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LABORATORY REACTOR DESIGN
AND THE
PRECISION OF PARAMETER ESTIMATES

by

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A thesis submitted to the School of Graduate Studies and Research in partial fulfilment of the requirements for the degree of
MASTER OF APPLIED SCIENCE
in the Department of Chemical Engineering
University of Ottawa

ISBN 0-315-89611-6

Canada

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Abstract

This study is concerned with investigating the dependence of the precision of estimated kinetic parameters on the type of reactor used for performing the kinetic measurements. Two ideal reactors, the plug-flow reactor (PFR) and the continuous-stirred-tank reactor (CSTR), were simulated using a Monte-Carlo computer simulation. Parameters were estimated using nonlinear multiresponse estimation techniques, and the distributional characteristics of the parameter estimates were calculated. Comparison between the reactors involved the study of overall measures of precision such as the size, shape and orientation of the 95% joint confidence region, and the determinant of the covariance matrix of the parameter estimates. Five variables were identified as having a possible affect on the precision: the nature of the reaction network, the kinetic model, the magnitudes of the rate parameters, the covariance structure of the responses, and the experimental design. The dependence of parameter precision on these variables is presented along with recommendations for determining the reactor type to give the most precise kinetic parameters.

Acknowledgements

I would like to thank Dr. David D. McLean for his advice and guidance through this research as well as for his encouragement. In addition, I would like to thank Mr. David Macleod for his patience and support. Finally, I thank Dr. Elizabeth Nielsen for her confidence in me and her optimism.

> "We hope that this algebraical analogue or model will perform in a way which resembles the real thing sufficiently closely to widen our understanding and to enable us to make useful predictions."[1]

[1] Gordon (1978)

Nomenclature

AREA	area of the approximate joint confidence region, $\det(\underline{V}(\hat{\theta})^{\frac{1}{2}})$.
A,B,C	reacting species and products of reaction.
C_i	concentration of the reacting species i.
C_{Ao}	initial concentration of the reacting species A.
$Cov(\hat{\theta}_i, \hat{\theta}_j)$	covariance between two parameters.
e	n×r matrix of deviations between the observed and predicted responses.
E	the n×r matrix defined as $\mathbf{E} = \mathbf{R}\,\Lambda^{\frac{1}{2}}$.
f	n×r matrix of values of the response functions.
$F_{p,n-p,1-\alpha}$	upper $100(1-\alpha)$ percentage point of an F distribution with p and (n-p) degrees of freedom.
k	total number of operating variables.
M	inverse of the approximate covariance matrix for the estimated parameters.
n	total number of conditions or runs.
$N(\mathbf{0},\Sigma)$	multivariate Normal distribution with a mean of zero and a covariance matrix $\underline{\Sigma}$.
p	total number of parameters.
r	total number of responses.
R	the n×r matrix of random Normal N(0,1) numbers.
s^2	the variance of a parameter estimate.
$S(\theta)$	objective function, $\det(\underline{e}^T\underline{e})$, the sum of squares of residuals and cross-products.

$S(\hat{\underline{\theta}})$ objective function evaluated at the optimal values of the parameter estimates.

$\mathbf{U}$ matrix whose columns are the normalized eigen vectors of $\mathbf{\Sigma}$.

$\mathbf{V}(\theta)$ p×p covariance matrix of parameters.

$V(\theta_i)$ marginal variance of an individual parameter.

x_1 scaled θ_1 (rate parameter).

x_2 scaled θ_2 (rate parameter).

x_3 scaled σ_A^2 (variance of C_A).

x_4 scaled σ_B^2 (variance of C_B).

x_5 scaled σ_C^2 (variance of C_C).

x_6 scaled σ_{AB} (covariance between C_A and C_B).

x_7 scaled σ_{AC} (covariance between C_A and C_C).

x_8 scaled σ_{BC} (covariance between C_B and C_C).

$\mathbf{X}_i$ n×p matrix of partial derivatives of the response function with respect to the parameters for the i'th response.

$\mathbf{Y}$ n×r matrix of values of the measured responses, i.e., y_{uv} is the measured value for the v'th response at the u'th experimental condition.

α probability.

ε n×r matrix of random errors associated with the measured responses.

θ p×1 vector of "true" values for the model parameters.

$\hat{\theta}$	p×1 vector of "estimated" values for the model parameters.
$\bar{\theta}$	the mean of a parameter estimate.
Λ	matrix of the eigenvalues of Σ.
ξ	k×n matrix of values of the operating variables.
$\rho(\theta_i, \theta_j)$	correlation between two parameters.
$\hat{\sigma}^2$	estimate of the pure error variance with (n-p) degrees of freedom.
σ_i^2	variance of the concentration of the reacting species i.
σ_{ij}	covariance between the concentrations of two reacting species.
σ^{ij}	i-j'th element of the inverse of the covariance matrix of the responses (Σ^{-1}).
τ	space time.

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1 INTRODUCTION

Models for chemical kinetics play a vital role in the design, control and optimization of chemical reactors. Since models are used to predict the rate of formation and depletion of chemicals in a process, the economic feasibility of a manufacturing process, or the choice of one process among alternatives, begins with the collection of kinetic data for the development of a model. Unreliable kinetic data may lead to the design of an inappropriate reactor for the process, a meaningless control strategy or an undependable estimate of the costs involved with a plant design. A reliable model provides a solid foundation on which to build sound chemical engineering decisions.

The reliability of the kinetic prediction using a model depends on the rate parameters in the model. Parameter reliability involves both accuracy and precision. Accuracy is of paramount importance, for without it, the kinetic predictions are meaningless. Precision refers to the degree of certainty associated with an estimate of the parameter. Engineering calculations made using more precise kinetic parameters would enable, for example, tighter process control or more confidence in reactor design.

Both the accuracy and precision of the parameter estimates are affected by the experimental conditions in the laboratory. The usual criteria for choosing a laboratory reactor have been concerned with parameter accuracy. For example, various criteria, such as physical performance, mixing properties, mass transfer and heat transfer characteristics, were used by Weekman (1974) to compare the ability of different laboratory reactors to supply accurate estimates of rate parameters. The precision of the kinetic parameters was not considered as a factor for choosing a laboratory reactor.

Hoffman et al. (1977) published a brief study of the effect of reactor type on parameter reliability and determined that a plug flow reactor will always give more precise parameter estimates than a continuous stirred tank reactor. However, the scope of their study was limited to the decomposition of a substance into various products through a parallel reaction network. This study also neglected the effect of the precision of the measured concentrations of the products of reaction, a factor which may influence parameter precision.

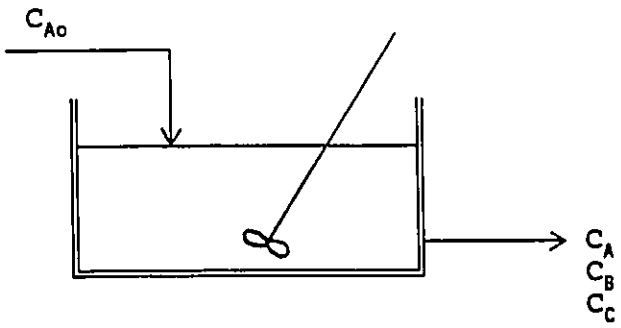
Despite the importance of having precise estimates of kinetic rate parameters, no other investigations into the effect of the choice of reactor type on parameter precision were found in the literature. Further investigation of the influence of reactor type on parameter precision is warranted.

At the outset, one might ask if there is any evidence that parameter precision may be influenced by the type of reactor used to obtain the kinetic data. It is known that the precision of the parameter estimates depend on the form of the reactor design equations (Draper and Hunter, (1966)). The reactor design equations, in turn, are based on both the kinetic model and the reactor type. Hence, the precision of the parameter estimates for a given kinetic model ultimately depends upon the reactor used.

1.1 Scope

In this study, the nature of the dependence between parameter precision and reactor type was studied by comparing the precision obtained using the two extreme ideal reactor types: the continuous stirred tank reactor (CSTR) and the plug flow reactor (PFR). These reactors exhibit the two extremes of mixing, as follows:

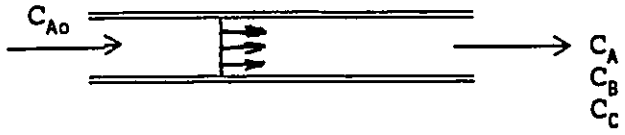
CSTR: **Schematic**



Mixing Properties:

The concentration of the reacting species and products of reaction are uniform within the reactor.

PFR: **Schematic**



Mixing Properties:

The composition varies from point to point along the flow path, but is uniform at a particular cross-section.

Therefore, any dependence that the precision of the kinetic parameters has on the reactor used will be evident. Moreover, for most bench-scale studies, there is a concerted effort to meet either of these two conditions.

The objectives of this study were:

i) To determine the reactor type which gives the most precise estimates of kinetic parameters, and

ii) To determine the factors which influence parameter precision and consequently the choice of reactor.

An analysis of the covariance matrix of the parameter estimates (see Section 2.4.1) identified five factors which may have an influence on the parameter precision:

1. the kinetic model,
2. the reaction network,
3. the magnitude of the rate parameters,
4. the precision of the experimental observations of the reaction, and
5. the experimental design.

This investigation was limited to studying first order kinetic models for the simple series and parallel networks given below:

<u>Series Network</u>: $A \xrightarrow{\theta_1} B \xrightarrow{\theta_2} C$

<u>Parallel Network</u>: $A \xrightarrow{\theta_1} B$

$A \xrightarrow{\theta_2} C$

For example, a first-order, series reaction is the hydration of acetaldehyde (Bell and Clunie (1951)). The liquid phase pyrolysis of α-pinene into dipentene and allo-ocimene is a first-order parallel reaction (Fuguitt and Hawkins (1947)).

The experimental design refers to the number of runs and the levels of the operating variables, in this case, the initial concentration of "A" and the space-time. Two experimental designs were considered. The first was a ten-run design setting the initial concentration of "A" at three levels and the space-time at an expected conversion of "A" of approximately 10%, 50% and 90%, plus a replicate run at the centre point. The second design added ten more runs to the first, at conditions designed to attain maximum improvement in the precision of the parameter estimates. This second design allowed the reactors to be compared under conditions giving the best parameter precision for each reactor type.

The remaining factors, the magnitude of the rate parameters and the precision of the experimental observations of the reaction, were studied according to a fractional factorial design.

1.2 Computer Simulation

To carry out this study, chemical reactions must be performed at set values for each of the five factors and the precision of the resulting parameter estimates determined. For the practical reasons of time, feasibility and economics, computer simulation was used. For example, performance of a series of experiments which have various values of the magnitudes of the rate parameters for a specific reaction network and model as well as various values for the precision of the experimental observations of the reaction is not feasible. Furthermore, for reasons which will be outlined below, the determination of parameter precision requires that the same experiment be repeated hundreds of times. This would be prohibitively expensive and unreasonable, even for a bench-scale study.

The major tasks for the computer were:

i) Simulation of experiments:

The computer simulated the outcome of an experiment given information on the reaction kinetics, the reactor type and the variation in the experimental observations of the reaction.

ii) Estimation of the kinetic parameters:

The data obtained by computer simulation was treated the same as data from "real" bench-scale experiments to estimate the rate parameters.

iii) The experimental design for precise parameter estimation:

The computer was also used to determine the run conditions required to improve the precision of the estimates of the kinetic parameters.

iv) Determination of the precision of the parameter estimates:

The precision of the rate parameters was determined using a Monte Carlo simulation, which repeats the same set of experiments many times. As a result, a large sample of estimated rate parameters was obtained from which the precision was calculated.

v) Assessment of the results:

Finally, the influence of the factors on parameter precision were modelled and the reactor type which gives the most precise parameter estimates was determined.

2 BACKGROUND

2.1 The General Model

A particularly useful form for a process model expresses the measured values of the responses as a function of the operating variables, the model parameters and an additive random error:

$$y = f(\xi, \theta) + \varepsilon \tag{1}$$

where **y** is the n×r matrix of values of the measured responses, i.e., y_{uv} is the measured value for the v'th response at the u'th experimental condition, or

$$y_{uv} = f_v(\xi_u, \theta) + \varepsilon_{uv} \qquad \begin{matrix} u=1,2,\ldots,n \\ v=1,2,\ldots,r \end{matrix} \tag{2}$$

f is an n×r matrix of values of the response functions,

ξ is the k×n matrix of values of the operating variables,

θ is the p×1 vector of "true" values for the model parameters,

ε is the n×r matrix of random errors associated with the measured responses,

n is the total number of conditions or runs,

r is the total number of responses,

k is the total number of operating variables and

p is the total number of parameters.

For this study, the measured responses were the concentrations of the three reacting species denoted by C_A, C_B and C_C. The operating variables were the initial concentration of "A" , C_{Ao}, and the space time, τ; the parameters were the rate constants θ_1 and θ_2. These values may be expressed in vector form as follows:

$$\boldsymbol{y}_u=[C_{Au} \quad C_{Bu} \quad C_{Cu}] \qquad \boldsymbol{\xi}_u=\begin{bmatrix} C_{Aou} \\ \tau_u \end{bmatrix}$$

$$\boldsymbol{f}_u=[f_{Au} \quad f_{Bu} \quad f_{Cu}] \qquad \boldsymbol{\theta}=\begin{bmatrix} \theta_1 \\ \theta_2 \end{bmatrix} \qquad (3)$$

$$\boldsymbol{\varepsilon}_u=[\varepsilon_{Au} \quad \varepsilon_{Bu} \quad \varepsilon_{Cu}]$$

The reactor design equations, **f**, were based upon both the kinetic model and the type of reactor used. Table 1 outlines the reactor design equations for the conditions in this study.

Table 1

The Reactor Design Equations

Study Conditions	Reactor Design Equations
First order-series reaction; Plug flow reactor	$\boldsymbol{f}^{T}=\begin{bmatrix} f_A \\ f_B \\ f_C \end{bmatrix}=\begin{bmatrix} C_{Ao}\exp(-\theta_1\tau) \\ \frac{C_{Ao}\theta_1}{\theta_2-\theta_1}\{\exp(-\theta_1\tau)-\exp(-\theta_2\tau)\} \\ C_{Ao}\left[1+\frac{\theta_2\exp(-\theta_1\tau)-\theta_1\exp(-\theta_2\tau)}{(\theta_1-\theta_2)}\right] \end{bmatrix}$
First order-series reaction; Continuous stirred tank reactor	$\boldsymbol{f}^{T}=\begin{bmatrix} f_A \\ f_B \\ f_C \end{bmatrix}=\begin{bmatrix} \frac{C_{Ao}}{\theta_1\tau+1} \\ \frac{C_{Ao}}{(\theta_1\tau+1)\ (\theta_2\tau+1)} \\ \frac{C_{Ao}\theta_1\theta_2\tau^2}{(\theta_1\tau+1)\ (\theta_2\tau+1)} \end{bmatrix}$
First order-parallel reaction; Plug flow reactor	$\boldsymbol{f}^{T}=\begin{bmatrix} f_A \\ f_B \\ f_C \end{bmatrix}=\begin{bmatrix} C_{Ao}\exp(-(\theta_1+\theta_2)\tau) \\ \frac{C_{Ao}\theta_1}{\theta_1+\theta_2}\{1-\exp(-(\theta_1+\theta_2)\tau)\} \\ \frac{C_{Ao}\theta_2}{\theta_1+\theta_2}\{1-\exp(-(\theta_1+\theta_2)\tau)\} \end{bmatrix}$
First order-parallel reaction; Continuous stirred tank reactor	$\boldsymbol{f}^{T}=\begin{bmatrix} f_A \\ f_B \\ f_C \end{bmatrix}=\begin{bmatrix} \frac{C_{Ao}}{1+(\theta_1+\theta_2)\tau} \\ \frac{C_{Ao}\theta_1\tau}{1+(\theta_1+\theta_2)\tau} \\ \frac{C_{Ao}\theta_2\tau}{1+(\theta_1+\theta_2)\tau} \end{bmatrix}$

2.2 Computer Simulation of Experiments

The task of obtaining simulated experimental data was accomplished by using Equation (1). In the first step or deterministic simulation, exact values of the concentrations of the reacting species were calculated from the design functions of Table 1 using the known values of the operating conditions and the rate parameters. In the second step, called the stochastic simulation, random errors associated with the measured reacting species were generated according to the multivariate Normal distribution $N(0,\Sigma)$. When these random errors were added to the deterministic values, simulated "measured" concentrations of the reacting species were obtained.

2.3 Parameter Estimation

Many methods are available for a kinetics investigator to estimate the rate parameters from measured kinetic data. For example, a single-response analysis technique such as Least Squares may be used to analyze the data from one of the measured reacting species. Alternatively, multiresponse estimation may be used when more than one species is measured. Since multiresponse analysis uses more of the available information about the reaction, parameters estimated using multiresponse techniques are more precise (Box and Draper

(1965); Ziegel and Gorman (1980)). For this reason, multiresponse analysis was used in this study.

The multiresponse estimation criterion used in this study was developed by Box and Draper (1965) and involves minimization of

$$S(\boldsymbol{\theta}) = \det(\boldsymbol{e}^T\boldsymbol{e}) \tag{4}$$

where **e** is the n×r matrix of deviations between the observed and predicted responses, whose elements are given by:

$$e_{uv} = y_{uv} - f_v(\boldsymbol{\xi}_u, \boldsymbol{\theta}) \tag{5}$$

Minimization of $S(\theta)$ with respect to θ involves an iterative procedure.

2.4 Precision

The most common method of expressing the precision of a parameter is in terms of a 100(1-α)% confidence interval, that is, a range of values that has a 100(1-α)% probability of containing the true value. This interval takes into account

the variance that is associated with the parameter along with its magnitude. The precision of a set of parameters is similarly expressed as a joint confidence region. This region has a specified probability of containing the true values of the set of parameters and explicitly takes into account the correlation between parameters in addition to the variance of the individual parameters.

2.4.1 The Covariance Matrix

All basic information concerning the precision of the estimates of the parameters is contained in the covariance matrix, defined as follows

$$V(\theta) = \begin{bmatrix} V(\theta_1) & Cov(\theta_1,\theta_2) & \cdots & Cov(\theta_1,\theta_p) \\ & V(\theta_2) & \cdots & Cov(\theta_2,\theta_p) \\ & & \cdots & \cdot \\ & & \cdots & \cdot \\ \underline{SYM} & & \cdots & V(\theta_p) \end{bmatrix} \qquad (6)$$

The marginal variance of an individual parameter, $V(\hat{\theta}_i)$, is found as the i'th diagonal element while the covariance between two parameters, $Cov(\hat{\theta}_i,\hat{\theta}_j)$, is found as the i-j'th off diagonal element of the covariance matrix. The correlation is a scale-independent relative measure of covariance and may be calculated from the variances and the covariance:

$$\rho(\theta_i, \theta_j) = \frac{Cov(\theta_i, \theta_j)}{\sqrt{V(\theta_i) \times V(\theta_j)}} \tag{7}$$

For a two parameter model,

$$V(\theta) = \begin{bmatrix} V(\theta_1) & Cov(\theta_1, \theta_2) \\ Cov(\theta_1, \theta_2) & V(\theta_2) \end{bmatrix} \quad \rho(\theta_1, \theta_2) = \frac{Cov(\theta_1, \theta_2)}{\sqrt{V(\theta_1) \times V(\theta_2)}} \tag{8}$$

For the multiresponse case, an approximate covariance matrix for the estimated parameters (Draper and Hunter, (1966)) is given by

$$V(\theta) = M^{-1} \tag{9}$$

where

$$M = \sum_{i=1}^{r} \sum_{j=1}^{r} X_i^T X_j \sigma^{ij} \tag{10}$$

and σ^{ij} is the i-j'th element of Σ^{-1}, the inverse of the covariance matrix of the responses, and

$\mathbf{X}_i$ is the n×p matrix of partial derivatives of the response function with respect to the parameters for the i'th response whose elements are:

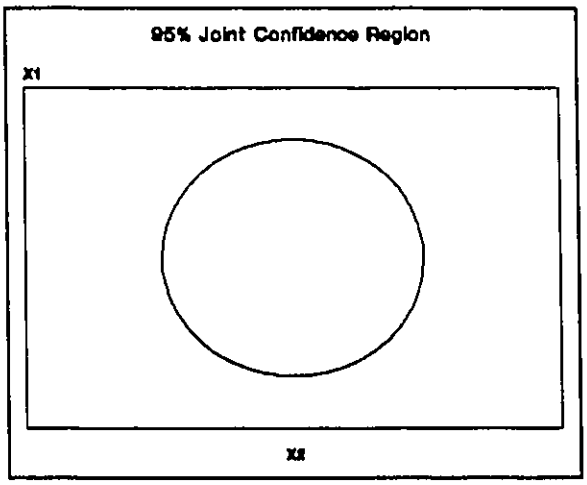
$$\{x_{ui}\}_v = \left.\frac{\partial f_v(\xi_u, \theta)}{\partial \theta_i}\right|_{\theta=\hat{\theta}} \qquad \begin{matrix} v=1,2,\ldots,r \\ u=1,2,\ldots,n \\ i=1,2,\ldots,p \end{matrix} \qquad (11)$$

The covariance matrix calculated using Equation (9) is only an approximation based upon linearization of the response functions about $\theta = \hat{\theta}$ and can be unreliable. Consequently, Monte Carlo simulations were used as will be described in Section 2.6. However, Equation (9) served as a useful tool to identify the factors that may influence the precision. The reaction network and kinetic model are two variables that will affect the design function, **f**. Three other variables are the magnitude of the rate parameters, $\theta = \hat{\theta}$, the experimental design, ξ and the variability of the concentration of reaction products, Σ.

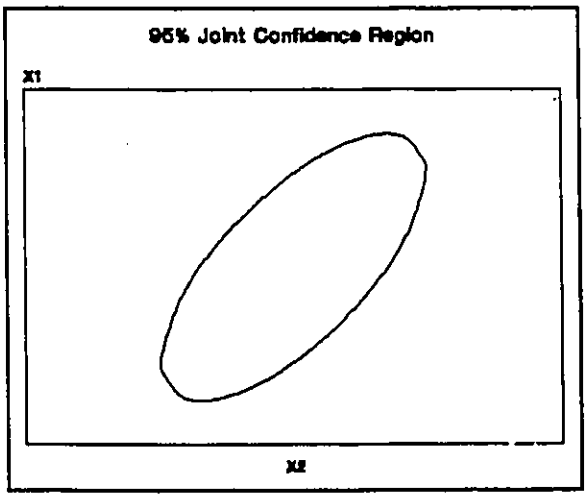
2.4.2 The Joint Confidence Region

The 100(1-α)% joint confidence region has a 100(1-α)% probability of containing the true values of the set of parameters. Examining parameter precision involves examining the size, shape and orientation of the joint confidence region. The smaller the joint confidence region, for a

specific probability, the more precise the set of parameters. Thus the size or "volume" of the joint confidence region is a principal measure of parameter precision. For two parameter models, this "volume" translates into a two-dimensional area, as shown in Figure 1.



(a) Zero Correlation



(b) Positive Correlation

Figure 1: The Effect of Correlation on the Shape of the Joint Confidence Region

The shape and orientation of the joint confidence region are affected by the correlation between parameters. For high correlations, the joint confidence region is highly attenuated and inferences concerning one parameter cannot be made independently of the other (Figure 1b). It is desirable to have zero correlation, if possible, so that each parameter estimate may be expressed independently of the other parameter estimates.

When the errors are Normally distributed, a 100(1-α)% confidence region for the parameters (Box and Tiao, (1973)) contains those values for which

$$S(\boldsymbol{\theta}) - S(\hat{\boldsymbol{\theta}}) \leq \hat{\sigma}^2 p F_{p,n-p,1-\alpha} \tag{12}$$

where $S(\theta)$ is the objective function (such as $\det(\mathbf{e}^T\mathbf{e})$);

$S(\hat{\theta})$ is the objective function evaluated at the optimal values of the parameter estimates;

$\hat{\sigma}^2$ is an estimate of the pure error variance with (n-p) degrees of freedom ; and

$F_{p,n-p,1-\alpha}$ is the upper 100(1-α) percentage point of an F distribution with p and (n-p) degrees of freedom.

For multiresponse analysis, Equation (12) is approximate. The shape of the contours are those of the objective function calculated according to Equation (4). Equation (12) is equivalent to

$$(\boldsymbol{\theta}-\hat{\boldsymbol{\theta}})^T \boldsymbol{V}^{-1} (\boldsymbol{\theta}-\hat{\boldsymbol{\theta}}) \leq p F_{p,n-p,1-\alpha} \tag{13}$$

Equation (13) is also approximate for the multiresponse analysis. The confidence region determined using Equation (13) is elliptical in shape, based on the covariance matrix of Equation (9).

If the measured responses are assumed to be Normally distributed with a constant variance, then the size or "volume" of the approximate confidence region is proportional to the square root of the determinant of the covariance matrix of the estimated rate parameters (Box and Lucas (1959); Draper and Hunter (1966)), that is

$$A \propto \sqrt{|\boldsymbol{V}(\hat{\boldsymbol{\theta}})|} \tag{14}$$

2.4.3 Monte-Carlo Simulation

An alternative method to estimate the dispersion of a set of parameters is Monte Carlo Simulation. The Monte Carlo method determines the actual dispersion of the parameter estimates by repeating a set of experiments many times while allowing the "measured" reacting species to vary according to the designated error structure of the data. This method overcomes the approximations introduced by the methods outlined in the previous sections.

Bard (1972) concluded that the size, shape and orientation of the approximate joint confidence regions estimated using Equations (12) or (13) depend upon the parameter estimates themselves. Moreover, the calculated joint confidence region often underestimates the coverage of the actual region (Donaldson and Schnabel (1987)). As the degree of uncertainty introduced by using the linearized approximate joint confidence regions is highly undesirable, the Monte Carlo method was chosen for this study.

2.5 Experimental Design for Precise Parameter Estimates

As observed in Section 2.4.1, the operating conditions influence the covariance matrix of the parameter estimates. The method used to choose operating conditions to improve the precision of the parameter estimates was the D-Optimal design

criterion of Draper and Hunter (1966).

This criterion determines the operating conditions which minimize the size of the expected approximate joint confidence region by minimizing det($\mathbf{V}(\hat{\theta})$) or by maximizing det($\mathbf{M}$). Because the evaluation of this criterion over the operating region may involve multiple maxima, a grid search is the usual method employed for determining the optimal run locations and was employed in this study.

3 PROCEDURE

3.1 Computer Simulation

The Monte-Carlo simulation involved repeating three tasks: simulating the experiments, estimating the rate parameters and determining the precision of the rate parameters (see Appendix A for the calculations involved). To perform this simulation, values for the following variables were required:

i) The reactor type (i.e., CSTR or PFR);

ii) The reaction network and model (i.e., first order series or parallel);

iii) the experimental design (i.e., the set of run conditions y_u and ξ_u),

iv) the rate parameters θ, and

v) the precision of the measured concentrations of the experimental observations of the reaction, V(y).

In this study, the simulation was repeated 200 times.

A "set" of experiments constituted performing a Monte-Carlo simulation for each reactor type (CSTR and PFR), for each kinetic model and reaction network (first-order series and parallel) and for each experimental design (the initial 10-run design and the 20-run design for precise parameter estimation). Since these factors were fixed for a particular set, what varied from one set to another were the magnitude of the rate parameters, θ, and the precision of the experimental observations of the reaction, $\mathbf{V}(\mathbf{y})$.

The objective of this study was to determine how the eight factors which constitute the magnitude of the rate parameters and the precision of the experimental observations of the reaction influence the precision of the parameter estimates. The investigation of these factors was set up as an interactive procedure. A 2^{8-3}_{IV} fractional factorial design with 5 centre point replicates was first set up to determine the main effects. If the information gleaned from this initial series of conditions was insufficient, more sets of experiments would be carried out as appropriate. The complete 37-set design and the values for the factors in this study are given in Tables 2 and 3.

Table 2

The 2^{8-3} Experimental Design for this Study in terms of the Scaled Factors in Table 3

Set	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
1	-1	-1	-1	-1	-1	-1	-1	-1
2	1	-1	-1	-1	-1	1	1	-1
3	-1	1	-1	-1	-1	1	1	1
4	1	1	-1	-1	-1	-1	-1	1
5	-1	-1	1	-1	-1	1	-1	-1
6	1	-1	1	-1	-1	-1	1	-1
7	-1	1	1	-1	-1	-1	1	1
8	1	1	1	-1	-1	1	-1	1
9	-1	-1	-1	1	-1	-1	1	1
10	1	-1	-1	1	-1	1	-1	1
11	-1	1	-1	1	-1	1	-1	-1
12	1	1	-1	1	-1	-1	1	-1
13	-1	-1	1	1	-1	1	1	1
14	1	-1	1	1	-1	-1	-1	1
15	-1	1	1	1	-1	-1	-1	-1
16	1	1	1	1	-1	1	1	-1
17	-1	-1	-1	-1	1	-1	-1	1
18	1	-1	-1	-1	1	1	1	1
19	-1	1	-1	-1	1	1	1	-1
20	1	1	-1	-1	1	-1	-1	-1
21	-1	-1	1	-1	1	1	-1	1
22	1	-1	1	-1	1	-1	1	1
23	-1	1	1	-1	1	-1	1	-1
24	1	1	1	-1	1	1	-1	-1
25	-1	-1	-1	1	1	-1	1	-1
26	1	-1	-1	1	1	1	-1	-1
27	-1	1	-1	1	1	1	-1	1
28	1	1	-1	1	1	-1	1	1
29	-1	-1	1	1	1	1	1	-1
30	1	-1	1	1	1	-1	-1	-1
31	-1	1	1	1	1	-1	-1	1
32	1	1	1	1	1	1	1	1
33	0	0	0	0	0	0	0	0
34	0	0	0	0	0	0	0	0
35	0	0	0	0	0	0	0	0
36	0	0	0	0	0	0	0	0
37	0	0	0	0	0	0	0	0

Table 3

(a) Values of the Factors

Factor	Lowest Value ($x_i = -1$)	Highest Value ($x_i = +1$)
θ_1	0.0085	0.085
θ_2	0.006	0.06
σ_A^2	0.00025	0.0025
σ_B^2	0.00064	0.0064
σ_C^2	0.00036	0.0036
$\sigma_{AB}, \sigma_{AC}, \sigma_{BC}$	0.1	0.7

(b) Values of the Scaled Factors

$$x_1 = (\theta_1 - 0.04675) / 0.03825$$

$$x_2 = (\theta_2 - 0.033) / 0.027$$

$$x_3 = (\sigma_A^2 - 0.001375) / 0.001125$$

$$x_4 = (\sigma_B^2 - 0.00352) / 0.00288$$

$$x_5 = (\sigma_C^2 - 0.00198) / 0.00162$$

$$x_6 = (\sigma_{AB} - 0.4) / 0.3$$

$$x_7 = (\sigma_{AC} - 0.4) / 0.3$$

$$x_8 = (\sigma_{BC} - 0.4) / 0.3$$

3.2 Generating Experimental Results

The computer simulated the outcome of an experiment given information on the reaction kinetics, the reactor type and the variation in the experimental observations of the reaction. This involved two steps: the deterministic simulation and the stochastic simulation.

