9599488130E-02	2.9732541282E-02	1.8428583273E-02	7.3036248443E-02
2.2089720185E-03	-4.0688481184E-04	1.4921576503E-03	1.3728530541E-04
-1.7519234801E-02	-4.1593209097E-02	-2.4638572676E-02	1.4274559065E-01
1.0823927294E-01	6.2671408130E-02	-3.4476647521E-01	3.3889875251E-03
1.4712848459E-02	1.3620325927E-02	-4.9372638440E-02	-5.3468335305E-03
7.9943762719E-02	1.3303856662E-01	8.6619008567E-02	7.4830068135E-03
-3.4693995703E-01	-2.2026834560E-01	-1.8116515620E-02	-1.5202517966E-02
-4.6645560217E-02	4.1086313526E-04	-1.5101846425E-03	-1.3973712535E-04
-3.0254613483E-01	-1.3576973989E-02	-3.3160397199E-02	-1.7510982111E-02
3.6853670741E-02	8.4284255354E-02	4.2114031023E-02	1.9873870203E-01

5.8464369659E-03	-5.5268825686E-04	2.0369923832E-03	2.6368810568E-04
-2.5826779483E-02	-3.7387208694E-02	-4.5213798943E-02	1.3436710838E-01
9.9484015684E-02	1.1283497570E-01	-3.2199325243E-01	7.4260533450E-03
1.9052880450E-02	7.1443350091E-03	-2.6119762183E-02	-4.0303879892E-03
8.8145441309E-02	1.0593060486E-01	1.3227160072E-01	8.0558441764E-03
-2.8211210627E-01	-3.3066432669E-01	-1.9447001546E-02	-2.5086021821E-02
-5.3708810475E-02	2.6342636456E-04	-9.7205584991E-04	-1.2700063524E-04
0.	0.	0.	0.
0.	0.	0.	0.
0.	0.	0.	0.
1.0015348281E-02	4.1170251191E-03	9.5867606560E-04	-1.6564259850E-02
-9.0031771720E-03	-2.8910218978E-03	4.1781756879E-02	-4.6625576246E-03
-5.2438198901E-03	6.5585653991E-02	-5.5402363178E-02	-7.8206427576E-02
0.	0.	0.	0.
0.	0.	0.	0.
0.	0.	0.	0.
-2.6769794322E-01	-2.2834515650E-02	-2.5649911753E-02	-2.0277432319E-02
6.0360746912E-02	6.2714308606E-02	4.8875878243E-02	1.4328280900E-01
1.4956654760E-02	-1.2986645711E-03	4.7665876865E-03	9.6068122569E-04
-5.0116719156E-02	-5.5315022269E-02	-1.6756491100E-02	1.4395097078E-01
1.4122334120E-01	4.0539960837E-02	-3.4851626266E-01	2.1569321481E-02
4.3964896424E-02	1.8164063855E-02	-6.5857727379E-02	-1.6323852779E-02
2.4657849857E-01	1.9174570324E-01	7.6422008528E-02	3.5930523755E-02
-4.9620125244E-01	-1.8945107226E-01	-8.8117196484E-02	-1.0513624931E-01
-1.4958649797E-01	2.3876158919E-03	-8.8781161957E-03	-1.7916533961E-03
-4.9397112864E-01	-1.1590735020E-02	-3.0649292305E-02	-1.5766367895E-02
3.1422444346E-02	7.7810369383E-02	3.7893429740E-02	1.8541865178E-01
4.7012499645E-03	-4.6601418456E-04	1.7181004154E-03	2.0955770868E-04
-2.2331051232E-02	-3.4964038031E-02	-4.6860811454E-02	1.3337953073E-01
9.3138624701E-02	1.1700719303E-01	-3.1949409075E-01	5.9823609180E-03
1.6735921267E-02	6.5835271655E-03	-2.4092903861E-02	-3.4865954230E-03
7.5559283640E-02	9.8468303448E-02	1.3567062095E-01	6.6785483877E-03
-2.6247822822E-01	-3.3921248788E-01	-1.6102978811E-02	-2.0021592568E-02
-4.6920217342E-02	2.0446376213E-04	-7.5451671298E-04	-9.2879955047E-03

END OF FILE

RUN	DEG.F.	SCFM*	N	RATIO	BED	S1	S2	S3	CONV.
1	482.90	6.05	4	6.488	77.0	2.759	.271	.233	51.25
2	485.18	6.07	4	6.488	77.0	2.913	.214	.219	52.55
3	483.93	6.06	4	6.488	77.0	2.844	.255	.215	52.57
4	498.64	9.04	4	8.858	77.0	3.036	.162	.213	53.42
5	498.36	9.03	4	8.858	77.0	2.928	.217	.213	53.58
6	484.99	6.07	4	6.488	77.0	2.859	.248	.215	52.50
7	484.23	6.06	4	6.488	77.0	2.858	.246	.217	52.76
9	468.05	6.06	4	3.949	77.0	3.092	.208	.164	50.00
10	482.98	6.05	4	6.488	77.0	2.810	.263	.221	52.92
11	483.16	6.05	4	6.488	77.0	2.834	.259	.216	53.07
12	499.25	9.08	4	4.036	77.0	3.513	.114	.087	59.04
14	483.91	6.06	4	6.488	77.0	2.869	.241	.217	53.81
15	483.12	6.05	4	6.488	77.0	2.816	.268	.216	53.23
16	498.55	6.15	4	6.488	77.0	3.193	.179	.149	62.05
17	499.34	6.07	4	8.588	77.0	3.037	.222	.173	62.55
18	499.78	6.07	4	8.588	77.0	2.966	.245	.182	60.77
19	484.31	6.06	4	6.488	77.0	2.813	.269	.216	55.03
20	484.78	6.07	4	6.488	77.0	2.857	.247	.217	54.35
21	468.08	9.13	4	8.946	77.0	1.851	.252	.549	30.54
22	468.65	9.14	4	8.946	77.0	1.821	.296	.529	31.22
23	483.99	6.06	4	6.488	77.0	2.810	.273	.214	53.66
24	483.21	6.05	4	6.488	77.0	2.812	.277	.211	53.86
25	499.85	6.22	4	3.911	77.0	3.526	.115	.082	65.30
27	483.44	6.06	4	6.488	77.0	2.837	.267	.210	53.40
28	482.70	6.05	4	6.488	77.0	2.811	.264	.220	53.49
29	468.53	9.11	4	3.962	77.0	2.703	.249	.266	42.97
30	468.06	9.11	4	3.962	77.0	2.534	.279	.303	42.45
31	484.01	6.06	4	6.488	77.0	2.866	.264	.202	54.48
33	467.38	6.17	4	8.700	77.0	2.099	.279	.447	39.56
34	467.88	6.17	4	8.700	77.0	2.126	.216	.481	37.21
35	483.35	4.14	4	6.390	77.0	2.827	.287	.199	47.18
36	483.18	4.14	4	6.390	77.0	2.943	.229	.200	47.26
37	483.61	5.96	3	7.340	77.0	2.099	.450	0.000	26.53
38	483.83	5.97	3	7.340	77.0	2.331	.335	0.000	22.94
39	484.27	5.97	3	7.340	77.0	2.064	.468	0.000	25.61
40	483.87	6.12	2	6.019	77.0	2.000	0.000	0.000	3.86
41	482.81	6.12	2	6.019	77.0	2.000	0.000	0.000	4.00
42	494.58	6.19	2	6.019	77.0	2.000	0.000	0.000	6.53
43	504.05	6.25	2	6.019	77.0	2.000	0.000	0.000	10.06
44	484.20	6.06	4	6.488	77.0	2.887	.240	.211	53.19
45	484.25	6.06	4	6.488	77.0	2.770	.282	.222	53.86
46	500.07	6.16	4	6.488	77.0	3.503	.080	.112	65.62
48	484.66	5.94	4	5.170	77.0	2.830	.273	.208	51.89
50	485.56	5.95	4	5.180	77.0	2.817	.265	.217	52.05
51	485.30	5.94	4	5.210	77.0	2.829	.269	.211	52.45
52	485.98	5.95	4	5.180	77.0	2.846	.266	.207	52.51
53	501.79	6.05	4	5.290	77.0	3.079	.211	.166	60.87
54	502.34	6.05	4	5.160	77.0	3.087	.215	.161	61.73
55	515.26	6.13	4	5.300	77.0	3.287	.183	.116	67.77
56	515.07	6.13	4	5.300	77.0	3.299	.177	.116	66.10
57	529.60	6.22	4	5.300	77.0	3.472	.144	.080	73.72
58	529.68	6.22	4	5.300	77.0	3.501	.137	.075	74.23
59	529.60	6.22	4	5.300	77.0	3.501	.140	.073	75.38
61	485.36	5.95	4	5.300	77.0	2.864	.251	.211	50.14
62	484.20	5.94	4	5.100	77.0	2.893	.257	.197	55.36

*The flowrate at minimum fluidization is ca. 0.6 scfm.

64	484.89	5.94	4	5.300	77.0	2.872	.258	.204	55.93
65	483.72	6.26	4	11.000	77.0	2.465	.292	.317	49.04
66	484.58	6.26	4	11.000	77.0	2.407	.296	.334	48.75
67	482.79	6.02	4	2.680	77.0	3.509	.107	.092	51.81
68	484.60	6.04	4	2.670	77.0	3.599	.085	.077	59.25
69	482.41	6.02	4	2.680	77.0	3.577	.092	.080	57.88
70	482.76	6.02	4	2.680	77.0	3.551	.097	.085	57.69
71	483.18	6.03	4	2.700	77.0	3.586	.089	.079	60.05
72	484.33	5.94	4	5.300	77.0	2.889	.254	.201	54.45
73	467.68	5.83	4	5.230	77.0	2.384	.286	.348	44.02
74	469.62	5.85	4	5.300	77.0	2.400	.288	.342	44.97
75	453.96	5.75	4	5.150	77.0	1.884	.237	.547	31.76
76	454.91	5.75	4	5.300	77.0	1.823	.237	.568	30.60
77	457.88	5.77	4	5.300	77.0	1.936	.252	.520	33.75
78	440.42	5.66	4	5.090	77.0	1.570	.186	.686	17.80
79	440.86	5.67	4	5.300	77.0	1.571	.182	.688	15.80
80	486.79	11.09	4	5.400	77.0	2.704	.275	.249	45.66
81	480.77	11.02	4	5.400	77.0	2.467	.285	.321	42.92
82	484.45	5.94	4	5.300	77.0	2.847	.264	.208	53.14
83	542.32	6.30	4	5.160	77.0	3.608	.111	.057	82.15
84	543.30	6.31	4	5.300	77.0	3.604	.115	.055	83.85
85	485.26	5.94	4	5.170	77.0	2.914	.253	.193	54.41
86	484.93	5.94	4	5.300	77.0	2.867	.262	.203	52.71
101	498.88	9.08	4	4.578	47.6	2.961	.255	.176	40.03
102	496.77	9.30	4	4.099	47.6	3.002	.270	.153	32.63
103	498.46	9.31	4	4.099	47.6	3.383	.116	.128	40.59
104	497.70	9.31	4	4.099	47.6	3.137	.234	.132	41.43
105	459.23	5.93	4	4.000	47.6	1.708	.217	.619	17.86
106	457.74	5.92	4	4.000	47.6	1.616	.216	.650	16.81
107	457.01	5.92	4	4.000	47.6	1.599	.225	.650	16.57
108	497.97	11.46	4	4.305	47.6	3.023	.252	.157	39.80
109	499.75	11.48	4	4.305	47.6	3.102	.236	.142	39.34
110	499.76	11.48	4	4.305	47.6	3.095	.235	.145	41.93
111	493.65	6.51	4	4.099	47.6	3.165	.214	.135	51.16
112	494.06	6.52	4	4.099	47.6	3.173	.221	.128	51.61
113	496.31	10.68	4	4.000	47.6	3.111	.234	.141	41.81
114	495.25	10.67	4	4.000	47.6	3.107	.230	.144	41.73
115	498.90	6.13	4	5.595	47.6	2.822	.288	.201	51.86
116	496.76	6.12	4	5.595	47.6	2.814	.277	.211	50.04
117	495.60	10.28	4	4.000	47.6	3.124	.238	.134	42.61
118	496.38	10.29	4	4.000	47.6	3.072	.241	.149	40.23
119	492.24	6.90	4	4.297	47.6	3.057	.240	.154	49.25
120	492.26	6.90	4	4.297	47.6	3.045	.238	.160	48.67
121	488.53	11.51	4	3.835	47.6	2.779	.273	.225	37.39
122	489.40	11.52	4	3.835	47.6	2.804	.271	.218	37.77
123	487.10	5.91	4	4.196	47.6	3.006	.242	.170	49.24
124	488.28	5.92	4	4.196	47.6	3.008	.247	.166	49.78
125	457.89	5.92	4	4.000	47.6	1.695	.212	.627	18.02
126	457.33	5=92	4	4.000	47.6	1.673	.212	.634	17.35

```
HPHD,T10.                                                    IAN S.
RUN(S)
SETINDF.
REDUCE.
LGO.
        6400 END RECORD
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     CALCULATION OF MOLE FRACTIONS FROM CHROMATOGRAPH ANALYSIS
C     A(1) AND X(1) ARE THE AREA AND ATTENUATION FOR THE COMBINED
C                                  H2-CH4-C2H6 PEAK
C     A(2) AND X(2) ARE FOR THE C3H8 PEAK
C     A(3) AND X(3) ARE FOR THE C4H10 PEAK
C     A(4) AND X(4) ARE FOR THE HYDROGEN PEAK
C     A(5) AND X(5) ARE FOR THE METHANE PEAK
C
      DIMENSION TITLE(20), A(5), X(5), CONVRT(5), AA(5), TEMP(7)
      DIMENSION EMF(7), TDIF(7), TCEROR(7), FEED(5), RAT(2,50)
      DATA CONVRT / 4.464, 0.1532, .10322, .07895, .0692 /
      DATA TCEROR/ 0.054, 0.038, 0.025, 0.004, 0.041, 0.024, 0.073/
      HEIGHT = 77.0
      NCOUNT = 0
      READ(5,800) TITLE
      WRITE(6,901) TITLE
C
   10 READ(5,801) SAMPLE, (A(I),X(I),I=1,5)
      IF(SAMPLE.LT.0.0)  GO TO 300
      IF(SAMPLE.NE.0.0)  GO TO 15
      WRITE(6,902)
      GO TO 10
   15 AA(1) = A(4)*X(4)*CONVRT(1)
      AA(2) = A(5)*X(5)*CONVRT(2)
      AA(3) = (A(1)*X(1)-(AA(1)/CONVRT(1)+AA(2)/CONVRT(2)))*CONVRT(3)
      AA(4) = A(2)*X(2)*CONVRT(4)
      AA(5) = A(3)*X(3)*CONVRT(5)
      VOLUME = 0.0
      DO 40 I=1,5
   40 VOLUME = VOLUME + AA(I)
      DO 60 I=1,5
   60 AA(I) = AA(I)*100.0/VOLUME
C
C     EMF  1-7 ARE THE MILLIVOLTS OF THE THERMOCOUPLES AT
C        1 BOTTOM OF THE REACTOR
C        2 6 INCHES UP THE REACTOR
C        3 1 FT UP THE REACTOR
C        4 2 FT UP THE REACTOR
C        5 3 FT UP THE REACTOR
C        6 THE FEED GAS
C        7 THE CIRCULATING OIL
      READ(5,802) EMF
      DO 100 J=1,7
      EMF(J) = EMF(J) - TCEROR(J)
  100 TEMP(J) = 480.00 - (10.110-EMF(J))*(20.00/0.457)
      TAVG = (TEMP(1)*3.+TEMP(2)*6.+TEMP(3)*9.+TEMP(4)*18.)/36.
      DO 120 J=1,7
  120 TDIF(J) = TEMP(J) - TAVG
C
C     CARBON IS THE NUMBER OF CARBONS IN THE PARAFIN FEED
C     FLOWH2 IS THE HYDROGEN ROTAMETER SETTING AT 4.0 PSIG
```

