DESIGNS AND MODELS FOR THE MIXTURE PROBLEM WITH CATEGORIZED COMPONENTS

By

JENGJUNG FANG

Bachelor of Business
Cheng-Kung University
Tainan, Taiwan
1983

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1989

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DESIGNS AND MODELS FOR THE MIXTURE

PROBLEM WITH CATEGORIZED

COMPONENTS

Thesis Approved:

Kenneth E Case

Thesis Advisor

Manjunath Kamath

[illegible]

M. P. Terrell

[illegible]

Thomas C. Collins

Dean of the Graduate College

PREFACE

The overall objective of the research is to extend the designs and models of the mixture experiments while the components are classified into categories. The multiple-centroid design, simplex-lattice by simplex-centroid design and their corresponding models are developed. The method of calculating estimates of parameters in the two models corresponding to the two designs is generalized. Method of using ratios of components as design variables is developed and illustrated. A method for obtaining D_N-optimal designs is suggested and D_N-optimal designs for models being linear, linear with cross-product terms, and quadratic are obtained. The design and model using mixture components and mixture-related variables as design variables are developed.

I would like to express my sincere appreciation to my major advisor, Professor Kenneth E. Case, for his superb suggestions, guidance, encouragement and support throughout this research. During my doctoral studies, Dr. Case gave me full confidence to complete it. Without his inspiration and assistance, the accomplishment of this dissertation would not have been possible.

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I also wish to dedicate this dissertation to my family and I hope my effort in graduate school has been worthy of my family's efforts.

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NOMENCLATURE

ACED = A branch-and-bound search algorithm to construct a catalog of A-, D-, G-, V-optimal designs

A-optimality = Minimize the trace of $(X^T X)^{-1}$

DETMAX = An algorithm for the construction of D-optimal designs

c_i = The proportion contribution of the i^{th} category

D-optimality = Maximize the determinant of $(X^T X)$

G-optimality = Minimize the maximum prediction variance $d = x_0(X^T X)^{-1} x_0 \sigma^2$ over a specified set of design points

h_i = The radius of the i^{th} component in an ellipsoidal region

(i, j) = A design consists of the i^{th} constituent point in the first category and the j^{th} constituent point in the second category

I_N = The N x N Identity matrix

m = The degree of a regression equation

q = The number of components in a mixture

q_i = The number of components in the i^{th} category

$\{q^c, m\}$ = A simplex-centroid design for a q-component mixture with a m^{th}-degree regression equation

$\{q^l, m\}$ = A simplex-lattice design for a q-component mixture with a m^{th}-degree regression equation

$\{q_1^c, q_2^c; m_1, m_2\}$ design = A multiple-centroid design by using a $\{q_1^c, m_1\}$ simplex-centroid design in the first category and a $\{q_2^c, m_2\}$ simplex-centroid design in the second category. Then combine the two designs by factorial arrangement into a multiple-centroid design.

$\{q_1^l, q_2^c; m_1, m_2\}$ design = A simplex-lattice by simplex-centroid design by using a $\{q_1^l, m_1\}$ simplex-lattice design in the first category and a $\{q_2^c, m_2\}$ simplex-centroid design in the second category. Then combine the two designs by factorial arrangement into the design.

$\{q_1^l, q_2^l; m_1, m_2\}$ design = A multiple-lattice design by using a $\{q_1^l, m_1\}$ simplex-lattice design in the first category and a $\{q_2^l, m_2\}$ simplex-lattice design in the second category. Then combine the two designs by factorial arrangement into a multiple-lattice design.

$\binom{q}{m}$ $= \dfrac{q!}{m!(q-m)!}$

R_A^2 = Adjusted coefficient of determination

r_i = The i^{th} ratio variable defined by mixture variables

$r_i^{'}$ = The i^{th} normalized ratio variable transformed from the i^{th} uncoded ratio variables

V-optimality = Minimize average value of d, $d = x_0(X^T X)^{-1} x_0 \sigma^2$, over a specified set of design points

w_i = The i^{th} mixture-related variable which is orthogonally transformed from mixture variables

$\boldsymbol{X}$ = The matrix of known constants in a regression equation

$\boldsymbol{x_0}$ = A point within factor space

x_{0i} = The center of the i^{th} component in an ellipsoidal region

x_i = The i^{th} component and the proportion of the i^{th} component

x_{ij} = The j^{th} component of the i^{th} category in a mixture

y = The response observed at a design point

Y = The vector of observed responses

$\hat{y}(\boldsymbol{x}_0)$ = The expected response at $\boldsymbol{x}_0$

z_i = The i^{th} process variable that may have effect on the blending properties of components