The deterministic simulation solved the design equations of Table 1 for the true values of C_A, C_B and C_C using the actual values of θ_1 and θ_2 and the run conditions of the experimental design. The ten-run experimental design set C_{Ao} at three levels and τ at an expected conversion of "A" at approximately 10%, 50% and 90%, plus a centre point replicate. The twenty-run design added ten more run conditions to the first design (see Section 3.4).

The stochastic simulation generated random experimental errors to add to the true values above. These errors were Normally distributed, $N(0,\Sigma)$, with the covariance matrix of the responses from the conditions specified in Table 2. The following equation was used to perform this task (Bard, (1974)).

$$\varepsilon = \mathbf{E}\ \mathbf{U} \qquad (15)$$

where ε is the n×r matrix of random errors associated with the measured responses,

$\mathbf{E}$ is the n×r matrix defined as

$$\mathbf{E} = \mathbf{R}\,\Lambda^{1/2} \tag{16}$$

$\mathbf{R}$ is the n×r matrix of random Normal N(0,1) numbers,

$\mathbf{U}$ is a matrix whose columns are the normalized eigen vectors of Σ, and

Λ is the matrix of the eigenvalues of Σ, such that

$$\mathbf{U}^T\,\Sigma = \Lambda\,\mathbf{U}^T \tag{17}$$

3.3 Parameter Estimation

The simulation program generated "experimental" data which was treated as though they were obtained in a laboratory. The kinetic parameters were estimated using nonlinear multiresponse estimation, since this procedure obtains more precise estimates. As explained in Section 2.3, the multiresponse estimation criterion involved minimization of $S(\theta)$ with respect to θ. Since this approach involved an iterative procedure, a quasi-Newton method was used to search the S surface for the minimum value. To simplify this task, the IBM subroutine "ZXMIN" was used in the computer program (see Appendix A).

3.4 Designing Experiments for Precise Parameter Estimation

The D-Optimal design criterion found the values for the parameters which minimized the size of the expected approximate joint confidence region by maximizing the determinant of **M**. Since the evaluation of this criterion over the operating region may involve multiple maxima, a grid search was employed to determine the optimal run locations for this study.

The value of det(**M**) was first evaluated for the initial ten-run experimental design, according to Equation (10). The operating region was then divided into a three by ten grid, that is, three levels of C_{Ao} and ten levels of τ, and the value of det(**M**) was evaluated for the first ten runs plus one other point from the grid. The designed run was that grid point for which det(**M**) was the largest. This point was added to the first ten conditions and the grid was searched again for the next designed run. The process stopped at ten additional runs, when there was no more improvement to the precision of the parameter estimates.

3.5 Evaluating Precision of the Parameter Estimates

The Monte Carlo simulation repeated the same set of experiments 200 times. This sample was used to estimate the location and dispersion statistics of the parameter estimates, according to the following equations:

i) the mean of a parameter estimate:

$$\bar{\theta} = \frac{1}{n} \sum_{i=1}^{n} \theta_i \qquad (18)$$

ii) the variance of a parameter estimate:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^{n} (\theta_i - \bar{\theta})^2 \qquad (19)$$

iii) the covariance between the two parameter estimates:

$$Cov(\theta_1, \theta_2) = \frac{1}{n-1} \sum_{i=1}^{n} (\theta_{1i} - \bar{\theta_1})(\theta_{2i} - \bar{\theta_2}) \qquad (20)$$

iv) the correlation between the parameter estimates was calculated according to Equation (7), and

v) the determinant of the covariance matrix:

$$\det(\mathbf{V}(\theta)) = s^2_{\theta 1} \cdot s^2_{\theta 2} - (\mathrm{Cov}(\theta_1, \theta_2))^2 \qquad (21)$$

3.6 Modelling of the Results

Two measures of precision were recorded for each set of experiments: the "area" of the joint confidence region, AREA (where AREA = $(\det(\underline{V}(\hat{\underline{\theta}})^{1/2}))$, and the correlation between the parameter estimates, ρ.

In order to compare reactors, the relative precision, that is, the ratio of the measures of precision for the CSTR to the PFR, was examined. This relative measure of precision was modelled against the scaled factors of this study. In this regard, single response (least-squares) parameter estimation was used. To perform this task, the Statistical Analysis System (SAS) was used to find the empirical model of the effects of the factors on the relative precision.

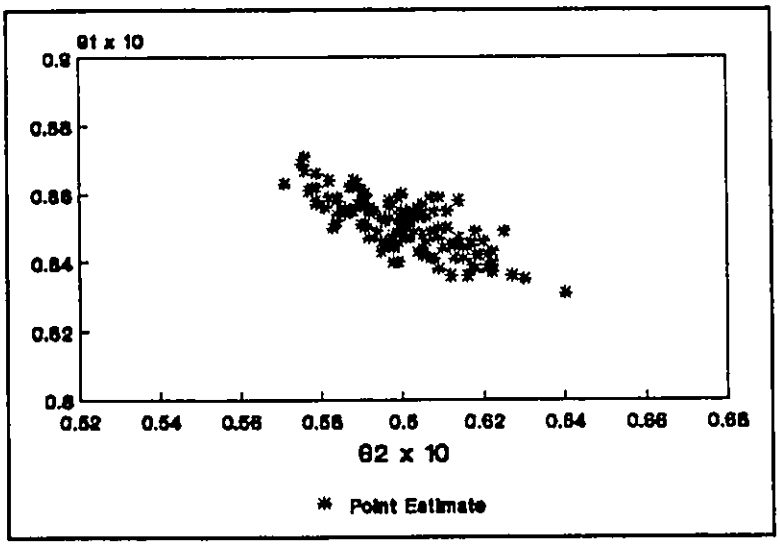
4 RESULTS AND DISCUSSION

The raw results are presented in Appendix B.

4.1 The Dispersion of the Parameter Estimates

As an example of the dispersion of the parameter estimates, Figure 2 displays the results for the series reaction network at the conditions of Set 12. The joint confidence regions appear elliptical in shape with the true values of the parameters at the centre point. In addition, the frequency of the estimates is thin at the outer edge of the ellipse and increases as the centre point is approached.

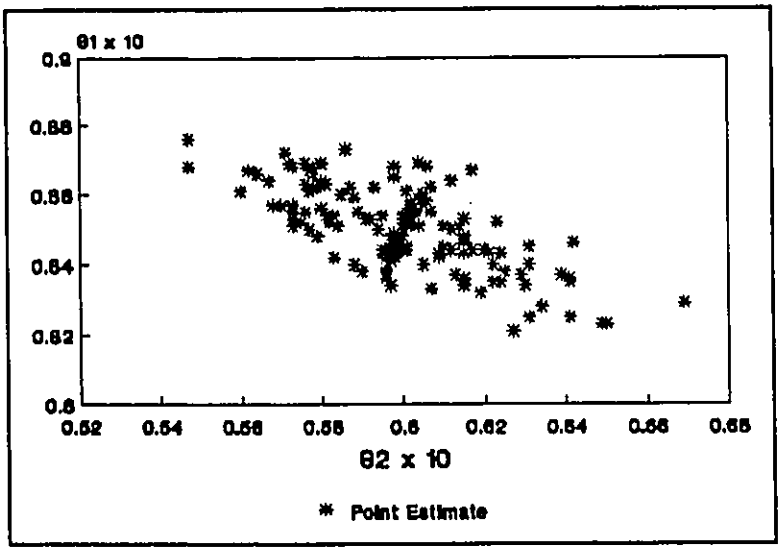
Figure 2 clearly displays that, for the conditions of Set 12, the area of the joint confidence region obtained using the CSTR is larger than that obtained using the PFR. Using Equation (14), the measure of the volume of the joint confidence region, to compare the reactors, the area from the CSTR was 2.76 times larger than that from the PFR.



(a) Plug Flow Reactor

$\hat{\theta}_{1(mean)}$ = 0.0851 $V(\hat{\theta}_1)$ = 4.52×10^{-7} $\rho(\theta_1,\theta_2)$ = -0.757

$\hat{\theta}_{2(mean)}$ = 0.0600 $V(\hat{\theta}_2)$ = 1.23×10^{-6} $\det(\underline{V}(\underline{\hat{\theta}}))^{1/2}$ = 4.87×10^{-7}



(b) Continuous Stirred Tank Reactor

$\hat{\theta}_{1(mean)}$ = 0.0850 $V(\hat{\theta}_1)$ = 1.03×10^{-6} $\rho(\theta1,\theta2)$ = -0.663

$\hat{\theta}_{2(mean)}$ = 0.0600 $V(\hat{\theta}_2)$ = -1.19×10^{-6} $\det(\underline{V}(\underline{\hat{\theta}}))^{1/2}$ = 1.35×10^{-6}

Figure 2: The Dispersion of the Parameter Estimates from a First-Order Series Reaction, Set Number 12

4.2 The Effect of Reactor Type on Parameter Precision

4.2.1 Area of the Joint Confidence Region

The main measure used to compare the precision obtained from both reactors is the ratio of the area of the joint confidence region obtained using the CSTR to that using the PFR. When the value for this ratio is greater than one, the area of the joint confidence region using the CSTR is greater than that using the PFR and, as a result, the PFR is the reactor type which would give the most precise estimates of kinetic parameters.

Table 4 compares the reactors by displaying the ratio of the area of the joint confidence region using the CSTR to that using the PFR, for the conditions of this study.

Table 4

Effect of Reactor Type on Parameter Precision

Confidence Region Area Ratio (CSTR/PFR)

Parallel Reaction Network			Series Reaction Network		
Set	10-Run Design	20-Run Design	Set	10-run Design	20-Run Design
1	1.91	1.73	1	2.83	2.50
2	1.42	2.09	2	0.85	0.70
3	1.54	1.65	3	1.32	2.53
4	1.29	1.37	4	3.22	2.42
5	1.72	1.43	5	3.14	2.29
6	1.84	1.96	6	0.66	0.63
7	0.92	1.07	7	1.83	3.24
8	1.32	1.32	8	3.28	3.32
9	1.24	1.12	9	3.52	2.29
10	1.49	1.39	10	0.58	0.58
11	1.69	1.80	11	1.27	2.34
12	1.50	1.73	12	2.76	2.51
13	1.73	1.52	13	3.01	2.20
14	1.55	1.56	14	0.72	0.76
15	1.37	1.36	15	1.95	2.13
16	1.21	1.18	16	2.71	2.69
17	1.93	1.81	17	2.19	2.30
18	1.58	1.40	18	0.52	0.60
19	1.74	1.70	19	1.93	1.64
20	1.45	1.33	20	3.05	2.31
21	1.13	1.00	21	3.21	3.70
22	1.30	1.61	22	0.46	0.52
23	1.68	1.64	23	1.80	2.09
24	1.21	1.32	24	3.53	2.73
25	1.56	1.49	25	2.71	2.25
26	1.67	1.44	26	0.56	0.55
27	1.73	1.55	27	1.72	2.06
28	1.40	1.28	28	2.49	2.35
29	1.29	1.63	29	2.54	3.36
30	1.58	1.47	30	0.79	0.94
31	1.92	1.66	31	2.99	2.72
32	1.78	1.63	32	2.63	1.85
33	1.61	1.65	33	2.82	2.42
34	1.47	1.84	34	4.03	2.16
35	1.81	1.64	35	2.62	2.63
36	1.33	1.44	36	2.72	2.38
37	1.45	1.33	37	2.80	2.24

Parallel Reaction Network

For the parallel reaction network, all values of the ratio for the twenty-run design were greater than one. Therefore, the precision of the parameter estimates was always better using a PFR to measure the kinetics of a first-order parallel reaction network. This same result was obtained by the study of Hoffman et al. (1977).

A physical interpretation of this result is that the most information about a parallel reaction is revealed in the initial stages of the reaction, and a PFR gives this type of information better than a CSTR.

The average confidence region area ratio for the twenty-run experimental design was 1.51. That is, on average, the area of the joint confidence region using the CSTR was 1.51 times larger than that using the PFR. This ratio ranged from 1.00 to 2.09 indicating that, for some conditions (i.e., Set 21), the reactor type had no effect of the choice of reactor, as the CSTR could produce equally precise parameter estimates as the PFR. At other conditions (i.e., Set 2), the parameters estimated using the PFR could be twice as precise as those using the CSTR.

For the ten-run experimental design, the average confidence region area ratio was 1.52. That is, the experimental design had negligible affect on the choice of reactor or on the average improvement in precision using a PFR. However, these ratios ranged from 0.92 to 1.93. At the conditions of Set 7, the CSTR produced slightly more precise parameter estimates. Therefore, the use of only the ten-run experimental design in this study might have led to a misleading interpretation for the conditions of Set 7.

Series Reaction Network

Table 4 shows that, for the series reaction network, there were some occasions when the CSTR gave a smaller area of the joint confidence region, that is, the ratio was less than one. Therefore, for a first-order series reaction network, the precision of the parameter estimates was not always better using a PFR to measure the kinetics of the reaction. This trend was apparent for both the ten-run and twenty-run designs.

When the confidence region area ratio was greater than one, the average ratio for the twenty-run experimental design was 2.49. This ratio ranged from 1.64 to 3.70, demonstrating that great improvements in the precision can be made by using a PFR to measure the reaction kinetics, at some conditions.

When the confidence region area ratio was less than one, the average ratio for the twenty-run experimental design was 0.66. That is, the area of the joint confidence region using the PFR was 1.52 times larger than that using the CSTR, on average. This ratio ranged from 0.52 to 0.94, signifying that using a CSTR at some conditions (i.e., Set 22), could make the parameter estimates as much as 1.92 times more precise than using a PFR.

The experimental design had negligible effect on these results, as the ten-run experimental design mirrored the results of the twenty-run design.

4.2.2 Correlation Between Parameter Estimates

A second measure of comparison of the precision obtained from both reactors was the ratio of the correlation between the parameter estimates, using the CSTR to the PFR. Table 5 presents this comparison.

Table 5

Effect of Reactor Type on Parameter Correlation

Correlation Ratio (CSTR/PFR)

Parallel Reaction Network			Series Reaction Network		
Set	10-Run Design	20-Run Design	Set	10-run Design	20-Run Design
1	2.94	0.86	1	0.89	0.57
2	0.48	0.92	2	-2.17	0.70
3	1.47	2.47	3	0.07	0.87
4	1.49	0.94	4	-0.39	0.35
5	1.59	0.99	5	-4.29	-1.26
6	-1.59	-1.44	6	5.58	0.98
7	0.88	0.95	7	0.95	1.16
8	1.07	0.98	8	-3.84	-1.43
9	-2.16	3.38	9	1.04	1.02
10	1.19	0.77	10	0.66	0.62
11	0.52	0.63	11	0.60	1.14
12	0.03	-0.21	12	0.88	1.05
13	1.48	1.34	13	0.99	0.83
14	1.58	1.27	14	-1.79	-4.37
15	1.01	1.10	15	0.90	1.06
16	-0.49	-0.58	16	1.12	1.00
17	1.89	0.95	17	-11.9	1.45
18	-0.24	-0.19	18	0.65	0.37
19	0.96	1.93	19	0.98	0.83
20	-0.24	-0.36	20	3.77	1.08
21	1.08	0.92	21	3.76	2.38
22	0.94	1.02	22	0.76	0.10
23	0.95	0.53	23	0.69	0.98
24	1.62	0.97	24	2.07	1.91
25	0.85	0.86	25	1.04	1.04
26	0.73	0.68	26	0.34	0.50
27	0.77	0.72	27	0.71	1.03
28	0.37	0.20	28	0.99	0.99
29	0.88	0.94	29	1.63	0.94
30	-0.22	-1.44	30	-7.47	0.02
31	0.97	1.20	31	-1.02	-1.16
32	3.66	1.12	32	0.87	0.95
33	26.7	1.01	33	0.61	1.11
34	-14.9	1.37	34	1.65	0.29
35	1.28	2.42	35	0.26	0.43
36	3.06	2.02	36	1.08	1.27
37	-33.8	1.15	37	0.48	0.89

For both the parallel and series reaction networks, the ratio was greater than one as often as it was less than one. The interpretation of this result is that the PFR produced a lower correlation as often as the CSTR, and no reactor was preferred.

It is interesting to note, however, that at the times when the CSTR gave a smaller area of the joint confidence region, the correlation was almost always lower for the CSTR as well, making the preference for the CSTR at these occasions two-fold.

Some high negative values for the relative correlation were obtained, for example, Sets 34 and 37 of the ten-run design for the series reaction network. An examination of the raw results in Appendix B shows that, at this condition, the correlation for the PFR was very nearly zero, sometimes negative in nature, whereas the correlation from the CSTR was a positive value, averaging 0.44. Since the PFR result was the denominator of the ratio measuring relative correlation, the high negative values were achieved.

4.3 Factors Influencing Parameter Precision

The objective of this study was to determine how the factors which constitute the magnitude of the rate parameters and the precision of the experimental observations of the reaction influence the precision of the parameter estimates. As indicated in Section 3.1, this investigation was first set up as a 2^{8-3}_{IV} fractional factorial design with 5 centre point replicates, in order to determine the main effects. Since the twenty-run design allows the reactors to be compared under conditions giving the best parameter precision for each reactor type, this analysis will be limited to examining the information gleaned from the twenty-run design. See Appendix C for the modelling calculations.

For the parallel reaction network, the precision of the parameter estimates was always better using a PFR to measure the kinetics. Modelling the relative area of the joint confidence region, that is, the area obtained using the CSTR to that using the PFR, gave the following empirical model:

$$(AREA_{CSTR} : AREA_{PFR}) = (AREA_{CSTR} : AREA_{PFR})_{mean} \qquad (21)$$

That is, the factors did not influence the choice of reactor.

For the series reaction network, an examination of Tables 2 and 4 reveal that the CSTR gave more precise parameter estimates when the values of θ_1 and θ_2 were high and low respectively. Thus, an initial glance at the results indicates that, for first-order series reactions, the PFR gave more precise parameter estimates, except when the reaction from "A" to "B" was fast and the reaction from "B" to "C" was slow. A possible explanation for this observation is that a CSTR is more capable of giving information about the final concentration of product "C" thereby obtaining a better estimate of θ_2.

Modelling the relative area of the joint confidence region yielded the following empirical equation:

$$\begin{aligned}(AREA_{CSTR} : AREA_{PFR}) &= 2.05 - 0.413\ x_1 + 0.429\ x_2 \\ &+ 0.133\ x_3 + 0.502\ (x_1x_2 + x_3x_6 + x_4x_7) \\ &- 0.128\ (x_1x_8 + x_5x_7) - 0.145\ (x_2x_5 + x_4x_8)\end{aligned} \tag{22}$$

However, tests for the adequacy of this model showed the need for a quadratic term (see Appendix C for this evaluation). As a result, further sets of experiments were carried out, according to Table 6. The following model of the ratio of the area of the joint confidence region obtained using the CSTR to that of the PFR with this additional information was obtained:

$$(AREA_{CSTR} : AREA_{PFR}) = 2.31 - 0.400\ x_1 + 0.447\ x_2 - 0.329\ x_2^2 + 0.133\ x_3 + 0.502\ (x_1x_2 + x_3x_6 + x_4x_7) - 0.128\ (x_1x_8 + x_5x_7) - 0.147\ (x_2x_5 + x_4x_8) \quad (23)$$

Table 6

(a) The Experimental Design to Obtain Quadratic Terms

Set	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
38	1.1	0	0	0	0	0	0	0
39	-1.1	0	0	0	0	0	0	0
40	0	1.1	0	0	0	0	0	0
41	0	-1.1	0	0	0	0	0	0

Results

Effect of Reactor Type on Parameter Precision for the Series Reaction Network

(b) Confidence Region Area Ratio (CSTR/PFR)

Set	10-Run Design	20-Run Design
38	5.94	3.41
39	4.13	5.57
40	7.79	5.60
41	0.47	0.74

(c) Correlation Ratio (CSTR/PFR)

Set	20-Run Design
38	0.60
39	-0.66
40	1.04
41	-0.56

Tests on the adequacy of this model showed no lack of fit (see Appendix C). However, in order to ascertain which of the second-order interactions were trivial, seven more sets of experiments were carried out (see Table 7).

The following final model of the relative area of the joint confidence region was obtained:

$$(AREA_{CSTR} : AREA_{PFR}) = 2.309 - 0.413\ x_1 + 0.434\ x_2 - 0.340\ x_2^2 + 0.119\ x_3 - 0.133\ x_1x_8 + 0.465\ x_3x_6 - 0.152\ x_4x_8 \quad (24)$$

There was no lack of fit for this final model (see Appendix C).

Table 7

(a) The Experimental Design to Obtain Second-Order Interactions[1]

Set	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
42	1	1	1	1	1	-1	-1	-1
43	1	1	1	1	1	-1	1	-1
44	1	1	1	1	-1	1	-1	-1
45	1	1	1	1	-1	1	1	-1
46	1	1	1	1	1	1	1	1
47	1	1	1	1	-1	1	1	1
48	1	1	1	1	1	1	1	-1

Results

(b) Effect of Reactor Type on Parameter Precision for the Series Reaction Network

Set	Confidence Region Area Ratio (CSTR/PFR) 20-Run Design	Correlation Ratio (CSTR/PFR) 20-Run Design
42	4.16	0.50
43	4.83	0.87
44	6.70	0.78
45	7.90	1.01
46	3.92	0.48
47	5.25	2.42
48	7.06	0.72

[1]Sets 42 to 45 are to differentiate $\theta_1\theta_2$, $\sigma_A^2\sigma_{AB}$ and $\sigma_B^2\sigma_{AC}$; sets 46 and 47 are to differentiate $\theta_1\sigma_{BC}$ and $\sigma_C\sigma_{AC}$; and sets 46 and 49 are to differentiate $\theta_2\sigma_C^2$ and $\sigma_B\sigma_{BC}$.

Equation (24) shows that three main factors, namely θ_1, θ_2 and σ_A^2, and three interactions, $\theta_1\sigma_{BC}$, $\sigma_A^2\sigma_{AB}$ and $\sigma_B^2\sigma_{BC}$, affected the choice of reactor. For the purposes of comparing the effects of the various factors, it is appropriate to examine the scaled values in order that the effect of each factor is given equal weight.

According to Equation (24), the effect of x_2 (scaled θ_2) is quadratic and independent of any interactions. As x_2 increases, the relative area ratio ($AREA_{CSTR}$: $AREA_{PFR}$) also increases to a maximum at approximately 0.68 (see Figure 3). As the value of x_2 increases further, the quadratic term becomes dominant causing the relative area ratio to decrease. Equation (24) predicts that a CSTR will give more precise parameter estimates than a PFR when x_2 is either very low or very high.

However, since this study only examined values of x_2 from -1.1 to +1.1, the prediction of the final model is limited to the effect of very low x_2. In addition, Figure 3 shows that, when all of the other factors are zero (i.e., at their centre points), the effect of x_2 alone will not cause the relative area ratio to be less than one. The values of the other identified factors must also work to decrease the ratio, in order for the CSTR to give more precise parameter estimates. Nevertheless, the magnitude of θ_2 influences the parameter

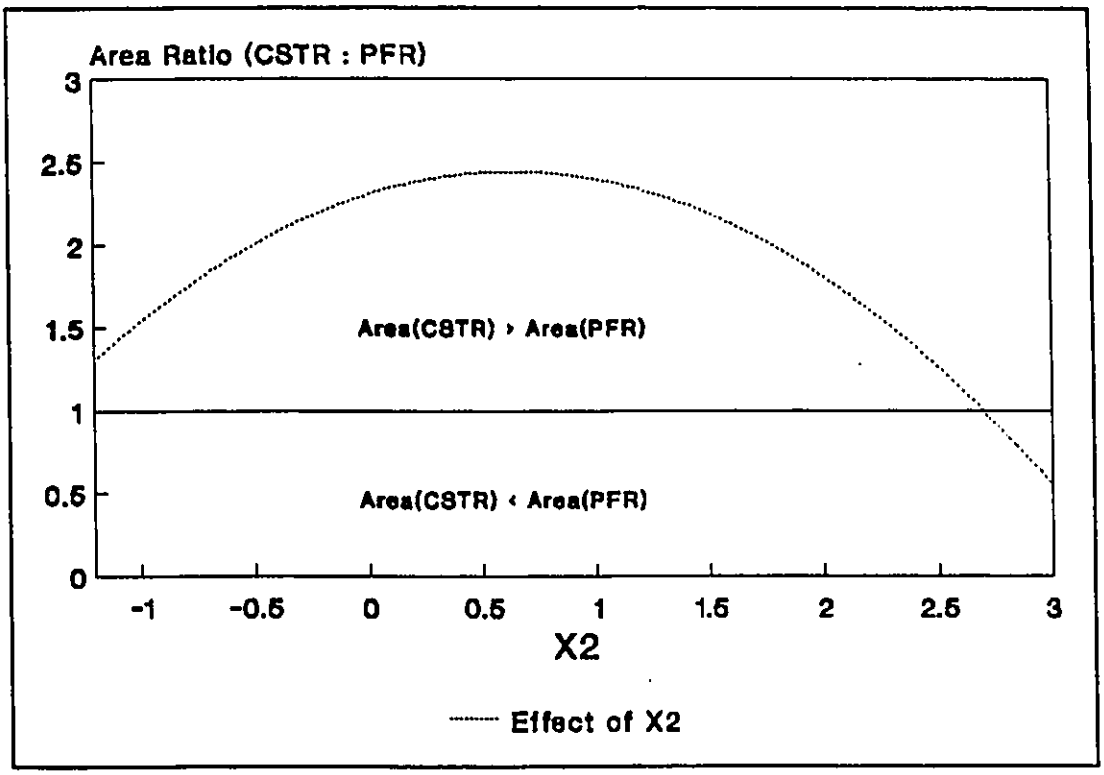


Figure 3: The Effect of x_2 on the Choice of Reactor[1]

[1] When the factors of Equation (24), other than x_2, are set to zero: $(AREA_{CSTR} : AREA_{PFR}) = 2.309 + 0.434\ x_2 - 0.340\ x_2^2$

precision and low values of θ_2 favour the choice of the CSTR over the PFR.

The effect of x_3 (scaled σ_A^2) is to make the relative area ratio increase and favour the PFR as x_3 increases. However, there is a strong interaction between x_3 and x_6 (scaled σ_{AB}) which may offset this effect (see Figure 4). When both x_3 and x_6 are high, or both x_3 and x_6 are low, the second-order interaction term is positive, thereby favouring the PFR. But when x_3 is high and x_6 is low, or x_3 is low and x_6 is high, the interaction effect decreases the relative area ratio to favour the CSTR.

Therefore, the final model of Equation (24) predicts that a CSTR will give more precise parameter estimates than a PFR when:

i) x_3 is less than -1.2 and x_6 is greater than 1.5; or

ii) x_3 is greater than 2 and x_6 is less than -1.5;

and all other factors are zero. However, since these predictions are outside the study conditions, the effects of x_3 and x_3x_6 must be combined with those of the other factors. Thus, the variance of the measured product "A" and the covariance between C_A and C_B influence parameter precision such

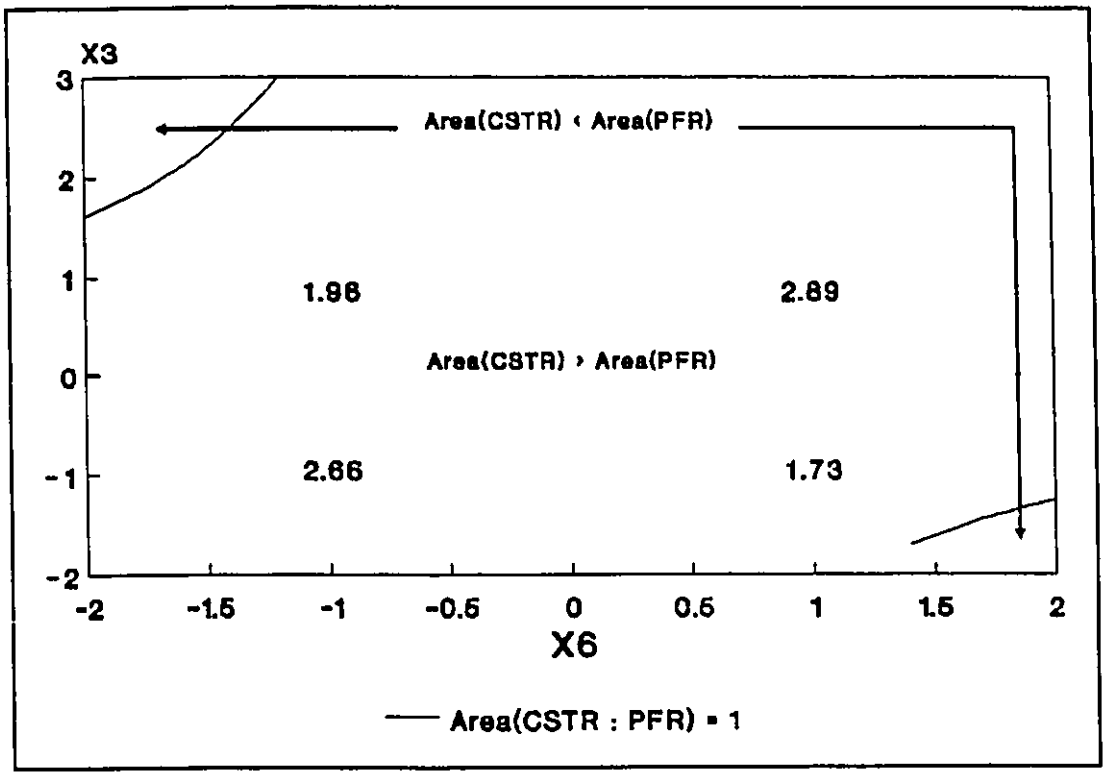


Figure 4: The Effects of x_3 and x_6 on the Choice of Reactor[2]

[2] When the factors of Equation (24), other than x_3 and x_6, are set to zero:
$(AREA_{CSTR} : AREA_{PFR}) = 2.309 + 0.119\ x_3 + 0.465\ x_3x_6$

that low values of σ_A^2 and high values of σ_{AB} favour the choice of the CSTR over the PFR.

The effect of x_1 (scaled θ_1) is such that, as x_1 increases, the relative area ratio decreases, to favour the CSTR. However, the interaction between x_1 and x_8 (scaled σ_{BC}) means that, when x_8 is low, the ratio decreases with increasing x_1 more slowly than when x_8 is high (see Figure 5).

Equation (24) predicts that a CSTR will give more precise parameter estimates than a PFR when x_1 is greater than 2, when x_8 is greater than 1 and all other factors are zero. Since this prediction is also outside the operating region of this study, the effects of θ_1 and $\theta_1\sigma_{BC}$ must be combined with those of the other factors.