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C     FLOWHC IS THE PARAFIN ROTAMETER READING AT 4.0 PSIG
      NCOUNT = NCOUNT + 1
      READ(5,802) CARBON, FLOWHC, FLOWH2
      H2 = FLOWH2*(13.4/100.)*((TAVG+460.)/530.)
      HYDCAR = FLOWHC*(3.495/100.)*((TAVG+460.)/530.)
      H2FEED = 0.0
      HCFEED = 0.0
      CONV = 0.0
      IF(A(4).EQ.0.0)  GO TO 230
      N = CARBON + 0.1
      N = N-1
      GO TO (200,210,220) N
  200 HYDCAR = HYDCAR*SQRT(2.06/1.049)
      HCFEED = AA(3) + AA(2)*0.5
      H2FEED = AA(1) + AA(2)*2.0 + AA(3)*3.0 - HCFEED*3.0
      CONV = 100.*(HCFEED-AA(3))/HCFEED
      X1 = 2.0
      X2 = 0.0
      X3 = 0.0
      FEED(1) = 0.0
      FEED(2) = HYDCAR/(HYDCAR+H2)
      FEED(3) = 0.0
      FEED(4) = 0.0
      FEED(5) = 1.0 - FEED(2)
      RAT(1,NCOUNT) = H2/HYDCAR
      GO TO 230
  210 HYDCAR = HYDCAR*SQRT(2.06/1.56)
      HCFEED = AA(4) + AA(3)*(2./3.) + AA(2)/3.
      H2FEED = AA(1)+AA(2)*2.+AA(3)*3.+AA(4)*4. - HCFEED*4.
      CONV = 100.*(HCFEED-AA(4))/HCFEED
      REACT = AA(2)/3.0 + AA(3)*2.0/3.0
      X1 = AA(2)/REACT
      X2 = AA(3)/REACT
      X3 = 0.0
      FEED(1) = 0.0
      FEED(2) = 0.0
      FEED(3) = HYDCAR/(HYDCAR+H2)
      FEED(4) = 0.0
      FEED(5) = 1.0 - FEED(3)
      RAT(1,NCOUNT) = H2/HYDCAR
      GO TO 230
  220 HCFEED = AA(5)+AA(4)*0.75+AA(3)*0.5+AA(2)*0.25
      H2FEED = AA(1)+AA(2)*2.0+AA(3)*3.0+AA(4)*4.0+AA(5)*5.0-HCFEED*5.
      CONV = 100.*(HCFEED-AA(5))/HCFEED
      REACT = AA(2)*.25+AA(3)*.5+AA(4)*.75
      X1 = AA(2)/REACT
      X2 = AA(3)/REACT
      X3 = AA(4)/REACT
      FEED(1) = 0.0
      FEED(2) = 0.0
      FEED(3) = 0.0
      FEED(4) = HYDCAR/(HYDCAR+H2)
      FEED(5) = 1.0 - FEED(4)
      RAT(1,NCOUNT) = H2/HYDCAR
      GO TO 230
  230 CONTINUE
      FLOW = H2 + HYDCAR
```

```
      RATIO = H2FEED/HCFEED
      RAT(2,NCOUNT) = RATIO
C
      NSAMPL = SAMPLE + 0.1
C     WRITE(6,900) NSAMPL, (AA(I),I=1,5), (TDIF(I),I=1,5), TDIF(7),
C    1  TAVG, RATIO, FLOW, CONV, X1, X2, X3
C     WRITE(7,965) NSAMPL,TAVG,FLOW,FEED,X1,X2,X3,CONV,HEIGHT
      GO TO 10
  300 WRITE(6,998)
C
  800 FORMAT(10A6/10A6)
  801 FORMAT( F5.0, 5(F10.1,F5.0))
  802 FORMAT(8F10.3)
  900 FORMAT(I5, F10.2, F8.2, F7.2, F7.2, F8.2,4X, 5(F5.1), F7.1, F10.2,
     1   F7.2, F7.2, F7.2, 3X, F6.2, 2F6.3)
  901 FORMAT(//1X,10A6/1X,10A6//1X,6HSAMPLE,13X,21HPRODUCT MOLE FRACTION
     1, 12X, 25HLOCAL TEMP - AVERAGE TEMP, 6X, 7HREACTOR, 2X, 4HFEED,
     2  4X, 4HEXIT, 3X, 4HCONV, 7X,11HSELECTIVITY/
     3   1X, 6HNUMBER, 5X, 2HH2, 5X, 3HCH4, 4X,4HC2H6, 3X, 4HC3H8, 3X,
     4  5HC4H10,  6X, 3HBTM,2X, 3H6IN, 2X, 3H1FT, 2X, 3H2FT, 2X, 3H3FT,
     5 3X, 3HOIL, 4X, 7HTEMP(F), 2X, 5HRATIO,  4X, 3HCFM, 12X, 4HC1H4,
     6  2X, 4HC2H6, 2X, 4HC3H8/)
  902 FORMAT(/)
  965 FORMAT(I3,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.2,F5.1)
  998 FORMAT(1H1'
  999 FORMAT(1X,2F10.4)
      END
'        6400 END RECORD
 FLUIDIZED BED REACTOR RUNS OF DEC 5 - 6 /69 AND JAN 10 /70
 SELECTIVITY  FEB 16  1970
1.   90.5       20.   23.8       10.   221.8      5.    72.4       2.    726.5
10.155     10.205     10.205     10.194     10.15      9.840      9.38
4.         13.        22.
2.   94.6       20.   46.1       5.    54.1       20.   143.4      1.    315.3
10.260     10.244     10.23      10.255     10.19      9.6        9.31
4.         13.        22.
3.   91.5       20.   43.9       5.    104.9      10.   137.6      1.    298.7
10.16      10.24      10.222     10.22      10.194     9.81       9.3
4.         13.        22.

4.   30.2       50.   34.2       5.    79.8       10.   155.3      1.    251.
10.265     10.598     10.587     10.573     10.573     9.763      9.735
4.         14.5       33.5
5.   77.1       20.   88.        2.    81.8       10.   156.       1.    624.3
10.326     10.584     10.57      10.563     10.565     9.39       9.918
4.         14.5       33.5

6.   88.8       20.   42.6       5.    102.2      10.   129.5      1.    291.8
10.284     10.25      10.227     10.242     10.208     9.51       9.4
4.         13.        22.
7.   95.9       20.   46.3       5.    109.2      10.   142.1      1.    314.9
10.23      10.237     10.226     10.221     10.19      9.65       9.32
4.         13.        22.

9.   129.1      20.   46.3       5.    160.8      10.   112.       1.    449.2
9.518      9.88       9.885      9.89       9.815      9.55       8.38
4.         20.        20.6
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10.  97.7        20.  48.4        5.  111.        10.  150.        1.  316.8
10.01        10.211       10.215       10.215       10.153       9.73        9.33
4.           13.          22.
11.  97.3        20.  46.9        5.  109.4       10.  147.5       1.  316.8
9.97         10.218       10.23        10.22        10.158       9.79        9.27
4.           13.          22.

12.  61.5        50.  13.6        10.  62.2        20.  92.4        1.  569.2
10.32        10.573       10.601       10.593       10.583       9.67        8.22
4.           28.5         30.

14.  100.        20.  48.2        5.  109.        10.  149.4       1.  329.1
10.118       10.223       10.24        10.223       10.18        9.9         9.35
4.           13.          22.
15.  99.         20.  47.7        5.  110.7       10.  151.2       1.  320.5
10.1         10.218       10.223       10.2         10.13        9.83        9.28
4.           13.          22.

16.  119.5       20.  37.7        5.  176.3        5.  138.1        1.  415.7
10.527       10.552       10.558       10.555       10.505       9.73        9.34
4.           13.          22.

17.  103.6       20.  95.7        2.  75.6        10.  151.6       1.  346.5
10.579       10.568       10.572       10.57        10.458       9.622       9.97
4.           10.          22.4
18.  96.7        20.  94.1        2.  76.3        10.  156.7       1.  316.7
10.578       10.585       10.588       10.577       10.52        9.57        9.97
4.           10.          22.4

19.  102.5       20.  49.7        5.  107.        10.  150.1       1.  332.8
10.234       10.234       10.228       10.224       10.204       9.182       9.21
4.           13.          22.
20.  100.2       20.  48.5        5.  107.2       10.  146.6       1.  329.3
10.243       10.235       10.236       10.24        10.165       10.144      9.25
4.           13.          22.

21.  75.3        10.  135.3       2.  128.        10.  187.7       1.  235.2
9.845        9.855        9.875        9.85         9.85         9.57        9.44
4.           15.          35.
22.  156.5       5.   136.4       2.  129.7       10.  181.4       1.  242.1
9.87         9.872        9.868        9.87         9.875        9.56        9.57
4.           15.          35.

23.  100.        20.  47.9        5.  110.1       10.  147.9       1.  323.7
10.232       10.23        10.234       10.208       10.172       10.173      9.22
4.           13.          22.
24.  101.5       20.  47.8        5.  110.6       10.  150.2       1.  328.
10.188       10.18        10.247       10.19        10.165       10.17       9.22
4.           13.          22.

25.  76.5        50.  8.0         20.  119.       10.  85.5        1.  356.7
10.571       10.564       10.6         10.582       10.466       10.26       9.24
4.           20.          20.4

27.  100.        20.  46.6        5.  110.6       10.  148.8       1.  324.9
10.2         10.213       10.242       10.19        10.184       10.15       9.21
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4.          13.         22.
28.  99.4          20.  49.0        5.  110.4          10.  150.5        1.  322.5
10.195      10.177      10.2         10.19      10.173      10.156       9.19
4.          13.         22.

29.  107.3         20.  33.9        10.  96.4          20.  129.9        1.  354.7
9.846       9.865       9.875        9.867      9.862       9.56         8.31
4.          30.         31.
30.  95.7          20.  70.9        5.  90.6           20.  134.         1.  306.
9.842       9.84        9.868        9.858      9.848       9.775        8.5
4.          30.         31.

31.  103.7         20.  11.6        20.  109.5          10.  145.7        1.  339.3
10.237      10.21       10.208       10.228     10.16       9.64         9.15
4.          13.         22.

33.  107.1         10.  155.3        2.  60.5           20.  171.8        1.  375.4
9.872       9.89        9.875        9.802      9.805       9.63         9.33
4.          10.4        23.6
34.  94.9          10.  146.4        2.  117.3          10.  180.7        1.  333.8
9.85        9.86        9.852        9.85       9.82        9.77         9.49
4.          10.4        23.6


35.  87.6          20.  38.2         5.  122.3          10.  146.6        1.  279.
10.160      10.227      10.198       10.210     10.085      10.138       9.30
 4.0        9.0         15.0
36.  88.1          20.  38.2         5.  121.7          10.  145.2        1.  289.9
10.150      10.233      10.180       10.211     10.070      10.210       9.270
 4.0        9.0         15.0

37.  92.2          10.  72.7         20.                    173.1        1.  284.
10.173      10.220      10.206       10.218     10.180      10.260       10.010
 3.0        10.0        22.0
38.  77.9          10.  69.1         20.                    179.7        1.  247.
10.198      10.221      10.215       10.219     10.190      10.290       10.078
 3.0        10.0        22.0
39.  40.1          20.  65.7         20.                    158.9        1.  240.6
10.212      10.240      10.230       10.223     10.190      10.262       9.830
 3.0        10.0        22.0

40.  94.1          20.                                     90.1         2.  87.4
10.228      10.223      10.225       10.210     10.210      10.080       10.078
2.          10.         22.
41.  98.5          20.                                     181.0        1.  95.
10.204      10.195      10.195       10.190     10.182      10.318       10.355
2.          10.         22.

42.  94.5          20.                                     183.2        1.  146.9
10.475      10.465      10.461       10.460     10.450      10.438       10.605
2.          10.         22.

43.  96.7          20.                                     180.4        1.  229.6
10.682      10.680      10.678       10.678     10.648      10.762       10.688
2.          10.         22.
```

```
44.  96.5       20.  45.       5.   107.       10.  148.8      1.   317.1
10.187      10.240     10.200     10.239     10.148     10.050     9.30
4.          13.        22.
45.  95.9       20.  47.8       5.   105.4      10.  145.6      1.   307.9
 10.209     10.226     10.200     10.242     10.135     10.280     9.30
4.          13.        22.