α = The unknown parameter in a regression equation

β = The unknown parameter in a regression equation

$\hat{\beta}$ = The ordinary least squares estimator of β

γ = The parameter in a regression equation

δ = The parameter in a regression equation

σ^2 = The variance of observed response

ρ^* = The radius of the largest sphere inside experimental region

ε = The vector of observation errors

η = The mean response to a mixture at a certain design point

$\bar{\eta}$ = The observed mean response to a mixture

η_i = The mean response observed at $x_i = 1$ in a single-simplex mixture problem

η_{ij} = The mean response observed at $x_i = x_j = 1/2$ in a single-simplex mixture problem

η_{ijk} = The mean response observed at $x_i = x_j = x_k = 1/3$ in a single-simplex mixture problem

η_{ijj} = The mean response observed at $x_i = 1/3$ and $x_j = 2/3$ in a single-simplex mixture problem

η_{iij} = The mean response observed at $x_i = 2/3$ and $x_j = 1/3$ in a single-simplex mixture problem

$\eta_{i,j}$ = The mean response observed at $x_i = x_j = 1$ in a multiple-simplex mixture problem

$\eta_{i,jk}$ = The mean response observed at $x_i = 1$ and $x_j = x_k = 1/2$ in a multiple-simplex mixture problem

$\eta_{ij,k}$ = The mean response observed at $x_i = x_j = 1/2$ and $x_k = 1$ in a multiple-simplex mixture problem

$\eta_{ij,kl}$ = The mean response observed at $x_i = x_j = 1/2$ and $x_k = x_l = 1/2$ in a multiple-simplex mixture problem

$\eta_{ijk,l}$ = The mean response observed at $x_i = x_j = x_k = 1/3$ and $x_l = 1$ in a multiple-simplex mixture problem

$\eta_{ijk,lm}$ = The mean response observed at $x_i = x_j = x_k = 1/3$ and $x_l = x_m = 1/2$ in a multiple-simplex mixture problem

CHAPTER 1

THE RESEARCH PROBLEM

The use of experimental designs has proven to be an efficient method to improve the quality of products and process. The objective of an experimental design, in general, is to obtain the best operating conditions possible, considering economical factors, by which better products are obtained. This is accomplished through the analysis of data collected at critical design points.

Box and Draper (1987) describe the iterative nature of the experimental learning process. It consists essentially of the successive and repeated use of the sequence

CONJECTURE --> DESIGN --> EXPERIMENT --> ANALYSIS.

Traditional designs such as randomized blocks, Latin squares, and factorial designs have been used by statisticians and engineers as building blocks in the iterative learning process.

The mixture experiment is another method used in the iterative learning process. In a mixture problem, the measured response is assumed to depend only on the proportions of the ingredients present in the mixture and not on the amount of the mixture. Designs of experiments on mixtures are different from traditional designs since orthogonal designs cannot be obtained without transforming the mixture variables into nonmixture variables.

The purpose of using design of experiments with mixtures is to obtain a sequence of settings of components called design points where one can collect observations and fit the observations into a desired model which describes the relationship between the measured response and the mixture component proportions. The model is then verified for adequacy using a lack-of-fit test. If the model is appropriate, then one can predict the measured response by the fitted model as long as the setting of the mixture component proportions is inside the factor space.

1.1 The Response Surface Problem

The analysis of experimental designs is based on response surface methodology. In a general response surface problem, one would like to describe an observable response y through a set of predictor variables $x_1, x_2, ..., x_q$. Response y is thus considered to be a function of predictor variables. The response y is usually assumed to be a continuous and quantitative variable. The predictor variables are either quantitative or qualitative and they are controllable or observable by the experimenter. The relationship between the response y and predictor variables is expressed as

$$y_k = f(x_{k1}, x_{k2}, ..., x_{kq}) + \varepsilon_k \text{, k=1, 2, ..., N,} \tag{1.1}$$

where y_k is the k^{th} value of N observations of the response, x_{ki} is the value of the i^{th} predictor variable for the k^{th} observation, and ε_k is the observation error which is not explained by the regression function.