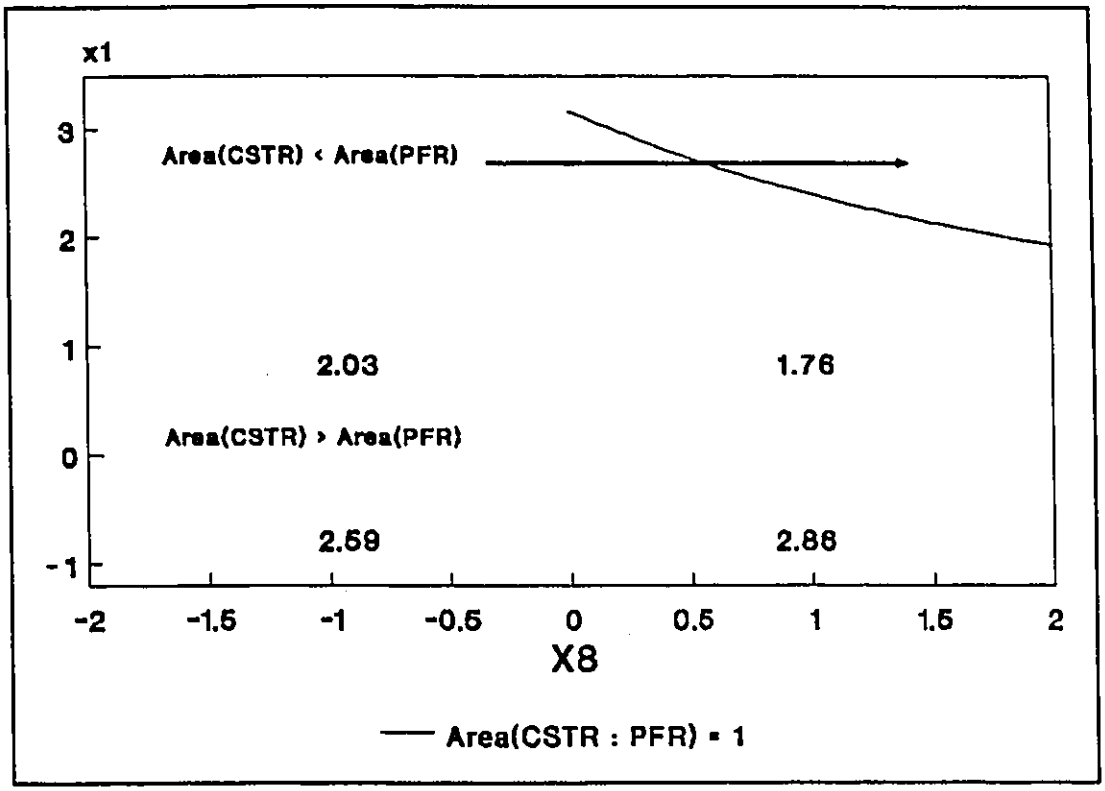


Figure 5: The Effects of x_1 and x_8 on the Choice of Reactor[3]

[3] When the factors of Equation (24), other than x_1 and x_8, are set to zero:
$(AREA_{CSTR} : AREA_{PFR}) = 2.309 - 0.413\ x_1 - 0.133\ x_1x_8$

The final term in the model of Equation (24) is the interaction x_4x_8 (scaled σ_8^2 and σ_{BC} respectively). When these values are either both high or both low, the relative area ratio is lower, favouring the CSTR (see Figure 6). However, when either x_4 is high and x_8 is low, or x_4 is low and x_8 is high, the ratio is higher. Since a high value of x_8 also enhances the effect of x_1, this model predicts that the preference for a CSTR, in terms of the precision of the rate parameters, is enhanced when x_4 and x_8 are both high.

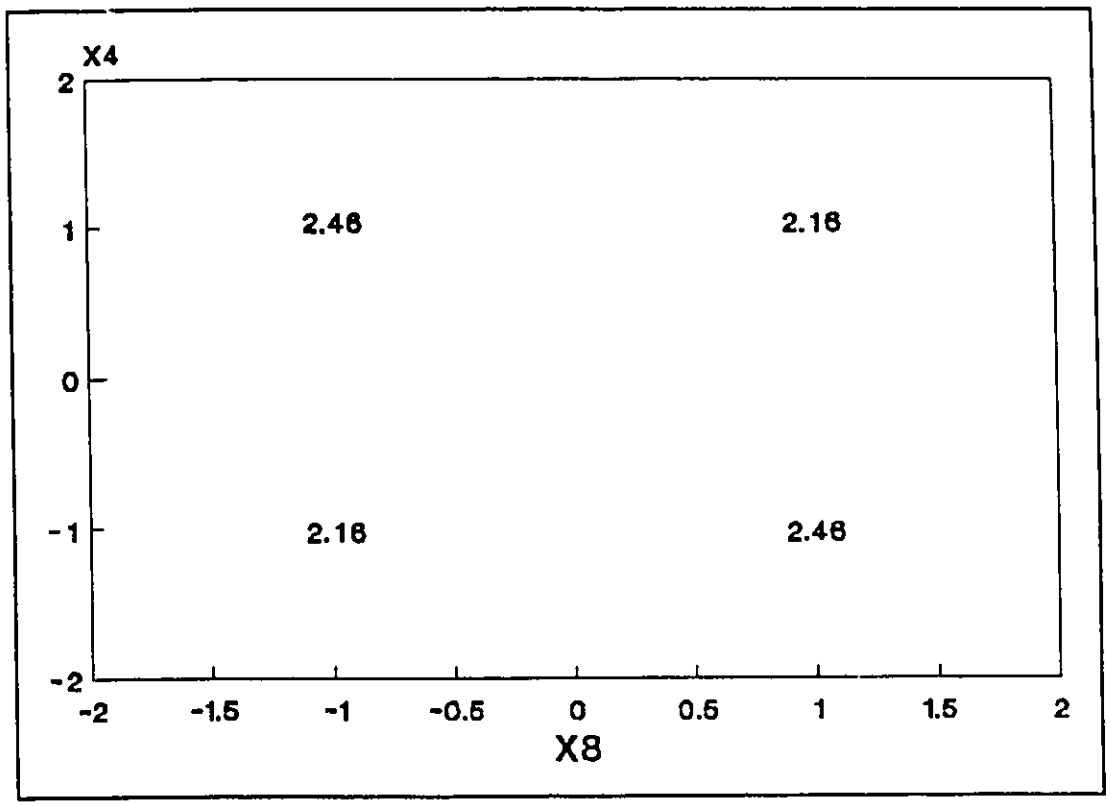


Figure 6: The Effects of x_4 and x_8 on the Choice of Reactor[4]

[4] When the factors of Equation (24), other than x_3 and x_6, are set to zero: $(AREA_{CSTR} : AREA_{PFR}) = 2.309 - 0.152\ x_4x_8$

The effects of the three main factors on the choice of reactor is shown in Figure 7. This figure exemplifies the trend noted in Section 4.2.1, that when x_1 was high and x_2 was low, (that is, when the rate from "A" to "B" was much faster than from "B" to "C"), the ratio of the area of the joint confidence region for the CSTR to that of the PFR was less than one. In addition, Equation (24) predicts that, when x_3 is low (that is, low variance of C_A), the CSTR would be favoured at lower values of x_1. Figure 7 also shows that the CSTR would be the preferred reactor when x_1 and x_2 are both high, although this prediction is outside the operating region for this study.

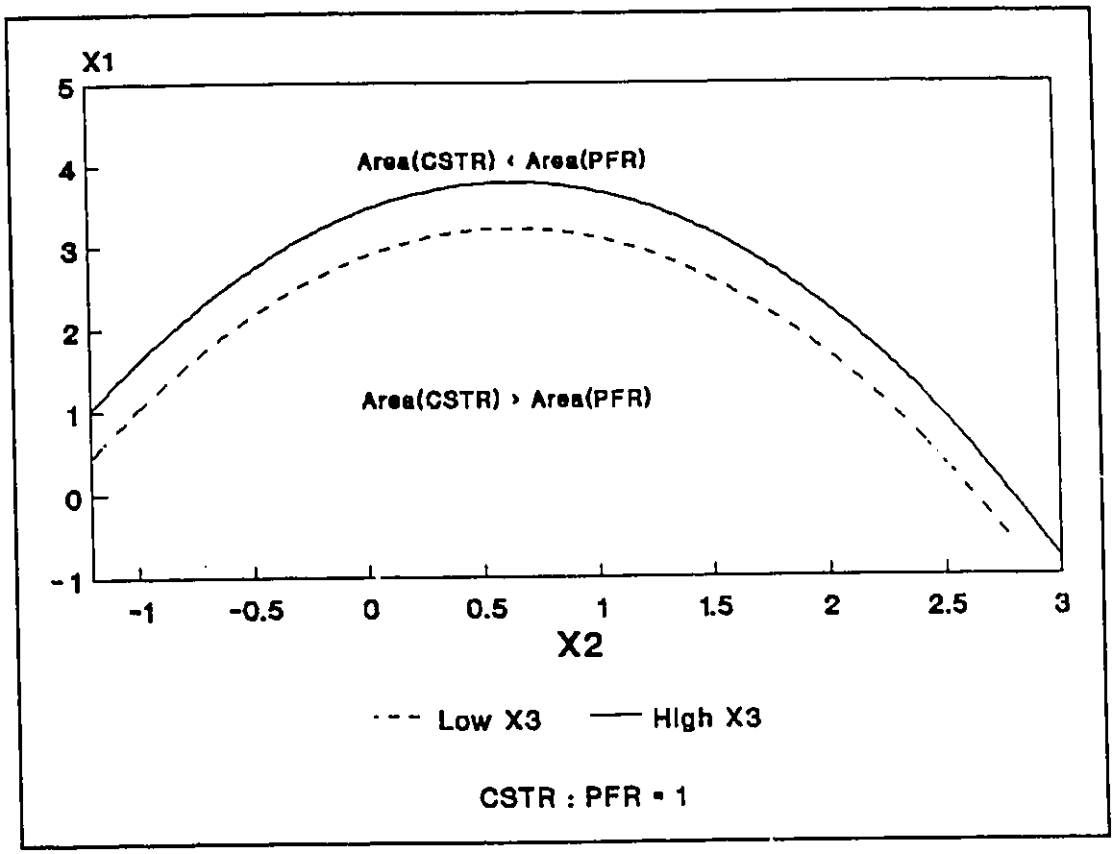


Figure 7: The Three Main Effects on the Choice of Reactor[5]

---

[5] When the factors of Equation (24), other than x_1, x_2 and x_3, are set to zero:

$$(AREA_{CSTR} : AREA_{PFR}) = 2.309 - 0.413\ x_1 + 0.434\ x_2 - 0.340\ x_2^2 + 0.119\ x_3$$

At this stage, it is important to examine the final model in terms of the original uncoded factors, in order to compare the reactors in real terms. Scaling the factors to their original values, using Table 3, gives the following model and Figure 8:

$$\begin{aligned}(AREA_{CSTR} : AREA_{PFR}) = {} & 1.92 - 6.16\ \theta_1 + 46.86\ \theta_2 \\ & - 445.33\ \sigma_A^2 + 70.37\ \sigma_B^2 - 1.894\ \sigma_{AB} \\ & + 1.16\ \sigma_{AC} - 11.59\ \theta_1\sigma_{BC} + 1377.78\ \sigma_A^2\sigma_{AB} \\ & - 175.93\ \sigma_B^2\sigma_{BC} - 466.39\ \theta_2^2\end{aligned} \qquad (25)$$

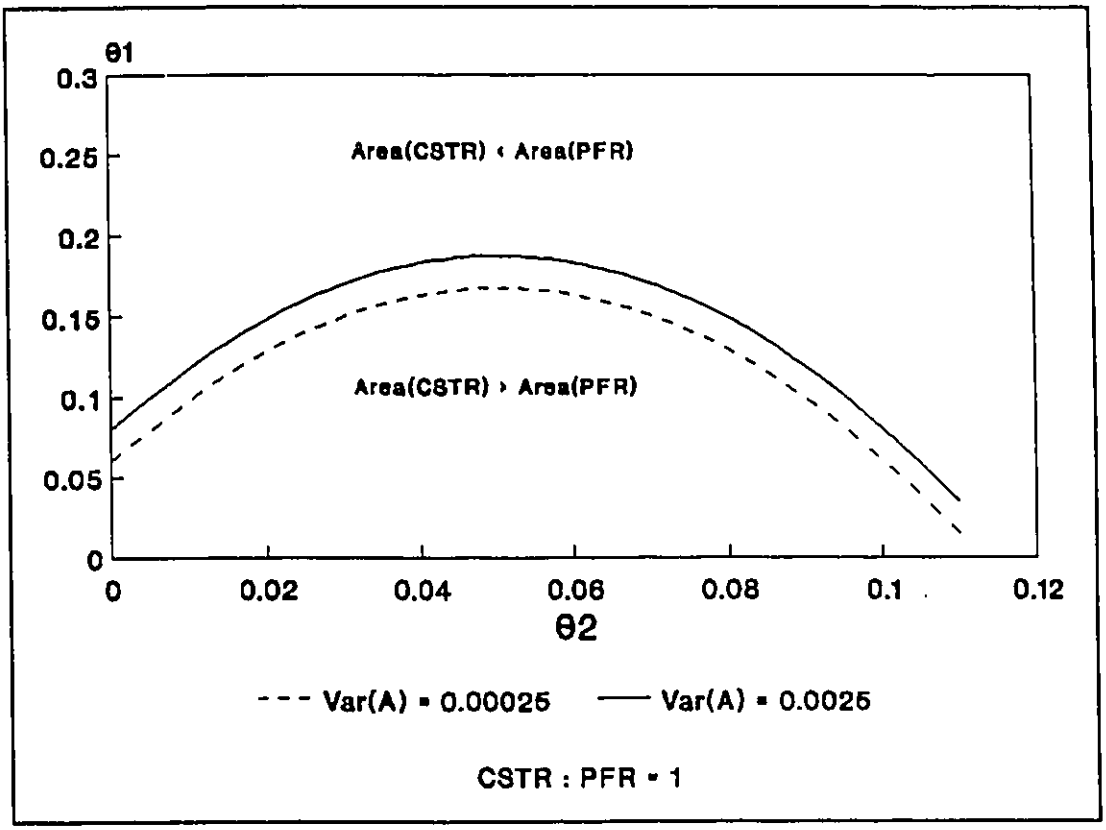


Figure 8: The Three Main Effects on the Choice of Reactor[6]

[6] Scaled to their "true" values.

4.4 Reproducibility

To examine the reproducibility of the results of this study, Table 8 displays the results for the five centre-point replicates, Sets 33 to 37 (see Appendix B for raw results). These results were used to estimate the pure-error variance of the data, in order to ascertain which factors affect the precision of the parameter estimates and consequently the choice of reactor.

In general, the results for the area of the joint confidence region are reproducible. Table 8a shows that the area of the joint confidence region fluctuated widely for the ten-run design but had moderated for the twenty-run design. This was particularly apparent for the series reaction network.

Table 8b shows that the correlation between parameter estimates for the parallel reaction network also fluctuated widely for the ten-run experimental design and moderated for the twenty-run design. The series reaction network, however, continued to display high variation in parameter correlation, even for the twenty-run experimental design. It appears that the reproducibility here was poor, perhaps indicating the need to use more than 200 Monte-Carlo simulations. As a result, a model of the effects of correlation on the choice of reactor

Table 8

Reproducibility of the Experiments (Centre-Point Replicates)

(a) Area of the Joint Confidence Region

(i) Parallel Reaction Network

Ten - Run Design			Twenty - Run Design		
CSTR ($x10^7$)	PFR ($x10^7$)	Ratio CSTR:PFR	CSTR ($x10^7$)	PFR ($x10^7$)	Ratio CSTR:PFR
12.3	7.64	1.61	2.92	1.77	1.65
12.5	8.48	1.47	2.84	1.55	1.84
13.1	7.23	1.81	2.65	1.63	1.64
10.7	8.04	1.33	2.66	1.84	1.44
11.2	7.73	1.45	2.46	1.85	1.33

(ii) Series Reaction Network

Ten - Run Design			Twenty - Run Design		
CSTR ($x10^7$)	PFR ($x10^7$)	Ratio CSTR:PFR	CSTR ($x10^7$)	PFR ($x10^7$)	Ratio CSTR:PFR
18.2	6.46	2.82	3.22	1.33	2.42
27.9	6.93	4.03	2.97	1.37	2.16
18.6	7.10	2.62	3.09	1.18	2.63
20.3	7.44	2.72	3.02	1.27	2.38
17.6	6.29	2.80	2.86	1.27	2.24

Table 8 (continued)

(b) Correlation Between Parameter Estimates

(i) Parallel Reaction Network

Ten - Run Design			Twenty - Run Design		
CSTR	PFR	Ratio	CSTR	PFR	Ratio
0.442	0.017	26.7	0.301	0.297	1.11
0.382	-0.026	-14.9	0.311	0.227	0.29
0.537	0.421	1.28	0.345	0.143	0.43
0.384	0.126	3.06	0.250	0.124	1.27
0.471	-0.014	-33.8	0.276	0.241	0.89

(ii) Series Reaction Network

Ten - Run Design			Twenty - Run Design		
CSTR	PFR	Ratio	CSTR	PFR	Ratio
-0.147	-0.240	0.61	-0.259	-0.233	1.11
-0.162	-0.098	1.65	-0.097	-0.332	0.29
-0.057	-0.222	0.26	-0.209	-0.487	0.43
-0.119	-0.175	1.08	-0.231	-0.182	1.27
-0.141	-0.294	0.48	-0.256	-0.288	0.89

would not be very sensitive to the factors in this study.

4.5 Applicability

In order to properly design a bench-scale investigation, an experimenter would have some knowledge of the reaction kinetics being studied and of the reactor conditions needed to obtain accurate estimates of the reaction parameters. With this knowledge, the findings of this study could be used determine the reactor type to use in order to obtain the most precise estimates of the parameters.

This study showed that the reaction network affected the choice of reactor. The parameter precision for a parallel reaction network was always better using a PFR, whereas some conditions of the series network made the CSTR the favoured reactor to obtain precise parameters. However, the empirical models obtained in this study cannot be expanded to other networks.

For the parallel reaction network, Hoffman et al. (1977) predicted that the PFR would also give more precise parameter estimates for second-order and higher models. The same behaviour would be expected from this study, due to the similar nature of these reactions. However, the effect of the kinetic model for series reactions of higher order is

uncertain from this study.

This study also showed that the experimental design had negligible effect on the choice of reactor. While vast improvement was made in the precision of the parameter estimates, the choice of reactor was not affected by the experimental design.

Finally, the magnitude of the rate parameters and the precision of the experimental observations of the reaction influenced choice of reactor for the series reaction network. An experimenter could use Equations (24) or (25) to predict which reactor should be used, when the values for the factors are within the levels chosen for this study.

In order to examine the ability of Equation (24) to make accurate predictions outside the conditions of this study, some exploratory experiments were carried out, as given in Table 9. These extra Sets explored the region of high θ_1 and intermediate θ_2 and of low θ_1 and high θ_2.

Table 9

Exploring The Region Outside This Study

x_1	x_2	Confidence Region Area Ratio (CSTR:PFR)
-0.96	1.26	1.73
-0.83	2.48	0.83
-0.70	3.70	0.93
1.39	-0.67	1.10
4.01	-0.11	1.06
5.31	-0.17	1.10

* The values for factors x_3 to x_8 were all -1.

Figure 9 superimposes the results from Table 9 over the model of Equation (24). Since the relative area ratio falls below 1 as x_2 increases, the final model predicts fairly well for low x_1 and high x_2. But for high x_1 and intermediate x_2, the model does not predict the results obtained. These exploratory results seem to indicate the need for an interactive term in x_1x_2 beyond the operating region of this study.

Nevertheless, this exercise demonstrates that an experimenter can take the approach used in this study, apply it to the kinetic model being investigated and determine the reactor type which will give the most precise estimates of the parameters.

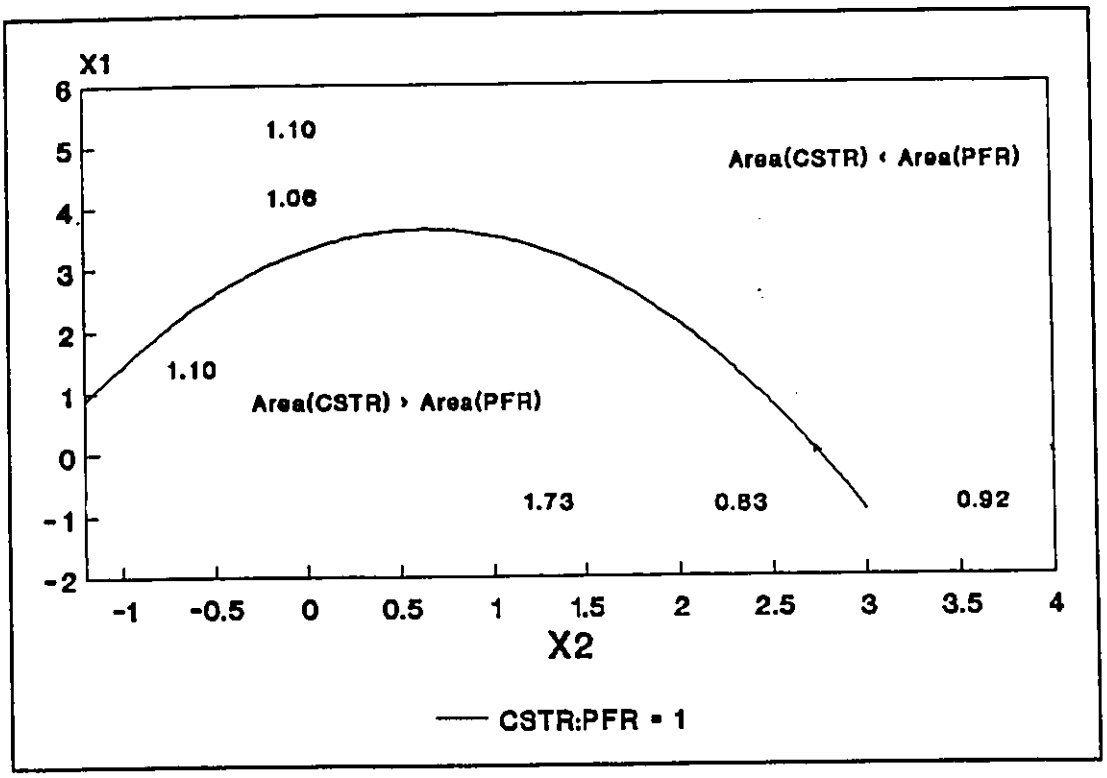


Figure 9: Exploring The Region Outside This Study

5 CONCLUSIONS

Parallel Reaction Network:

1. The precision of the parameter estimates was always better using a PFR to measure the kinetics of a first-order parallel reaction network. The most information about a parallel reaction is revealed in the initial stages of the reaction, and a PFR gives this type of information better than a CSTR.

2. On average, the area of the joint confidence region using the CSTR was 1.51 times larger than that using the PFR.

3. The magnitude of the rate parameters and the covariance structure of the responses did not influence the choice of reactor.

4. The correlation between parameter estimates was not a factor in choosing reactor type. The PFR produced a lower correlation between parameter estimates as often as the CSTR.

Series Reaction Network:

5. For the first-order series reaction network, the precision of the parameter estimates was not always better using a PFR to measure the kinetics of the

reaction. The PFR gave more precise parameter estimates, except when the reaction from "A" to "B" was fast and the reaction from "B" to "C" was slow. A CSTR is more capable of giving information about the final concentration of product "C" thereby obtaining a better estimate of θ_2.

6. When the PFR was more precise, the area of the joint confidence region was 2.49 times smaller, on average, than that using the CSTR.

7. When the CSTR was more precise, the average area of the joint confidence region was 1.52 times smaller than that using the PFR.

8. Three main factors, namely the magnitudes of the rate parameters, θ_1 and θ_2, and the variance of the measured product "A", σ_A^2, affected the choice of reactor, as well as three interactions, $\theta_1\sigma_{BC}$, $\sigma_A^2\sigma_{AB}$ and $\sigma_B^2\sigma_{BC}$.

9. The following conditions favour the choice of the CSTR over the PFR: high magnitude of θ_1, low θ_2, low σ_A^2, high σ_B^2, high σ_{AB} and high σ_{BC}.

10. When the CSTR was more precise, in terms of area of the joint confidence region, the correlation also tended to be lower using the CSTR.

Other Conclusions:

11. While vast improvement was made in the precision of the parameter estimates through the use of designed experiments, the choice of reactor was not affected by the experimental design.

6 RECOMMENDATIONS

It is recommended that a kinetics experimenter consider the precision of the parameter estimates when choosing a laboratory reactor. The approach of this study can be applied to ascertain the reactor type which will give the most precise estimates of the parameters for the kinetic model being investigated.

Since the predictions of this study are limited by the levels of the factors used in this investigation, a study of the effects of the factors outside the operating region of this work is also recommended. Using more than 200 Monte-Carlo simulations for this research is advised.

7 REFERENCES

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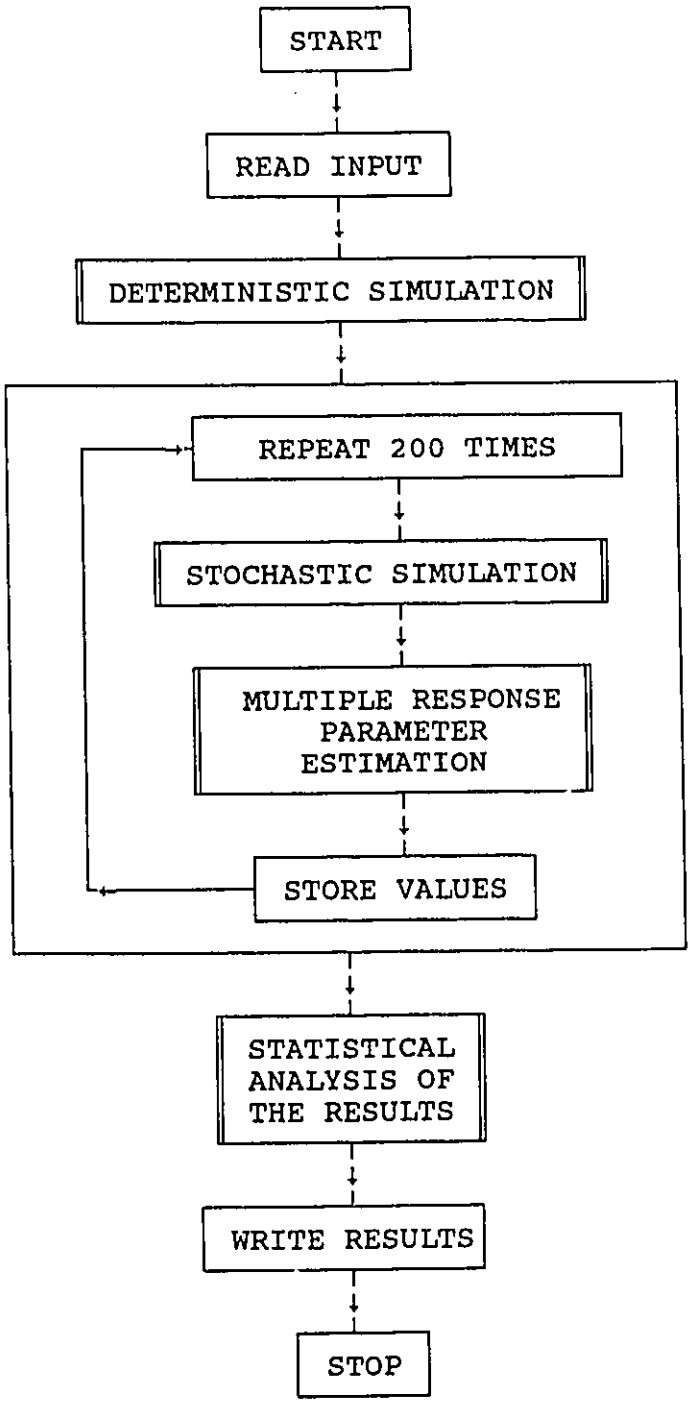
Appendix A

Program to Perform a Monte-Carlo Simulation

Program Algorithm



Program to Perform a Monte-Carlo Simulation

Input Required:

INFO: Q the reactor and network
(1 = PFR, series reaction;
2 = CSTR, series reaction;
3 = PFR, parallel reaction;
4 = CSTR, parallel reaction)

K1 magnitude of θ_1

K2 magnitude of θ_2

NR number of runs (10)

NV number of variables (3: C_A, C_B, C_C)

PLT option to write stored values of the parameter estimates to a file (0 = no; 1 = yes)

MLE estimation procedure (0 = Bayesian estimates; 1 = maximum liklihood estimates)

NRUN set number

DSEED seed number to start the random Normal number generator

EXPM: ND number of designed runs (0 = initial 10-run design; 10 = add the ten designed runs)

CONC: CAO initial concentration for "A" for each run

DCONC: DCAO initial concentration of "A" for the designed runs

TIME: T space time for the reaction to proceed

DTIME: DT space time for the designed runs

COVARM: covariance matrix for the responses

Program to Perform a Monte-Carlo Simulation

Program Listing:

```
C
C       PROGRAM TO SIMULATE A CHEMICAL REACTOR
C
C
C ***************************************************************
C
C                              INPUT SECTION
C
C
C ***************************************************************
      INTEGER Q,PLT,MLE,NRUN
      COMPLEX W(3),Z(3,3)
      REAL K1,K2,CA0(50),T(50),DCA0(50),DT(50),A(3,3),C(3,5
      0)
      REAL WK(50),NORM,EVR(3),VTR(3,3)
      REAL STDEV,R(50),ERR(3,50),D(3,50),RESP(3,50)
      REAL X(2),H(3),G(2),F,WW(6),B1(300),B2(300),SS(3,3)
      REAL AINV(3,3),WKAREA(18)
      DOUBLE PRECISION DSEED
      COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
      EXTERNAL FUNCT,FUNC
      DATA NN/2/,NSIG/4/,MAXFN/500/,IOPT/0/
      DATA N/3/,IJOB/1/,IZ/3/,IA/3/,NZERO/0/,M/200/,NMBR/0/
      ,NHS/0/
      DATA XXX1/0.0/,XXX2/0.0/,BB1/0.0/,BB2/0.0/BB3/0.0/,ID
      GT/4/
      NAMELIST /INFO/ Q,K1,K2,NR,NV,PLT,MLE,NRUN,DSEED
      NAMELIST /EXPM/ ND
      NAMELIST /TIME/ T /CONC/ CA0 /COVARM/ A /DCONC/ DCA0
      /DTIME/ DT
C
C       READ DATA FROM INPUT FILE
C
      READ (5,INFO)
      READ (5,EXPM)
      READ (5,CONC)
      READ (5,DCONC)
      READ (5,TIME)
      READ (5,DTIME)
      READ (5,COVARM)
      IF(ND.EQ.0) GO TO 800
      DO 1 J=1,ND
         NR=NR+1
         CA0(NR)=DCA0(J)
         T(NR)=DT(J)
1     CONTINUE
800   CONTINUE
C
C       WRITE INPUT DATA TO OUTPUT FILE
C
      WRITE (6,100)
100   FORMAT(///T20,'PARAMETER ESTIMATES FOR THE')
```