46.  60.5       50.  87.5       2.   186.6      5.   111.2      1.   281.8
10.590      10.590     10.561     10.600     10.465     10.461     8.830
4.          13.        22.
-1.0
            END OF FILE
```

```
HPHD,T10.                                                    IAN S.
RUN(S)
SETINDF.
REDUCE.
LGO.
         6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)                                                    4
C     FLUID BED DATA ANALYSIS RUNS 48 - 86 N2 USED TO CALIB. CHROM.
C     CALCULATION OF MOLE FRACTIONS FROM CHROMATOGRAPH ANALYSIS
C     A(1) AND NATTEN(1) ARE THE INTEGRATION AND THE ATTENUATION FOR THE
C        C2H6 PEAK
C     A(2) AND NATTEN(2) FOR C3H8 PEAK
C     A(3) AND NATTEN(3) FOR CH4 PEAK
C     A(4) AND NATTEN(4) FOR C4H10 PEAK
C
      DIMENSION TITLE(20), A(4), NATTEN(4), X(5), CALIB(4), TEMP(5),
     1  EMF(5), TDIF(5),TCEROR(7), FEED(5)
      DIMENSION RAT(3,50)
      DATA CALIB/ 1.483, 1.839, 1.000, 2.131 /
      DATA TCEROR/ 0.054, 0.038, 0.025, 0.004, 0.041, 0.024, 0.073/
      HEIGHT = 77.0
      READ(5,800) TITLE
      WRITE(6,901) TITLE
C
      NCOUNT = 0
   10 READ(5,801) NSAMPL,CALIBR,(A(I),NATTEN(I),I=1,4)
      IF(NSAMPL.LT.0) GO TO 300
      IF(NSAMPL.NE.0) GO TO 15
      WRITE(6,902)
      GO TO 10
   15 SUM = 0.0
      XMULT = 77.066/CALIBR
      DO 30 J=1,4
      ATTEN = NATTEN(J)
      X(J) = (A(J)*ATTEN*XMULT/CALIB(J))*100.0*(CALIB(4)/8498.)
   30 SUM = SUM + X(J)
      X(5) = 100.0 - SUM
C
C     EMF  1-7 ARE THE MILLIVOLTS OF THE THERMOCOUPLES AT
C        1 BOTTOM OF THE REACTOR
C        2 6 INCHES UP THE REACTOR
C        3 1 FT UP THE REACTOR
C        4 2 FT UP THE REACTOR
C        5 3 FT UP THE REACTOR
      READ(5,803) EMF
      IF(EMF(1).EQ.0.0) GO TO 125
      DO 100 J=1,5
      EMF(J) = EMF(J) - TCEROR(J)
  100 TEMP(J) = 480.00 - (10.110-EMF(J))*(20.00/0.457)
      TAVG = (TEMP(1)*3.+TEMP(2)*6.+TEMP(3)*9.+TEMP(4)*18.)/36.
      DO 120 J=1,5
  120 TDIF(J) = TEMP(J) - TAVG
      GO TO 180
  125 CONTINUE
      DO 130 J=2,5
      EMF(J) = EMF(J) - TCEROR(J)
  130 TEMP(J) = 480.00 - (10.110-EMF(J))*(20.00/0.457)
      TAVG = (TEMP(2)*9. + TEMP(3)*9. + TEMP(4)*18.)/36.
```

```
      DO 140 J=2,5
  140 TDIF(J) = TEMP(J) - TAVG
  180 CONTINUE
C
C     NCARBN IS THE NUMBER OF CARBONS IN THE PARAFIN FEED
C     FLOWH2 IS THE H2 FEED RATE IN SCFM
C     FLOWHC IS THE PARAFIN FELD RATE IN SCFM
      READ(5,802) NCARBN,FLOWHC,FLOWH2
      IF(NCARBN.NE.4)  STOP
      REAC = X(1)*0.5 + X(2)*0.75 + X(3)*0.25
      CONV = 100.*REAC/(REAC+X(4))
      AAA = (X(3) + X(1)*2. + X(2)*3. + X(4)*4.)/4.
      X1 = X(3)/REAC
      X2 = X(1)/REAC
      X3 = X(2)/REAC
C     THIS SECTION ADDED DUE TO ERROR IN MEASURING RATIO FROM
C      CHROMATOGRAPH FOR RUNS 48 TO 86
C     FEED RATIOS OBTAINED BY COMPARING TO SIMILAR FLOW METER SETTINGS
C        FROM RUNS 1 - 46
      READ(5,804) RATIO
  804 FORMAT(F10.3)
      NCOUNT = NCOUNT + 1
      RAT(1,NCOUNT) = RATIO
      RAT(2,NCOUNT) = FLOWH2/FLOWHC
      C4 = X(4) + 0.25*X(3) + 0.5*X(1) + 0.75*X(2)
      RAT(3,NCOUNT) = (100.0-C4)/C4
      FEED4 = 100.0/(RATIO+1.0)
      FEEDH = 100.0 - FEED4
      REAC = FEED4*CONV/100.0
      X(4) = FEED4 - REAC
      X(1) = REAC*X2
      X(2) = REAC*X3
      X(3) = REAC*X1
      X(5) = 100.0 - (X(1)+X(2)+X(3)+X(4))
      FLOW = (FLOWHC+FLOWH2)*(460.+TAVG)/530.
      FEED(1) = 0.0
      FEED(2) = 0.0
      FEED(3) = 0.0
      FEED(4) = FEED4/(FEED4+FEEDH)
      FEED(5) = 1.0 - FEED(4)
C
C     WRITE(6,900) NSAMPL,  X(5),X(3),X(1),X(2),X(4), (TDIF(I),I=1,5),
C    1             TAVG, RATIO, FLOW, CONV, X1,X2,X3
C     WRITE(7,965) NSAMPL,TAVG,FLOW,FEED,X1,X2,X3,CONV,HEIGHT
      GO TO 10
  300 WRITE(6,998)
C
  800 FORMAT(10A6/10A6)
  801 FORMAT(I5,F10.1,4(F10.1,I5))
  802 FORMAT(I5,5X,2F10.3)
  803 FORMAT(8F10.3)
  901 FORMAT(//1X,10A6/1X,10A6//1X,6HSAMPLE,13X,21HPRODUCT MOLE FRACTION
     1,  8X, 25HLOCAL TEMP - AVERAGE TEMP,10X, 7HREACTOR, 2X, 4HFEED,
     2  4X, 4HEXIT, 3X, 4HCONV, 7X,11HSELECTIVITY/
     3   1X, 6HNUMBER, 5X, 2HH2, 5X, 3HCH4, 4X,4HC2H6, 3X, 4HC3H8, 3X,
     4  5HC4H10,  6X, 3HBTM,2X, 3H6IN, 2X, 3H1FT, 2X, 3H2FT, 2X, 3H3FT,
     5           10X, 7HTEMP(F), 2X, 5HRATIO,  4X, 3HCFM, 12X, 4HC1H4,
```

```
     6  2X, 4HC2H6, 2X, 4HC3H8/)
   902 FORMAT(/)
   900 FORMAT(I5, F10.2, F8.2, F7.2, F7.2, F8.2,4X, 5(F5.1),10X,F7.2,
     1   F7.2, F7.2, F7.2, 3X, F6.2,2F6.3)
   965 FORMAT(I3,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.2,F5.1)
   998 FORMAT(1H1)
   999 FORMAT(1X,3F10.4)
       END
          6400 END OF RECORD

    48 81.42      17.9          4 33.8          2 125.          4 87.3
            10.285      10.228      10.212      10.206
     4      0.553       2.78
5.17
    50 81.42      17.4          4 35.4          2 124.7         4 86.9
            10.302      10.245      10.236      10.230
     4      0.553       2.78
5.18
    51 81.42      17.7          4 34.4          2 125.5         4 85.7
            10.300      10.245      10.225      10.200
     4      0.553       2.78
5.21
    52 81.42      17.6          4 34.0          2 127.0         4 86.0
            10.318      10.260      10.240      10.230
     4      0.553       2.78
5.18

    53 81.42      15.9          4 31.1          2 78.2          8 69.6
            10.673      10.620      10.605      10.595
     4      0.553       2.78
5.29
    54 81.42      16.8          4 62.3          1 162.4         4 139.0
            10.700      10.633      10.610      10.610
     4      0.553       2.78
5.16

    55 75.6       25.2          2 39.4          1 38.1         16 47.0
            10.988      10.926      10.910      10.900
     4      0.553       2.78
5.3
    56 75.6       26.4          2 42.9          1 83.0          8 110.
            10.975      10.911      10.915      10.875
     4      0.553       2.78
5.3

    57 82.5       24.0          2 33.2          1 97.7          8 85.5
            11.302      11.246      11.248      11.208
     4      0.553       2.78
5.3
    58 79.15      23.4          2 31.7          1 100.8         8 85.2
11.05       11.315      11.280      11.275      11.235
     4      0.553       2.78
5.3
    59 79.15      25.9          2 33.4          1 109.0         8 86.7
11.05       11.320      11.270      11.275      11.235
     4      0.553       2.78
```

```
5.3
   61 81.42       5.8          2 12.1          1 22.3          4 16.5
10.105      10.310      10.255      10.255      10.210
    4       0.553       2.78
5.3
   63 81.3       18.2          4 34.6          2 137.9         4 81.9
10.08       10.290      10.220      10.230      10.220
    4       0.553       2.78
5.10
   64 81.3       17.2          4 33.8          2 129.3         4 75.6
10.13       10.300      10.240      10.240      10.235
    4       0.553       2.78
5.3

   65 79.7       10.2          4 27.5          2 58.1          4 104.4
10.16       10.255      10.213      10.210      10.210          10.030
    4       0.293       3.22
11.0
   66 79.7       18.1          2 50.7          1 99.4          2 92.5
10.19       10.280      10.235      10.225      10.230
    4       0.293       3.22
11.0

   67 79.6       6.2           4 13.3          2 68.7          8 38.8
9.8         10.290      10.215      10.215      10.150          6.65
    4       0.957       2.43
2.68
   68 79.6       10.7          4 48.3          1 153.          8 62.3
9.9         10.330      10.250      10.250      10.12
    4       0.957       2.43
2.67
   69 79.6       6.2           2 13.3          1 81.2          4 35.2
9.83        10.290      10.20       10.20       10.11           7.48
    4       0.957       2.43
2.68
   70 79.6       10.0          1 10.9          1 61.8          4 54.4
9.90        10.280      10.205      10.205      10.11
    4       0.957       2.43
2.68
   71 79.6       22.5          4 49.5          1 153.          8 121.
9.9         10.285      10.220      10.215      10.12           6.64
    4       0.957       2.43
2.70

   72 80.7       17.0          4 33.5          2 130.6         4 80.6
10.10       10.295      10.222      10.23       10.21           9.41
    4       0.553       2.78
5.3

   73 80.15      31.5          2 47.5          2 88.5          4 100.6
9.77        9.905       9.850       9.840       9.83            9.25
    4       0.553       2.78
5.23
   74 80.15      32.0          2 47.1          2 90.0          4 97.8
9.81        9.942       9.89        9.89        9.87
    4       0.553       2.78
```

```
5.30
   75 80.15      19.1          2 54.7          2 51.2          4 124.4
9.520      9.560      9.530      9.530      9.520                9.38
    4      0.553      2.78
5.15
   76 80.15      17.4          2 51.7          2 90.3          2 119.7
9.525      9.590      9.555      9.550      9.540                9.36
    4      0.553      2.78
5.3
   77 80.15      20.8          2 53.1          2 107.6         2 116.2
9.60       9.655      9.61       9.624      9.615                9.45
    4      0.553      2.78
5.3
   78 80.0       8.5           2 38.9          2 24.2          4 151.7
9.245      9.250      9.220      9.215      9.218                9.30
    4      0.553      2.78
5.09
   79 80.0       13.8          1 32.4          2 80.4          1 145.3
9.25       9.260      9.222      9.23       9.23                 9.29
    4      0.553      2.78
5.3
   80 80.0       15.0          4 33.7          2 99.6          4 93.4
10.28      10.32      10.27      10.28      10.29                9.60
    4      1.01       5.20
5.4
   81 80.0       14.3          4 39.9          2 83.4          4 95.8
10.14      10.180     10.140     10.140     10.16                9.37
    4      1.01       5.20
5.4
   82 80.0       16.5          4 32.3          2 120.          4 79.2
10.17      10.280     10.220     10.230     10.205               9.40
    4      0.553      2.78
5.3
   83 80.0       23.1          2 29.1          1 63.1          16 64.8
11.46      11.595     11.562     11.55      11.48                10.2
    4      0.553      2.78
5.16
   84 80.0       23.0          2 27.5          1 121.5         8 110.7
11.49      11.605     11.575     11.58      11.565
    4      0.553      2.78
5.3
   85 80.0       17.4          4 32.9          2 135.          4 82.7
10.22      10.295     10.243     10.242     10.21                9.15
    4      0.553      2.78
5.17
   86 80.0       16.7          4 32.1          2 123.3         4 82.2
10.220     10.305     10.25      10.22      10.20
    4      0.553      2.78
5.3
-9999
          END OF FILE
```

```
HPHD,T377.
RUN(S)
SETINDF.
REDUCE.
LOAD(INPUT)
LGO.
      6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     MAIN SEARCH PROG. FOR CATALYST ACTIVITY AND INTERCHANGE
C     SHAW JUNE 1972
C
      COMMON/BLK1/VARIND(7,100),VARDEP(4,100),CALDEP(4,100),NRUN(100),
     1               NRUNS,KCOUNT,     H2EMUL(100),HEIGHT(100),Z2(4)
      COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KEMUL,OUT(5),S1,S2,S3,CONV,
     1              X,IPRINT,EMULH2
      COMMON/BLK3/ A(13)
      COMMON /BLK4/ SUMM(100)
      COMMON /BLK5/ SUMN,AKE(7),KM,SMIN
      COMMON /BLK8/ MCYC,MAXK,MKAT,NSTEP,ALPHA,BETA,EPS(7),V(7,7),AFK(7)
      DIMENSION XX(100),XPHI(100),DIF(4),TITLE(12),AVGDIF(4)
C
      READ(5,804) TITLE
      WRITE(6,983) TITLE
      READ(5,500) KM,MCYC,MAXK,MKAT,NSTEP
      READ(5,501)(EPS(I),I=1,KM)
      READ(5,501)(AKE(I),I=1,KM)
      READ(5,501) ALPHA,BETA
      SMIN=1.0E30
      V(1,1) = 1.0
      V(1,2) = 0.0
      V(2,1) = 0.0
      V(2,2) = 1.0
      READ(5,801) NRUNS
      DO 5 I=1,NRUNS
      READ(5,802) NRUN(I),(VARIND(J,I),J=1,7),(VARDEP(J,I),J=1,4),
     1            HEIGHT(I)
      VARDEP(4,I) = 1.0 - VARDEP(4,I)*0.01
    5 WRITE(6,988)NRUN(I),(VARIND(J,I),J=1,7),(VARDEP(J,I),J=1,4),
     1            HEIGHT(I),NRUN(I)
      A(1) = 51000.
      A(3) = 30000.
      A(4) = 16000.
      A(5) = 15.6604
      A(6) = 10.6292
      A(7) = 12.2399
      A(8) = 6.8140
      A(9) = -2.348
      A(10) = -2.151
      A(12) = 4.5208
      A(13) = -2.2115
      A(2) = A(3) + 10000.
      A(11) = A(4) + 10000.
      WRITE(6,996) (A(I),I=1,13)
      A(5) = 10.0**A(5)
      A(6) = 10.0**A(6)
      A(7) = 10.0**A(7)
      A(8) = 10.0**A(8)
      A(12) = 10.0**A(12)
```