An appropriate model is generally selected to approximate the true relationship between response y and the predictor variables. Usually a model linear in the parameters is chosen. A linear response model may be written in matrix form as

$$Y = X\beta + \varepsilon, \tag{1.2}$$

where $\boldsymbol{Y}$ is an Nx1 vector of observed response values, $\boldsymbol{X}$ is an Nxp matrix of known constants, $\boldsymbol{\beta}$ is a px1 vector of unknown parameters, and $\boldsymbol{\varepsilon}$ is an Nx1 vector of random errors. It is usually assumed that E(ε)=0 and Var(ε)=$\sigma^2\boldsymbol{V}$, where $\boldsymbol{V}$ is a NxN matrix. Most often $\boldsymbol{V}=\boldsymbol{I}_N$ (the NxN identity matrix). Since E(ε)=0, the model (1.2) can be alternately expressed as

$$\eta = \mathrm{E}(\boldsymbol{Y}) = \boldsymbol{X}\boldsymbol{\beta}. \tag{1.3}$$

If Var(ε)=$\sigma^2\boldsymbol{I}_N$, then the ordinary least squares estimator of $\boldsymbol{\beta}$ is given by

$$\hat{\boldsymbol{\beta}} = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{X}^{\mathrm{T}}\boldsymbol{Y}, \tag{1.4}$$

and has variance

$$\mathrm{Var}(\hat{\boldsymbol{\beta}}) = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\sigma^2. \tag{1.5}$$

If $\boldsymbol{x}_0$ is a point within the factor space constructed by the values of design points (predictor variables), the predicted response and its variance for the expected mean response at $\boldsymbol{x}_0$ are

$$\hat{y}(\boldsymbol{x}_0) = \boldsymbol{x}_0^{\mathrm{T}}\hat{\boldsymbol{\beta}}, \tag{1.6}$$

and

$$\begin{aligned} \mathrm{Var}[\hat{y}(\boldsymbol{x}_0)] &= \mathrm{Var}[\boldsymbol{x}_0^{\mathrm{T}}\hat{\boldsymbol{\beta}}] \\ &= \boldsymbol{x}_0^{\mathrm{T}}(\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{x}_0\sigma^2. \end{aligned} \tag{1.7}$$

Designs of experiments are usually used to set up the values of predictor variables such that the response y is predicted through those predictor variables efficiently and precisely. Orthogonal designs of predictor variables are often employed such that the factor effects of predictor variables are not confounded with each other. Computer-aided design of experiments permits one to obtain designs which meet certain criteria under the assumption that the response model is true. One design which minimizes the generalized variance of the elements of the estimated parameters in the model is called a D-optimal design. A sequential design is often desirable through augmenting the initial design when the initial fitted model is suspected to be inadequate.

1.2 Mixture Experiments

The mixture problem is one subproblem of the response surface problem. A mixture experiment involves mixing two or more components (ingredients) together to form some end product, and measuring one or more properties of the resulting mixture or end product. In the general mixture problem, the measured response is assumed to be dependent only on the proportions of the ingredients present in the mixture and not on the amount of the mixture (Cornell 1990, Scheffe' 1958). Examples of mixture problems are the tensile strength of an alloy of different metals, the wear-resistance of a mixture of different kinds of rubbers, and the octane rating of a blend of different gasoline stocks. The effect of a fertilizer which is a mixture of certain components, on the yield of a crop would not be an example, because this yield would depend not only on the proportions of the components but also on the total amount of the mixture. The purpose of a mixture experiment is to predict empirically the response y to any mixture of components.

In a mixture problem, the response to a mixture of q components is a function of the proportions $x_1, x_2, \ldots, x_q$ of components in the mixture. Since x_i represents the proportion of the i^{th} component in the mixture, the following constraints hold:

$$0 \le x_i \le 1 \, (i = 1, 2, \ldots, q); \sum_{i=1}^{q} x_i = 1. \qquad (1.8)$$

The factor space in the mixture problem is thus reduced from q dimensions of unconstrained components to q-1 dimensions of constrained components since the sum of the values of all components equals unity. The (q-1)-dimensional space constructed by the q components is called a (q-1)-dimensional simplex.