Program Listing: (continued)

```
      IF (Q.EQ.1) WRITE (6,101)
      IF (Q.EQ.2) WRITE (6,102)
      IF (Q.EQ.3) WRITE (6,103)
      IF (Q.EQ.4) WRITE (6,104)
101   FORMAT(T20,'SERIES REACTION IN A PFR')
102   FORMAT(T20,'SERIES REACTION IN A CSTR')
103   FORMAT(T20,'PARALLEL REACTION IN A PFR')
104   FORMAT(T20,'PARALLEL REACTION IN A CSTR')
      WRITE (6,105) NRUN
105   FORMAT(/T27,'RUN NUMBER ',I3)
      WRITE (6,110)
110   FORMAT(///,T20,'THE INITIAL RUN CONDITIONS ARE')
      WRITE (6,111)
111   FORMAT(/T20,'_____')
      WRITE (6,112)
112   FORMAT(/T21,'RUN NO',T33,'CA0',T45,'T')
      WRITE (6,113)
113   FORMAT(T20,'_____'/)
      DO 2 J=1,NR
         WRITE (6,114) J,CA0(J),T(J)
114      FORMAT(T20,I4,T32,F5.2,T41,F8.3)
2     CONTINUE
      WRITE (6,120)
120   FORMAT(////T20,'THE RESPONSE COVARIANCE MATRIX ')
      WRITE (6,121)
121   FORMAT(' ',T20,'_____')
      DO 3 J=1,NV
         WRITE (6,123) A(J,1),A(J,2),A(J,3)
123      FORMAT (/T21,F9.6,2X,F9.6,2X,F9.6)
3     CONTINUE
      WRITE (6,130)
130   FORMAT(///T20,'THE TRUE VALUES OF THE CONSTANTS ARE')
      WRITE (6,131) K1,K2
131   FORMAT(//T20,'K1=',T24,F5.4,T35,'K2=',T39,F5.4)
C *************************************************************
C
C                    DETERMINISTIC SIMULATION
C
C *************************************************************
      WRITE(6,150)
150   FORMAT(///T20,'THE FINAL CONCENTRATIONS ARE')
      WRITE(6,152)
152   FORMAT(//T21,'RUN NO',T30,'A',T37,'B',T44,'C')
      WRITE(6,153)
153   FORMAT(' ',T20,'_____'/)
      DO 4 J=1,NR
         IF(Q.EQ.1) CALL PFRSER(K1,K2)
         IF(Q.EQ.2) CALL CSTRSE(K1,K2)
         IF(Q.EQ.3) CALL PFRPAR(K1,K2)
         IF(Q.EQ.4) CALL CSTRPA(K1,K2)
```

Program Listing: (continued)

```
          WRITE(6,154) J,C(1,J),C(2,J),C(3,J)
154       FORMAT(T20,I4,T27,F5.2,T35,F5.2,T42,F5.2)
4       CONTINUE
C ***************************************************************
C
C                          STOCHASTIC SIMULATION
C
C ***************************************************************
C
C       CALCULATE EIGEN VALUES AND VECTORS OF THE COVARIANCE
C       AND NORMALIZE THE VECTORS
        CALL EIGRF(A,N,IA,IJOB,W,Z,IZ,WK,IER)
        DO 10 L=1,N
           NORM=0.0
           EVR(L)=REAL(W(L))
           IF(EVR(L).LT.0.0) GO TO 996
           DO 11 K=1,N
              VTR(K,L)=REAL(Z(K,L))
              NORM=NORM+VTR(K,L)**2
11         CONTINUE
           NORM=SQRT(NORM)
           DO 12 I=1,N
              VTR(I,L)=VTR(I,L)/NORM
12         CONTINUE
10      CONTINUE
C
C        CALCULATE THE INVERSE OF THE RESPONSE COVARIANCE MAT
C        (REQUIRED FOR THE MAXIMUM LIKELIHOOD ESTIMATION)
C
        IF(MLE.NE.1) GO TO 820
        CALL LINV2F(A,NV,IA,AINV,IDGT,WKAREA,IER)
C
C       GENERATE THE MULTIPLE VALUES FOR THE PARAMETERS
C
820     WRITE(6,200) DSEED
200     FORMAT(//T20,'THE INITIAL SEED IS     ',F8.0)
        IF(MLE.EQ.0) WRITE(6,201)
        IF(MLE.EQ.1) WRITE(6,202)
201     FORMAT(//T15,'BAYESIAN ESTIMATION; THE ESTIMATES ARE'
202     FORMAT(//T11,'MAXIMUM LIKELIHOOD ESTIMATION; THE ESTI
        MATES ARE')
        IF(MLE.EQ.0) WRITE(6,300)
        IF(MLE.EQ.1) WRITE(6,301)
300     FORMAT(//T12,'K1',T26,'K2',T39,'/S/MIN',T53,'LOOPS',T
        64,'NSIG')
301     FORMAT(//T12,'K1',T26,'K2',T38,'(MLF)MIN',T53,'LOOPS'
        ,T64,'NSIG')
        WRITE(6,302)
302     FORMAT(T2,'_____________________________________
```

Program Listing: (continued)

```
     +____________________'/)
      G1=K1
      G2=K2
      DO 20 KKK=1,M
         GO TO 805
815         NMBR=NMBR+1
            WRITE(6,303)
303         FORMAT(T2,'***** PARAMETERS HAVE BEEN REDETERMI
            NED *****')
            IF(NMBR.EQ.800) GO TO 998
         GO TO 805
835         NHS=NHS+1
            WRITE(6,308)
308         FORMAT(T2,'##### PARAMETERS HAVE BEEN REDETERMI
            NED #####')
            IF(NHS.EQ.290) GO TO 997
C
C     INITIALIZE THE K'S AND C'S TO THEIR ORIGINAL VALUES
C
805      IERROR=0
         K1=G1
         K2=G2
         DO 21 J=1,NR
            IF(Q.EQ.1) CALL PFRSER(K1,K2)
            IF(Q.EQ.2) CALL CSTRSE(K1,K2)
            IF(Q.EQ.3) CALL PFRPAR(K1,K2)
            IF(Q.EQ.4) CALL CSTRPA(K1,K2)
21       CONTINUE
C
C     CALCULATE THE E MATRIX
C
         DO 22 J=1,NV
            STDEV=SQRT(EVR(J))
            CALL GGNML(DSEED,NR,R)
            DO 23 L=1,NR
               ERR(J,L)=R(L)*STDEV
23          CONTINUE
22       CONTINUE
C
C     CALCULATE RANDOM ERROR MATRIX ( E * U )
C
         DO 24 I=1,NV
            DO 25 J=1,NR
               SUM=0.0
               DO 26 L=1,NV
                  SUM=SUM+VTR(I,L)*ERR(L,J)
26             CONTINUE
               D(I,J)=SUM
25          CONTINUE
24       CONTINUE
```

Program Listing: (continued)

```
C
C       ADD RANDOM ERROR TO FINAL CONCENTRATIONS
C
           DO 28 J=1,NV
              DO 29 K=1,NR
                 RESP(J,K)=D(J,K)+C(J,K)
                 IF(RESP(J,K).LE.0.0) GO TO 810
                 GO TO 29
810                 RESP(J,K)=0.0
                    IERROR=IERROR+1
29             CONTINUE
28          CONTINUE
C ***************************************************************
C
C                    MULTIPLE RESPONSE PARAMETER ESTIMATION
C
C ***************************************************************
C
C       BAYESIAN APPROACH -- RESPONSE COVARIANCE MATRIX ASSUM
C       ED UNKNOWN
C       MINIMIZE THE DETERMINANT OF THE S MATRIX
C       AND WRITE THE FINAL PARAMETERS OUT
C

              IF(MLE.EQ.1) GO TO 825
              X(1)=K1*10.0
              X(2)=K2*10.0
              CALL ZXMIN(FUNCT,NN,NSIG,MAXFN,IOPT,X,H,G,F,WW,IER)
              IF(IER.EQ.130) GO TO 815
              IF(IER.EQ.129) GO TO 835
              NZERO=NZERO+IERROR
              B1(KKK)=X(1)/10.0
              B2(KKK)=X(2)/10.0
              IF(M.GT.300) GO TO 830
              WRITE (6,304) KKK,B1(KKK),B2(KKK),F,WW(2),WW(3)
304           FORMAT(T1,I3,1X,3(E14.7,1X),2(E10.3,1X))
              GO TO 830
C
C          MAXIMUM LIKELIHOOD APPROACH -- RESPONSE COVARIANCE K
C          NOWN
C          MINIMIZE THE OBJECTIVE FUNCTION
C
825           X(1)=K1*10.0
              X(2)=K2*10.0
              CALL ZXMIN(FUNC,NN,NSIG,MAXFN,IOPT,X,H,G,F,WW,IER)
              IF(IER.EQ.130) GO TO 815
              IF(IER.EQ.129) GO TO 835
              NZERO=NZERO+IERROR
              B1(KKK)=X(1)/10.0
```

Program Listing: (continued)

```
            B2(KKK)=X(2)/10.0
            IF(M.GT.100) GO TO 830
            WRITE (6,307) KKK,B1(KKK),B2(KKK),F,WW(2),WW(3)
307         FORMAT(T1,I3,1X,3(E14.7,1X),2(E10.3,1X))
C ***********************************************************
C
C                STATISTICAL ANALYSIS OF THE REACTION PARAMETER
C
C ***********************************************************
830         XXX1=XXX1+B1(KKK)
            XXX2=XXX2+B2(KKK)
            ESS=ESS+F
            WORK=WORK+WW(2)
            SIG=SIG+WW(3)
20        CONTINUE
          XMEAN1=XXX1/M
          XMEAN2=XXX2/M
          ESS=ESS/M
          WORK=WORK/M
          SIG=SIG/M
          DO 32 I=1,M
             BB1=BB1+(XMEAN1-B1(I))**2
             BB2=BB2+(XMEAN2-B2(I))**2
             BB3=BB3+(B1(I)-XMEAN1)*(B2(I)-XMEAN2)
32        CONTINUE
          VAR11=BB1/(M-1)
          VAR22=BB2/(M-1)
          COV12=BB3/(M-1)
          PREC=VAR11*VAR22-(COV12**2)
          CORR=COV12/((VAR11*VAR22)**0.5)
C ***********************************************************
C
C                              OUTPUT OF RESULTS
C
C ***********************************************************
          IF(M.GT.100) WRITE(6,400) M
400       FORMAT(//T20,'RUNS WERE REPEATED',I6,'  TIMES',//)
          WRITE(6,401) XMEAN1,XMEAN2,ESS,WORK,SIG
401       FORMAT(/T1,'MEAN',3(E14.7,1X),2(E10.3,1X))
          WRITE(6,402) VAR11,COV12
402       FORMAT(/T10,'COVARIANCE MATRIX OF K1 AND K2:  ',2(E12
          .5,2X))
          WRITE(6,403) COV12,VAR22
403       FORMAT(T43,2(E12.5,2X))
          WRITE(6,404) PREC
404       FORMAT(/T10,'DETERMINANT OF COVARIANCE MATRIX:  ',E12
          .5)
          WRITE(6,405) CORR
405       FORMAT(/T10,'CORRELATION OF K1 AND K2:  ',E12.5)
          IF(NZERO.NE.0) WRITE(6,406) NZERO
```

Program Listing: (continued)

```
406     FORMAT(/T10,'THERE WERE ',I3,' RESPONSES LESS THAN ZE
        RO')
        IF(NMBR.NE.0) WRITE(6,407) NMBR
407     FORMAT(/T10,'THERE WERE',I4,
     +   ' PARAMETERS REDETERMINED DUE TO ROUNDOFF ERROR')
        IF(NHS.NE.0) WRITE(6,408) NHS
408     FORMAT(/T10,I3,'  PARAMETERS REDETERMINED; HESSIAN NO
        T POSITIVE D
       +EFINITE')
C ***************************************************************
C
C                       PLOT OPTION FOR THE JOINT CONFIDENCE REG
C                        ION
C ***************************************************************
        IF(PLT.EQ.0) GO TO 999
        WRITE(6,450)
450     FORMAT(///T20,'THE PARAMETERS ARE WRITING TO THE PLOT
        I/P FILE'/)
        WRITE(7,500) M,Q,NR,NG,MLE
500     FORMAT(T10,I4,T20,I2,T30,I3,T40,I3,T50,I3)
        WRITE(7,501) NRUN,XMEAN1,XMEAN2,2*VAR11,2*VAR22,CORR
501     FORMAT(T2,I3,T6,F9.6,T16,F9.6,T26,2(E11.4,2X),F6.3)
        DO 45 I=1,M
           WRITE(7,502) B1(I),B2(I)
502        FORMAT(T10,E15.7,T30,E15.7)
45      CONTINUE
        GO TO 999
C ***************************************************************
C
C       END OF PROGRAM
C
C ***************************************************************
996     WRITE(6,505)
505     FORMAT(/T10,'****PROGRAM TERMINATED; NEGATIVE RESPONS
        E EIGENVALUE
       +****',/)
        GO TO 999
997     WRITE(6,503)
503     FORMAT(/T10,'*****PROGRAM TERMINATED; HESSIAN NOT POS
        ITIVE DEFINI
       +TE*****',/)
        GO TO 999
998     WRITE(6,504) NMBR
504     FORMAT(/T10,'PROGRAM TERMINATED',/T10,
     +   'ROUNDOFF ERROR BECAME SIGNIFICANT',I4,' TIMES')
999     STOP
        END
C ***************************************************************
C
```

Program Listing: (continued)

```
C      THE CALCULATION OF CA,CB,CC FOR THE
C      PFR REACTOR AND SERIES REACTIONS
C
C ***************************************************************

       SUBROUTINE PFRSER(K1,K2)
       COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
       REAL K1,K2,CA0(50),T(50),C(3,50),RESP(3,50)
       INTEGER J,Q
       C(1,J)=CA0(J)*EXP(-K1*T(J))
       IF (K1.EQ.K2) GO TO 840
          C(2,J)=(CA0(J)*K1/(K2-K1))*(EXP(-K1*T(J))-EXP(-K2*
          T(J)))
          GO TO 845
840    C(2,J)=K1*CA0(J)*T(J)/(EXP(K1*T(J)))
       C(3,J)=CA0(J)-C(1,J)-C(2,J)
       GO TO 850
845    C(3,J)=CA0(J)*(1+(K2*EXP(-K1*T(J))-K1*EXP(-K2*T(J)))/
       (K1-K2))
850    RETURN
       END
C ***************************************************************
C
C      THE CALCULATION OF CA,CB,CC FOR THE
C      CSTR REACTOR AND SERIES REACTIONS
C
C ***************************************************************

       SUBROUTINE CSTRSE(K1,K2)
       COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
       REAL K1,K2,CA0(50),T(50),C(3,50),RESP(3,50)
       INTEGER J,Q
       C(1,J)=CA0(J)/(K1*T(J)+1)
       C(2,J)=(CA0(J)*K1*T(J))/((K1*T(J)+1)*(K2*T(J)+1))
       C(3,J)=(CA0(J)*K1*K2*T(J)**2)/((K1*T(J)+1)*(K2*T(J)+1))
       RETURN
       END
C ***************************************************************
C
C      THE CALCULATION OF CA,CB,CC FOR THE
C      PFR REACTOR AND PARALLEL REACTIONS
C
C ***************************************************************

       SUBROUTINE PFRPAR(K1,K2)
       COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
       REAL K1,K2,CA0(50),T(50),C(3,50),RESP(3,50)
       INTEGER J,Q
       C(1,J)=CA0(J)*EXP((-K1-K2)*T(J))
       C(2,J)=(CA0(J)*K1/(K2+K1))*(1-EXP((-K1-K2)*T(J)))
```

Program Listing: (continued)

```
      C(3,J)=(CA0(J)*K2/(K1+K2))*(1-EXP((-K1-K2)*T(J)))
      RETURN
      END
C *****************************************************************
C
C     THE CALCULATION OF CA,CB,CC FOR THE
C     CSTR REACTOR AND PARALLEL REACTIONS
C
C *****************************************************************

      SUBROUTINE CSTRPA(K1,K2)
      COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
      REAL K1,K2,CA0(50),T(50),C(3,50),RESP(3,50)
      INTEGER J,Q
      C(1,J)=CA0(J)/(1+(K1+K2)*T(J))
      C(2,J)=(CA0(J)*K1*T(J))/(1+(K1+K2)*T(J))
      C(3,J)=(CA0(J)*K2*T(J))/(1+(K1+K2)*T(J))
      RETURN
      END
C *****************************************************************
C
C     THE CALCULATION OF THE DETERMINANT OF MATRIX S
C
C *****************************************************************
C
C     CALCULATION OF THE MATRIX S
C
      SUBROUTINE FUNCT(NN,X,F)
      COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
      REAL SS(3,3),X(NN),C(3,50),RESP(3,50),T(50),K1,K2,CA0
     )(50)
      INTEGER Q,J
      K1=X(1)/10.0
      K2=X(2)/10.0
      DO 5 J=1,NR
         IF(Q.EQ.1) CALL PFRSER(K1,K2)
         IF(Q.EQ.2) CALL CSTRSE(K1,K2)
         IF(Q.EQ.3) CALL PFRPAR(K1,K2)
         IF(Q.EQ.4) CALL CSTRPA(K1,K2)
5     CONTINUE
      DO 1 I=1,NV
         DO 2 J=1,NV
            SUM=0.0
            DO 3 K=1,NR
               SUM=SUM+(RESP(I,K)-C(I,K))*(RESP(J,K)-C(J,K))
3           CONTINUE
            SS(I,J)=SUM
2        CONTINUE
1     CONTINUE
C
```

Program Listing: (continued)

```
C       CALCULATION OF THE DETERMINANT
C
        DET1=(SS(1,1)*SS(2,2)*SS(3,3))+2*(SS(1,2)*SS(1,3)*SS(
        2,3))
        DET2=(SS(1,1)*(SS(2,3)**2))+(SS(2,2)*(SS(1,3)**2))+(S
        S(3,3)*
       + (SS(1,2)**2))
        DET=DET1-DET2
        F=DET
        RETURN
        END
C ***************************************************************
C
C       THE CALCULATION OF THE OBJECTIVE FUNCTION FOR MAX-LIK
C       ELIHOOD
C ***************************************************************
C
C       CALCULATION OF THE MATRIX S
C
        SUBROUTINE FUNC(NN,X,F)
        COMMON /XPS/ Q,C,NV,NR,RESP,CA0,T,J,AINV
        REAL SS(3,3),X(NN),C(3,50),RESP(3,50),T(50),K1,K2,CA0
        (50)
        REAL AINV(3,3),WKAREA(50)
        INTEGER Q,J
        K1=X(1)/10.0
        K2=X(2)/10.0
        DO 5 J=1,NR
           IF(Q.EQ.1) CALL PFRSER(K1,K2)
           IF(Q.EQ.2) CALL CSTRSE(K1,K2)
           IF(Q.EQ.3) CALL PFRPAR(K1,K2)
           IF(Q.EQ.4) CALL CSTRPA(K1,K2)
5       CONTINUE
        DO 1 I=1,NV
           DO 2 J=1,NV
              SUM=0.0
              DO 3 K=1,NR
                 SUM=SUM+(RESP(I,K)-C(I,K))*(RESP(J,K)-C(J,K))
3             CONTINUE
              SS(I,J)=SUM
2          CONTINUE
1       CONTINUE
C
C       CALCULATION OF THE OBJECTIVE FUNCTION
C
        SUM=0.0
        DO 6 I=1,NV
           DO 7 J=1,NV
              SUM=SUM+AINV(I,J)*SS(I,J)
7          CONTINUE
6       CONTINUE
        F=SUM
        RETURN
```

Program to Perform a Monte-Carlo Simulation

Input File:

```
&INFO O=2,K1=0.085,K2=0.06,NR=10,NV=3,PLT=0,MLE=0,NRUN=46,
DSEED= 43200 ,
&END
&EXPM ND=10,&END
&CONC CA0=1.00,1.00,1.00,2.00,2.00,2.00,2.00,3.00,3.00,3.00,
&END
&DCONC DCA0=3.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,&END
&TIME T=1.307,11.76,105.9,1.307,11.76,11.76,105.9,1.307,11.7
6,105.9,
&END
&DTIME DT=21.18,21.18,21.18,21.18,21.18,21.18,21.18,21.18,21
.18,
21.18,&END
&COVARM A(1,1)=0.00250,A(1,2)=0.00280,A(1,3)=0.00210,A(2,1)=
0.00280,
A(2,2)=0.00640,A(2,3)=0.00336,A(3,1)=0.00210,A(3,2)=0.00336,
A(3,3)=0.00360,&END
```

Execution Program to Randomize the Seed for the Random Normal Number Generator:

```
&TRACE OFF
CMSEX TIME
&READ VARS &SEED *
&ONE = &PIECE OF &SEED 1 2
&IF &ONE = 00 &ONE = 25
&TWO = &PIECE OF &SEED 4 2
&IF &TWO = 00 &TWO = 25
&THR = &PIECE OF &SEED 7 2
&IF &THR = 00 &THR = 25
&SEED = &MULT OF &ONE &TWO &THR
&STACK 2
&STACK DEL
&STACK U
&STACK I DSEED= &SEED ,
&STACK C/DSE/ DSE/
&STACK FILE
X DETIN DATA A
FORTVS DETER
GLOBAL TXTLIB VLNKMLIB FORTLIB VFORTLIB CMSLIB IMSLSLIB PLOT
LIB
FI 5 DISK DETIN DATA A
FI 6 DISK DETOUT DATA A
FI 7 DISK PLOT DATA A
LOAD DETER ( CLEAR START
EXEC SENDFILE DETOUT DATA TO 289293 AT  UOTTAWA
EXEC SENDFILE DETIN DATA TO 289293  AT UOTTAWA
&EXIT
```

Program to Design Additional Experiments for Precise Parameter Estimation

Program Listing:

```
C ************************************************************
C
C      EXPERIMENTAL DESIGN BASED ON THE DRAPER AND HUNTER CRI
C      TERION
C ************************************************************
C
       INTEGER Q
       REAL DET(30)
       REAL A(3,3),AINV(3,3),WKAREA(18)
       REAL K1,K2,CA0(40),T(40),GCA0(30),GT(30)
       REAL X(40,2,3),XTX(2,2),MM(2,2),V(2,2)
       COMMON /XX/ CA0,T,J,X,K1,K2
       DATA IA/3/,IDGT/4/
       NAMELIST /INFO/ Q,NR,NV,K1,K2,NN,NG,NI
       NAMELIST /TIME/ T /CONC/ CA0 /COVARM/ A /GTIME/ GT /G
       CONC/ GCA0
C
C      READ DATA FROM INPUT FILE
C
       READ (5,INFO)
       READ (5,CONC )




       READ (5,TIME )
       READ (5,GCONC)
       READ (5,GTIME)
       READ (5,COVARM)
C
C      WRITE INPUT DATA TO OUTPUT FILE
C
       WRITE (6,100)
100    FORMAT(////T20,'DRAPER & HUNTER EXPERIMENTAL DESIGN')
       IF (Q.EQ.1) WRITE (6,110)
       IF (Q.EQ.2) WRITE (6,111)
       IF (Q.EQ.3) WRITE (6,112)
       IF (Q.EQ.4) WRITE (6,113)
110    FORMAT(T20,'FOR THE SERIES REACTION IN A PFR   ')
111    FORMAT(T20,'FOR THE SERIES REACTION IN A CSTR  ')
112    FORMAT(T20,'FOR THE PARALLEL REACTION IN A PFR ')
113    FORMAT(T20,'FOR THE PARLLEL REACTION IN A CSTR  ')
       WRITE (6,101)
101    FORMAT(/T20,'THE INITIAL RUN CONDITIONS ARE')
       WRITE (6,102)
102    FORMAT(/T20,'_______________________________')
       WRITE (6,103)
```

Program Listing: (continued)

```
103     FORMAT(/T21,'RUN NO', T33,'CA0',T45,'T')
        WRITE (6,104)
104     FORMAT(/T20,'_______________________________')
        DO 1 J=1,NR
           WRITE (6,105) J,CA0(J),T(J)
105        FORMAT(T20,I4,T32,F5.2,T41,F8.3)
1       CONTINUE
        WRITE(6,115)
115     FORMAT(/T23,'THE GRID LOCATIONS ARE')
        WRITE(6,116)
116     FORMAT(/T20,'_____________________________')
        WRITE(6,117)
117     FORMAT(/T21,'GRID NO',T33,'CA0',T45,'T')
        WRITE(6,118)
118     FORMAT(/T20,'_____________________________')
        DO 2 J=1,NG
           WRITE(6,119) J,GCA0(J),GT(J)
119        FORMAT(T20,I4,T32,F5.2,T41,F8.3)
2       CONTINUE
        WRITE (6,120)
120     FORMAT(//T20,'THE RESPONSE COVARIANCE MATRIX')
        WRITE (6,121)
121     FORMAT(' ',T20,'_________________________________')
        DO 3 J=1,NV
           WRITE (6,122) A(J,1),A(J,2),A(J,3)
122        FORMAT(T21,F8.6,2X,F8.6,2X,F8.6)
3       CONTINUE
        WRITE (6,123)
123     FORMAT(/T20,'THE TRUE VALUES OF THE CONSTANTS ARE')
        WRITE (6,124) K1,K2
124     FORMAT(/T20,'K1=',T24,F6.4,T35,'K2=',T39,F6.4)
C ***********************************************************
C
C       EXPERIMENTAL DESIGN
C
C ***********************************************************
        WRITE (6,150)
150     FORMAT(/T20,'THE DESIGNED RUN CONDITIONS ARE')
        WRITE (6,151)
151     FORMAT(/T20,'_______________________________________')
        WRITE (6,152)
152     FORMAT(/T21,'RUN NO',T33,'CA0',T45,'T',T54,'DETERMINA
        NT')
        WRITE (6,153)
153     FORMAT(/T20,'_______________________________________')
C
C      INVERSION OF THE RESPONSE COVARIANCE MATRIX
C
```

Program Listing: (continued)

```
      CALL LINV2F(A,NV,IA,AINV,IDGT,WKAREA,IER)
C
C     FIRST CALCULATE THE DETERMINANT OF THE SCREENING DESI
C     GN
C     INITIALIZE THE PARTIAL DERIVATIVES: [X]
C
         DO 17 J=1,NR
            IF(Q.EQ.1) CALL PFRSER
            IF(Q.EQ.2) CALL CSTRSE
            IF(Q.EQ.3) CALL PFRPAR
            IF(Q.EQ.4) CALL CSTRPA
17       CONTINUE
C
C     CALCULATE THE INVERSE COVARIANCE MATRIX OF THE PARAME
C     TERS, MM
            DO 18 L=1,NN
               DO 19 M=1,NN
                  MM(L,M)=0.0
                  XTX(L,M)=0.0
19             CONTINUE
18          CONTINUE
            DO 20 II=1,NV
               DO 21 JJ=1,NV
                  DO 22 I=1,NN
                     DO 23 MMM=1,NN
                        SUM=0.0
                        DO 24 K=1,J
                           SUM=SUM+X(K,I,II)*X(K,MMM,JJ)
24                      CONTINUE
                        XTX(I,MMM)=SUM*AINV(II,JJ)
23                   CONTINUE
22                CONTINUE
                  DO 25 L=1,NN
                     DO 26 M=1,NN
                        MM(L,M)=MM(L,M)+XTX(L,M)
                        XTX(L,M)=0.0
26                   CONTINUE
25                CONTINUE
21             CONTINUE
20          CONTINUE
C
C     TAKE THE DETERMINANT OF THE MM MATRIX
C
          XDET=MM(1,1)*MM(2,2)-MM(1,2)*MM(2,1)
         WRITE (6,203) NR,XDET
203      FORMAT( T20,I4,T53,E12.5)
C
C     REPEAT THE DESIGN FOR THE DESIRED NUMBER OF RUNS
```

Program Listing: (continued)

```
C
      DO 4 KKK=1,NI
C
C     INITIALIZE THE PARTIAL DERIVATIVES: [X]
C
         DO 5 J=1,NR
            IF(Q.EQ.1) CALL PFRSER
            IF(Q.EQ.2) CALL CSTRSE
            IF(Q.EQ.3) CALL PFRPAR
            IF(Q.EQ.4) CALL CSTRPA
5        CONTINUE
C
C     REPEAT FOR EACH ADDITIONAL POINT ON THE GRID
C
         J=NR+1
C
C     CALCULATE [X]
C
         DO 6 LLL=1,NG
            CA0(J)=GCA0(LLL)
            T(J)=GT(LLL)
            IF(Q.EQ.1) CALL PFRSER
            IF(Q.EQ.2) CALL CSTRSE
            IF(Q.EQ.3) CALL PFRPAR
            IF(Q.EQ.4) CALL CSTRPA
C
C     CALCULATE THE INVERSE COVARIANCE MATRIX OF THE PARAME
C     TERS, MM
            DO 7 L=1,NN
               DO 8 M=1,NN
                  MM(L,M)=0.0
                  XTX(L,M)=0.0
8              CONTINUE
7           CONTINUE
            DO 9 II=1,NV
               DO 10 JJ=1,NV
                  DO 11 I=1,NN
                     DO 12 MMM=1,NN
                        SUM=0.0
                        DO 13 K=1,J
                           SUM=SUM+X(K,I,II)*X(K,MMM,JJ)
13                      CONTINUE
                        XTX(I,MMM)=SUM*AINV(II,JJ)
12                   CONTINUE
11                CONTINUE
                  DO 14 L=1,NN
                     DO 15 M=1,NN
```

Program to Design Additional Experiments for Precise Parameter Estimation

Program Listing: (continued)

```
                              MM(L,M)=MM(L,M)+XTX(L,M)
                              XTX(L,M)=0.0
15                         CONTINUE
14                      CONTINUE
10                   CONTINUE
9                 CONTINUE
C
C       TAKE THE DETERMINANT OF THE MM MATRIX
C
                  DET(LLL)=MM(1,1)*MM(2,2)-MM(1,2)*MM(2,1)
C                 WRITE (6,200) DET(LLL),J
C00               FORMAT(T5,G12.5,5X,I2)
6              CONTINUE
C
C       DETERMINE THE CONDITIONS AT WHICH THE DETERMINANT IS
C       LARGEST
               N=1
               XDET1=DET(N)
               DO 16 K=2,NG
                  IF (DET(K).LT.XDET1) GO TO 16
                  N=K
                  XDET1=DET(N)
16             CONTINUE
C
C      STOP IF DESIGN DOESN'T IMPROVE PRECISION DURING THE NI
C      RUNS
               TEST=(XDET**(-0.50))
               TEST1=(XDET1**(-0.50))
               IF(((TEST-TEST1)/TEST).LT.(0.05)) GO TO 998
C
C      ASSIGN THE DESIGNED RUN TO THESE CONDITIONS
C
               XDET=XDET1
               NR=NR+1
               CAO(NR)=GCAO(N)
               T(NR)=GT(N)
               WRITE (6,201) NR,CAO(NR),T(NR),XDET
201            FORMAT( T20,I4,T32,F6.1,T41,F8.2,T53,E12.5)
4           CONTINUE
            GO TO 999
998         WRITE (6,202) J,CAO(J),T(J),XDET1
202         FORMAT(///T20,I4,T32,F6.1,T41,F8.2,T53,E12.5//)
999         STOP
            END
C ************************************************************
C
C       EVALUATION OF PARTIAL DERIVATIVES FOR PFR SERIES KINE
C       TICS
```