```
      WRITE(6,993)
      CALL SEARCH
C
  405 WRITE(6,992)
      SSUMM = 0.0
      DO 408 J=1,4
  408 AVGDIF(J) = 0.0
      DO 410 I=1,NRUNS
  410 SSUMM = SSUMM + SUMM(I)
      DO 450 I=1,NRUNS
      SUMM(I) = SUMM(I)*100.0/SSUMM
      DO 440 J=1,4
      DIF(J) = VARDEP(J,I) - CALDEP(J,I)
  440 AVGDIF(J) = AVGDIF(J) + DIF(J)*DIF(J)
C     WRITE(7,998) K,NRUN(I),(VARIND(J,I),J=1,2),H2EMUL(I),DIF
  450 WRITE(6,997) NRUN(I),(VARIND(J,I),J=1,7),(DIF(J),J=1,4),
     1             HEIGHT(I),NRUN(I),AKE(1),SUMM(I)
      DIV = NRUNS
      DO 455 J=1,4
  455 AVGDIF(J) = AVGDIF(J)/DIV
      WRITE(6,990) (AVGDIF(J),J=1,4)
      EACH = SSUMM/NRUNS
      WRITE(6,999) SSUMM,EACH
C
C     DO 600 I=1,NRUNS
C 600 WRITE(7,777) K,NRUN(I),((VARDEP(J,I),CALDEP(J,I)),J=1,4)
C
      STOP
C
  500 FORMAT(515)
  501 FORMAT(10F8.1)
  777 FORMAT(I2,I3,3X,2F7.3,3X,2F6.3,3X,2F6.3,3X,2F6.1)
  801 FORMAT(2I5,7F10.3)
  802 FORMAT(I3,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.2,F5.1)
  804 FORMAT(12A6)
  983 FORMAT(1H1,2X,12A6/)
  988 FORMAT(I4,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.4,F5.1,I4)
  990 FORMAT(///2X, 8HVARIANCE, 4F20.10)
  992 FORMAT(1H1, 35X, 31HOBSERVED MINUS PREDICTED VALUES//)
  993 FORMAT(////)
  996 FORMAT(2X, 15HTHE A VECTOR IS,4F7.0, 6F9.4, F7.0, 2F9.4)
  997 FORMAT(I4,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.4,F5.1,I4,3X,F7.4,
     1F6.1)
  998 FORMAT(I2,I3,F8.2,F7.2,F6.3,4F9.4)
  999 FORMAT(////2X,21HTHE TOTAL RESIDUAL IS,F17.5/2X, 29HTHE AVERAGE PE
     1R EXPERIMENT IS, F10.5///)
      END
      SUBROUTINE OBJECT
      COMMON/BLK1/VARIND(7,100),VARDEP(4,100),CALDEP(4,100),NRUN(100),
     1            NRUNS,KCOUNT,     H2EMUL(100),HEIGHT(100),Z2(4)
      COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KEMUL,OUT(5),S1,S2,,3,CONV,
     1              X,IPRINT,EMULH2
      COMMON /BLK4/ SUMM(100)
      COMMON /BLK5/ SUMN,AKE(7),KM,SMIN
      DIMENSION CVARIN(3,3), NUSE(3), CVRIN3(3,3)
      DATA CVRIN3 / +5.15875E+00, +1.15851E+00, -1.11377E+01,
     1              +1.15851E+00, +9.48350E+00, -1.89154E+01,
```

```
     2               -1.11377E+01, -1.89154E+01, 6.24919E+02/
C     DATA CVRIN3 / +1.6309E+01, -8.89845 00, +5.3325E+02,
C    1              -8.8984E+00, +1.7375E+01, -4.2757E+02,
C    2              +5.3325E+02, -4.2757E+02, +2.3489E+04/
      DATA CVARIN / 1339.2, 4290.9, -206.6, 4290.9, 31645.9, -5883.7,
     1   -206.6, -5883.7, 8229.8 /
      DATA NUSE / 1, 3, 4 /
      CACT = AKE(1)
      X = AKE(2)
      RATIO = 1.0
      SUMN = 0.0
      DO 100 I=1,NRUNS
      HO = HEIGHT(I)
      T = VARIND(1,I)
      FLOW = VARIND(2,I)
      FEED(1) = VARIND(3,I)
      FEED(2) = VARIND(4,I)
      FEED(3) = VARIND(5,I)
      FEED(4) = VARIND(6,I)
      FEED(5) = VARIND(7,I)
C     CALL KATWEN(0)
      CALL KATWEN(1)
      H2EMUL(I) = EMULH2
      CALDEP(1,I) = S1
      CALDEP(2,I) = S2
      CALDEP(3,I) = S3
      CALDEP(4,I) = 1.0 - CONV*0.01
      SUMM(I) = 0.0
      DO 40 J1=1,3
      J = NUSE(J1)
      DO 40 JJ1=1,3
      JJ = NUSE(JJ1)
      ERR = CVRIN3(J1,JJ1)*(VARDEP(J,I)-CALDEP(J,I))*(VARDEP(JJ,I)-CALDE
     1P(JJ,I))
C     ERR = CVARIN(J1,JJ1)*(VARDEP(J,I)-CALDEP(J,I))*(VARDEP(JJ,I)-CALDE
C    1P(JJ,I))
      IF(J1.EQ.JJ1)  Z2(J1) = ERR
   40 SUMM(I) = SUMM(I) + ERR
      SUMN = SUMN + SUMM(I)
      QQ = 1.0E+03*EXP(-0.5*SUMM(I))
C     QQ = 1.0E+13*EXP(-0.5*SUMM(I))
      RATIO = RATIO*QQ
C     WRITE(6,998) NRUN(I),(VARIND(J,I),J=1,7),(CALDEP(J,I),J=1,4),
C    1             HEIGHT(I),NRUN(I),X,SUMM(I),(Z2(J),J=1,4),TT
  100 CONTINUE
      WRITE(6,999) X,CACT,SUMN,RATIO
      RETURN
  998 FORMAT(I4,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.4,F5.1,I4,F6.3,
     14F9.2,F2.0,F5.2)
  999 FORMAT(1X,2F13.7,2E20.8/)
      END
        6400 END OF RECORD
        6400 END OF RECORD
 KATWEN(1) FOR INTER AND CACT  * ORC KIN. PAR. ERRORS FOR WEIGHTING
     2    4    6   12
0.01    -0.005
1.32    0.25
```

1.2 0.8

32

84	543.30	6.31	0.00	0.0000	0.0000	.1587	.8413	3.604	.115	.055	83.85	77.0
1	483. 3	6.06	0.00	0.0000	0.0000	.1335	.8665	2.844	.255	.215	52.57	77.0
5	498.36	9.03	0.00	0.0000	0.0000	.1014	.8986	2.928	.217	.213	53.58	77.0
7	484.23	6.06	0.00	0.0000	0.0000	.1335	.8665	2.858	.246	.217	52.76	77.0
9	468.05	6.06	0.00	0.0000	0.0000	.2021	.7979	3.092	.208	.164	50.00	77.0
11	483.16	6.05	0.00	0.0000	0.0000	.1335	.8665	2.834	.259	.216	53.07	77.0
12	499.25	9.08	0.00	0.0000	0.0000	.1986	.8014	3.513	.114	.087	59.04	77.0
15	483.12	6.05	0.00	0.0000	0.0000	.1335	.8665	2.816	.268	.216	53.23	77.0
18	499.78	6.07	0.00	0.0000	0.0000	.1043	.8957	2.966	.245	.182	60.77	77.0
20	484.78	6.07	0.00	0.0000	0.0000	.1335	.8665	2.857	.247	.217	54.35	77.0
22	468.65	9.14	0.00	0.0000	0.0000	.1005	.8995	1.821	.296	.529	31.22	77.0
24	483.21	6.05	0.00	0.0000	0.0000	.1335	.8665	2.812	.277	.211	53.86	77.0
25	499.85	6.22	0.00	0.0000	0.0000	.2036	.7964	3.526	.115	.082	65.30	77.0
28	482.70	6.05	0.00	0.0000	0.0000	.1335	.8665	2.811	.264	.220	53.49	77.0
30	468.06	9.11	0.00	0.0000	0.0000	.2015	.7985	2.534	.279	.303	42.45	77.0
31	484.01	6.06	0.00	0.0000	0.0000	.1335	.8665	2.866	.264	.202	54.48	77.0
34	467.88	6.17	0.00	0.0000	0.0000	.1031	.8969	2.126	.216	.481	37.21	77.0
45	484.25	6.06	0.00	0.0000	0.0000	.1335	.8665	2.770	.282	.222	53.86	77.0
46	500.07	6.16	0.00	0.0000	0.0000	.1335	.8665	3.503	.080	.112	65.62	77.0
52	485.98	5.95	0.00	0.0000	0.0000	.1618	.8382	2.846	.266	.207	52.51	77.0
54	502.34	6.05	0.00	0.0000	0.0000	.1623	.8377	3.087	.215	.161	61.73	77.0
56	515.07	6.13	0.00	0.0000	0.0000	.1587	.8413	3.299	.177	.116	66.10	77.0
59	529.60	6.22	0.00	0.0000	0.0000	.1587	.8413	3.501	.140	.073	75.38	77.0
64	484.89	5.94	0.00	0.0000	0.0000	.1587	.8413	2.872	.258	.204	55.93	77.0
66	484.58	6.26	0.00	0.0000	0.0000	.0833	.9167	2.407	.296	.334	48.75	77.0
72	484.33	5.94	0.00	0.0000	0.0000	.1587	.8413	2.889	.254	.201	54.45	77.0
74	469.62	5.85	0.00	0.0000	0.0000	.1587	.8413	2.400	.288	.342	44.97	77.0
77	457.88	5.77	0.00	0.0000	0.0000	.1587	.8413	1.936	.252	.520	33.75	77.0
79	440.86	5.67	0.00	0.0000	0.0000	.1587	.8413	1.571	.182	.688	15.80	77.0
81	480.77	11.02	0.00	0.0000	0.0000	.1563	.8438	2.467	.285	.321	42.92	77.0
82	484.45	5.94	0.00	0.0000	0.0000	.1587	.8413	2.847	.264	.208	53.14	77.0
86	484.93	5.94	0.00	0.0000	0.0000	.1587	.8413	2.867	.262	.203	52.71	77.0

END OF FILE

```
HPHD,T10.                                                    IAN S.
RUN(S)
SETINDF.
REDUCE.
LGO.
'        6400 END OF RECORD
      PROGRAM TST (INPUT,OUTPUT,PUNCH,TAPE5=INPUT,TAPE6=OUTPUT,TAPE7=PUN
     1CH)
C     FLUIDIZED BED DATA ANALYSIS RUNS 101 - 126
C     A(1) AND NATTEN(1) ARE THE INTEGRATION AND THE ATTENUATION FOR THE
C        C2H6 PEAK
C     A(2) AND NATTEN(2) FOR C3H8 PEAK
C     A(3) AND NATTEN(3) FOR CH4 PEAK
C     A(4) AND NATTEN(4) FOR C4H10 PEAK
C
      DIMENSION TITLE(20), A(4), NATTEN(4), X(5),  CALIB(4), TEMP(4),
     1  EMF(4), TDIF(5),TCEROR(4), FEED(5)
      DIMENSION RAT(2,26)
      DATA CALIB/ 1.483, 1.839, 1.020, 2.131 /
      DATA TCEROR/ 0.054, 0.038, 0.025, 0.041 /
      WRITE(6,998)
      HE+GHT = 47.6
      READ(5,800) TITLE
      WRITE(6,901) TITLE
C
      DO 250 NCOUNT =1,26
   10 READ(5,801) NSAMPL,FLOWH2,FLOWHC,(A(I),NATTEN(I),I=1,4)
      IF(NSAMPL.LT.0) GO TO 300
   15 SUM = 0.0
      DO 30 J=1,4
      ATTEN = NATTEN(J)
      X(J) = (A(J)*ATTEN/CALIB(J))*100.0*(CALIB(4)/8498.)
   30 SUM = SUM + X(J)
      X(5) = 100.0 - SUM
C
C     EMF  1-4 ARE THE MILLIVOLTS OF THE THERMOCOUPLES AT
C        1 BOTTOM OF THE REACTOR
C        2 6 INCHES UP THE REACTOR
C        3 1 FT UP THE REACTOR
C        4 2 FT UP THE REACTOR
C     EMF READ AS DATA ON 0 - 100 SCALE ON RECORDER AND THEN CONVERTED
      READ(5,803) NN,(EMF(J),J=1,4)
      DO 60 J=1,4
   60 EMF(J) = 10.281 - (50.0-EMF(J))*(0.397/20.0)
      DO 100 J=1,4
      EMF(J) = EMF(J) - TCEROR(J)
  100 TEMP(J) = 480.00 - (10.110-EMF(J))*(20.00/0.457)
      TAVG = (TEMP(1)*3.+TEMP(2)*6.+TEMP(3)*12.)/21.
      DO 120 J=1,4
  120 TDIF(J) = TEMP(J) - TAVG
C
C     FLOWH2 IS THE H2 FEED RATE IN SCFM
C     FLOWHC IS THE PARAFIN FEED RATE IN SCFM
      REAC = X(1)*0.5 + X(2)*0.75 + X(3)*0.25
      CONV = 100.*REAC/(REAC+X(4))
      AAA = (X(3) + X(1)*2. + X(2)*3. + X(4)*4.)/4.
      X1 = X(3)/REAC
      X2 = X(1)/REAC
      X3 = X(2)/REAC
```

```
      RAT(1,NCOUNT) = FLOWH2/FLOWHC
      C4 = X(4) + 0.25*X(3) + 0.5*X(1) + 0.75*X(2)
      RAT(2,NCOUNT) = (100.0-C4)/C4
      RATIO = RAT(1,NCOUNT)
      FEED4 = 100.0/(RAT(1,NCOUNT) + 1.0)
      FEEDH = 100.0 - FEED4
      REAC = FEED4*CONV/100.0
      X(4) = FEED4 - REAC
      X(1) = REAC*X2
      X(2) = REAC*X3
      X(3) = REAC*X1
      X(5) = 100.0 - (X(1)+X(2)+X(3)+X(4))
      FLOW = (FLOWHC+FLOWH2)*(460.+TAVG)/530.
      FEED(1) = 0.0
      FEED(2) = 0.0
      FEED(3) = 0.0
      FEED(4) = FEED4/(FEED4+FEEDH)
      FEED(5) = 1.0 - FEED(4)
C
C     WRITE(6,900) NSAMPL,  X(5),X(3),X(1),X(2),X(4), (TDIF(I),I=1,5),
C    1             TAVG, RATIO, FLOW, CONV, X1,X2,X3
C     WRITE(7,965) NSAMPL,TAVG,FLOW,FEED,X1,X2,X3,CONV,HEIGHT
  250 CONTINUE
  300 WRITE(6,998)
C
  800 FORMAT(10A6/10A6)
  801 FORMAT(I3,3X,F5.3,2X,F5.3,2X,4(F5.1,1X,I2,2X))
  802 FORMAT(I5,5X,2F10.3)
  803 FORMAT(I3,7X,4F10.1)
  901 FORMAT(//1X,10A6/1X,10A6//1X,6HSAMPLE,13X,21HPRODUCT MOLE FRACTION
     1,  8X, 25HLOCAL TEMP - AVERAGE TEMP,10X, 7HREACTOR, 2X, 4HFEED,
     2  4X, 4HEXIT, 3X, 4HCONV, 7X,11HSELECTIVITY/
     3   1X, 6HNUMBER, 5X, 2HH2, 5X, 3HCH4, 4X,4HC2H6, 3X, 4HC3H8, 3X,
     4  5HC4H10,  6X, 3HBTM,2X, 3H6IN, 2X, 3H1FT, 2X, 3H2FT, 2X, 3H3FT,
     5            10X, 7HTEMP(F), 2X, 5HRATIO,  4X, 3HCFM, 12X, 4HC1H4,
     6  2X, 4HC2H6, 2X, 4HC3H8/)
  902 FORMAT(/)
  900 FORMAT(I5, F10.2, F8.2, F7.2, F7.2, F8.2,4X, 5(F5.1),10X,F7.2,
     1   F7.2, F7.2, F7.2, F7.2, 3X, F6.2,2F6.3)
  965 FORMAT(I3,F7.2,F6.2,F5.2,4F7.4,F6.3,2F5.3,F7.2,F5.1)
  998 FORMAT(1H1)
  999 FORMAT(1X,2F10.4)
      END
        6400 END OF RECORD
  F.B.R. DATA JULY 1972