One method to model the mixture problem is using the q components of mixture as the predictor variables, called mixture variables, directly to describe the measured response. Scheffe' (1958) introduces the simplex-lattice design and its associated model for three components. In a q-component mixture problem, the proportions used for each component take the (m+1) equally spaced values from 0 to 1, x_i=0,1/m, 2/m, ..., 1, and all possible mixtures with these proportions for each component are used. Such a design is called a $\{q^l, m\}$ simplex-lattice design where the superscript *l* represents lattice. It can be shown that the number of design points in the $\{q^l, m\}$ lattice is

$$\binom{q+m-1}{m} = \frac{(q+m-1)!}{m!(q-1)!}.$$

Scheffe' (1958) derives a canonical polynomial model which can be fitted by the design points on the $\{q^l, m\}$ simplex-lattice. The first-degree canonical polynomial for design points on the $\{q^l, 1\}$ simplex-lattice is

$$y = \sum_{i=1}^{q} \beta_i x_i + \varepsilon.$$

The second-degree canonical polynomial model for design points on the $\{q^l, 2\}$ simplex-lattice is

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j + \varepsilon.$$

Similarly, the cubic model for design points on the $\{q^l, 3\}$ simplex-lattice is

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j + \sum_{i<j<k}\sum\sum^{q} \beta_{ijk} x_i x_j x_k + \sum_{i<j}\sum^{q} \delta_{ij} x_i x_j (x_i - x_j) + \varepsilon.$$

A special case of the cubic model which is referred to as a "special cubic polynomial" is

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j} \sum^{q} \beta_{ij} x_i x_j + \sum_{i<j<k} \sum \sum^{q} \beta_{ijk} x_i x_j x_k + \varepsilon.$$

The number of parameters in the $\{q^l, m\}$ canonical polynomial can be shown to be $\binom{q+m-1}{m}$ which is exactly the same as the number of the design points on the $\{q^l, m\}$ simplex-lattice.

Scheffe' (1963) develops the simplex-centroid design and its corresponding model for any number of components. The design points in the q-component simplex-centroid design correspond to q permutations of (1, 0, 0, ..., 0), $\binom{q}{2}$ permutations of (1/2, 1/2, 0, ..., 0), $\binom{q}{3}$ permutations of (1/3, 1/3, 1/3, 0, ..., 0), ..., and so on, with the overall centroid point (1/q, 1/q, ..., 1/q). The polynomial model associated with the q-component simplex-centroid design is

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j} \sum^{q} \beta_{ij} x_i x_j + \sum_{i<j<k} \sum \sum^{q} \beta_{ijk} x_i x_j x_k + \ldots + \beta_{12\ldots q} x_1 x_2 \ldots x_q + \varepsilon.$$

It can be shown that the number of distinct design points in the q-component simplex-centroid design is equal to the number of parameters in the corresponding model which is equal to $2^q - 1$.

For the simplex-lattice and simplex-centroid designs, the design points are uniformly distributed on the boundary of the factor space. There is no design point inside the simplex except at the overall centroid. Both models have the property that the model corresponding to its design has the number of parameters in the model equal to the number of distinct design points such that the parameters in the model are determined uniquely from the design points of its associated design.

Kenworthy (1963) introduces factorial arrangements with mixtures using ratios as design variables. The response is thus a function of ratios and indirectly is a function of components in the mixture. Lambrakis (1968a) develops a multiple-lattice design for experiments with mixtures of n "major" components (categories) where each major component is itself a mixture of several other components and each category of components contributes a fixed proportion to the total mixture. Each category is represented in every mixture by one or more of its member components. This type of mixture problem is also called the mixture problem for categorized components. Suppose one would like to make a fruit cocktail consisting of two major categories - liquids and solids. The liquids can be at least one of three kind of liquors (minor components) while the solids can be at least one of two kind of fruits (minor components). Also assume that the proportion of liquid in the mixture is 80% while the proportion of solids is 20%. Then this is a mixture problem with two categories. For example, the $\{p^{l}, 3\}$ simplex-lattice for the first category of components and the $\{q^{l}, 2\}$ simplex-lattice for the second category of components, will be combined into the $\{p^{l}, q^{l}; 3, 2\}$ double lattice. The factor space of the $\{p^{l}, q^{l}; 3, 2\}$ double lattice can be expressed as

$$u_1 + u_2 + u_3 = 1,\ v_1 + v_2 = 1, \text{ and } u_i, v_i \geq 0.$$

The canonical polynomial corresponding to the $\{p^{l}, 3\}$ simplex-lattice is

$$y = \sum_{i=1}^{p} \alpha_i u_i + \sum_{i<j}\sum^{p} \alpha_{ij} u_i u_j + \sum_{i<j<k}\sum\sum^{p} \alpha_{ijk} u_i u_j u_k + \sum_{i<j}\sum^{p} \delta_{ij} u_i u_j (u_i - u_j) + \varepsilon,$$

and the canonical polynomial corresponding to the $\{q^{l}, 2\}$ simplex-lattice is

$$y = \sum_{i=1}^{q} r_i\, v_i + \sum_{i<j}\sum^{q} r_{ij} v_i v_j + \varepsilon.$$