Program Listing: (continued)

```
C ***************************************************************
C
      SUBROUTINE PFRSER
      COMMON /XX/ CA0,T,J,X,K1,K2
      REAL K1,K2,CA0(40),T(40),X(40,2,3)
      X(J,1,1)=-CA0(J)*T(J)*EXP(-K1*T(J))
      X(J,2,1)=0.0
      IF (K1.EQ.K2) GO TO 840

      X(J,1,2)=-CA0(J)*(EXP(-K1*T(J))*(K1*T(J)*(K2-K1)-K2)+
      K2*EXP(-K2*
     +       T(J)))/((K2-K1)**2)
      X(J,2,2)=CA0(J)*K1*(EXP(-K2*T(J))*(T(J)*(K2-K1)+1)-EX
      P(-K1*T(J))
     +       )/((K2-K1)**2)
      GO TO 845
840   X(J,1,2)=CA0(J)*T(J)*(1-K1*T(J))*EXP(-K1*T(J))
      X(J,2,2)=X(J,1,2)
845   X(J,1,3)=-X(J,1,1)-X(J,1,2)
      X(J,2,3)=-X(J,2,1)-X(J,2,2)
      RETURN
      END
C ***************************************************************
C
C     EVALUATION OF PARTIAL DERIVATIVES FOR CSTR SERIES KIN
C     ETICS
C ***************************************************************
C
      SUBROUTINE CSTRSE
      COMMON /XX/ CA0,T,J,X,K1,K2
      REAL K1,K2,CA0(40),T(40),X(40,2,3)
      X(J,1,1)=-CA0(J)*T(J)/((K1*T(J)+1)**2)
      X(J,2,1)=0.0
      X(J,1,2)= CA0(J)*T(J)/((K2*T(J)+1)*(K1*T(J)+1)**2)
      X(J,2,2)=-CA0(J)*K1*T(J)**2/((K1*T(J)+1)*((K2*T(J)+1)
      **2))
      X(J,1,3)=-X(J,1,1)-X(J,1,2)
      X(J,2,3)=-X(J,2,1)-X(J,2,2)
      RETURN
      END
C ***************************************************************
C
C     EVALUATION OF PARTIAL DERIVATIVES FOR PFR PARALLEL KI
C     NETICS
C ***************************************************************
```

Program to Design Additional Experiments for Precise Parameter Estimation

Program Listing:

```
C
      SUBROUTINE PFRPAR
      COMMON /XX/ CA0,T,J,X,K1,K2
      REAL K1,K2,CA0(40),T(40),X(40,2,3)
      X(J,1,1)=-CA0(J)*T(J)*EXP(-(K1+K2)*T(J))
      X(J,2,1)=X(J,1,1)
      X(J,1,2)= CA0(J)*(EXP(-(K1+K2)*T(J))*(K1*T(J)*(K2+K1)
     -K2)+K2)/((
     +         K2+K1)**2)
      X(J,2,2)= CA0(J)*K1*(EXP(-(K1+K2)*T(J))*((K1+K2)*T(J)
     +1)-1)/((K1
     +         +K2)**2)
      X(J,1,3)=CA0(J)*K2*(EXP(-(K1+K2)*T(J))*((K1+K2)*T(J)+
     1)-1)/((K1-
     +         K2)**2)
      X(J,2,3)=CA0(J)*(EXP(-(K1+K2)*T(J))*(K2*(K1+K2)*T(J)-
     K1)+K1)/((K1
     +         +K2)**2)
      RETURN
      END
C ***************************************************************
C
C     EVALUATION OF PARTIAL DERIVATIVES FOR CSTR PARALLEL K
C     INETICS
C ***************************************************************
C
      SUBROUTINE CSTRPA
      COMMON /XX/ CA0,T,J,X,K1,K2
      REAL K1,K2,CA0(40),T(40),X(40,2,3)
      X(J,1,1)=-CA0(J)*T(J)/((1+(K1+K2)*T(J))**2)
      X(J,2,1)=X(J,1,1)
      X(J,1,2)= CA0(J)*T(J)*(1+K2*T(J))/((1+(K1+K2)*T(J))**
     2)
      X(J,2,2)=-CA0(J)*K1*T(J)**2/((1+(K1+K2)*T(J))**2)
      X(J,1,3)=-CA0(J)*K2*T(J)**2/((1+(K1+K2)*T(J))**2)
      X(J,2,3)= CA0(J)*T(J)*(1+K1*T(J))/((1+(K1+K2)*T(J))**
     2)
      RETURN
      END
```

Program to Design Additional Experiments for Precise Parameter Estimation

Input File:

```
&INFO Q=2,NR=10,NV=3,K1=0.085,K2=0.06,NN=2,NG=30,NI=10,&END
&CONC CA0=1.00,1.00,1.00,2.00,2.00,2.00,2.00,3.00,3.00,3.00,
&END
&TIME T=1.307,11.76,105.9,1.307,11.76,11.76,105.9,1.307,11.7
6,105.9,
&END
&GCONC GCA0=1.0,1.0,1.0,1.0,1.0,1.0,1.0,1.0,1.0,1.0,2.0,2.0,
2.0,2.0,2.0,
&END
2.0,2.0,2.0,2.0,2.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,3.0,
&GTIME GT=10.59,21.18,31.77,42.36,52.95,63.54,74.13,84.72,95
.31,105.9,
10.59,21.18,31.77,42.36,52.95,63.54,74.13,84.72,95.31,105.9,
10.59,21.18,31.77,42.36,52.95,63.54,74.13,84.72,95.31,105.9,
&END
&COVARM A(1,1)=0.00250,A(1,2)=0.00280,A(1,3)=0.00210,A(2,1)=
0.00280,
A(2,2)=0.00640,A(2,3)=0.00336,A(3,1)=0.00210,A(3,2)=0.00336,
A(3,3)=0.00360,&END
```

Execution Program

```
&TRACE OFF
FORTVS  DESIGN
GLOBAL TXTLIB VLNKMLIB FORTLIB VFORTLIB CMSLIB IMSLSLIB PLOT
LIB
FI 5 DISK DESIGN DATA A (LRECL 80 RECFM F
FI 6 DISK DESIGN RESULT A
LOAD DESIGN ( CLEAR START
EXEC SENDFILE DESIGN RESULT TO 289293 AT UOTTAWA
&EXIT
```

Appendix B

Results

Parallel Reaction Network:

Plug Flow Reactor:

10-Run Design		20-Run Design	
$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$	$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$
4.1427E-17	0.13682	2.2329E-18	0.36497
1.5124E-15	-0.68081	1.5624E-16	-0.87070
1.6612E-15	0.16383	1.1933E-16	0.14407
1.0509E-13	0.44504	1.1850E-14	0.73931
6.0003E-17	0.45732	3.7909E-18	0.70488
7.7192E-14	-0.11500	3.7048E-15	-0.06278
4.0741E-15	0.92860	1.1585E-16	0.84792
7.3280E-14	0.87853	6.0959E-15	0.97076
4.3205E-18	-0.20184	2.1189E-19	0.16182
6.3522E-15	0.49808	4.3756E-16	0.55567
1.3698E-14	-0.32028	7.8744E-16	-0.33651
3.8415E-13	-0.41360	1.4959E-14	-0.35067
9.5443E-17	0.53614	4.0582E-18	0.60646
4.7805E-13	0.45773	2.1405E-14	0.56714
2.3949E-13	0.72236	1.1486E-14	0.66697
4.0508E-13	-0.42984	1.8959E-14	-0.36444
4.4553E-17	0.33028	2.4366E-18	0.52057
3.3900E-14	-0.14965	1.5008E-15	-0.26178
3.7157E-15	-0.89788	2.2449E-16	-0.93689
1.4195E-12	-0.44339	8.5781E-14	0.15791
3.4362E-17	0.83488	2.1896E-18	0.94670
1.5101E-13	0.70737	3.9085E-15	0.76064
1.1246E-13	0.43268	6.8366E-15	0.48264
3.3531E-12	0.43354	1.8301E-13	0.74015
2.5553E-16	-0.86098	1.4582E-17	-0.86127
3.2381E-13	-0.81231	2.4024E-14	-0.85506
1.6173E-14	-0.77942	9.4901E-16	-0.80958
2.7507E-13	-0.73382	1.5499E-14	-0.64901
3.8782E-16	-0.84115	1.6323E-17	-0.82629
6.4264E-12	-0.24445	4.1223E-13	-0.01614
5.8863E-13	0.67274	3.2052E-14	0.49865
4.9300E-12	0.13243	2.4668E-13	0.29666
5.8427E-13	0.01655	3.1409E-14	0.29695
7.1920E-13	-0.02573	2.3895E-14	0.22785
5.2208E-13	0.42061	2.6025E-14	0.14294
6.4716E-13	0.12561	3.4025E-14	0.12363
5.9726E-13	-0.01394	3.4180E-14	0.24066

Parallel Reaction Network:

Continuous Stirred Tank Reactor:

10-Run Design		20-Run Design	
$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$	$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$
1.5094E-16	0.40211	6.6886E-18	0.31349
3.0518E-15	-0.32409	6.8295E-16	-0.79818
3.9529E-15	0.24095	3.2562E-16	0.35561
1.7399E-13	0.66249	2.2191E-14	0.69740
1.7817E-16	0.72538	7.7261E-18	0.69701
2.6073E-13	0.18273	1.4249E-14	0.09070
3.4147E-15	0.81611	1.3265E-16	0.80582
1.2741E-13	0.94064	1.0605E-14	0.95608
6.6332E-18	0.43525	2.6528E-19	0.54648
1.4051E-14	0.59132	8.5037E-16	0.42871
3.8910E-14	-0.16605	2.5641E-15	-0.21038
8.6627E-13	-0.01295	4.4990E-14	0.07206
2.8586E-16	0.79334	9.3825E-18	0.81201
1.1450E-12	0.72460	5.1830E-14	0.71844
4.4807E-13	0.72931	2.1339E-14	0.73128
5.8995E-13	0.21219	2.6393E-14	0.21273
1.6605E-16	0.62416	7.9454E-18	0.49661
8.5033E-14	0.03585	2.9212E-15	0.05023
1.1209E-14	-0.86022	6.5012E-16	-0.87035
3.0028E-12	0.10423	1.5163E-13	-0.05740
4.3778E-17	0.89774	2.1938E-18	0.87227
2.5473E-13	0.66754	1.0089E-14	0.77735
3.1557E-13	0.41042	1.8498E-14	0.25726
4.9246E-12	0.70229	3.1735E-13	0.71697
6.1985E-16	-0.73446	3.2210E-17	-0.74376
9.0582E-13	-0.59336	5.0146E-14	-0.58493
4.8424E-14	-0.59589	2.2665E-15	-0.58281
5.3723E-13	-0.26861	2.5366E-14	-0.12716
6.4104E-16	-0.73975	4.3358E-17	-0.77494
1.5967E-11	0.05300	8.8803E-13	0.02326
2.1625E-12	0.65518	8.8369E-14	0.59686
1.5549E-11	0.48497	6.5743E-13	0.33078
1.5118E-12	0.44240	8.5160E-14	0.30100
1.5529E-12	0.38211	8.0927E-14	0.31120
1.7192E-12	0.53794	7.0331E-14	0.34529
1.1511E-12	0.38400	7.0580E-14	0.24998
1.2623E-12	0.47099	6.0700E-14	0.27567

Series Reaction Network:

Plug Flow Reactor:

10-Run Design		20-Run Design	
$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$	$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$
2.7644E-17	-0.20396	1.0813E-18	-0.25888
1.4599E-15	0.03558	1.6968E-16	-0.18700
1.3604E-15	-0.29030	7.7075E-17	-0.50900
3.2544E-14	-0.08462	4.0524E-15	-0.45374
3.9359E-17	-0.05609	1.8413E-18	-0.08529
7.1405E-14	-0.04335	3.1812E-15	-0.19798
1.9657E-15	-0.82657	7.6761E-17	-0.80756
2.4522E-14	-0.09861	9.6689E-16	-0.30209
4.2769E-18	-0.87215	1.9528E-19	-0.91983
3.8030E-15	0.51435	1.8806E-16	0.57566
1.7400E-14	-0.30321	6.2348E-16	-0.22813
2.3717E-13	-0.75678	9.8385E-15	-0.80404
5.2012E-17	-0.69400	2.2144E-18	-0.84765
1.9998E-13	0.04622	1.0355E-14	0.05549
2.5428E-13	-0.79194	1.2438E-14	-0.78303
2.2316E-13	-0.76589	8.7962E-15	-0.88939
5.2229E-17	-0.03251	1.4282E-18	0.07307
2.1220E-14	0.32909	7.2261E-16	0.47931
1.6173E-15	0.36648	1.8833E-16	0.65809
8.0187E-13	0.06381	3.8035E-14	0.16742
8.9021E-18	0.20959	2.4461E-19	0.30888
8.3082E-14	0.40664	2.7443E-15	0.44396
1.7613E-13	-0.33039	5.4302E-15	-0.36964
1.0616E-12	0.36674	5.9004E-14	0.33323
1.8798E-16	-0.49708	9.1704E-18	-0.60150
2.7781E-13	0.28774	1.2385E-14	0.34276
2.4106E-14	0.58436	1.0890E-15	0.71694
2.6970E-13	-0.73984	9.8691E-15	-0.83651
3.2451E-16	-0.26247	9.7673E-18	-0.44059
3.2374E-12	0.02144	1.3298E-13	0.07952
1.0750E-12	-0.52978	2.6470E-14	-0.55106
5.4296E-12	-0.22220	2.0144E-13	-0.35024
4.1719E-13	-0.24036	1.7653E-14	-0.23349
4.7980E-13	-0.09825	1.8816E-14	-0.33169
5.0385E-13	-0.22155	1.3833E-14	-0.48745
5.5408E-13	-0.17497	1.8116E-14	-0.18192
3.9596E-13	-0.29385	1.6194E-14	-0.28768

Series Reaction Network:

Plug Flow Reactor:

10-Run Design		20-Run Design	
$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$	$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$
1.5207E-12	-0.11832	6.3717E-14	-0.25068
4.1205E-14	-0.35109	1.0859E-15	0.49415
1.8664E-12	-0.27187	6.7671E-14	-0.41491
6.6740E-14	0.13441	1.6584E-15	0.04741
		1.447E-12	-0.2023
		4.835E-13	-0.6904
		5.813E-14	-0.5782
		9.136E-15	-0.8853
		1.609E-13	-0.3108
		2.520E-14	-0.3108
		8.139E-14	-0.4616

Series Reaction Network:

Continuous Stirred Tank Reactor:

10-Run Design		20-Run Design	
$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$	$\det(\underline{V}(\underline{\theta}))$	$\rho(\theta_1,\theta_2)$
2.2120E-16	-0.18214	6.7682E-18	-0.14679
1.0545E-15	-0.07719	8.4286E-17	-0.15219
2.3676E-15	-0.01890	4.9429E-16	-0.44246
3.3810E-13	0.03330	2.3641E-14	-0.15659
3.8836E-16	0.24056	9.6973E-18	0.10752
3.1147E-14	-0.24205	1.2608E-15	-0.19477
6.6032E-15	-0.78761	8.0435E-16	-0.93969
2.6429E-13	0.37859	1.0634E-14	0.43062
5.2851E-17	-0.90709	1.0203E-18	-0.93665
1.2968E-15	0.33672	6.3433E-17	0.35535
2.8160E-14	-0.18070	3.4077E-15	-0.25951
1.8129E-12	-0.66271	6.2220E-14	-0.84047
4.7162E-16	-0.68800	1.0750E-17	-0.70707
1.0464E-13	-0.08281	5.9247E-15	-0.24256
9.6993E-13	-0.71550	5.6512E-14	-0.82736
1.6360E-12	-0.86086	6.3527E-14	-0.89277
2.5090E-16	0.38680	7.5816E-18	0.10570
5.8126E-15	0.21316	2.5821E-16	0.17824
6.0255E-15	0.35916	5.0676E-16	0.54503
7.4400E-12	0.24052	2.0368E-13	0.18110
9.1805E-17	0.78873	3.3490E-18	0.73606
1.7509E-14	0.30720	7.3589E-16	0.04498
5.6913E-13	-0.22709	2.3805E-14	-0.36336
1.3216E-11	0.75880	4.4119E-13	0.63700
1.3789E-15	-0.51463	4.6351E-17	-0.62343
8.8169E-14	0.09904	3.7551E-15	0.17069
7.1166E-14	0.41722	4.6083E-15	0.74034
1.6708E-12	-0.73405	5.4460E-14	-0.82403
2.0910E-15	-0.42790	5.5549E-17	-0.41364
2.0000E-12	-0.16007	1.1761E-13	0.00166
9.6317E-12	-0.51420	1.9611E-13	-0.59436
3.7543E-11	-0.19257	6.8797E-13	-0.33402
3.3201E-12	-0.14694	1.0342E-13	-0.25860
7.7998E-12	-0.16251	8.8125E-14	-0.09708
3.4539E-12	-0.05655	9.5518E-14	-0.20872
4.1027E-12	-0.18854	9.1468E-14	-0.23132
3.1020E-12	-0.14063	8.1566E-14	-0.25638

Series Reaction Network:

Continuous Stirred Tank Reactor:

10-Run Design		20-Run Design	
det($\underline{V}(\underline{\theta})$)	$\rho(\theta_1,\theta_2)$	det($\underline{V}(\underline{\theta})$)	$\rho(\theta_1,\theta_2)$
9.0388E-12	0.04371	2.1704E-13	-0.14927
1.7030E-13	-0.35785	6.0510E-15	-0.32606
1.4530E-11	-0.34064	3.7888E-13	-0.43093
3.1125E-14	0.09276	1.2319E-15	-0.02667
		6.014E-12	-0.1010
		2.334E-12	-0.6027
		3.895E-13	-0.4492
		7.220E-14	-0.8927
		6.302E-13	-0.1494
		1.322E-13	-0.7525
		5.747E-13	-0.3334

Appendix C

Significance Tests

1. Test for lack of fit:

Compare R to $F_{n-p-\nu p, \nu p}$, where

$$R = \frac{(SSR - \nu_p \sigma_p^2) \; / \; (n-p-\nu_p)}{\sigma_p^2}$$

If R > F, the model displays lack of fit.

2. Test for the need for additional terms in a model:

Compare Q to $F_{\nu A-\nu B, \nu p}$, where

$$Q = \frac{SSR_A - SSR_B}{\sigma_p^2 \; (p_B - p_A)}$$

Modelling Results

1. Parallel Reaction Network:

Full model of the ratio of the area of the joint confidence region for the CSTR to that of the PFR (37 sets):

analysis of variance

SAS

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	31	1.90959676	0.06159990	1.709	0.2889
ERROR	5	0.18023315	0.03604663		
C TOTAL	36	2.08982991			

ROOT MSE	0.1898595	R-SQUARE	0.9138
DEP MEAN	1.517359	ADJ R-SQ	0.3791
C.V.	12.51249		

1. Parallel Reaction Network (continued):

1/2 of full model

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR H0: PARAMETER=0	PROB > |T|
INTERCEP	1	1.51735938	0.03121271	48.614	0.0001
K1	1	-0.002704072	0.03356273	-0.081	0.9389
K2	1	-0.03234889	0.03356273	-0.964	0.3794
VA	1	-0.04763585	0.03356273	-1.419	0.2150
VB	1	-0.01886722	0.03356273	-0.562	0.5983
VC	1	-0.01072133	0.03356273	-0.319	0.7623
VAB	1	-0.003995043	0.03356273	-0.119	0.9099
VAC	1	0.03652446	0.03356273	1.088	0.3261
VBC	1	-0.07463318	0.03356273	-2.224	0.0768
K1K2	1	-0.07743757	0.03356273	-2.307	0.0691
K1VA	1	0.04785949	0.03356273	1.426	0.2132
K1VB	1	-0.02481310	0.03356273	-0.739	0.4929
K1VC	1	-0.05997316	0.03356273	-1.787	0.1340
K1VAB	1	-0.02914206	0.03356273	-0.868	0.4249

1. Parallel Reaction Network (continued):

2/2 of full model

K1VAB	1	-0.02914206	0.03356273	-0.868	0.4249
K1VAC	1	0.06867345	0.03356273	2.046	0.0961
K1VBC	1	0.01378072	0.03356273	0.411	0.6984
K2VC	1	0.04945225	0.03356273	1.473	0.2006
K2VBC	1	0.04040590	0.03356273	1.204	0.2825
VAVB	1	0.06029550	0.03356273	1.797	0.1324
VAVC	1	0.04588009	0.03356273	1.367	0.2299
VAVAC	1	0.03433964	0.03356273	1.023	0.3532
VAVBC	1	0.03558727	0.03356273	1.060	0.3375
VCVAB	1	-0.03434104	0.03356273	-1.023	0.3531
VABVBC	1	0.003608255	0.03356273	0.108	0.9186
K1K2VC	1	0.01582386	0.03356273	0.471	0.6572
K1K2VBC	1	0.02529583	0.03356273	0.754	0.4850
K1VAVB	1	-0.06253986	0.03356273	-1.963	0.1214
K1VAVC	1	0.02576907	0.03356273	0.768	0.4773
K1VAVAC	1	-0.04946711	0.03356273	-1.474	0.2005
K1VAVBC	1	0.04884465	0.03356273	1.455	0.2053
K1VCVAB	1	0.08073585	0.03356273	2.406	0.0612
K1VABVBC	1	0.02080719	0.03356273	0.620	0.5624

2. Series Reaction Network:

2.1 Full Model (37 sets):

Model of the ratio of the area of the joint confidence region for the CSTR to that of the PFR.

analysis of variance

SAS

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	31	24.19012350	0.78032656	5.581	0.0316
ERROR	5	0.69914824	0.13982965		
C TOTAL	36	24.88927174			

ROOT MSE	0.373938	R-SQUARE	0.9719
DEP MEAN	2.053283	ADJ R-SQ	0.7977
C.V.	18.21171		

2.1 Full Model (37 sets) (continued):

1/2 of full model

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR H0: PARAMETER=0	PROB > |T|
INTERCEP	1	2.05328330	0.06147503	33.400	0.0001
K1	1	-0.41304995	0.06610353	-6.249	0.0015
K2	1	0.42906418	0.06610353	6.491	0.0013
VA	1	0.13322860	0.06610353	2.015	0.0999
VB	1	-0.09176088	0.06610353	-1.388	0.2238
VC	1	-0.06647361	0.06610353	-1.006	0.3608
VAB	1	0.00655468 9	0.06610353	0.099	0.9249
VAC	1	-0.09945637	0.06610353	-1.505	0.1928
VBC	1	0.08480078	0.06610353	1.283	0.2558
K1K2	1	0.50225177	0.06610353	7.598	0.0006
K1VA	1	-0.04551061	0.06610353	-0.688	0.5218
K1VB	1	0.02911595	0.06610353	0.440	0.6780
K1VC	1	-0.04307102	0.06610353	-0.652	0.5434
K1VAB	1	0.02988184	0.06610353	0.452	0.6702

2.1 Full Model (37 sets) (continued):

2/2 of full model

K1VAB	1	0.02988184	0.06610353	0.452	0.6702
K1VAC	1	-0.01047761	0.06610353	-0.159	0.8803
K1VBC	1	-0.12822871	0.06610353	-1.940	0.1101
K2VC	1	-0.14687756	0.06610353	-2.222	0.0769
K2VBC	1	0.04161940	0.06610353	0.630	0.5566
VAVB	1	-0.08637843	0.06610353	-1.307	0.2482
VAVC	1	0.04677750	0.06610353	0.708	0.5108
VAVAC	1	-0.08769437	0.06610353	-1.327	0.2420
VAVBC	1	0.06546461	0.06610353	0.990	0.3675
VCVAB	1	-0.00505225	0.06610353	-0.076	0.9420
VABVBC	1	0.00899765	0.06610353	0.136	0.8971
K1K2VC	1	0.04543984	0.06610353	0.687	0.5224
K1K2VBC	1	-0.03847029	0.06610353	-0.582	0.5858
K1VAVB	1	0.02828531	0.06610353	0.428	0.6865
K1VAVC	1	-0.10584838	0.06610353	-1.601	0.1702
K1VAVAC	1	-0.06047635	0.06610353	-0.915	0.4022
K1VAVBC	1	-0.09118757	0.06610353	-1.379	0.2263
K1VCVAB	1	-0.08020051	0.06610353	-1.213	0.2792
K1VABVBC	1	-0.00735975	0.06610353	-0.111	0.9157

2.2 Reduced Model (37 sets):

analysis of variance

FINAL MODEL FOR AREA RATIO SERIES NETWORK

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	6	21.20731665	3.53455277	28.799	0.0001
ERROR	30	3.68195510	0.12273184		
C TOTAL	36	24.88927174			

ROOT MSE	0.350331	R-SQUARE	0.8521
DEP MEAN	2.053283	ADJ R-SQ	0.8225
C.V.	17.06199		

2.2 Reduced Model (37 sets) (continued):

reduced model

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR H0: PARAMETER=0	PROB > |T|
INTERCEP	1	2.05328330	0.05759407	35.651	0.0001
K1	1	-0.41304995	0.06193036	-6.670	0.0001
K2	1	0.42906418	0.06193036	6.928	0.0001
VA	1	0.13322860	0.06193036	2.151	0.0336
K1K2	1	0.50225177	0.06193036	8.110	0.0001
K1VBC	1	-0.12822871	0.06193036	-2.071	0.0471
K2VC	1	-0.14687756	0.06193036	-2.372	0.0243

2.2 Reduced Model (37 sets) (continued):

1/2 predictions

FINAL MODEL FOR AREA RATIO

OBS	ACTUAL	PREDICT VALUE	STD ERR PREDICT	RESIDUAL	STD ERR RESIDUAL	STUDENT RESIDUAL
1	2.5019	2.1312	0.1623	0.3707	0.3105	1.1939
2	0.7048	0.5570	0.1623	0.1478	0.3105	0.4759
3	2.5324	2.5350	0.1623	-.002613	0.3105	-.008415
4	2.4150	2.4570	0.1623	-0.0419	0.3105	-0.1351
5	2.2949	2.3976	0.1623	-0.1027	0.3105	-0.3309
6	0.6295	0.8235	0.1623	-0.1940	0.3105	-0.6247
7	3.2371	2.8015	0.1623	0.4356	0.3105	1.4029
8	3.3163	2.7234	0.1623	0.5929	0.3105	1.9096
9	2.2858	2.3876	0.1623	-0.1019	0.3105	-0.3281
10	0.5808	0.3006	0.1623	0.2802	0.3105	0.9024
11	2.3379	2.2786	0.1623	0.0593	0.3105	0.1910
12	2.5148	2.7134	0.1623	-0.1986	0.3105	-0.6398
13	2.2033	2.6541	0.1623	-0.4508	0.3105	-1.4519
14	0.7564	0.5670	0.1623	0.1894	0.3105	0.6099
15	2.1315	2.5450	0.1623	-0.4135	0.3105	-1.3317
16	2.6874	2.9799	0.1623	-0.2925	0.3105	-0.9420
17	2.3040	2.6814	0.1623	-0.3774	0.3105	-1.2154
18	0.5978	0.5943	0.1623	.0034329	0.3105	0.0111

2.2 Reduced Model (37 sets) (continued):

2/2 predictions

FINAL MODEL FOR AREA RATIO SERIES NETWORK

OBS	ACTUAL	PREDICT VALUE	STD ERR PREDICT	RESIDUAL	STD ERR RESIDUAL	STUDENT RESIDUAL
19	1.6404	1.9848	0.1623	-0.3444	0.3105	-1.1094
20	2.3141	2.4197	0.1623	-0.1056	0.3105	-0.3400
21	3.7002	2.9479	0.1623	0.7523	0.3105	2.4230
22	0.5178	0.8608	0.1623	-0.3430	0.3105	-1.1046
23	2.0938	2.2513	0.1623	-0.1575	0.3105	-0.5073
24	2.7345	2.6861	0.1623	0.0483	0.3105	0.1557
25	2.2482	2.4249	0.1623	-0.1767	0.3105	-0.5692
26	0.5506	.8508	0.1623	-0.3002	0.3105	-0.9667
27	2.0571	2.2413	0.1623	-0.1842	0.3105	-0.5931
28	2.3491	2.1632	0.1623	0.1859	0.3105	0.5987
29	2.3848	2.6914	0.1623	-0.3066	0.3105	-0.9875
30	0.9404	1.1173	0.1623	-0.1768	0.3105	-0.5695
31	2.7219	2.5077	0.1623	0.2142	0.3105	0.6898
32	1.8480	2.4297	0.1623	-0.5816	0.3105	-1.8733
33	2.4204	2.0533	0.0576	0.3671	0.3456	1.0625
34	2.1641	2.0533	0.0576	0.1109	0.3456	0.3208
35	2.6278	2.0533	0.0576	0.5745	0.3456	1.6624
36	2.3824	2.0533	0.0576	0.3291	0.3456	0.9523
37	2.2443	2.0533	0.0576	0.1910	0.3456	0.5527

SUM OF RESIDUALS 6.86118E-14
SUM OF SQUARED RESIDUALS 3.681955
PREDICTED RESID SS (PRESS) 5.616776

2.2 Reduced Model (37 sets) (continued):

Estimate σ_p^2 using the 5 centre-point replicates:
(2.4204, 2.1641, 2.6278, 2.3824, 2.2443)

Therefore, $\sigma_p^2 = 0.031831$, $\nu_p = 4$

Reduced model:

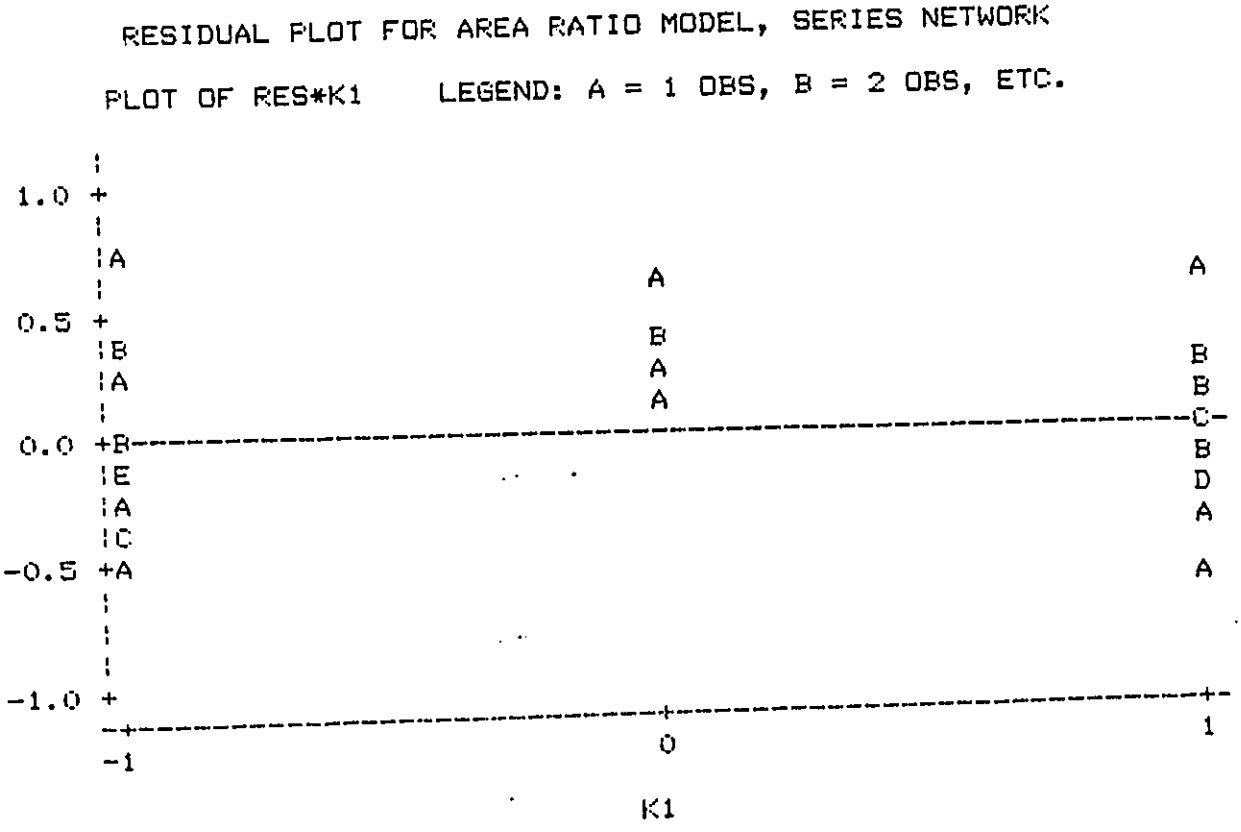
$$(A_{CSTR}:A_{PFR}) = 2.05 - 0.413\,x_1 + 0.429\,x_2 + 0.133\,x_3 + 0.502\,(x_1x_2 + x_3x_6 + x_4x_7) - 0.128\,(x_1x_8 + x_5x_7) - 0.147\,(x_2x_5 + x_4x_8)$$

SSR = 3.6820, n = 37 and p = 7.