101    4.120  0.900     9.2 08    31.5 02    73.4 08    19.4 32
101        66.         65.5       64.1       59.
102    4.140  1.010     2.9 08    16.3 01    22.2 08    31.9 08
102        61.6        63.6       61.9       57.5
103    4.140  1.010    13.9 04    19.1 04   139.6 08    63.1 16
103        65.         64.5       64.        61.
104    4.140  1.010    14.1 08    19.7 04   130.0 08    61.2 16
104        61.5        64.8       63.2       60.
105    2.736  0.684     4.3 08    15.2 08    46.5 04    65.4 16
105        20.3        20.2       18.3       15.
106    2.736  0.684     5.5 08    41.0 04    56.5 04    45.2 32
```

```
106       19.5        18.2        16.5        12.5
107   2.736  0.684    10.2 04     36.6 04     49.9 04     82.1 16
107       19.2        17.4        15.5        12.
108   5.145  1.195    15.0 08     11.6 08    123.6 08     64.6 16
108       64.5        66.         62.4        62.
109   5.145  1.195     8.9 08     13.3 04     80.5 08     41.8 16
109       65.2        67.         65.3        64.5
110   5.145  1.195    15.2 08     23.3 04    137.8 08    128.8 08
110       65.3        67.8        64.9        63.6
111   2.910  0.710    15.6 08     12.2 08     79.2 16     49.9 16
111       62.5        59.4        57.5        49.5
112   2.910  0.710    17.4 08     25.0 04    171.7 08    106.0 08
112       63.8        59.8        57.8        48.
113   4.736  1.184    15.4 08     23.0 04    141.0 08     65.9 16
113       61.9        63.4        61.         58.5
114   4.736  1.184    15.6 08     48.6 02    144.9 08    136.1 08
114       60.8        61.7        60.         59.
115   2.876  0.514    16.5 08     28.5 04    111.2 08     38.2 16
115       68.         65.4        63.7        55.5
116   2.876  0.514    31.2 04     58.8 02    109.0 08     80.8 08
116       64.7        64.         60.9        52.
117   4.560  1.140    15.4 08     21.5 04    139.3 08    125.5 08
117       62.2        62.4        60.         58.
118   4.560  1.140    10.0 04     15.3 02     87.7 04     88.6 04
118       62.7        62.9        61.2        58.
119   3.115  0.725    17.3 08     27.5 04    151.4 08    106.6 08
119       59.5        58.         56.1        48.
120   3.115  0.725    16.8 08     56.0 02    148.0 08    107.1 08
120       59.3        58.4        56.         48.
121   5.100  1.330    15.6 08     31.9 04    109.3 08     68.8 16
121       54.         54.         52.         50.5
122   5.100  1.330    15.8 08     31.5 04    112.4 08     69.0 16
122       54.         55.5        53.         51.5
123   2.673  0.637    15.7 08     27.3 04    134.0 08     96.0 08
123       54.5        52.         50.         35.
124   2.673  0.637    17.9 08     29.9 04    150.0 08    105.1 08
124       56.         53.         51.5        39.5
125   2.736  0.684    11.7 04     42.8 04     64.2 04     90.0 16
125       19.7        18.5        16.6        13.0
126   2.736  0.684    22.4 02     41.5 04    121.5 02     90.3 16
126       19.         17.8        16.         12.8
          END OF FILE
```

```
      SUBROUTINE KATWEN(KATBUB)
C     KATO AND WEN MODEL FOR FLUIDIZED BED REACTOR
C     CHEM. ENG. SCI.,PG. 1351 , VOL. 24,1969.
C     MODIFIED SHAW MARCH 1972
C     IF KATBUB IS  0  NO BUBBLE REACTION
C     IF KATBUB IS  1  BUBBLE REACTION
      COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KLMUL,OUT(5),S1,S2,S3,CONV,
     1              XFAC,IPRINT,EMULH2
      COMMON/BLK3/ A(13)
      DIMENSION VC(20),VE(20),WFB(20),WFB2(20),RKBC(20),RKP1C(20),
     1RKE2C(20),WKBVE(20),WKBVC(20),WKPE(20),WKPB(20),CH1(20),CH(20)
C
      DBMAX = 10.0
      AREA=324.
      EPSO = 0.557
      EPB = 0.449
      HMF = HO*1.043
      UMF = 0.77
      UEMUL = UMF
      HN = 20.
      TEMP = (T-32.0)*(5.0/9.0) + 273.1
      U = FLOW*1.46042
      RHOS = 0.957
      DP = 0.015
C     PRELIMINARY CALCULATIONS
      NPANIC = 0
      NITER=1
      GRAV=980.
      RT=82.06*TEMP
      RTT=1.99*TEMP
      VF=AREA*U
      RKBE=CACT*A(5)*EXP(-A(1)/RTT)
      RKP1E=CACT*A(6)*EXP(-A(2)/RTT)
      RKP2=1.0+A(7)*EXP(-A(3)/RTT)
      RKE=1.0+A(8)*EXP(-A(4)/RTT)
      RKBE=RT*RKBE
      RKP1E=RT*RKP1E
      RKE2E = RT*CACT*A(12)*EXP(-A(11)/RTT)
      UDIFF=U-UMF
      DOM=(1.4*RHOS*DP*U)/UMF
      DO =. 0.3261*(UDIFF*HN)**0.4
      HDBMAX = (DBMAX-DO)*UMF/(1.4*RHOS*DP*U)
      DBMEAN = DBMAX - 1.0
    2 G2=0.711*(GRAV*DBMEAN)**0.50
      DBSAVE = DBMEAN
      HT = HMF*(1.0+(U-UMF)/G2)
      DBMEAN = ((DBMAX-DO)*0.5*HDBMAX + DBMAX*(HT-HDBMAX))/HT
      IF(ABS(DBSAVE-DBMEAN).GT.0.0001)  GO TO 2
      EPS = EPSO
      VOIDC = (1.0-EPS)/(1.0-EPB)
      G3=2.0+DOM
      G4=2.0-DOM
      IF(KATBUB.EQ.1)  G5 = (8.0*AREA*(HT-HO))/(3.1416*HT)
      IF(KATBUB.EQ.0)  G5 = (6.0*AREA*(HT-HO))/(3.1416*HT)
      G6=(HO*(1.0-EPSO))/HT
      G7=(HO*(1.0-EPSO))/(2.0*HT*(HT-HO))
C     CALCULATE MECHANICAL CHARACTERISTICS OF THE REACTOR
      HTC=0.0
      G9=UMF/EPS
```

```
      NSTAGE=0
      DO 90 I=1,20
      DHT = (2.0*DO*G3**(I-1))/(G4**I)
      IF(DHT.GE.DBMAX) DHT = DBMAX
      HTC=HTC+DHT
      DBUB = DHT
      IF(HTC.LT.HT)  GO TO 70
      DHT = HT - (HTC-DHT)
      NSTAGE=I
   70 BUBN = (G5/(DBUB*DBUB))*(DHT/DBUB)
      UBR=0.711*(GRAV*DBUB)**0.50
      G8 = (BUBN*3.1416*DBUB*DBUB*DBUB)/6.0
      G10=UBR-G9
      IF(KATBUB.EQ.1)  VC(I) = G8*((3.0*G9)/G10+0.250)
      IF(KATBUB.EQ.0)  VC(I) = (G8*3.0*G9)/G10
      VB=(G8*(UBR+2.0*G9))/(UBR-G9)
      VE(I) = AR5A*DHT - VB
      FO = XFAC*(11.0/DBUB)
      FON=(FO*(UBR-G9))/(UBR+2.0*G9)
      RKBC(I)=RK2E*VOIDC
      RKP1C(I)=RKP1E*VOIDC
      RKE2C(I) = RKE2E*VOIDC
      WFB(I)=FON*VB
      WFB2(I)=WFB(I)*WFB(I)
      WKBVE(I)=RKBC(I)*VE(I)
      WKBVC(I)=RKBC(I)*VC(I)
      WKPE(I)=(RKP1C(I)*VE(I))/RKP2
      WKPB(I)=(RKP1C(I)*VC(I))/RKP2
C     WRITE(6,997) I,DHT,HTC,EPS,BUBN,VC(I),VB,VE(I),FON
      IF(NSTAGE.GE.1) GO TO 110
      IF(I.NE.20)  GO TO 90
      WRITE(6,998)
      STOP
   90 CONTINUE
C
C     ITERATIONS ON MASS BALANCES OF EACH STAGE
  110 DO 280 K=1,NSTAGE
      IF(K.GT.1)  GO TO 140
      F1 = VF*FEED(1)
      F2 = VF*FEED(2)
      F3 = VF*FEED(3)
      F4 = VF*FEED(4)
      F5 = VF*FEED(5)
      PB5 = FEED(5)
      PE5 = FEED(5)
      GOTO150
  140 F4=VF*PB4
      F5=VF*PB5
      F1=VF*PB1
      F2=VF*PB2
      F3=VF*PB3
  150 IF(NITER.GT.1)  PB5 = CHI(K)
      NNN=1
      NPNK=0
      PE5=PE5
      GOTO270
  190 PDIFF=PE5-PCALC
```

```
      IF(NPNK-1)195,211,214
  195 IF(PDIFF.LE.0.0)  GO TO 210
      NNN = 1
      NPNK=1
      GOTO212
  210 NNN=1
      NPNK=2
      GOTO215
  211 IF(PDIFF.LE.0.0) GO TO 213
  212 PE5R=PE5
      PDIFR=PDIFF
      PE5 = PE5 - 0.06
      IF(PE5.GT.0.0)  GO TO 270
      NPANIC = NPANIC + 1
      PE5 = 0.0001
      IF(NPANIC.LT.10)  GO TO 270
      WRITE(6,996)
      CONV = 0.0
      S1 = 0.0
      S2 = 0.0
      S3 = 0.0
      EMULH2 = 0=0
      DO 205 J=1,5
  205 OUT(J) = 0.0
      RETURN
  213 PDIFL=PDIFF
      PE5L=PE5
      GOTO260
  214 IF(PDIFF.GT.0.0)  GO TO 216
  215 PE5L=PE5
      PDIFL=PDIFF
      PE5=PE5+0.01
      GOTO270
  216 PDIFR=PDIFF
      PE5R=PE5
      GOTO260
  220 PDIFF=PE5-PCALC
      IF(ABS(PDIFF).LE.1.0E-8)  GO TO 280
      PE5L=PE5R
      PDIFL=PDIFR
      PE5R=PE5
      PDIFR=PDIFF
  260 PE5=(PE5L*PDIFR-PE5R*PDIFL)/(PDIFR-PDIFL)
      NNN=2
      CALCULATE KINETICS AND COMPOSITION CHANGE IN EACH STAGE
  270 PI1=PB5**A(9)
      PI2=PE5**A(9)
      PI3=PB5**A(10)
      PI4=PE5**A(10)
      PI5 = PB5**A(13)
      PI6 = PE5**A(13)
      Z1=WFB(K)-WFB2(K)/(WFB(K)+WKBVE(K)*PI2)
      Z2=Z1+WKBVC(K)*PI1+VF
      PB4=F4/Z2
      Z3=WFB(K)+WKBVF(K)*PI2
      PE4=(WFB(K)*PB4)/Z3
      ZK1=0.9*RKBC(K)*PB4*PI1
```

```
      RB4=ZK1/0.9
      ZK2=0.9*RKBC(K)*PE4*PI2
      RE4=ZK2/0.9
      ZK4=WFB(K)+WKPF(K)*PI4
      ZK5=(VE(K)*ZK2)/(RKP2*ZK4)
      Z4=F3+WFB(K)*ZK5+(VC(K)*ZK1)/RKP2
      Z5=WFB(K)-WFB2(K)/(ZK4)
      Z6=WKPB(K)*PI3+VF
      PB3=Z4/(Z5+Z6)
      PE3=(WFB(K)*PB3)/ZK4+ZK5
      RB3=(RKP1C(K)*PB3*PI3-ZK1)/RKP2
      RE3=(RKP1C(K)*PE3*PI4-ZK2)/RKP2
      ZIAN1 =   (VE(K)*(1.1*RE4+RE3))/RKE
      ZIAN2 =   (VC(K)*(1.1*RB4+RB3))/RKE
      ZIAN3 = VC(K)*RKE2C(K)*PI5/RKE
      WKEE  = VE(K)*RKE2C(K)*PI6/RKE
      ZIAN4 = WFB(K) + WKEE
      PB2 =(WFB(K)*ZIAN1/ZIAN4+ZIAN2+F2)/(WFB(K)-WFB2(K)/ZIAN4+ZIAN3+VF)
      PE2 =  (WFB(K)*PB2+ZIAN1)/ZIAN4
      RB2 =  -(1.1*RB4+RB3-RKE2C(K)*PB2*PI5)/RKE
      RE2 =  -(1.1*RE4+RE3-RKE2C(K)*PE2*PI6)/RKE
      RB1=-(4.0*RB4+3.0*RB3+2.0*RB2)
      RE1=-(4.0*RE4+3.0*RE3+2.0*RE2)
      PB1=(F1-VE(K)*RE1-VC(K)*RB1)/VF
      PE1=(WFB(K)*PB1-VE(K)*RE1)/WFB(K)
      RB5=3.0*RB4+2.0*RB3+RB2
      RE5=3.0*RE4+2.0*RE3+RE2
      ZK8=(VE(K)*RE5)/WFB(K)
      PCALC IS PE5
      PCALC=(F5-WFB(K)*ZK8-VC(K)*RB5-VF*ZK8)/VF
      CH(K)=ZK8+PE5
      PB5=CH(K)
      IF(NNN-1)190,190,220
  200 CONTINUE
      CHECK CONVERGENCE ON HYDROGEN PARTIAL PRESSURES IN BUBBLE PHASE
      IF(NITER.EQ.1)  GO TO 340
      DMAX=ABS(CH9(1)-CH(1))
      DO330I=2,NSTAGE
      DDIF=ABS(CHI(I)-CH(I))
  330 IF(DDIF.GT.DMAX)  DMAX = DDIF
      IF(DMAX.LE.1.0E-6)  GO TO 380
  340 DO350I=1,NSTAGE
  350 CHI(I)=CH(I)
      NITER=NITER+1
      IF(NITER.LT.6)  GO TO 110
      WRITE(6,999)
      STOP