Then, the regression function for the $\{p^{l}, q^{l}; 3, 2\}$ double lattice is

$$y = \sum_{i=1}^{p}\sum_{j=1}^{q} \alpha_{i,j} u_i v_j + \sum_{i=1}^{p}\sum_{j<k}\sum^{q} \alpha_{i,jk} u_i v_j v_k + \sum_{i<j}\sum^{p}\sum_{k=1}^{q} \alpha_{ij,k} u_i u_j v_k + \ldots +$$
$$\sum_{i<j<k}\sum\sum^{p}\sum_{l<m}\sum^{q} \alpha_{ijk,lm} u_i u_j u_k v_l v_m + \varepsilon.$$

Another method to depict the shape of the surface over the simplex consists of q-1 transformed variables. The q-1 transformed variables are called mixture-related variables (M.R.V.) since they are transformed orthogonally from mixture variables. Standard designs such as a factorial design can be used on the q-1 variables for exploring response. Claringbold (1955) develops one method to transform the q dependent variables to q-1 M.R.V.'s.

Cornell and Good (1970) develop another method for mixture experiments where mixture components are categorized. The experimentation is performed in an ellipsoid region which is expressed analytically by

$$\sum_{i=1}^{q}\left(\frac{x_i - x_{0i}}{h_i}\right)^2 \leq 1,$$

where x_{0i} and h_i are chosen by the experimenter so as to give appropriate location and spread to the interval of interest for the i^{th} component x_i in the particular application. The ellipsoid is totally inside the multiple simplexes constructed by all sets of components in categories. A transformation is made from q mixture variables to q-k mixture-related variables where k is the number of categories. The transformation makes rotatable response surface designs possible. Process variables are introduced into this problem by Cornell (1971).

While the measured response in the mixture problem depends only on the proportions of components present in the mixture, sometimes the measured response might also depend on the variables which are not components of the mixture. Example such as the yield of a crop depends not only on the component proportions of fertilizers but also on the amount of fertilizer. The quality of alloy depends on its ingredients and the temperature and pressure in the manufacturing process. The variables other than component proportions which might have effects on the measured response to mixture are called process variables. Scheffe' (1963) illustrates a simplex-centroid by factorial design where process variables are in a factorial arrangement. Piepel and Cornell (1987) obtain D-optimal designs for the mixture amount problem.

1.3 The Problem with Current Designs on Mixture Experiments for Categorized Components

The Mixture problem for categorized components is first introduced by Lambrakis (1968a). Lambrakis develops a multiple simplex-lattice design for this problem where the region of the interest is any point in the multiple simplexes. Suppose the components in the q-component multiple simplex-lattice design are divided into k categories and each category has q_i components in it such that $q_1 + q_2 + ... + q_k = q$. Also assume the $\{q_i^l, m_i\}$ simplex-lattice design is selected on the components of the i^{th} category. The number of design points required in the multiple simplex-lattice design becomes

$$\prod_{i=1}^{k} \binom{q_i + m_i - 1}{m_i}.$$

For a 9-component and 3-category multiple simplex-lattice design with 3 components in each category, if a $\{3^l, 2\}$ simplex-lattice design is selected on the components in each category, the number of design points required for the $\{3^l, 3^l, 3^l; 2, 2, 2\}$ triple simplex-lattice design is 216 which is large and quite often it becomes infeasible to experimenters. Thus alternative designs and models should be considered instead of the multiple simplex-lattice design.

Cornell and Good (1970) expand the mixture problem for categorized components where the region of interest is an ellipsoid inside the multiple simplexes. The factor space of interest defined by the mixture components in the problem is no longer a set of multiple simplexes but a fraction of the multiple simplexes. Because of this one cannot explore the response surface over the whole set of multiple simplexes. Cornell (1971) expands process variables into consideration and the region of interest on the components is an ellipsoid.