Since R = 4.30 and $F_{26,4} = 5.77$, there is no lack of fit.

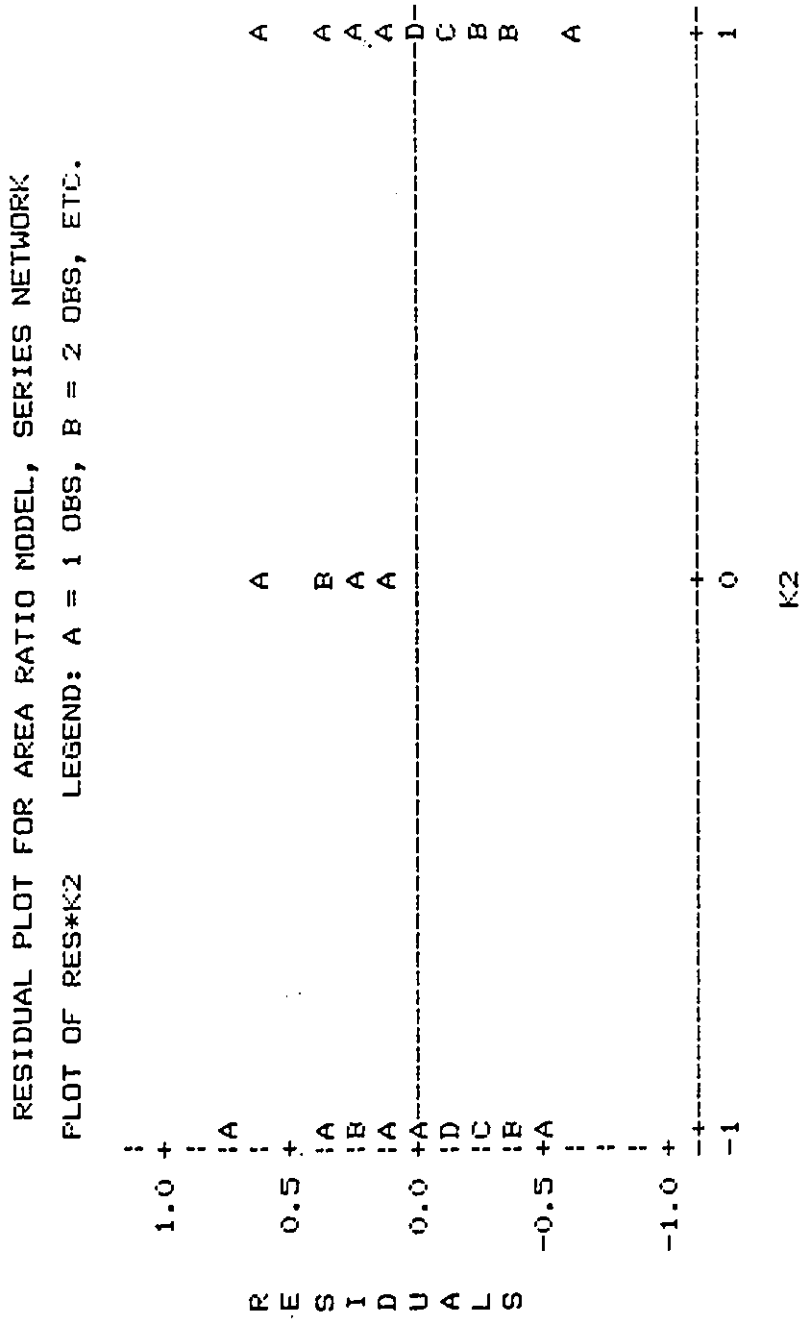
Residual Plots:

res vs k1



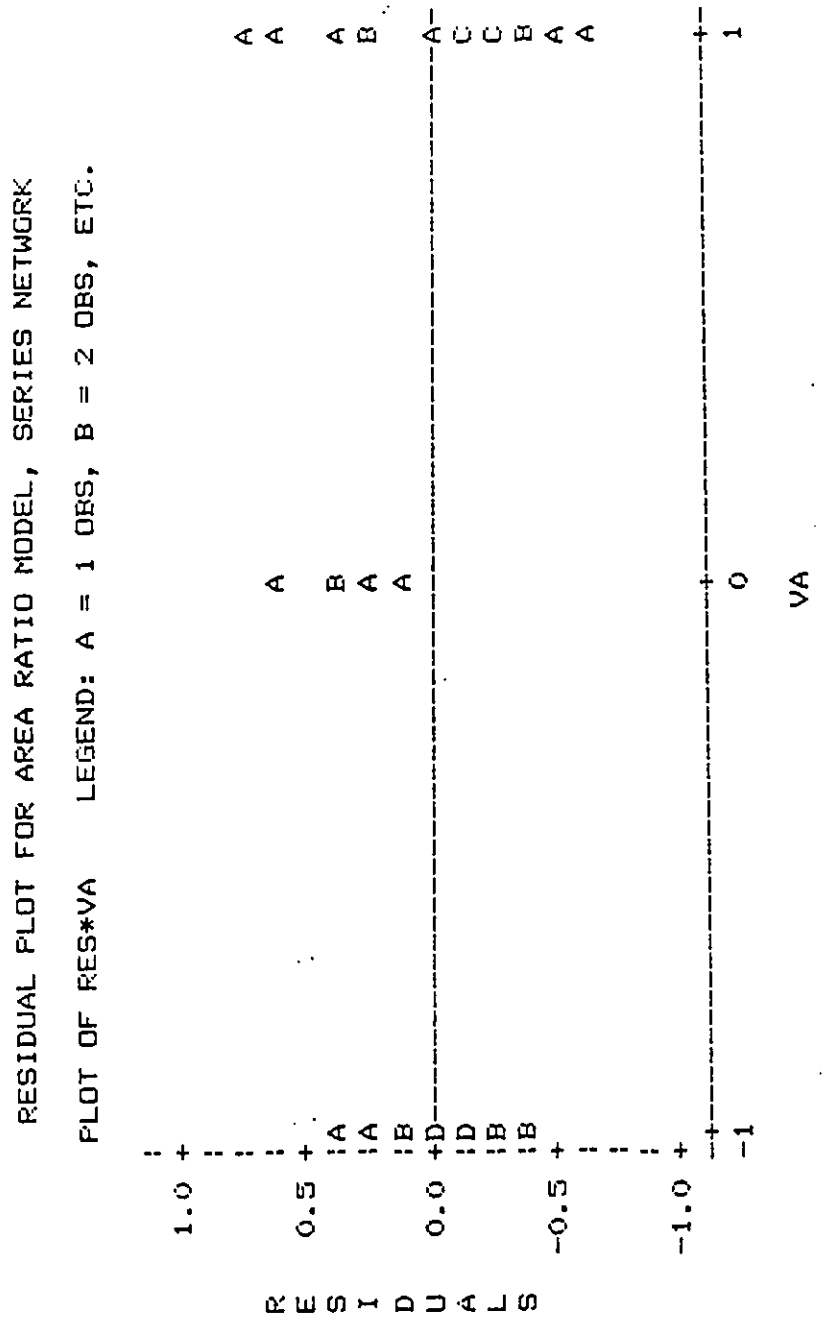
2.2 Reduced Model (37 sets) (continued):

res vs k2



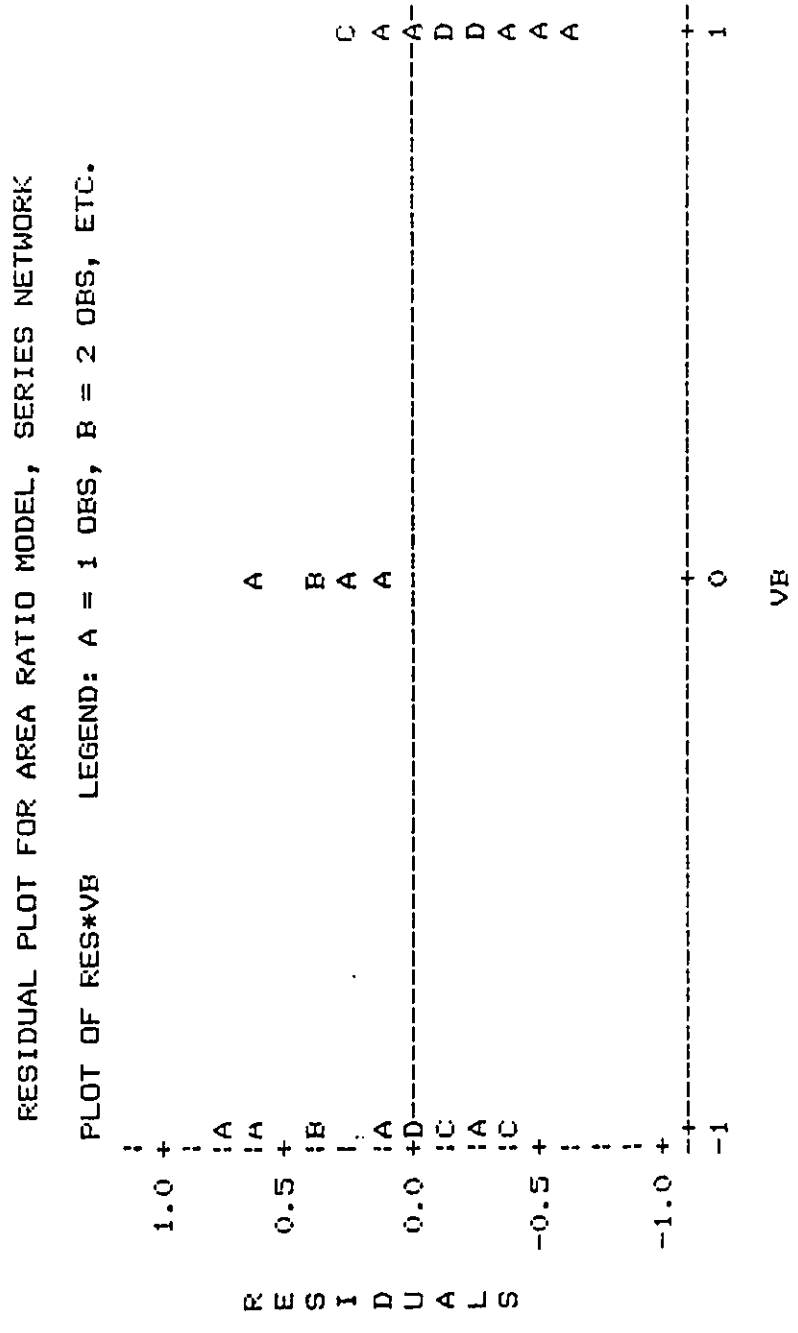
2.2 Reduced Model (37 sets) (continued):

res vs va



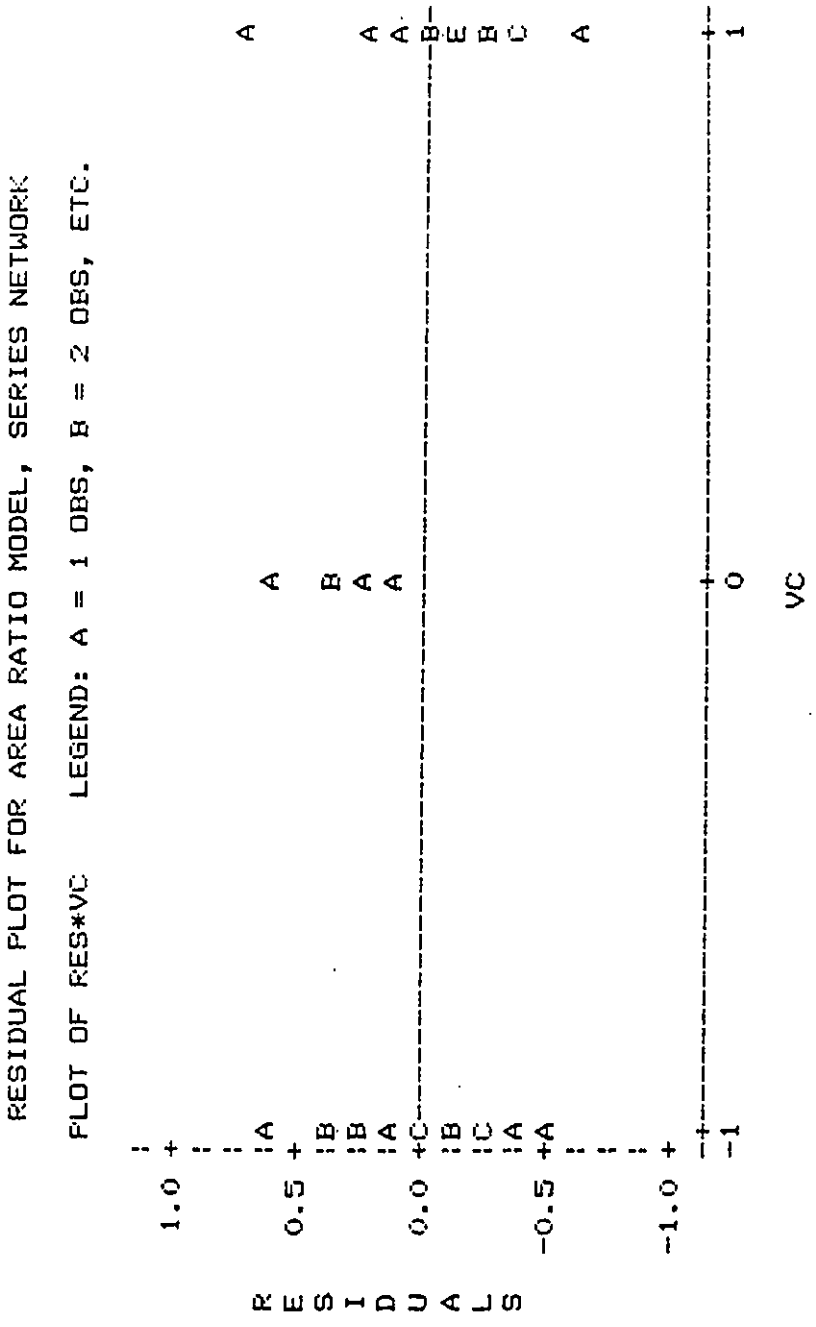
2.2 Reduced Model (37 sets) (continued):

res vs vb



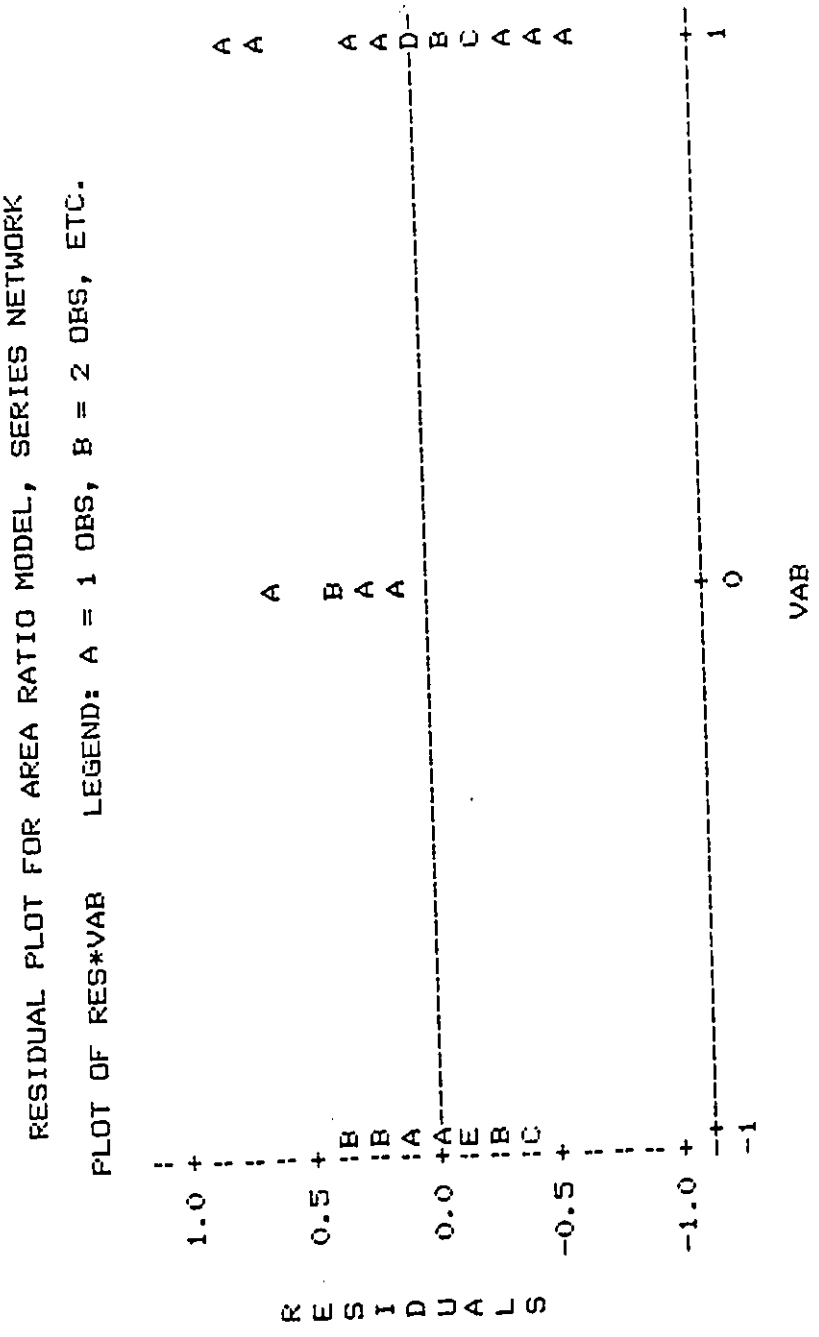
2.2 Reduced Model (37 sets) (continued):

res vs vc



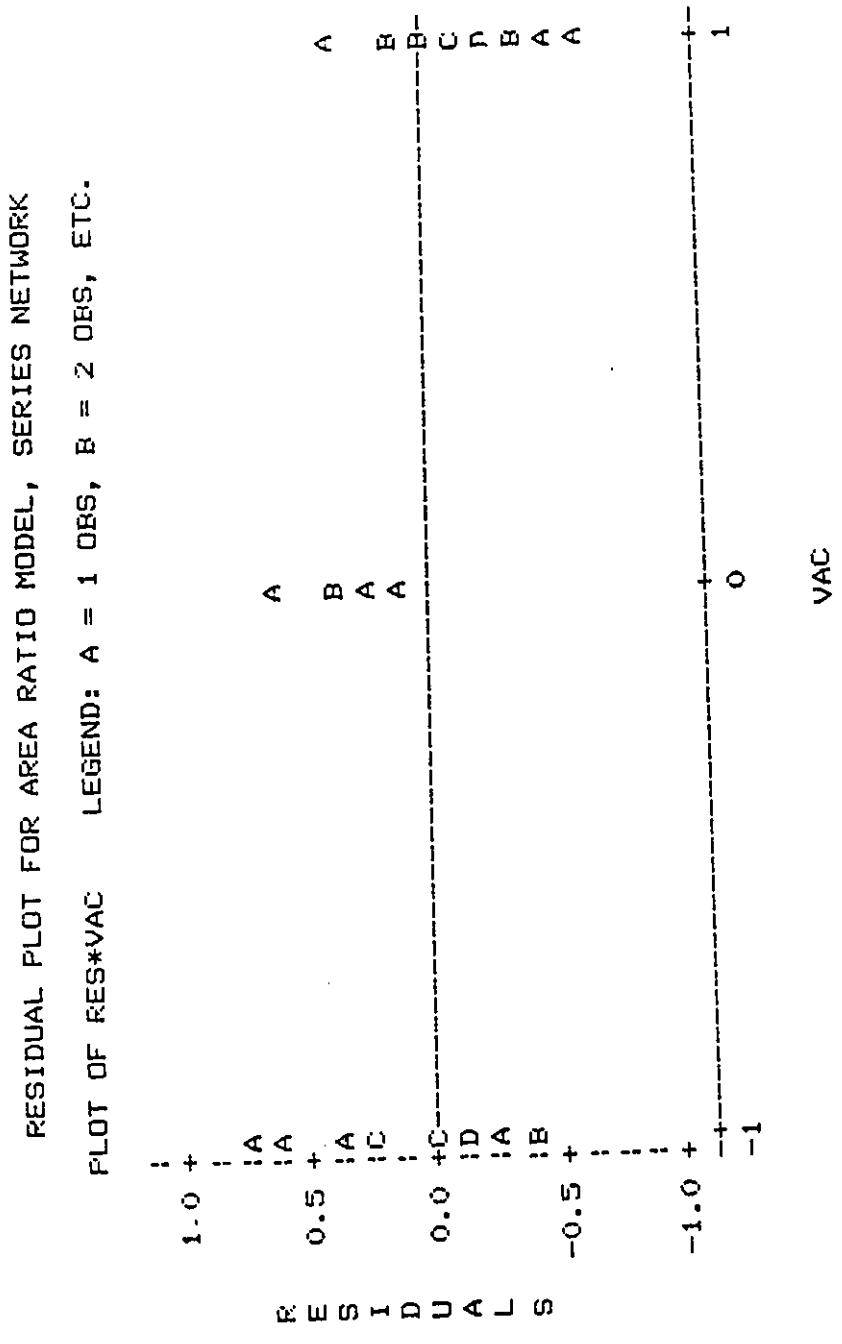
2.2 Reduced Model (37 sets) (continued):

res vs vab



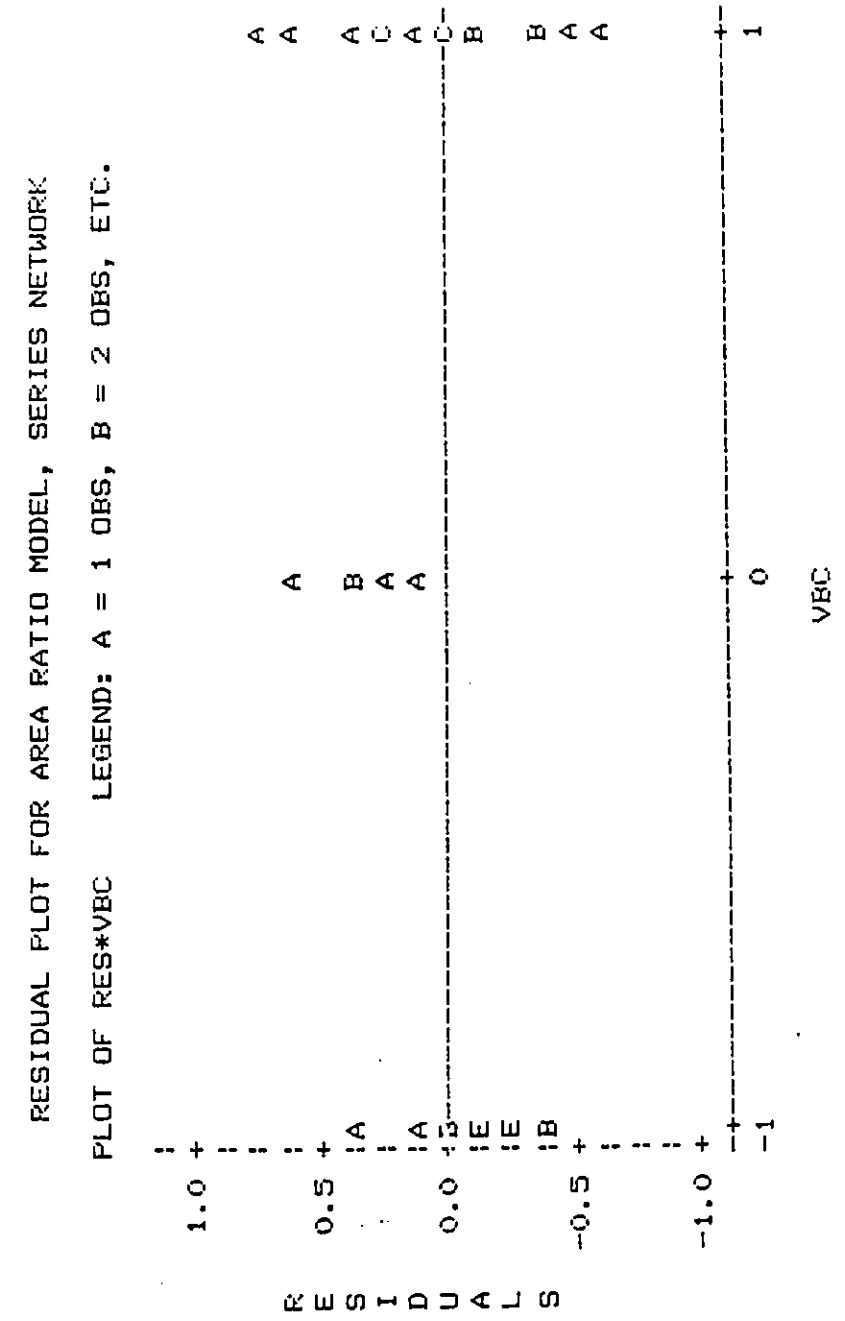
2.2 Reduced Model (37 sets) (continued):

res vs vac



2.2 Reduced Model (37 sets) (continued):

res vs vbc



Residual plots indicate that a quadratic term is needed.

A Q-Test is needed to confirm this:

2.3 Reduced Model (37 sets) Plus a Quadratic Term:

analysis of variance

SAS

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	7	21.77917490	3.11131070	29.011	0.0001
ERROR	29	3.11009685	0.10724472		
C TOTAL	36	24.88927174			

ROOT MSE	0.3274824	R-SQUARE	0.8750
DEP MEAN	2.053283	ADJ R-SQ	0.8449
C.V.	15.94921		

2.3 Reduced Model (37 sets) Plus a Quadratic Term (continued):

reduced model

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR H0: PARAMETER=0	PROB > |T|
INTERCEP	1	2.36779248	0.14645458	16.167	0.0001
K1	1	-0.41304995	0.05789126	-7.135	0.0001
K2	1	0.42906418	0.05789126	7.412	0.0001
VA	1	0.13322860	0.05789126	2.301	0.0287
K1K2	1	0.50225177	0.05789126	8.676	0.0001
K1VBC	1	-0.12822871	0.05789126	-2.215	0.0348
K2VC	1	-0.14687756	0.05789126	-2.537	0.0168
K1K1	1	-0.36365123	0.15748124	-2.309	0.0283

SSR_8 = 3.1109

Since Q = 18.0 and $F_{1,4}$ = 7.71, there is a need for a quadratic term.