  380 OUT(1) = PB1
      OUT(2) = PB2
      OUT(3) = PB3
      OUT(4) = PB4
      OUT(5) = PB5
      IF(FEED(4).EQ.0.0)  GO TO 390
      F = FEED(4)
      DD = FEED(4) - PB4
```

```
      S3 = OUT(3)/DD
      S2 = OUT(2)/DD
      GO TO 410
  390 IF(FEED(3).EQ.0.0)  GO TO 400
      F = FEED(3)
      DD = FEED(3) - PB3
      S3 = 0.0
      S2 = OUT(2)/DD
      GO TO 410
  400 F = FEED(2)
      DD = FEED(2) - PB2
      S3 = 0.0
      S2 = 0.0
  410 CONV = 100.0*DD/F
      S1 = OUT(1)/DD
      EMULH2 = PE5
      RETURN
  996 FORMAT(2X, 40HEMULSION CONC OF H2 KEEPS GOING NEGATIVE)
  997 FORMAT(1X,I3,F6.2,F7.2,F7.4,F6.2,4E9.2)
  998 FORMAT(2X, 46HNOT ENOUGH DIMENSIONS FOR THE NUMBER OF STAGES)
  999 FORMAT(//6X,42HBED DID NOT CONVERGE IN MAXIMUM ITERATIONS)
      END



      SUBROUTINE KWMIX
C        KATO AND WEN WITH EMULSION PERFECTLY MIXED
C     CHEM. ENG. SCI.,PG. 1351 , VOL. 24,1969.
C     MODIFIED SHAW MARCH 1972
C     IF KATBUB IS  0  NO BUBBLE REACTION
C     IF KATBUB IS  1  BUBBLE REACTION
      COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KEMUL,OUT(5),S1,S2,S3,CONV,
     1              XFAC,IPRINT,EMULH2
      COMMON/BLK3/ A(13)
      COMMON/BLK7/ PE(5)
      DIMENSION VC(20),VE(20),WFB(20),WFB2(20),RKBC(20),RKP1C(20),
     1RKE2C(20),WKBVE(20),WKBVC(20),WKPE(20),WKPB(20),CHI(20),CH(20)
      DIMENSION PO(5),BB(5),PB(5),OPE(5)

      LOOP = 0
      XSAVE = XFAC
      XFAC = XFAC*1.9
      CALL ORCMIX
      XFAC = XSAVE
      DRMAX = 10.0
      AREA=324.
      EPSO = 0.557
      EPB = 0.449
      HMF = HO*1.043
      UMF = 0.77
      UEMUL = UMF
      HN = 20.
      TEMP = (T-32.0)*(5.0/9.0) + 273.1
      U = FLOW*1.46042
      RHOS = 0.957
      DP = 0.015
C     PRELIMINARY CALCULATIONS
      NPANIC = 0
```

```
      NITER=1
      GRAV=980.
      RT=82.06*TEMP
      RTT=1.99*TEMP
      VF=AREA*U
      RKBE=CACT*A(5)*EXP(-A(1)/RTT)
      RKP1E=CACT*A(6)*EXP(-A(2)/RTT)
      RKP2=1.0+A(7)*EXP(-A(3)/RTT)
      RKE=1.0+A(8)*EXP(-A(4)/RTT)
      RKBF=RT*RKBF
      RKP1E=RT*RKP1E
      RKE2E = RT*CACT*A(12)*EXP(-A(11)/RTT)
      UDIFF=U-UMF
      DOM=(1.4*RHOS*DP*U)/UMF
      DO = 0.3261*(UDIFF*HN)**0.4
      HDBMAX = (DBMAX-DO)*UMF/(1.4*RHOS*DP*U)
      DBMEAN = DBMAX - 1.0
    2 G2=0.711*(GRAV*DBMEAN)**0.50
      DBSAVE = DBMEAN
      HT = HMF*(1.0+(U-UMF)/G2)
      DBMEAN = ((DBMAX-DO)*0.5*HDBMAX + DBMAX*(HT-HDBMAX))/HT
      IF(ABS(DBSAVE-DBMEAN).GT.0.0001)  GO TO 2
      EPS = EPSO
      VOIDC = (1.0-EPS)/(1.0-EPB)
      G3=2.0+DOM
      G4=2.0-DOM
      G5 = (6.0*AREA*(HT-HO))/(3.1416*HT)
      G6=(HO*(1.0-EPSO))/HT
      G7=(HO*(1.0-EPSO))/(2.0*HT*(HT-HO))
C     CALCULATE MECHANICAL CHARACTERISTICS UP THE REACTOR
      HTC=0.0
      G9=UMF/EPS
      NSTAGE=0
      VEMUL = 0.0
      XFLOW = 0.0
      DO 90 I=1,20
      DHT = (2.0*DO*G3**(I-1))/(G4**I)
C
C     CONSTANT BUBBLE SIZE UP THE REACTOR
C     DHT = DBMEAN
C
      IF(DHT.GE.DBMAX) DHT = DBMAX
      HTC=HTC+DHT
      DBUB = DHT
      IF(HTC.LT.HT)  GO TO 70
      DHT = HT - (HTC-DHT)
      NSTAGE=I
      SAVDHT = DHT
   70 BUBN = (G5/(DBUB*DBUB))*(DHT/DBUB)
      UBR=0.711*(GRAV*DBUB)**0.50
      G8 = (BUBN*3.1416*DBUB*DBUB*DBUB)/6.0
      G10=UBR-G9
      VC(I) = (G8*3.0*G9)/G10
C
C     NO SOLIDS IN BUBBLE
      VC(I) = 0.0
C
```

```
      VB=(G8*(UBR+2.0*G9))/(UBR-G9)
      VE(I) = AREA*DHT - VB
      FO = XFAC*(1.0/DBUB)
      FON=(FO*(UBR-G9))/(UBR+2.0*G9)
      RKBC(I)=RKBE*VOIDC
      RKP1C(I)=RKP1L*VOIDC
      RKF2C(I) = RKF2E*VOIDC
      WFB(I)=FON*VB
      XFLOW = XFLOW + WFB(I)
      WFB2(I)=WFB(I)*WFB(I)
      WKBVE(I)=RKBC(I)*VE(I)
      WKBVC(I)=RKBC(I)*VC(I)
      WKPE(I)=(RKP1C(I)*VE(I))/RKP2
      WKPB(I)=(RKP1C(I)*VC(I))/RKP2
      WRITE(6,997) I,DHT,HTC,LPS,BUBN,VC(I),VB,VE(I),FON
      VEMUL = VEMUL + VE(I)
      IF(NSTAGE.GE.1) GO TO 110
      IF(I.NE.20)  GO TO 90
      WRITE(6,998)
      STOP
   90 CONTINUE
C
C     ITERATIONS ON MASS BALANCES OF EACH STAGE
  110 CONTINUE
      AREAEM = VE(NSTAGE)/SAVDHT
      DO 115 I=1,5
  115 BB(I) = AREAEM*UEMUL*FEED(I)
      DO 300 K=1,NSTAGE
      IF(K.GT.1)  GO TO 140
      F1 = VF*FEED(1)
      F2 = VF*FEED(2)
      F3 = VF*FEED(3)
      F4 = VF*FEED(4)
      F5 = VF*FEED(5)
      PB(5) = FEED(5)
      GOTO150
  140 F5 = VF*PB(5)
      F4 = VF*PB(4)
      F3 = VF*PB(3)
      F2 = VF*PB(2)
      F1 = VF*PB(1)
  150 IF(NITER.GT.1)  PB(5) = CHI(K)
      NNN=1
      NPNK=0
      PF5 = PB(5)
      GOTO270
  190 PDIFF=PF5-PCALC
      IF(NPNK-1)195,211,214
  195 IF(PDIFF.LE.0.0)  GO TO 210
      NNN = 1
      NPNK=1
      GOTO212
  210 NNN=1
      NPNK=2
      GOTO215
  211 IF(PDIFF.LE.0.0) GO TO 213
  212 PF5R=PF5
```

```
      PDIFR=PDIFF
      PE5 = PE5 - 0.05
      IF(PE5.GT.0.0)  GO TO 270
      NPANIC = NPANIC + 1
      PE5 = 0.0001
      IF(NPANIC.LT.10)  GO TO 270
      WRITE(6,996)
      CONV = 0.0
      S1 = 0.0
      S2 = 0.0
      S3 = 0.0
      EMULH2 = 0.0
      DO 205 J=1,5
  205 OUT(J) = 0.0
      RETURN
  213 PDIFL=PDIFF
      PE5L=PE5
      GOTO260
  214 IF(PDIFF.GT.0.0)  GO TO 216
  215 PE5L=PE5
      PDIFL=PDIFF
      PE5=PE5+0.01
      GOTO270
  216 PDIFR=PDIFF
      PE5R=PE5
      GOTO260
  220 PDIFF=PE5-PCALC
      IF(ABS(PDIFF).LE.1.0E-7)  GO TO 280
      PE5L=PE5R
      PDIFL=PDIFR
      PE5R=PE5
      PDIFR=PDIFF
  260 PE5=(PE5L*PDIFR-PE5R*PDIFL)/(PDIFR-PDIFL)
      NNN=2
C     CALCULATE KINETICS AND COMPOSITION CHANGE IN EACH STAGE
  270 PB(5) = PE5
      PI1 = PB(5)**A(9)
      PI3 = PB(5)**A(10)
      PI5 = PB(5)**A(13)
      PB(4) = (F4+WFB(K)*PE(4))/(WFB(K)+VF+WKBVC(K)*PI1)
      ZK1 = 0.9*RKBC(K)*PB(4)*PI1
      RB4 = ZK1/0.9
      PB(3) = (F3+WFB(K)*PE(3)+VC(K)*ZK1/RKP2)/(WFB(K)+VF+WKPB(K)*PI3)
      RB3 = (RKP1C(K)*PB(3)*PI3-ZK1)/RKP2
      ZIAN3 = VC(K)*RKE2C(K)*PI5/RKE
      PB(2) = (F2+WFB(K)*PE(2)+VC(K)*(1.1*RB4+RB3)/RKE)/
     1        (WFB(K)+VF+ZIAN3)
      RB2 = -(1.1*RB4+RB3-RKE2C(K)*PB(2)*PI5)/RKE
      RB1=-(4.0*RB4+3.0*RB3+2.0*RB2)
      PB(1) = (F1-VC(K)*RB1+WFB(K)*PL(1))/(VF+WFB(K))
      RB5=3.0*RB4+2.0*RB3+RB2
      PB(5) = (F5-VC(K)*RB5+WFB(K)*PE(5))/(VF+WFB(K))
      CH(K) = PB(5)
      PCALC = PB(5)
      IF(NNN-1)190,190,220
  280 CONTINUE
      DO 282 I=1,5
```

```
282 BB(I) = BB(I) + WFB(I)*PB(I)
300 CONTINUE
    CHECK CONVERGENCE ON EMULSION HYDROGEN PRESSURE
    FLOWIN = 0.0
    DO 312 I=1,5
312 FLOWIN = FLOWIN + BB(I)
    DO 313 I=1,5
313 PO(I) = BB(I)/FLOWIN
    TAU = VEMUL/FLOWIN
    WRITE(6,995)  PB,PE,PO,TAU
    LOOP = LOOP + 1
    DO 320 I=1,5
320 OPE(I) = PE(I)
330 PI2 = PE(5)**A(9)
    PI4 = PE(5)**A(10)
    PI6 = PE(5)**A(13)
    SAVE5 = PE(5)
    PE(4) = PO(4)/(1.0+RKBC(1)*PI2*TAU)
    R4 =  RKBC(1)*PI2*PE(4)
    TERM = 1.0 + RKP1C(1)*PI4*TAU/RKP2
    PE(3) = (PO(3)+0.9*R4*TAU/RKP2)*(1.0/TERM)
    R3 = -(0.9*R4-RKP1C(1)*PI4*PE(3))/RKP2
    TERM = 1.0 + RKE2C(1)*PI6*TAU/RKE
    PE(2) = (PO(2)+(1.1*R4+R3)*TAU/RKE)*(1.0/TERM)
    R2 = -(1.1*R4+R3-RKE2C(1)*PI6*PE(2))/RKE
    PE(1) =  PO(1) + (4.0*R4+3.0*R3+2.0*R2)*TAU
    PE(6) = PO(5) -(3.0*R4+2.0*R3+R2)*TAU
    IF(ABS(PE(5)-SAVE5).GT.0.0005) GO TO 330
    IF(LOOP.LT.18)  GO TO 360
    WRITE(6,993) T,FLOW,FEED
    STOP
360 IF(ABS(OPE(5)-PE(5)).LT.0.0001)  GO TO 380
    GO TO 110

C

380 F1 = UEMUL/U
    F2 = (U-UEMUL)/U
    DO 385 I=1,5
385 OUT(I) = F1*PE(I) + F2*PB(I)
    IF(FEED(4).EQ.0.0)  GO TO 390
    F = FEED(4)
    DD = FEED(4) - OUT(4)
    S3 = OUT(3)/DD
    S2 = OUT(2)/DD
    GO TO 410
390 IF(FEED(3).EQ.0.0)  GO TO 400
    F = FEED(3)
    DD = FEED(3) - OUT(3)
    S3 = 0.0
    S2 = OUT(2)/DD
    GO TO 410
400 F = FEED(2)
    DD = FEED(2) - OUT(2)
    S3 = 0.0
    S2 = 0.0
410 CONV = 100.0*DD/F
    S1 = OUT(1)/DD
```

```
      EMULH2 = PE(5)
      RETURN
  993 FORMAT( 29H TOO MANY LOOPS   YOU BLEW IT,7F10.4)
  995 FORMAT(1X,3(5F8.6,1X),F5.1)
  996 FORMAT(2X, 40HEMULSION CONC OF H2 KEEPS GOING NEGATIVE)
  997 FORMAT(1X,I3,F6.2,F7.2,F7.4,F6.2,4E9.2)
  998 FORMAT(2X, 46HNOT ENOUGH DIMENSIONS FOR THE NUMBER OF STAGES)
  999 FORMAT(//6X,42HBED DID NOT CONVERGE IN MAXIMUM ITERATIONS)
      END



      SUBROUTINE ORCMIX
      PERFECTLY MIXED MODEL
      COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KEMUL,OUT(5),S1,S2,S3,CONV,
     1              XFAC,IPRINT,EMULH2
      COMMON/BLK3/A(13)
      COMMON/BLK7/ PE(5)