In addition to the work of Lambrakis (1968a) and Cornell and Good (1970), there are other possible designs and models which can be used in the mixture problem for categorized components. For example one can use ratios as design variables in this problem.

1.4 Research Objectives

The overall objective of the research is to extend the designs and models of mixture experiments while the components are classified into categories. To complete this objective, several subobjectives and tasks must be met. The subobjectives are:

(1) Develop q-component designs and models using mixture variables as design variables. This will include :

(1.1) Simplex-lattice by simplex-centroid designs and the associated models. This requires that the first set of components form a simplex-lattice design and the second set of components form a simplex-centroid design and then combine them into one design.

(1.2) Multiple-centroid designs and the associated models. For double-centroid design, this requires the first set of components form a simplex-centroid design and the second set of components form a simplex-centroid design. Then they are combined into one design.

(1.3) Interpretation of the coefficients in the fitted regression model associated with the multiple-centroid design.

(2) Develop designs and models using ratios as design variables. This requires transforming the mixture variables into ratio variables, and use

of the ratio variables as design variables. Then standard designs can be applied to the ratio variables.

(3) Develop D-optimal designs and models. This require choosing a set of candidate design points. The D-optimal designs are obtained by the DETMAX algorithm (already available in the MIXSOFT software package) based on the assumption that the model under consideration is true.

(4) Develop designs and models using both mixture components and mixture-related variables as design variables at the same time. For example, one can use mixture variables as design variables on the components in the first category and use mixture-related variables as design variables on the components in the second category. This makes the designs similar to mixture experiments involving process variables.

(5) Compare the performance among the multiple-lattice design, multiple-centroid design, design using ratios of components, D-optimal design, and the design using both mixture components and mixture-related variables as design variables.

1.5 Contributions

All the of above items are new developments not previously covered in the literature. This research provides benefits to both theoreticians and practitioners, resulting in contributions to the area of experiments with mixtures. This study becomes the first of its kind to provide the following in the mixture problems for categorized components :

(1) Simplex-lattice X simplex-centroid design and the associated models.

(2) Multiple simplex-centroid designs and the associated models.

(3) Designs and models using ratios as design variables.

(4) D-optimal designs.

(5) Designs and models using both mixture components and mixture-related variables as design variables at the same time.

(6) Comparison among the multiple-lattice design, multiple-centroid design, designs using ratios of components, D-optimal designs, and designs using both mixture components and mixture-related variables as design variables.

All of these are new developments that provide alternative methods to practitioners in the designing and modeling of mixture problems with components in categories.

CHAPTER 2

LITERATURE SURVEY

The problem of mixture experiments is first introduced by Claringbold (1955). The first formal theory for experiments with mixtures of q components whose purpose is the empirical prediction of the response to any mixture of the components is presented by Scheffe' (1958). Since then, various extensions and modifications of mixture problems have been developed. The mixture problem , in general, is divided into two areas:

(1) The values of all components are bounded between 0 and 1. This kind of mixture problem is called the unconstrained mixture problem.

(2) The values of some components are bounded with positive lower bounds or upper bounds. This kind of mixture problem is called the constrained mixture problem.

Claringbold (1955) presents a problem with mixtures in a paper on the joint action of related hormones and notes that the factor space for experiments with mixtures is a simplex. In a q-component mixture (q≥3) let x_i be the proportion (by volume, weight, moles, etc.) of the i^{th} component in the mixture and also let x_i denote the i^{th} component itself, so that

$$x_i \geq 0 \text{ (i=1,2,...,q), and } \quad x_1 + x_2 + ... + x_q = 1. \qquad (2.1)$$

The factor space for q=3 could be plotted in a 3-dimensional space as shown in Figure 2.1. The triangle ABC in Figure 2.1 which is constructed by restriction (2.1) is a simplex since any pair of the 3 vertices has a distance the same as that of