2.4 Full Model (48 sets):

Model of the ratio of the area of the joint confidence region for the CSTR to that of the PFR with additional sets to obtain the quadratic term and the specific second-order interactions.

analysis of variance

SAS

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	30	26.26307328	0.87543578	9.614	0.0001
ERROR	17	1.54803569	0.09106092		
C TOTAL	47	27.81110897			

ROOT MSE	0.301763	R-SQUARE	0.9443
DEP MEAN	2.082667	ADJ R-SQ	0.8461
C.V.	14.48926		

2.4 Full Model (48 sets) (continued):

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR HO: PARAMETER=0	PROB > |T|
INTERCEP	1	2.36779248	0.13495253	17.545	0.0001
K1	1	-0.39603961	0.05032955	-7.869	0.0001
K2	1	-0.45139958	0.05032955	-8.969	0.0001
VA	1	0.13799019	0.05211021	2.649	0.0169
VB	1	-0.08699929	0.05211021	-1.670	0.1133
VC	1	-0.07701249	0.05211021	-1.472	0.1592
VAB	1	-0.01131628	0.05211021	-0.217	0.8307
VAC	1	-0.09469478	0.05211021	-1.817	0.0869
VBC	1	0.07426190	0.05211021	1.420	0.1739
K1K2	1	0.11079263	0.05230875	0.514	0.6135
K1VA	1	-0.04074902	0.05211021	-0.782	0.4450
K1V3	1	-0.03387754	0.05211021	-0.650	0.5243
K1VC	1	-0.05360991	0.05230875	-1.025	0.3198
K1VAB	1	0.03464343	0.05211021	0.665	0.5151
K1VAC	1	-0.00571601	0.05211021	-0.110	0.9139
K1V3C	1	-0.16455208	0.14467596	-1.137	0.2712
K2VC	1	-0.05218508	0.19126481	-0.273	0.7893
K2V3C	1	0.03108052	0.05230875	0.594	0.5502
VAVB	1	-0.08161684	0.05211021	-1.566	0.1357
VAVC	1	0.03623861	0.05230875	0.693	0.4979
VAVAB	1	0.15944187	0.21572040	0.739	0.4699
VAVAC	1	-0.08293278	0.05211021	-1.591	0.1299
VAV3C	1	0.05492572	0.05230875	1.050	0.3094
V3VAC	1	0.23677886	0.15771396	1.501	0.1515
V3V3C	1	-0.20960153	0.19382276	-1.081	0.2946
VCVAB	1	-0.01559411	0.05230875	-0.298	0.7692
VCVAC	1	-0.00254448	0.13809603	-0.197	0.8541
VA3VBC	1	-0.00154512	0.05230875	-0.030	0.9769
K1K1	1	-0.21875435	0.20865542	-1.048	0.3091
K2K2	1	-0.62294327	0.20865542	-2.986	0.0083
V1V1	1	-0.48280799	0.26958226	-1.791	0.0911

2.5 Reduced Model (48 sets):

analysis of variance

SAS

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	7	23.92082440	3.40297491	34.113	0.0001
ERROR	40	3.99028457	0.09975711		
C TOTAL	47	27.91110897			

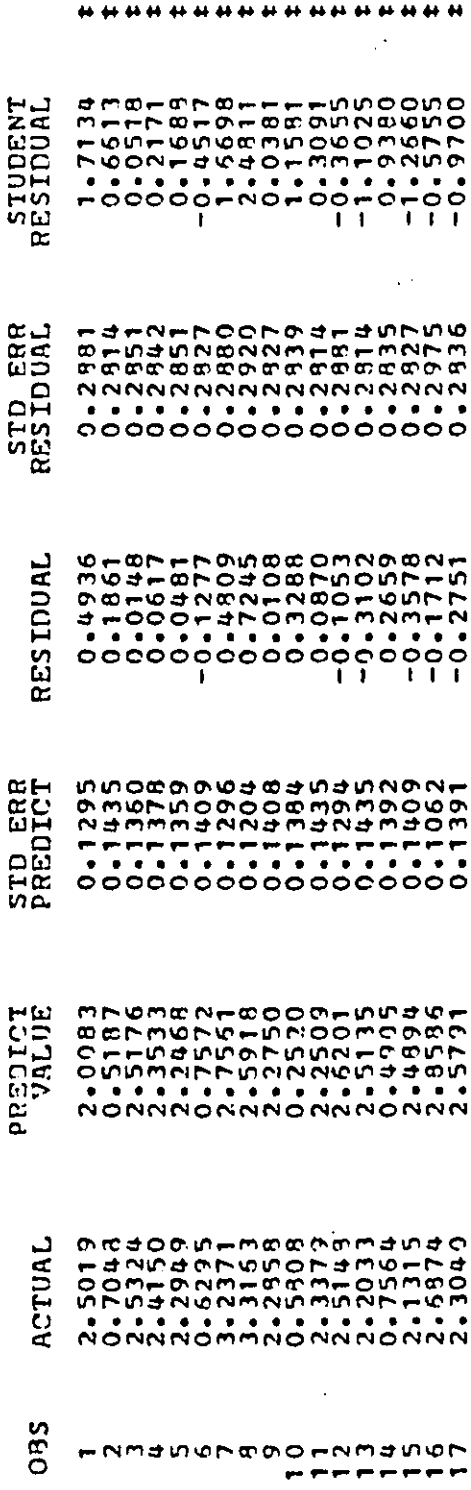
ROOT MSE	0.3159435	R-SQUARE	0.8565
DEP MEAN	2.082667	ADJ R-SQ	0.8314
C.V.	15.16534		

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR HO: PARAMETER=0	PROB > |T|
INTERCEP	1	2.30915923	0.11868806	19.456	0.0001
K1	1	-0.41346583	0.05091559	-8.121	0.0001
K2	1	0.43397336	0.05091559	8.523	0.0001
VA	1	0.11924611	0.05256966	2.268	0.0289
K1VBC	1	-0.13337528	0.05171455	-2.579	0.0137
VAVAB	1	0.46468392	0.05103101	9.106	0.0001
VBVBC	1	-0.15202412	0.05171455	-2.940	0.0054
K2K2	1	-0.34041907	0.12759698	-2.668	0.0110

2.5 Reduced Model (48 sets) (continued):

1/2 predictions



OBS	ACTUAL	PREDICT VALUE	STD ERR PREDICT	RESIDUAL	STD ERR RESIDUAL	STUDENT RESIDUAL
1	2.5019	2.0083	0.1295	0.4936	0.2881	1.7134
2	0.7044	0.5187	0.1435	0.1861	0.2814	0.6613
3	2.5324	2.5176	0.1360	0.0148	0.2842	0.0518
4	2.4150	2.3533	0.1378	0.0617	0.2851	0.2171
5	2.2949	2.2468	0.1359	0.0481	0.2827	0.1689
6	0.6295	0.7572	0.1409	-0.1277	0.2880	-0.4517
7	3.2371	2.7561	0.1296	0.4809	0.2920	1.6698
8	3.3153	2.5918	0.1204	0.7245	0.2927	2.4811
9	2.2858	2.2750	0.1408	0.0108	0.2939	0.0381
10	0.5308	0.2520	0.1384	0.3288	0.2914	1.1581
11	2.3373	2.2509	0.1435	0.0870	0.2881	0.3091
12	2.5149	2.6201	0.1294	-0.1053	0.2814	-0.3655
13	2.2033	2.5135	0.1435	-0.3102	0.2835	-1.1025
14	0.7564	0.4905	0.1392	-0.2659	0.2827	-0.9380
15	2.1315	2.4894	0.1409	-0.3578	0.2827	-1.2660
16	2.6874	2.8586	0.1062	-0.1712	0.2975	-0.5755
17	2.3049	2.5791	0.1391	-0.2751	0.2936	-0.9700

2.5 Reduced Model (48 sets) (continued):

2/2 predictions

FINAL MODEL FOR AREA RATIO SERIES NETWORK

OBS	ACTUAL	PREDICT VALUE	STD ERR PREDICT	RESIDUAL	STD ERR RESIDUAL	STUDENT RESIDUAL
18	0.5978	0.5560	0.1435	0.0418	0.2914	0.1434
19	1.5404	1.9468	0.1384	-0.3065	0.2939	-1.0794
20	2.3141	2.3160	0.1378	-0.001935	0.2942	-0.006809
21	3.7002	2.9176	0.1384	0.8826	0.2839	3.1089
22	0.5178	0.7945	0.1409	-0.2767	0.2927	-0.9788
23	2.0938	2.1353	0.1392	-0.0916	0.2935	-0.3230
24	2.7345	2.5545	0.1204	0.1799	0.2920	0.6162
25	2.2482	2.3123	0.1408	-0.0641	0.2927	-0.2268
26	0.5506	0.8228	0.1360	-0.2721	0.2851	-0.9546
27	2.0571	2.2135	0.1435	-0.1565	0.2814	-0.5562
28	2.3491	2.0493	0.1330	0.2998	0.2965	1.0466
29	2.3848	2.5508	0.1435	-0.1660	0.2814	-0.5901
30	0.9404	1.0613	0.1296	-0.1208	0.2880	-0.4195
31	2.7219	2.4521	0.1409	0.2698	0.2827	0.9545
32	1.8480	2.2878	0.1189	-0.4397	0.2926	-1.5029
33	2.4204	2.3092	0.1187	0.1113	0.2927	0.3802
34	2.1641	2.6278	0.1187	-0.1450	0.2927	-0.4955
35	2.6278	2.3092	0.1187	0.3186	0.2927	1.0885
36	2.3824	2.3092	0.1187	0.0732	0.2927	0.2501
37	2.2443	2.3092	0.1187	-0.0649	0.2927	-0.2217
38	1.8456	1.8543	0.1311	-0.008727	0.2874	-0.3034
39	2.3606	2.7640	0.1314	-0.4034	0.2872	-1.4046
40	2.3562	2.3746	0.0814	-0.008433	0.3052	-0.4276
41	0.8619	1.4199	0.0906	-0.5580	0.3026	-1.8442
42	2.0387	1.9222	0.1127	0.1095	0.2950	0.3710
43	2.1971	1.9292	0.1127	0.2679	0.2950	0.9080
44	2.5885	2.8586	0.1062	-0.2700	0.2975	-0.9079
45	2.8112	2.8586	0.1062	-0.0474	0.2975	-0.1593
46	1.9791	2.2878	0.1189	-0.3087	0.2926	-1.0551
47	2.2904	2.2878	0.1189	0.002643	0.2926	0.009034
49	2.6573	2.8586	0.1062	-0.2013	0.2975	-0.6768

SUM OF RESIDUALS 1.381E-13
SUM OF SQUARED RESIDUALS 3.990285
PREDICTED RESID SS (PRESS) 5.741224

2.5 Reduced Model (48 sets) (continued):

Reduced model:

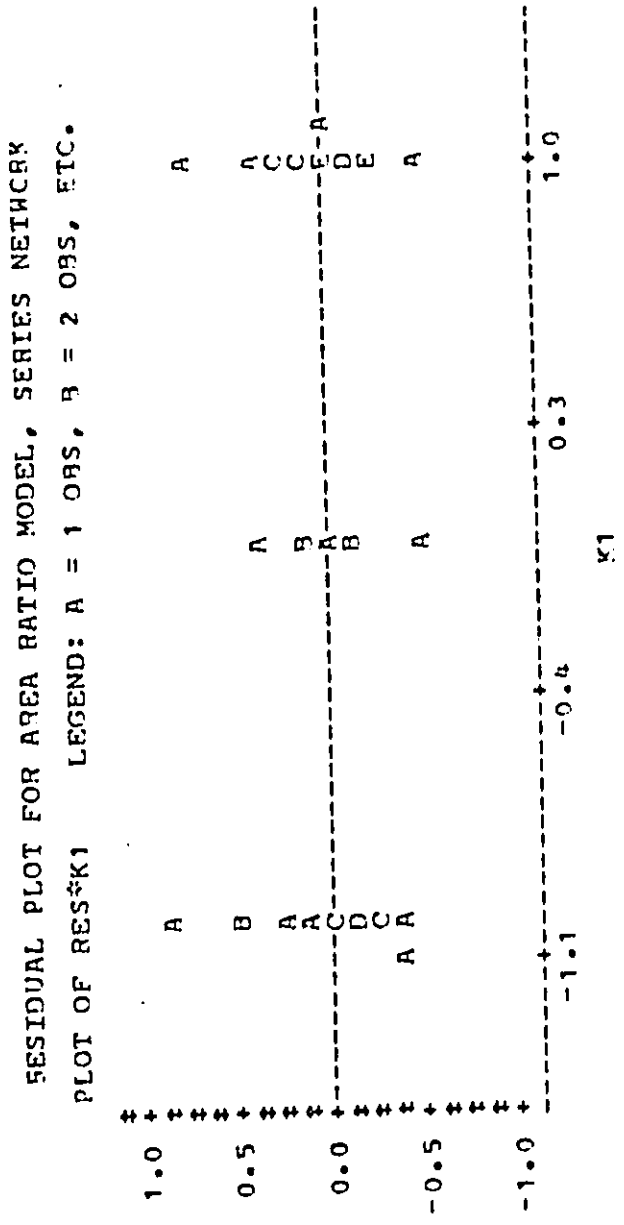
$$(A_{CSTR}:A_{PFR}) = 2.309 - 0.413\ x_1 + 0.434\ x_2 - 0.340\ x_2^2 + 0.119\ x_3 - 0.133\ x_1x_8 + 0.465\ x_3x_6 - 0.152\ x_4x_8$$

also, from this model, SSR = 3.9903, n = 48 and p = 8.

Since R = 3.37 and $F_{36,4} = 5.74$, there is no lack of fit.

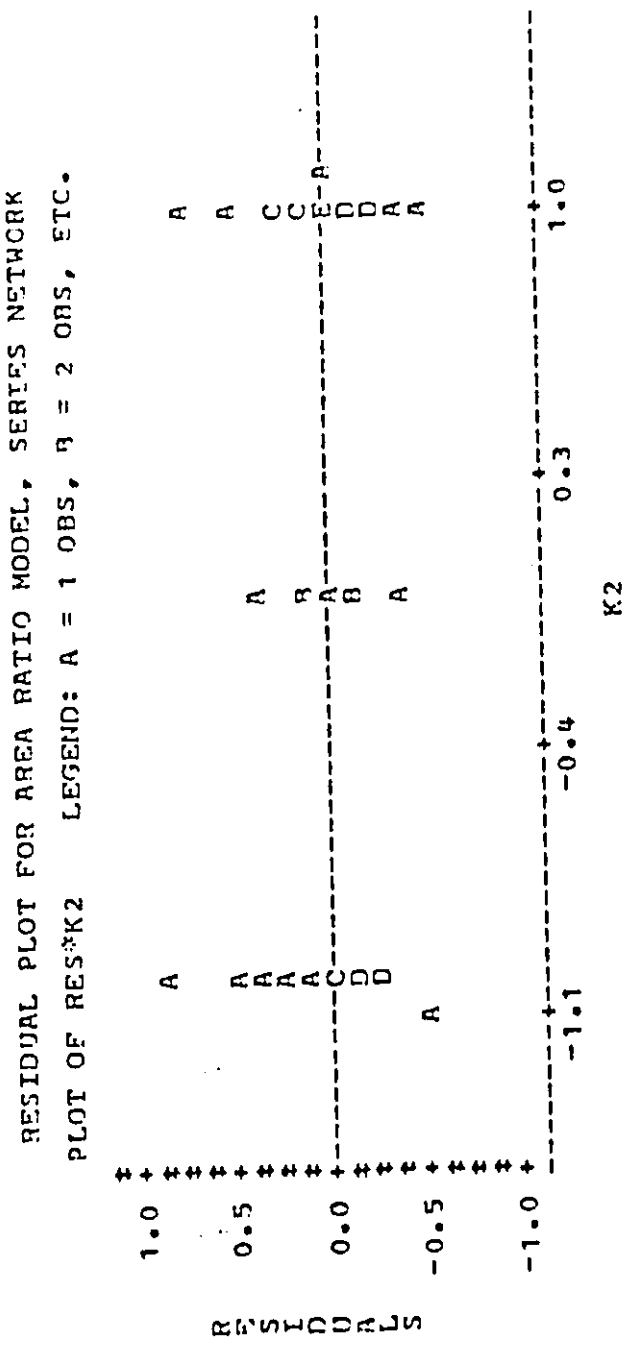
Residual Plots:

res vs k1



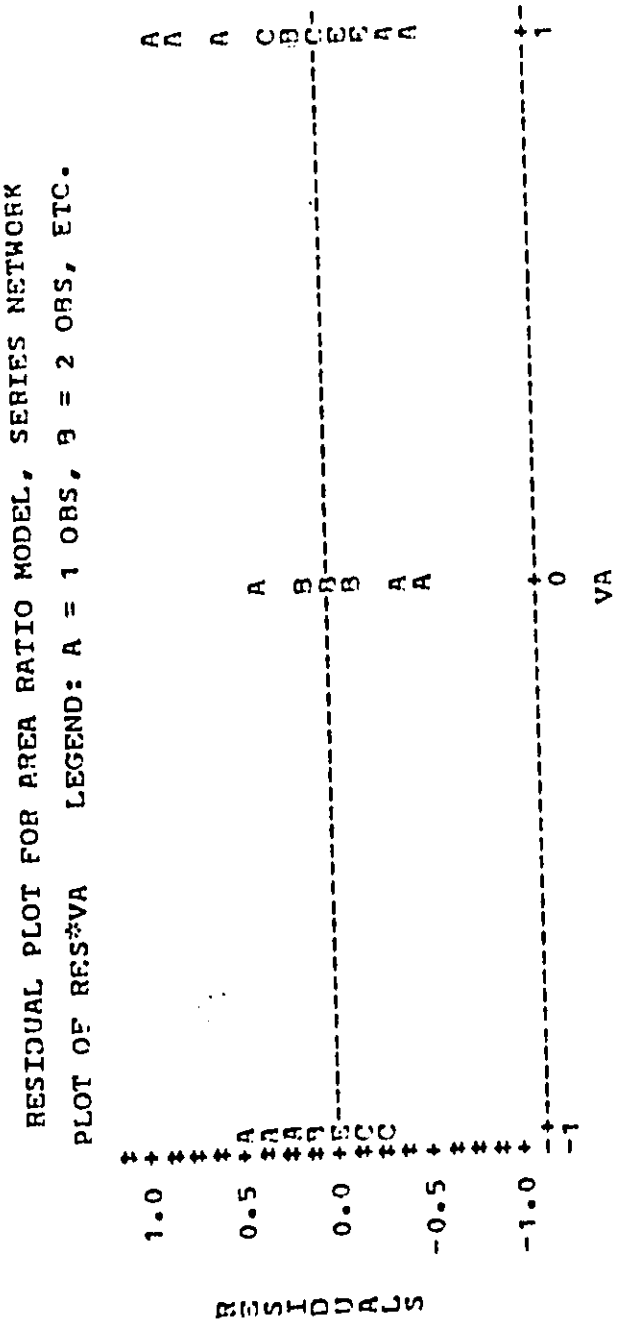
2.5 Reduced Model (37 sets) (continued):

res vs k2



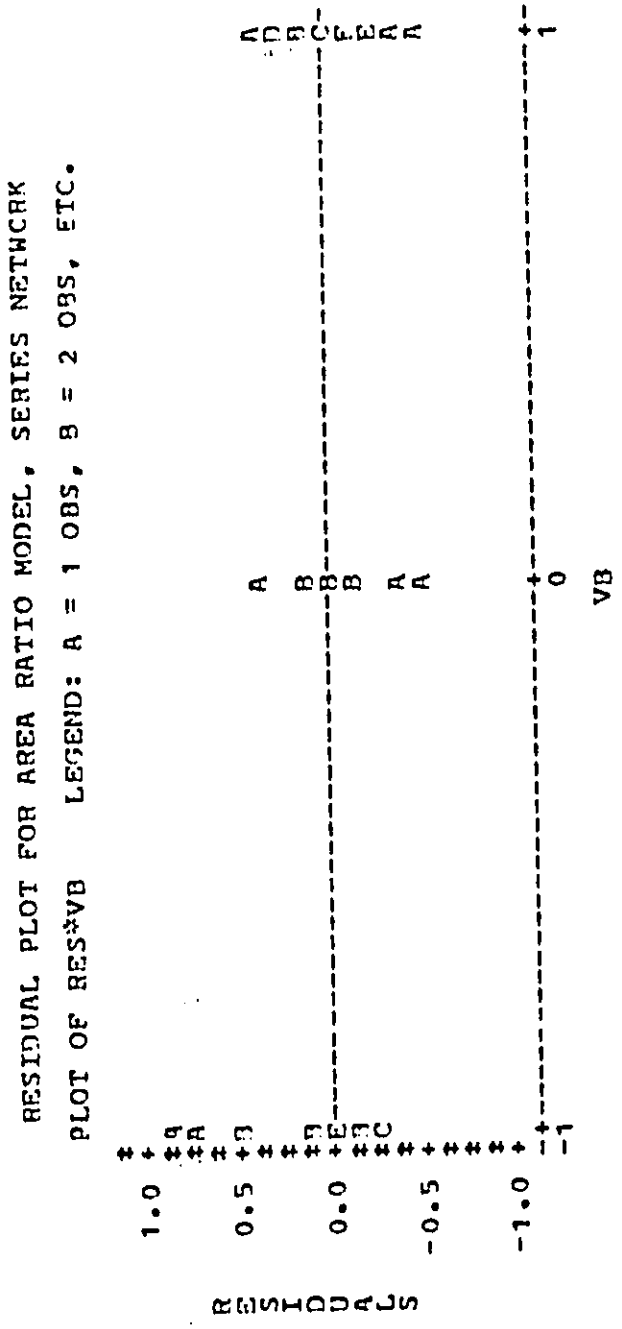
2.5 Reduced Model (37 sets) (continued):

res vs va



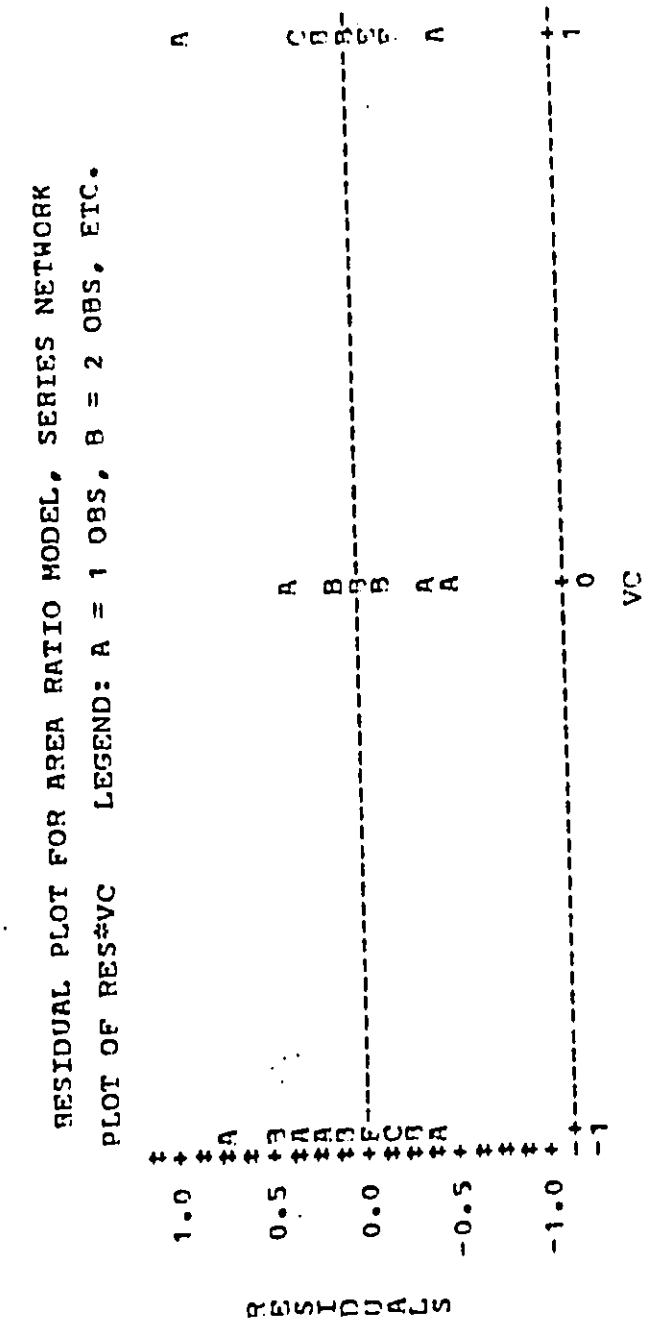
2.5 Reduced Model (37 sets) (continued):

res vs vb



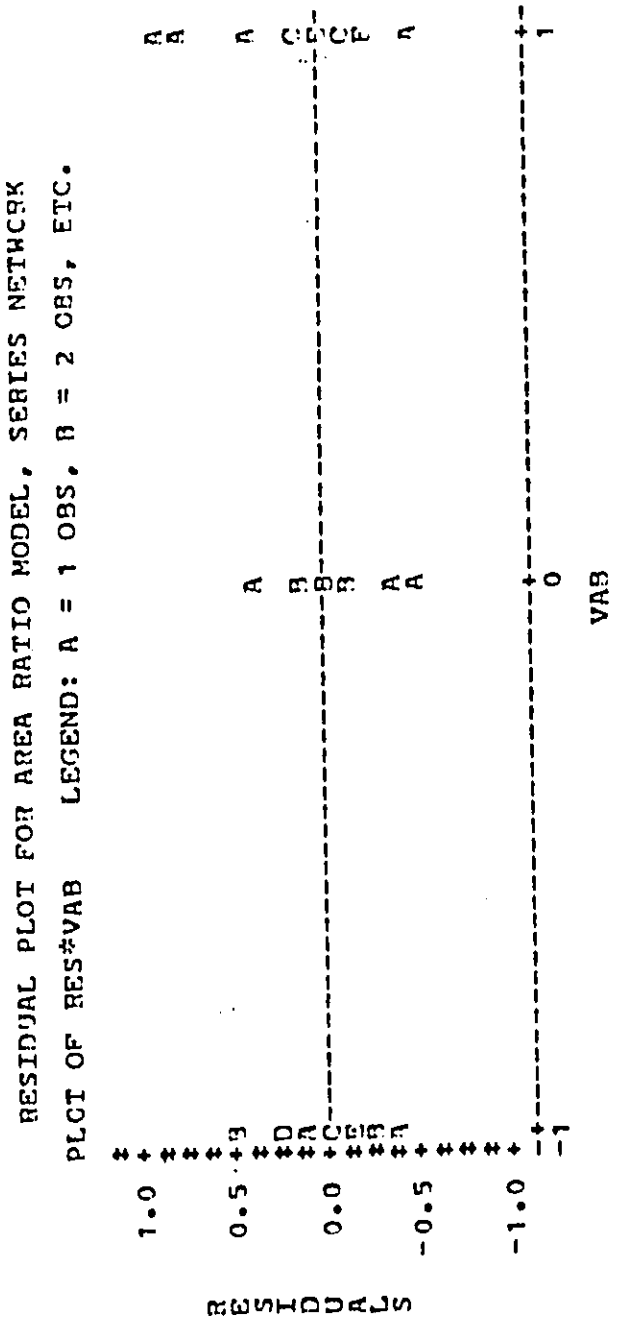
2.5 Reduced Model (37 sets) (continued):

res vs vc



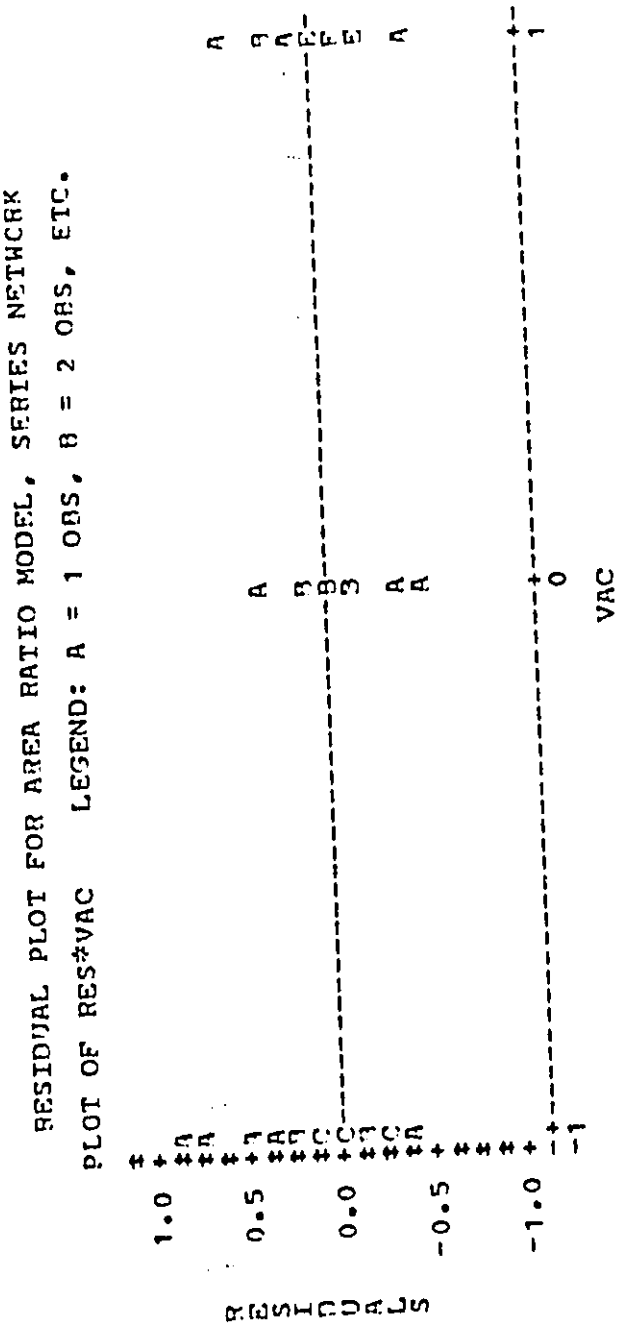
2.5 Reduced Model (37 sets) (continued):

res vs vab



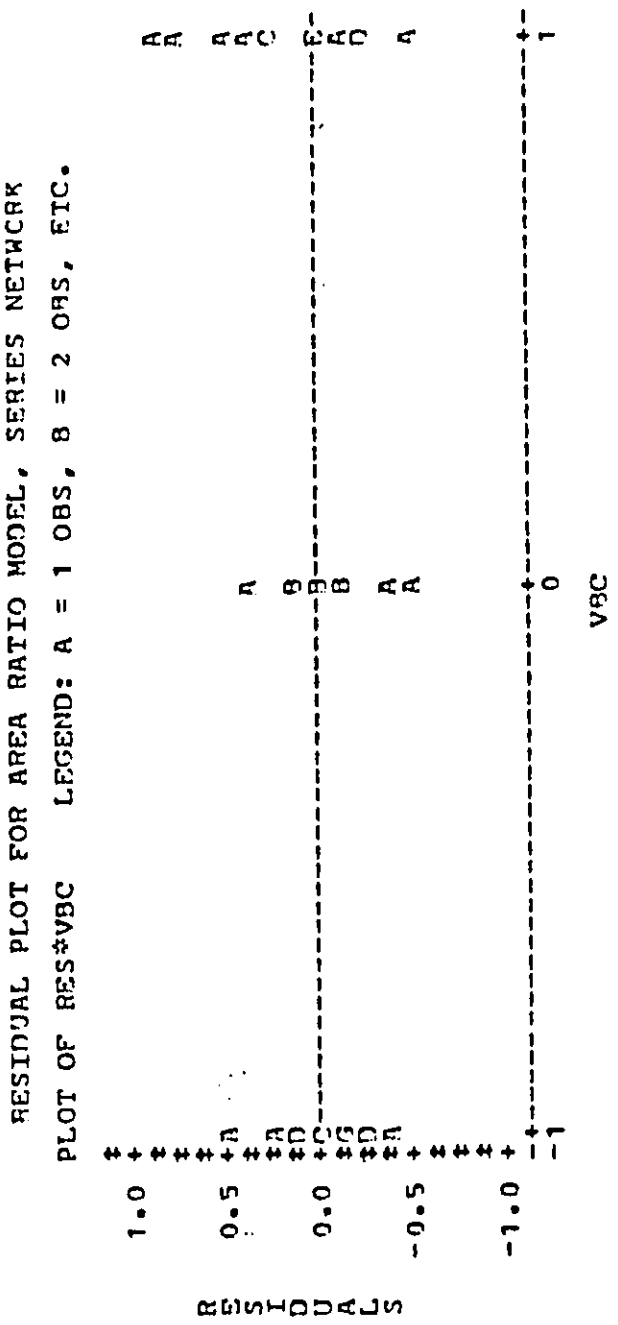
2.5 Reduced Model (37 sets) (continued):

res vs vac



2.5 Reduced Model (37 sets) (continued):

res vs vbc



The residual plots showed no inadequacies.