      U = FLOW*1.46042
      TEMP = (T-32.)*(5./9.) + 273.1
      GRAV = 980.0
      DBMAX = 10.0
      UMF = 0.77
      UEMUL = UMF
      HN = 20.0
      RHOS = 0.957
      DP = 0.015
      HMF = HO*1.043
      DO = 0.3261*(((U-UEMUL)*HN)**0.4)
      G1 = 1.0
      UX = U/G1
      HDBMAX = (DBMAX-DO)*UMF/(1.4*RHOS*DP*U)
      DBMEAN = DBMAX - 0.9
    2 HT = HMF*(1.0 + (U-UEMUL)/(0.711*SQRT(980.0*DBMEAN)))
      DBSAVE = DBMEAN
      DBMEAN = ((DBMAX-DO)*0.5*HDBMAX + DBMAX*(HT-HDBMAX))/HT
      IF(ABS(DBSAVE-DBMEAN).GT.0.0001)  GO TO 2
      Q = XFAC*11.0/DBMEAN
      X = Q*HT/(0.711*SQRT(GRAV*DBMEAN))
      NH2 = 0
      NSW=1
      MSW = 1
      TOL=0.000001
      RTT=1.99*TEMP
      FAC = (1.0-0.557)/(1.0-0.449)
      RKB=CACT*FAC*A(5)*EXP(-A(1)/RTT)
      RKP1=CACT*FAC*A(6)*EXP(-A(2)/RTT)
      RKP2=A(7)*EXP(-A(3)/RTT)
      RKE2 = CACT*FAC*A(12)*EXP(-A(11)/RTT)
      RKF=A(8)*EXP(-A(4)/RTT)
      EXPX = EXP(X)
      GAM = (U*(1.0-(1.0-UEMUL/U)/EXPX))/(82.06*TEMP*HMF)
      P5 = FEED(5)

      REACTION KINETICS FOR EMULSION WHERE THE ONLY REACTION OCCURS
```

```
800 Y2 = P5**A(9)
    P42 = (FEED(4)*GAM)/(GAM + RKB*Y2)
    RB = RKB*P42*Y2
    Z1=0.9*RB
    Z3 = RKP1*(P5**A(10))
    P32 = (Z1+FEED(3)*GAM*(1.0+RKP2))/(Z3+GAM*(1.0+RKP2))
    RP2=(Z1-Z3*P32)/(1.0+RKP2)
    Z4 = RKE2*(P5**A(13))
    P22 = (1.1*RB-RP2+(1.0+RKE)*GAM*FEED(2))/(Z4+(1.0+RKE)*GAM)
    RE2 = (1.1*RB-RP2-Z4*P22)/(1.0+RKE)
    P12=(4.0*RB-3.0*RP2-2.0*RE2)/GAM
    P52 = (FEED(5)*GAM - 3.0*RB + 2.0*RP2 + RE2)/GAM
    SEARCH SO THAT GUESSED H2 WILL BE THE SAME AS THE CALCULATED H2
    PDIF=P5-P52
    IF(NSW.EQ.2)  GO TO 703
    IF(PDIF.LE.0.0)  GO TO 700
    MSW =2
    PRT=P5
    P5 = P5 - 0.10
    DIFR=PDIF
    IF(P5.GE.0.0)  GO TO 800
    P5 = 0.0001
    IF(NH2.EQ.0) GO TO 701
    P52 = 0.0001
    IPRINT = -999
    GO TO 704
701 NH2 = 1
    GOTO800
700 IF(MSW.EQ.1) WRITE(6,996) IPRINT,P5,P52,PDIF
    PLT=P5
    DIFL=PDIF
    NSW=2
    GO TO 750
703 IF(ABS(PDIF).LT.TOL) GO TO 704
    IF(ABS(PDIF).LT.ABS(DIFR).OR.ABS(PDIF).LT.ABS(DIFL)) GO TO 710
    WRITE(6,999) IPRINT,P5,P52,PLT,PRT,PDIF,DIFL,DIFR
710 IF(ABS(DIFR).LT.ABS(DIFL)) GO TO 730
    IF(PLT.GT.P5)  GO TO 715
    PRT = P5
    DIFR = PDIF
    GO TO 750
715 PRT = PLT
    DIFR = DIFL
    PLT = P5
    DIFL = PDIF
    GO TO 750
730 IF(PRT.LT.P5)  GO TO 735
    PLT = P5
    DIFL = PDIF
    GO TO 750
735 PLT = PRT
    DIFL = DIFR
    PRT = P5
    DIFR = PDIF
750 P5 = PLT - DIFL*(PRT-PLT)/(DIFR-DIFL)
    GOTO800
```

```
704 PB1 = P12 + (FEED(1)-P12)/EXPX
    PB2 = P22 + (FEED(2)-P22)/EXPX
    PB3 = P32 + (FEED(3)-P32)/EXPX
    PB4 = P42 + (FEED(4)-P42)/EXPX
    PB5 = P52 + (FEED(5)-P52)/EXPX
    F1 = UEMUL/U
    F2 = (U-UEMUL)/U
    OUT(1) = F1*P12+PB1*F2
    OUT(2) = F1*P22+PB2*F2
    OUT(3) = F1*P32+PB3*F2
    OUT(4) = F1*P42+PB4*F2
    OUT(5) = F1*P52+PB5*F2
380 IF(FEED(4).EQ.0.0)  GO TO 390
    F = FEED(4)
    DD = FEED(4) - OUT(4)
    S3 = OUT(3)/DD
    S2 = OUT(2)/DD
    GO TO 410
390 IF(FEED(3).EQ.0.0)  GO TO 400
    F = FEED(3)
    DD = FEED(3) - OUT(3)
    S3 = 0.0
    S2 = OUT(2)/DD
    GO TO 410
400 F = FEED(2)
    DD = FEED(2) - OUT(2)
    S3 = 0.0
    S2 = 0.0
410 CONV = 100.0*DD/F
    S1 = OUT(1)/DD
    EMULH2 = P52
    PE(1) = P12
    PE(2) = P22
    PE(3) = P32
    PE(4) = P42
    PE(5) = P52

    RETURN
996 FORMAT(1X, 40HNEGATIVE ON FIRST STEP OF SEARCH FOR P52, 5X,I3,3F15
   ,.4)
999 FORMAT( 1X, 45H THE ORCUTT SEARCH MAY BLOW UP FOR IPRINT =  ,I4,
   17E11.4)
    END



    SUBROUTINE ORCPLG
    ORCUTT F.B.R. MODEL PLUG FLOW IN THE EMULSION
       MINIMUM STEP SIZE OF 0.4 CM  SHAW   20/4/72

    COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KEMUL,OUT(5),S1,S2,S3,CONV,
   1              XFAC,IPRINT,EMULH2
    COMMON/BLK3/ A(13)
    DIMENSION CN(10),C(10),C1(10),DC(10),C2(10),C3(10),C4(10),CN1(10),
   1          CDX(10),CIN(10),R(5)
```

```
      HMF = HO*1.043
      U = FLOW*1.46042
      UMF = 0.77
      UEMUL = UMF
      GRAV = 980.0
      DBMAX = 10.0
      HN = 20.0
      RHOS = 0.957
      DP = 0.015
      DO = 0.3261*(((U-UEMUL)*HN)**0.4)
      G1 = 1.0
      UX = U/G1
      HDBMAX = (DBMAX-DO)*UMF/(1.4*RHOS*DP*U)
      DBMEAN = DBMAX - 0.9
    2 HT = HMF*(1.0 + (U-UEMUL)/(0.711*SQRT(980.0*DBMEAN)))
      DBSAVE = DBMEAN
      DBMEAN = ((DBMAX-DO)*0.5*HDBMAX + DBMAX*(HT-HDBMAX))/HT
      IF(ABS(DBSAVE-DBMEAN).GT.0.0001)  GO TO 2
      Q = XFAC*11.0/DBMEAN
      Y = Q*HT/(0.711*SQRT(GRAV*DBMEAN))
      TEMP = (T-32.)*(5./9.) + 273.1
      NEQ=10
      NK=0
      Y=0.0
      NSTOP = 0
      DY = 0.3
      IHALF=0
      JHALF=0
      RTT = 1.99*TEMP
      FAC = (1.0-0.557)/(1.0-0.449)
      RKB = FAC*CACT*A(5)*EXP(-A(1)/RTT)
      RKF=A(8)*EXP(-A(4)/RTT)
      RKB2 = FAC*CACT*A(12)*EXP(-A(11)/RTT)
      RKP1 = FAC*CACT*A(6)*EXP(-A(2)/RTT)
      RKP2=A(7)*EXP(-A(3)/RTT)
      Z1 = 82.06*TEMP/UEMUL
      Z3=X/HT
      Z2 = Z3*(U-UEMUL)/UEMUL
      DO 4 J=1,5
      JJ = J + 5
      CN(J) = FEED(J)
    4 CN(JJ) = CN(J)
      KREF=1
      DO5 I=1,NEQ
    5 CIN(I)=CN(I)

   10 YCHECK = Y + DY
      IF(NK.EQ.0.AND.YCHECK.GT.HT)  DY = HT - Y
      DO20 I=1,NEQ
   20 C(I)=CN(I)
      N=1
      GOTO400
   30 DO 40 I=1,NEQ
      C1(I)=DC(I)
   40 C(I)=CN(I)+C1(I)/2.0
      N=2
      GOTO400
```

```
   50 DO60 I=1,NEQ
      C2(I)=DC(I)
   60 C(I)=CN(I)+C2(I)/2.0
      N=3
      GOTO400
   70 DO80 I=1,NEQ
      C3(I)=DC(I)
   80 C(I)=CN(I)+C3(I)
      N=4
      JHALF=0
      GOTO400
C     AT THIS POINT 4 RUNG KUTTA STEPS HAVE BEEN DONE
   90 DO100 I=1,NEQ
      C4(I)=DC(I)
  100 CN1(I)=CN(I)+(C1(I)+2.0*C2(I)+2.0*C3(I)+C4(I))/6.0
      IF(NK-1) 110,130,150
  110 DY=DY/2.0
      NK=1
      DO120 I=1,NEQ
  120 CDX(I)=CN1(I)
      GOTO10
  130 DO140 I=1,NEQ
  140 CN(I)=CN1(I)
      Y=Y+DY
      NK=2
      GOTO10
  150 DO160 I=1,NEQ
  160 CN(I)=(16.0*CN1(I)-CDX(I))/15.0
      Y = Y - DY
      DY=DY*2.0
      NK=0
      Y=Y+DY
      NCOUNT=0
      DO 171 I=1,NEQ
      EPSL = (ABS(CDX(I)-CN1(I)))/15.0
      IF(EPSL.LE.1.0E-08)  NCOUNT = NCOUNT+1
      IF(EPSL.LE.1.0E-06)  GO TO 171
      GO TO 208
C     GOTO209
  171 CONTINUE
      IF(NCOUNT.GE.NEQ) GO TO 220
      IHALF=0
      GOTO230
C     STEP SIZE MUST BE HALVED
  208 IF(DY.GT.0.3)  GO TO 209
      DY = 0.3
      IHALF = 0
      GO TO 230
  209 DO210 I=1,NEQ
  210 CN(I)=GIN(I)
      Y=Y-DY
      DY=DY/2.0
      IHALF=IHALF+1
      IF(IHALF.LT=6)  GO TO 10
      WRITE(6,999) T,FLOW,FEED
      STOP
  220 DY=DY*2.0
```

```
      IHALF=0
C     THESE VALUES OF CIN AND CN ARE THE FINAL VALUES AT THE
C     END OF A STAGE
  230 DO240 I=1,NEQ
  240 CIN(I)=CN(I)
      IF(Y.EQ.HT)  GO TO 280
      GOTO10
C     DIFFERENTIAL EQUATIONS
  400 DO 430 I=1,NEQ
  430 IF(C(I).LT=0.0)  C(I) = 0.0
  460 IF(C(5).GT.0.0)  GO TO 465
      C(5) = 0.0001
      NSTOP = NSTOP + 1
      WRITE(6,997) Y,T,FLOW,FEED
      IF(NSTOP.LT.20)  GO TO 465
      STOP
  465 R(4) = RKB*C(4)*(C(5)**A(9))
      R(3) = -(0.9*R(4) - RKP1*C(3)*(C(5)**A(10)))/(1.0+RKP2)
      R(2) = -(1.1*R(4)+R(3)-RKE2*C(2)*(C(5)**A(13)))/(1.0+RKE)
      R(1) = -(4.0*R(4)+3.0*R(3)+2.0*R(2))
      R(5) = 3.0*R(4) + 2.0*R(3) + R(2)
      Z4=-DY*Z1
      Z5=-DY*Z2
      WW6=Z3*DY
      DO 470 J=1,5
      JJ = J + 5
      W1 = C(J) - C(JJ)
      DC(J) = Z4*R(J) + Z5*W1
  470 DC(JJ) = WW6*W1
      GOTO(30,50,70,90),N
C
C     FINAL CALCULATIONS ---  PROBLEM IS SOLVED
  280 DO 610 I=1,5
  610 OUT(I) = (UEMUL*CN(I) + (U-UEMUL)*CN(I+5))/U
      IF(FEED(4).EQ.0.0)  GO TO 620
      F = FEED(4)
      DD = FEED(4) - OUT(4)
      S3 = OUT(3)/DD
      S2 = OUT(2)/DD
      GO TO 640
  620 IF(FEED(3)=EQ.0.0)  GO TO 630
      F = FEED(3)
      DD = FEED(3) - OUT(3)
      S3 = 0.0
      S2 = OUT(2)/DD
      GO TO 640
  630 F = FEED(2)
      DD = FEED(2) - OUT(2)
      S3 = 0.0
      S2 = 0.0
  640 CONV = 100.0*DD/F
      S1 = OUT(1)/DD
      EMULH2 = C(5)
      RETURN

  997 FORMAT(1X,8F12.5)
  998 FORMAT( 2X, 22HSTOP FOR JHALF COUNTER/1X,2F8.3,10F6.3,F7.2,F6.2,
```

```
     1  5F7.4/)
 999 FORMAT( 2X, 22HSTOP FOR IHALF COUNTER,7E15.8)
     END



     SUBROUTINE PARROW
     PARTRIDGE AND ROWE FLUIDIZED BED MODEL
     COMMON /BLK2/ FEED(5),T,FLOW,CACT,HO,KEMUL,OUT(5),S1,S2,S3,CONV,
    1              XFAC,IPRINT,EMULH2
     COMMON/BLK3/ A(13)
     DIMENSION CN(10),C(10),C1(10),DC(10),C2(10),C3(10),C4(10),CN1(10),
    1          CDX(10),CIN(10),R(10)
     GRAV=980.0
     PRESS = 1.0
     DBMAX = 10.0
     DELTP = 0.04
     HN = 20.0
     RHOS = 0.957
     DP = 0.015
     UMF = 0.77
     U1=UMF
     UO=UMF
     AREA=324.
     U2 = FLOW*1.46042
     U=U2
     UDIFF=U2-UM6
     G=UDIFF*HN
     DO = 0.3261*G**0.4
     G1=1.0+0.5*DELTP/PRESS
     UX=U2/G1
     HMF = HO*1.043
     HDBMAX = (DBMAX-DO)*UMF/(1.4*RHOS*DP*U)
     DBMEAN = DBMAX - 0.9
   2 HT = HMF*(1.0 + UDIFF/(0.711*SQRT(980.0*DBMEAN)))
     DBSAVE = DBMEAN
     DBMEAN = ((DBMAX-DO)*0.5*HDBMAX + DBMAX*(HT-HDBMAX))/HT
     IF(ABS(DBSAVE-DBMEAN).GT.0.0001)  GO TO 2
     EPSO = 0.557
     EPB = 0.449
     VOIDC=(1.0-EPSO)/(1.0-EPB)
     TEMP = (T-32.0)*(5.0/9.0) + 273.1
     RT=1.99*TEMP
     RRRB = VOIDC*CACT*82.06*TEMP*A(5)*EXP(-A(1)/RT)
     RRRP1 = VOIDC*CACT*82.06*TEMP*A(6)*EXP(-A(2)/RT)
     RRRE2 = VOIDC*CACT*82.06*TEMP*A(12)*EXP(-A(11)/RT)
     RKP2 = A(7)*EXP(-A(3)/RT)
     RKE = A(8)*EXP(-A(4)/RT)
     RKB1 = RRRB
     RKP11 = RRRP1
     RKE21 = RRRE2
     DO 4 J=1,5
     CN(J) = FEED(J)
   4 CN(J+5) = FEED(J)
     KFIN=0
     NEQ=10
```

```
      NU=0
      NK=0
      Y=0.0
      DY=0.1
      IHALF=0
      JHALF=0
      NSWIT=0
      KRET=1
      GOTO600
    9 DO5 I=1,NEQ
    5 CIN(I)=CN(I)
   10 DO20 I=1,NEQ
   20 C(I)=CN(I)
      N=1
      GOTO400
   30 DO 40 I=1,N5Q
      C1(I)=DC(I)
   40 C(I)=CN(I) C1(I)/2.0
      N=2
      GOTO400
   50 DO60 I=1,N5Q
      C2(I)=DC(I)
   60 C(I)=CN(I)+32(I)/2.0
      N=3
      GOTO400
   70 DO80 I=1,NEQ
      C3(I)=DC(I)
   80 C(I)=CN(I)+C3(I)
      N=4
      GOTO400
   90 DO100 I=1,NEQ
      C4(I)=DC(I)
  100 CN1(I)=CN(I)+(C1(I)+2.0*C2(I)+2.0*C3(I)+C4(I))/6.0
      JHALF=0
      IF(NK-1) 110,130,150
  110 DY=DY/2.0
      NK=1
      DO120 I=1,NEQ
  120 CDX(I)=CN1(I)
      GOTO10
  130 DO140 I=1,NEQ
  140 CN(I)=CN1(I)
      Y=Y+DY
      KRET=2
C     LEAVE OUT NEXT STATEMENT FOR PARTRIDGE ROWE MODEL
C     DB AND UX H5LD CONSTANT OVER ONE INTEGRATION STEP SIZE
C     GO TO 600
  145 Y=Y-DY
      NK=2
      GOTO10
  150 DO160 I=1,NEQ
  160 CN(I)=(16.0*CN1(I)-CDX(I))/15.0
      DY=DY*2.0
      NK=0
      Y=Y+DY
      KRET=3
      GOTO600
```

```
164   CONTINUE
      IF(KFIN)165,165,280
165   IF(Y-HT) 170,250,250
170   NCOUNT=0
      DO 171 I=1,NEQ
      EPSL = (ABS(CDX(I)-CN1(I)))/15.0
      IF(EPSL.LE.1.0E-08)  NCOUNT = NCOUNT+1
      IF(EPSL.LE.1.0E-06)  GO TO 171
      GOTO209
171   CONTINUE
      IHALF=0
      IF(NCOUNT.EQ.NEQ)  DY = DY*2.0
      GOTO230
209   DO210 I=1,NEQ
210   CN(I)=CIN(I)
      Y=Y-DY
      DY=DY/2.0
      IHALF=IHALF+1
      IF(IHALF.LT.5) GO TO 10
      WRITE(6,998)
      STOP
230   DO240 I=1,NEQ
240   CIN(I)=CN(I)
      THESE VALUES OF CIN AND CN ARE THE FINAL VALUES AT THE
      END OF A STAGE
      GOTO10
250   IF(KFIN) 260,260,280
260   KFIN=1
      Y=Y-DY
      KRET=4
      GOTO600
265   DY=HT-Y
      Y=Y+DY
      DO 270 I=1,NEQ
270   CN(I)=CIN(I)
      GOTO10
      CHECK FOR NEGATIVE COMPOSITION
400   KNEG = 0
      DO430 I=1,NEQ
430   IF(C(I).LT.0.0)  KNEG = 1
      IF(KNEG.EQ.0) GO TO 460
      DY=DY/2.0
      JHALF=JHALF+1
      IF(JHALF.LT.5)  GO TO 330
      WRITE(6,999)
      STOP
330   IF(NK - 1) 10,371,373
371   NK=0
      GOTO10
373   NK=0
      DO372I=1,NEQ
372   CN(I)=CIN(I)
      GOTO10
      DIFFERENTIAL EQUATIONS
600   R(9) = RKBC*C(9)*(C(10)**A(9))
      R(8) = -(0.9*R(9)-RKP1C*C(8)*(C(10)**A(10)))/(1.0+RKP2)
      R(7) = -(1.1*R(9)+R(8)-RKE2C*C(7)*(C(10)**A(13)))/(1.0+RKE)
```

```
      R(6) = -(4.0*R(9)+3.0*R(8)+2.0*R(7))
      R(10) = 3.0*R(9)+2.0*R(8)+R(7)
      R(4) = RKB1*C(4)*(C(5)**A(9))
      R(3) = -(0.9*R(4)-RKP11*C(3)*(C(5)**A(10)))/(1.0+RKP2)
      R(2) = -(1.1*R(4)+R(3)-RKE21*C(2)*(C(5)**A(13)))/(1.0+RKE)
      R(1) = -(4.0*R(4)+3.0*R(3)+2.0*R(2))
      R(5) = 3.0*R(4)+2.0*R(3)+R(2)
      QT=DY/UI
      QQ=DY/UC
      Z2 = AC/AI
      DO 480 J=1,5
      JJ = J+5
      Z1 = (C(JJ)-C(J))*QBLK
      DC(J) = QT*(-R(J)+Z1*Z2)
  480 DC(JJ) = -QQ*(R(JJ)+Z1)
      GOTO(30,50,70,90),N
      INTERMEDIATE CALCULATIONS
   30 G1=1.0+((1.0-Y/HT)*DELTP)/PRESS
      UX=U2/G1
      DB = (1.4*RHOS*DP*Y*UX)/UMF+DO
      IF(DB.GT.DBMAX)  DB = DBMAX
      ALPHA = 0.711*SQRT(GRAV*DB)*EPSO/UMF
      ALPHA=22.26*SQRT(DB)*EPSO/UMF
      GB = AREA*(UX-UMF)
      GC=GB*(1.0+EPSO/(ALPHA-1.0))
      AC=(GB*EPSO)/(UO*(ALPHA-1.0))
      AI=AREA-AC
      UC=GC/AC
      CORC = 1.17/(ALPHA + 0.17)
      RKRC=CORC*RRRB
      RKP1C=CORC*RRRP1
      RKE2C = RRRE2*CORC
      QE = (11.0/DB)*(ALPHA-1.0)/(ALPHA+0.17)
         QBLK=FO*(ALPHA-1)/(0.17+ALPHA)....FO=11./DB SEE KATO AND WEN)
      QBLK = XFAC*QE
      QBLK=0.733
      GOTO(9,145,164,265),KRET

  280 DO610I=1,5
  610 OUT(I) = (UO*CN(I)+(U-UO)*CN(I+5))/U
      IF(FEED(4).EQ.0.0)  GO TO 620
      F = FEED(4)
      DD = FEED(4) - OUT(4)
      S3 = OUT(3)/DD
      S2 = OUT(2)/DD
      GO TO 640
  620 IF(FEED(3).EQ.0.0)  GO TO 630
      F = FEED(3)
      DD = FEED(3) - OUT(3)
      S3 = 0.0
      S2 = OUT(2)/DD
      GO TO 640
  630 F = FEED(2)
      DD = FEED(2) - OUT(2)
      S3 = 0.0
      S2 = 0.0
  640 CONV = 100.0*DD/F
```

```
      S1 = OUT(1)/DD
      EMULH2 = CN(5)
      RETURN
  900 FORMAT(1X,F25.10)
  998 FORMAT(1X, 42HSTEP SIZE CUT TOO MANY TIMES  ***  STOP****)
  999 FORMAT(1X, 48HCOMPOSITIONS KEEP GOING NEGATIVE  ***  STOP ***)
      END
```

APPENDIX K

SUGGESTED EXPERIMENTAL DESIGN TECHNIQUE FOR ESTIMATING PARAMETERS IN ONE REACTOR THAT ARE TO BE USED IN ANOTHER REACTOR MODEL

The object of this study was to model a fluidized bed reactor. The kinetic parameters were estimated in the packed bed reactor and then were used in the fluidized bed model. The interchange parameter and the catalyst activity were estimated by minimizing $\underset{\sim}{w}^T \underset{\sim}{A}^{-1} \underset{\sim}{w}$ the weighted difference between the model predictions and the observed experimental results. The precision of the fluidized bed model predictions, not the kinetic parameters, was the major importance. The precision of the estimated parameters was only of importance inasmuch as it affected the precision of the reactor model predictions.

Available experimental design techniques that select operating conditions so as to obtain the most precise estimates of the kinetic parameters are not appropriate for applications such as the type presented in this study. The standard design techniques minimize the confidence region for the parameters which means maximizing $\left| \underset{\sim}{X}^T \underset{\sim}{A}^{-1} \underset{\sim}{X} \right|$ where $\underset{\sim}{X}$ is the matrix of derivatives of the responses with respect to the parameters in the experimental system used to estimate these parameters. The matrix $\underset{\sim}{A}$ represents the variance-covariance matrix of the experimental responses.

For this study, the operating conditions in the packed bed reactor, where the kinetic parameters were estimated, should be selected so as to minimize the uncertainty in the fluidized bed model predictions resulting from these parameters.

In the fluidized bed define for a single experiment u:

$$\underset{rxl}{\underset{\sim}{w}_u} \qquad \underset{\sim}{Y}_{u\$} - \underset{\sim}{\eta}_u \quad . \qquad \text{K.1}$$

where $\underset{u}{Y}$ is the vector of observed responses, $\underset{u}{\eta}$ is the predicted response and r is the number of responses per trial in the fluidized bed. The i'th predicted response is given by

$$\eta_i = f_i(\underset{u}{\xi}, \underset{}{\theta}, \frac{k}{k_o}, \theta^*) \qquad K.2$$

where f is some functional relationship, $\underset{u}{\xi}$ is the vector of control variables for the u'th trial and $\underset{}{\theta}$ is the vector of kinetic parameters estimated from the packed bed study. The parameters $\frac{k}{k_o}$ and θ^* are the catalyst activity and the interchange respectively and are estimated from the fluidized bed experiments. Now linearising:

$$\underset{rx1}{\underset{u}{w}} = \underset{u}{x} (\underset{}{\theta} - \underset{}{\theta}) \qquad K.3$$

where

$$\underset{rxp}{\underset{u}{X}} = \left[\frac{\partial f_i(\underset{u}{\xi}, \underset{}{\theta}, \frac{k}{k_o}, \theta^*)}{\partial \underset{j}{\theta}}\right]_{\theta = \theta} \qquad K.4$$

and $\underset{}{\theta}$ is some vector of the kinetic parameters and $\underset{}{\theta}$ is their best estimate. p is the number of these parameters.

Then: $$V(\underset{u}{w}) = (\underset{u}{x}\, V(\underset{}{\theta})^{-1}\, \underset{u}{x}^T)^{-1} = V(\underset{u}{\eta}) \qquad K.5$$

where $V(\underset{}{\theta})$ is the variance of the kinetic parameters and $V(\underset{u}{\eta})$ is the variance of the model prediction of the fluidized bed model at the best estimate of all the required parameters in the model. But from equation G.8 written in terms of the entire data set for the packed bed data:

$$V(\underset{}{\theta}) = \frac{1}{n\left(\frac{p}{r'}\right)} (\underset{}{X}^T \underset{}{A}^{-1} \underset{}{X})^{-1} \qquad K.6$$

where r' is the number of responses per trial in the packed bed experiments.

Therefore: $$V(\underline{w}_u) = \left[\underline{X}_u \left[\frac{1}{n-r} \left(\frac{R}{r} \right) (\underline{X}^T \underline{A}^{-1} \underline{X})^{-1} \right]^{-1} \underline{X}_u^T \right]^{-1} \equiv \underline{K}^{-1} \quad K.7$$

Thus: $$Df(\underline{w}_u) = \frac{\exp(-\frac{1}{2} \underline{w}_u^T \underline{K}^{-1} \underline{w}_u)}{(2\pi)^{r/2} |K|^{1/2}} \quad K.8$$

Therefore, when designing experiments in the packed bed reactor to estimate the kinetic parameters, they could be designed so as to minimize the generalized variance of $\underline{w}_u$. This can be accomplished using the design criterion to be described.

SUGGESTED EXPERIMENTAL DESIGN TECHNIQUE FOR PACKED BED REACTOR STUDY

This design technique can be employed once initial experiments have been performed in the packed bed reactor since these trials will provide parameter estimates and a value of $\underline{\Sigma}$ the variance-covariance matrix. It is also necessary to evaluate the matrix $\underline{x}_u$ once the initial parameter estimates are available. If the fluidized bed model is non-linear, $\underline{x}_u$ should be evaluated at the specific range of control variables to be used in the fluidized bed reactor. Control variables for the packed bed reactor are then selected so as to minimize the generalized variance of the predictions of the fluidized bed model at the set of control variables $\underline{\xi}_u$.

Using the exact same set of possible control variables that were used to select those shown in Table 4.5 according to the cirterion of minimizing $\underline{X}^T \underline{A}^{-1} \underline{X}$ a second set were chosen so as to minimize K^{-1} in equation K.7. Slightly different values were selceted as the best, even though the exact same set of possible control variables were used in both cases. The two sets of control variables are shown below:

$\lvert \underline{X}^T \underline{A}^{-1} \underline{X} \rvert$ CRITERION (TABLE 4.5)			$\left\lvert \left[\underline{X}_u \left[\frac{1}{n-p} (\underline{X}^T \underline{A}^{-1} \underline{X})^{-1} \right]^{-1} \underline{X}_u^T \right]^{-1} \right\rvert$ CRITERION		
^oF	ml./sec.	RATIO	^oF	ml./sec.	RATIO
488	1.1	3.6	493	2.4	3.2
489	1.5	3.2	489	1.5	3.2
496	2.0	3.2	488	2.4	3.3
500	2.4	3.3	488	1.2	3.4
516	2.0	3.8	487	1.2	3.9
488	2.1	3.2	488	2.1	3.2

The second and the sixth set of operating conditions are the same for both methods. However, the new proposed method selected lower temperatures. This can be explained by the fact that the prediction errors of the fluidized bed model are more serious at lower temperatures where the model is less sensitive to the interchange parameter and more sensitive to the kinetic parameters. Thus, for the experiments to be designed the simple criterion of $\underline{X}^T \underline{A}^{-1} \underline{X}$ which minimizes the uncertainty in the kinetic parameters may not be the best design criterion for cases such as described here.