2.6 Correlation Ratio (full model):

Model of the ratio of the correlation between the parameter estimates for the CSTR to that of the PFR.

analysis of variance

SAS

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	30	37.39830924	1.24661031	1.787	0.1047
ERROR	17	11.85936058	0.69760945		
C TOTAL	47	49.25766982			

ROOT MSE	0.8352302	R-SQUARE	0.7592
DEP MEAN	0.6507119	ADJ R-SQ	0.3344
C.V.	128.3564		

2.6 Correlation Ratio (full model) (continued):

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR HO: PARAMETER=0	PROB > |T|
INTERCEP	1	0.798231801	0.37352629	2.137	0.0474
K1	1	-0.251307351	0.13930388	-1.804	0.0890
K2	1	-0.289306411	0.13930388	-2.077	0.0533
VA	1	-0.224778961	0.14423245	-1.558	0.1375
V3	1	-0.066629191	0.14423245	-0.462	0.6500
VC	1	-0.343225571	0.14478198	-2.371	0.0298
VA3	1	0.097227691	0.14423245	0.674	0.5093
VAC	1	0.248659741	0.14423245	1.724	0.1029
VBC	1	-0.172252201	0.14478198	-1.190	0.2505
K1K2	1	1.175311461	0.59605421	1.972	0.0651
K1VA	1	-0.177352121	0.14423245	-1.230	0.2355
K1V3	1	-0.138696531	0.14423245	-0.962	0.3497
K1VC	1	-0.071898321	0.14478198	-0.497	0.6259
K1VA3	1	0.196423441	0.14423245	1.362	0.1910
K1VAC	1	0.234252571	0.14423245	1.624	0.1227
K1V3C	1	-0.430947791	0.40043913	-1.076	0.2969
K2VC	1	-1.203753461	0.52938939	-2.274	0.0362
K2V3C	1	-0.097443561	0.14478198	-0.673	0.5100
VAV3	1	-0.132067681	0.14423245	-0.916	0.3727
VAVC	1	-0.289049931	0.14478198	-1.996	0.0622
VAVA3	1	-0.488712791	0.59707841	-0.819	0.4244
VAVAC	1	-0.233506151	0.14423245	-1.619	0.1239
VAVBC	1	-0.152128311	0.14478198	-1.051	0.3091
V3VAC	1	-0.504566551	0.43652619	-1.156	0.2537
V3V3C	1	1.072330121	0.53646936	1.999	0.0619
VCVAB	1	-0.035407831	0.14478198	-0.245	0.8097
VCVAC	1	-0.024995091	0.38222697	-0.065	0.9485
VAVBC	1	-0.140715241	0.14478198	-0.972	0.3447
K1K1	1	-0.686298921	0.57752372	-1.188	0.2510
K2K2	1	-0.462972051	0.57752372	-0.802	0.4338
VAVA	1	0.982147301	0.74615913	1.316	0.2056

2.7 Correlation Ratio (reduced model):

analysis of variance

FINAL MODEL FOR CORRELATION RATIO SERIES

ANALYSIS OF VARIANCE

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE	PROB>F
MODEL	5	15.64572518	3.12914504	3.910	0.0053
ERROR	42	33.51194464	0.80028440		
C TOTAL	47	49.25766982			

ROOT MSE	0.8945862	R-SQUARE	0.3176
DEP MEAN	0.6507119	ADJ R-SQ	0.2364
C.V.	137.4781		

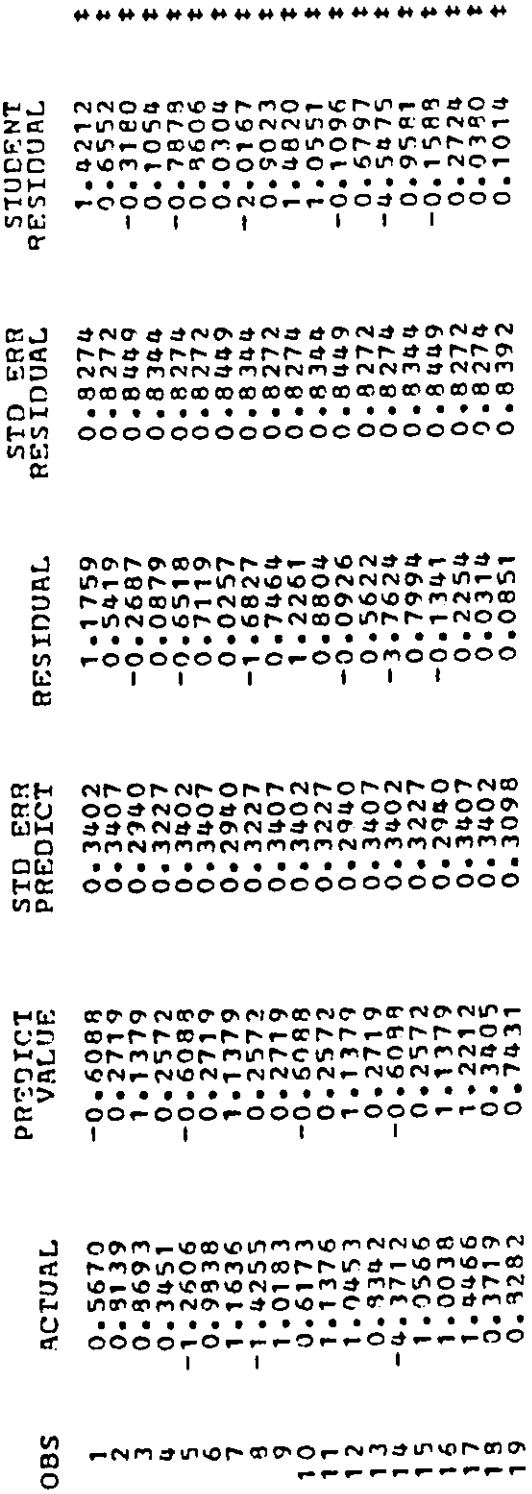
reduced model

PARAMETER ESTIMATES

VARIABLE	DF	PARAMETER ESTIMATE	STANDARD ERROR	T FOR HO: PARAMETER=0	PROB > |T|
INTERCEP	1	0.62334263	0.13181904	4.729	0.0001
K2	1	0.31716048	0.14216217	2.231	0.0311
VC	1	0.35879202	0.15230985	2.356	0.0232
K1VBC	1	-0.44037643	0.15230985	-2.891	0.0061
K2VC	1	-0.73347221	0.26486566	-2.769	0.0083
VBVBC	1	0.61761532	0.26561237	2.325	0.0250

2.7 Correlation Ratio (reduced model) (continued):

1/2 predictions



OBS	ACTUAL	PREDICT VALUE	STD ERR PREDICT	RESIDUAL	STD ERR RESIDUAL	STUDENT RESIDUAL
1	0.5670	-0.6088	0.3402	1.1759	0.8274	1.4212
2	0.3139	-0.2719	0.3407	0.5419	0.8272	0.6552
3	0.8693	1.1379	0.2940	-0.2687	0.8449	-0.3180
4	0.3451	-0.2572	0.3227	-0.0879	0.8344	-0.1054
5	-1.2606	-0.6088	0.3402	-0.6518	0.8274	-0.7879
6	-0.9838	-0.2719	0.3407	-0.7119	0.8272	-0.8606
7	1.1636	1.1379	0.2940	0.0257	0.8449	0.0304
8	-1.4255	1.2572	0.3227	-1.6827	0.8344	-2.0167
9	-1.0183	0.2719	0.3407	-0.7464	0.8272	-0.9023
10	0.6173	-0.6088	0.3402	1.2261	0.8274	1.4820
11	1.1376	-0.2572	0.3227	0.8804	0.8344	1.0551
12	1.0453	1.1379	0.2940	-0.0926	0.8449	-0.1096
13	-0.9342	0.2719	0.3407	-0.5622	0.8272	-0.6797
14	-4.3712	-0.6088	0.3402	-3.7624	0.8274	-4.5475
15	-1.0566	-0.2572	0.3227	-0.7994	0.8344	-0.9581
16	1.0038	1.1379	0.2940	-0.1341	0.8449	-0.1588
17	1.4466	1.2212	0.3407	0.2254	0.8272	0.2724
18	0.3719	0.3405	0.3402	0.0314	0.8274	0.0380
19	0.9282	0.7431	0.3098	0.0851	0.8392	0.1014

2.7 Correlation Ratio (reduced model) (continued):

2/2 predictions

FINAL MODEL FOR CORRELATION RATIO SERIES

OBS	ACTUAL	PREDICT VALUE	STD ERR PREDICT	RESIDUAL	STD ERR RESIDUAL	STUDENT RESIDUAL
20	1.0817	1.6239	0.3275	-0.5421	0.8325	-0.6512
21	2.3930	1.2212	0.3407	1.1618	0.8272	1.4045
22	0.1013	0.3405	0.3402	-0.2391	0.8274	-0.2890
23	0.9830	0.7431	0.3098	0.2399	0.8392	0.2959
24	1.9116	1.6238	0.3275	0.2878	0.8325	0.3457
25	1.0365	0.3405	0.3402	0.6960	0.8274	0.8412
26	0.4980	1.2212	0.3407	-0.7232	0.8272	-0.8743
27	1.0326	1.6238	0.3275	-0.5912	0.8325	-0.7101
28	0.9951	0.7431	0.3098	0.2420	0.8392	0.2884
29	0.9938	0.3405	0.3402	0.5984	0.8274	0.7232
30	0.0209	1.2212	0.3407	-1.2003	0.8272	-1.4511
31	1.0786	1.6238	0.3275	-0.5452	0.8325	-0.6550
32	0.9537	0.7431	0.3098	0.2106	0.8392	0.2510
33	1.1075	0.6233	0.1318	0.4842	0.8848	0.5472
34	0.2927	0.6233	0.1318	-0.3307	0.8848	-0.3737
35	0.4282	0.6233	0.1318	-0.1952	0.8848	-0.2206
36	1.2715	0.6233	0.1318	0.6482	0.8848	0.7326
37	0.8912	0.6233	0.1318	0.2679	0.8848	0.3027
38	0.5955	0.6233	0.1318	-0.0279	0.8848	-0.0315
39	-0.5598	0.6233	0.1318	-1.2832	0.8848	-1.4502
40	1.0386	0.9722	0.1903	0.0664	0.8741	0.0760
41	-0.5625	0.2745	0.2178	-0.8370	0.8677	-0.9647
42	-0.4993	0.3896	0.4563	-0.1107	0.7695	-0.1438
43	0.8730	0.3896	0.4563	0.4844	0.7695	0.6295
44	0.7769	1.1379	0.2940	-0.3611	0.8443	-0.4273
45	1.0084	1.1379	0.2940	-0.1296	0.8449	-0.1534
46	0.4807	0.7431	0.3098	-0.2624	0.8392	-0.3126
47	2.4212	1.4924	0.5226	0.9287	0.7260	1.2792
48	0.7223	0.3886	0.4563	0.3337	0.7695	0.4337

SUM OF RESIDUALS 5.05013E-14
SUM OF SQUARED RESIDUALS 33.61194
PREDICTED RESID SS (PRESS) 45.67117

2.7 Correlation Ratio (reduced model) (continued):

Reduced model:

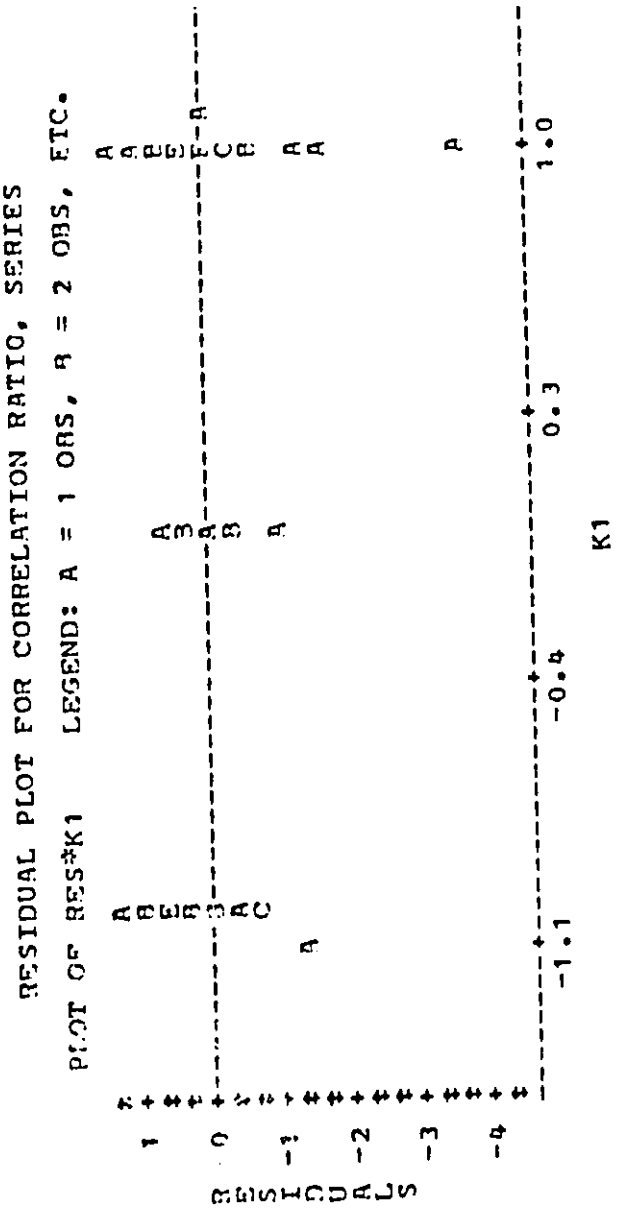
$$(\rho_{CSTR} : \rho_{PFR}) = 0.613 + 0.317\ x_2 - 0.359\ x_5 - 0.440\ x_1x_8 - 0.733\ x_2x_8 + 0.618\ x_4x_8$$

SSR = 36.62, n = 48, p = 6, $\sigma_p^2 = 0.18019$ and $\nu_p = 4$

Since R = 5.16 and $F_{38,4} = 5.72$, there is no lack of fit.

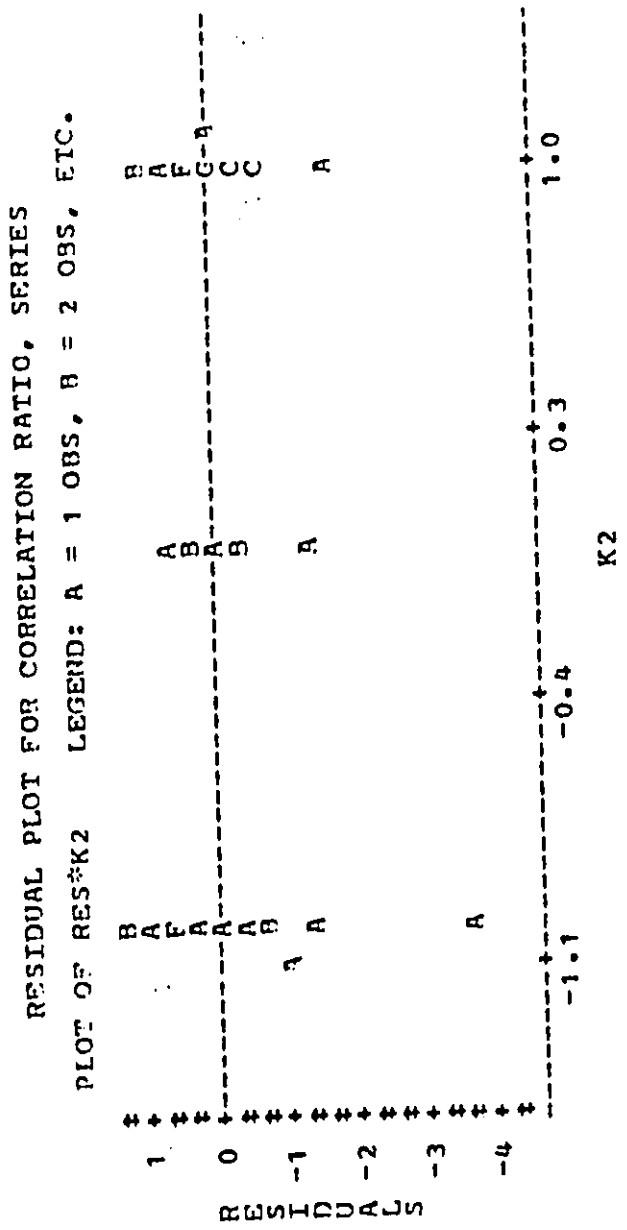
Residual Plots:

res vs k1



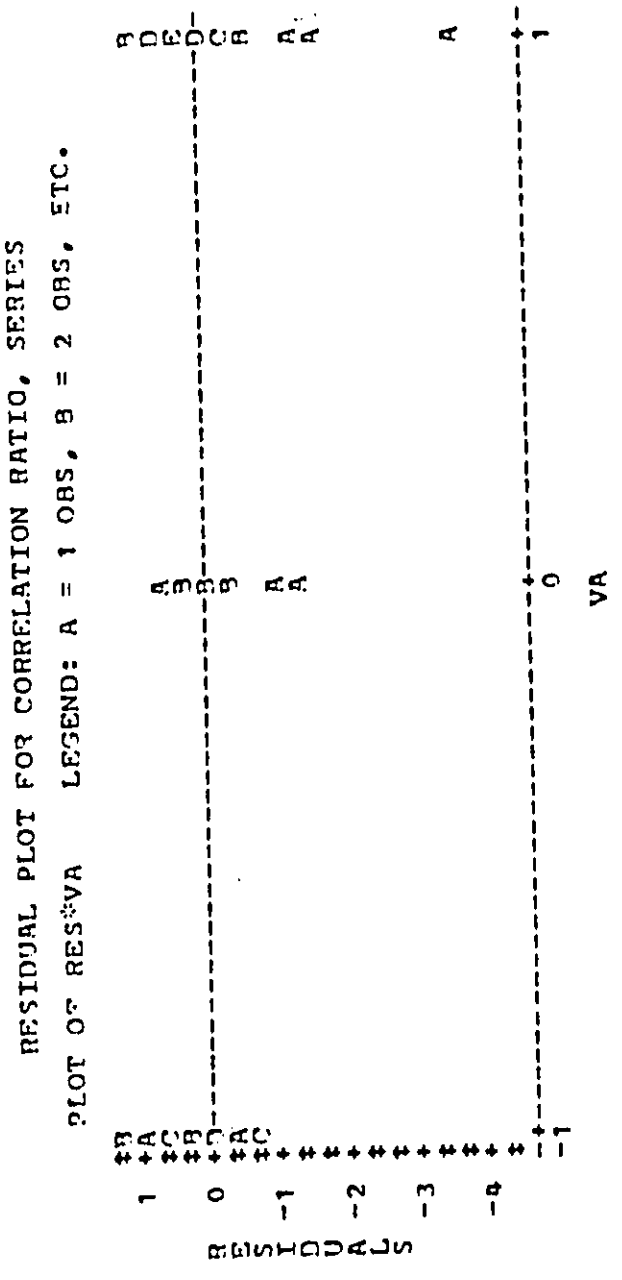
2.7 Correlation Ratio (reduced model) (continued):

res vs k2



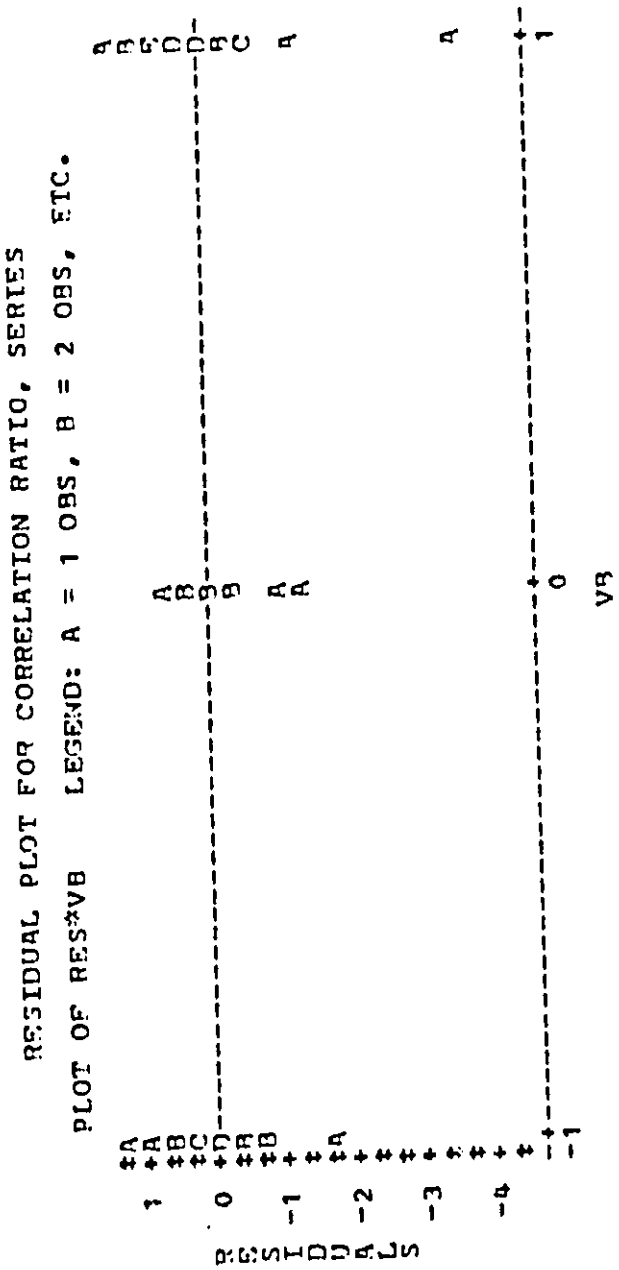
2.7 Correlation Ratio (reduced model) (continued):

res vs va



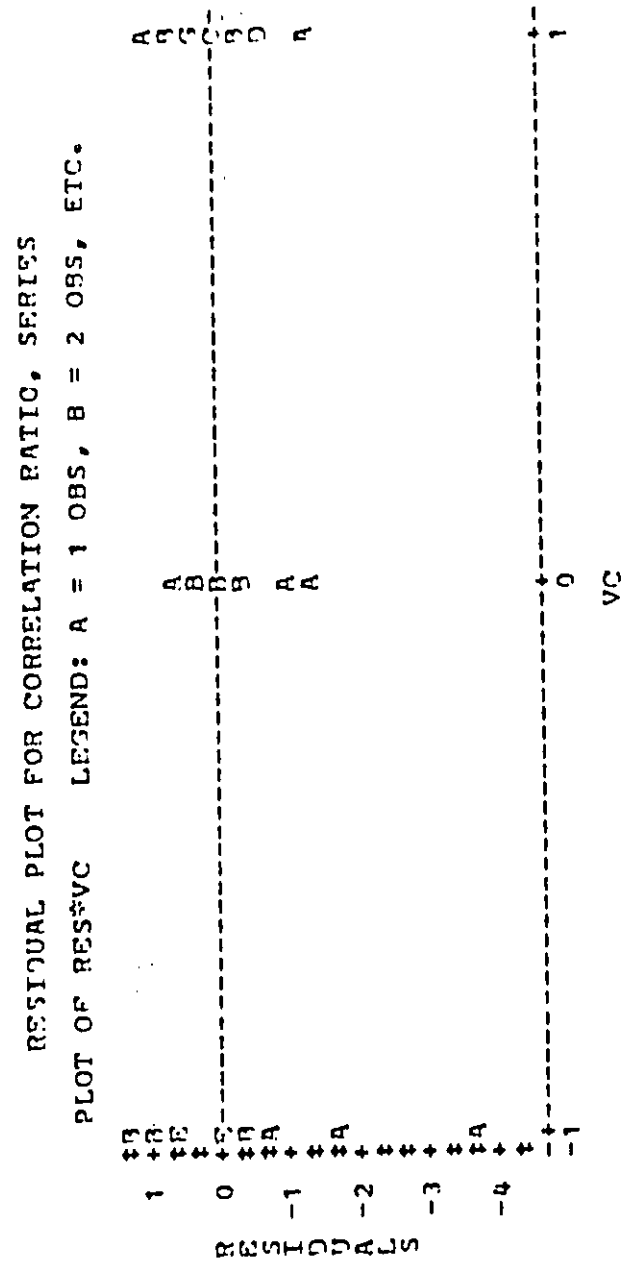
2.7 Correlation Ratio (reduced model) (continued):

res vs vb



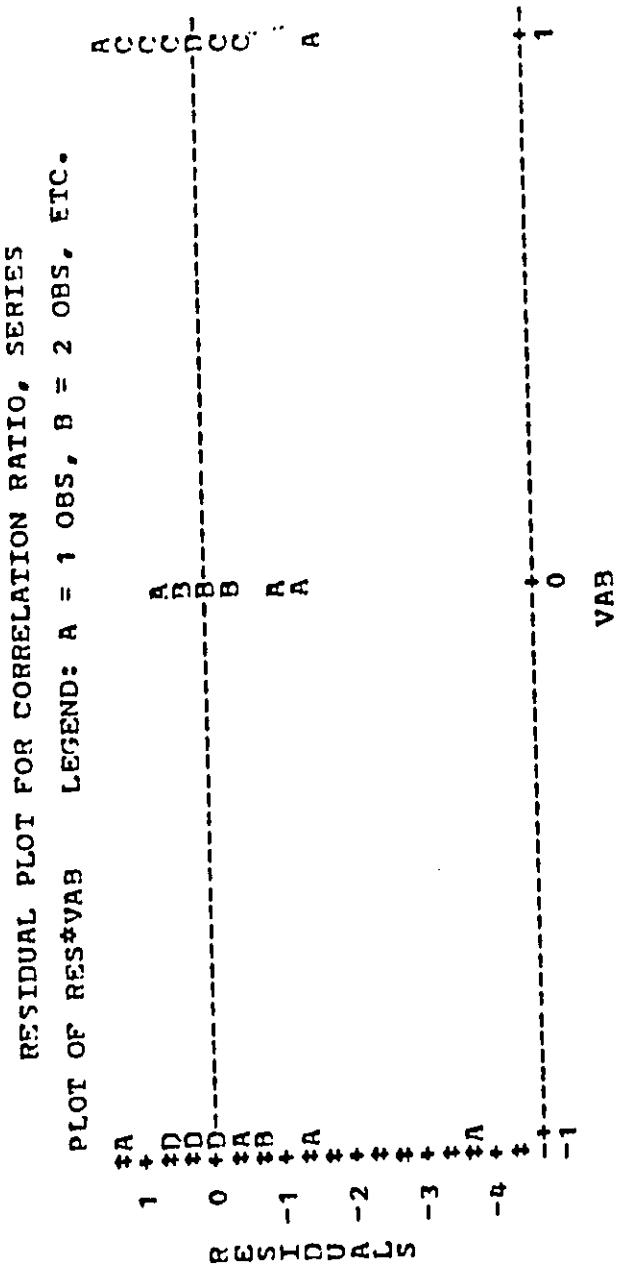
2.7 Correlation Ratio (reduced model) (continued):

res vs vc



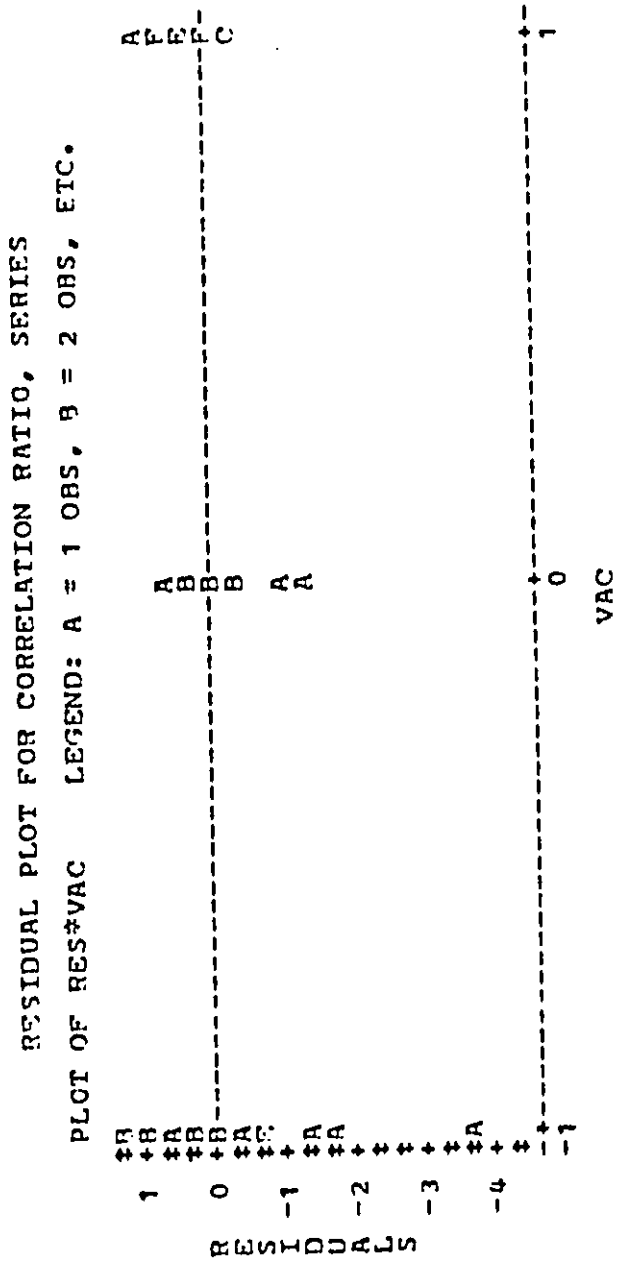
2.7 Correlation Ratio (reduced model) (continued):

res vs vab



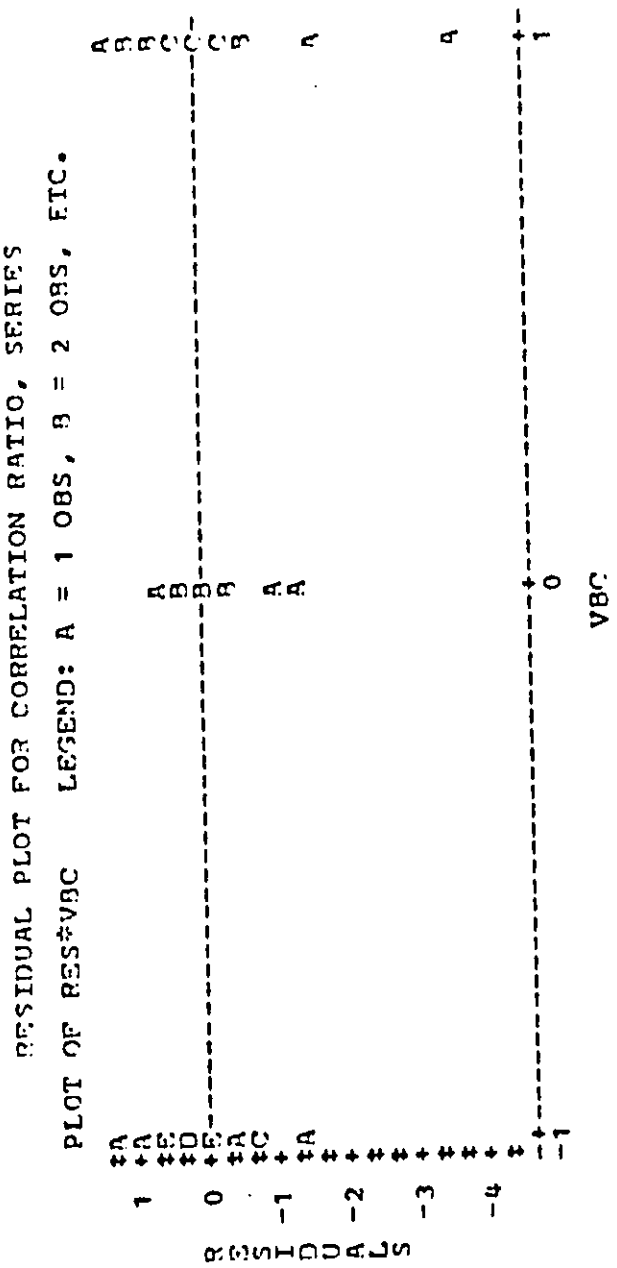
2.7 Correlation Ratio (reduced model) (continued):

res vs vac



2.7 Correlation Ratio (reduced model) (continued):

res vs vbc



The residual plots showed no inadequacies.