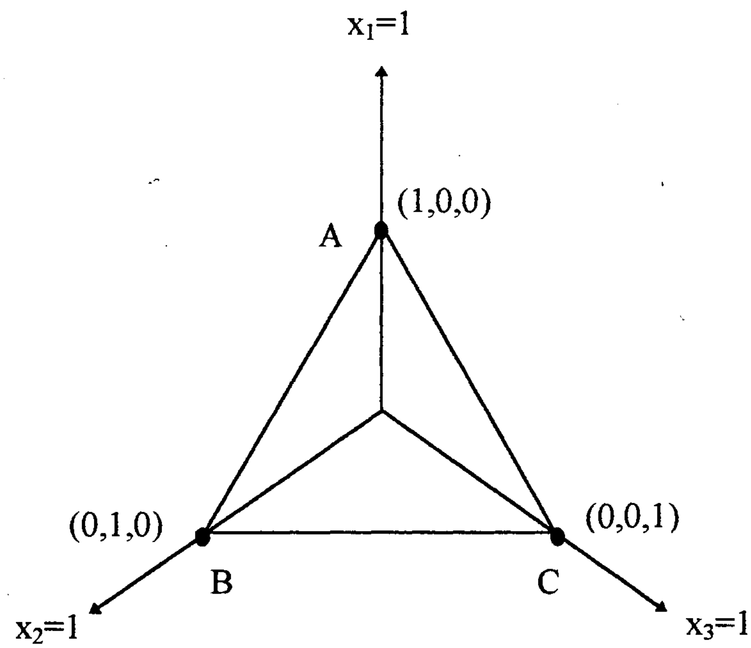


Figure 2.1 Factor Space of a Three-Component Mixture Problem

every other pair of vertices on the triangle. Triangle ABC is generally plotted as in Figure 2.2.

For mixture experiments, one generally would like to obtain a designed experiment which has design points uniformly and symmetrically distributed on and inside the factor space. However, the best design is based on the personal objective of the experimenters. The following designs and models are important subjects which one must understand while applying mixture experiments to one's problem.

2.1 Simplex-Lattice Design and the Associated Model

Scheffe' (1958) proposes a simplex-lattice design for exploring the whole factor space (simplex) where the design points are uniformly distributed on the boundary of the factor space. In a q-component mixture problem, the proportions used for each component take the (m+1) equally spaced values from 0 to 1, x_i=0, 1/m, 2/m, ..., 1, and all possible mixtures with these proportions for each component are used. Such a design is called $\{q^{l}, m\}$ lattice design. $\{3^{l}, 2\}$, $\{3^{l}, 3\}$ and $\{4^{l}, 2\}$ lattices are pictured in Figure 2.3. When the design points of the $\{q^{l}, m\}$ simplex-lattice are plotted onto the (q-1) dimensional simplex, these design points appear in a symmetrical pattern with respect to the vertices and the sides of the simplex. It can be shown that the number of design points in the $\{q^{l}, m\}$ lattice is

$$\binom{q+m-1}{m} = \frac{(q+m-1)!}{m!(q-1)!}.$$

Scheffe' (1958) also derives a canonical polynomial model which can be fitted by the design points on the $\{q^{l}, m\}$ simplex-lattice. The general linear regression function in q variables is

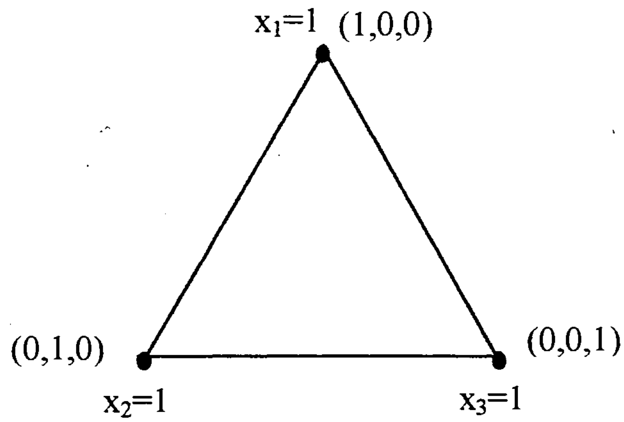
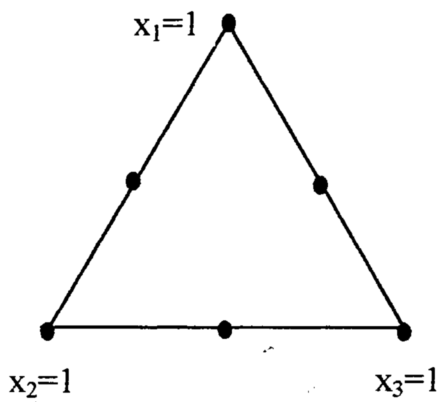
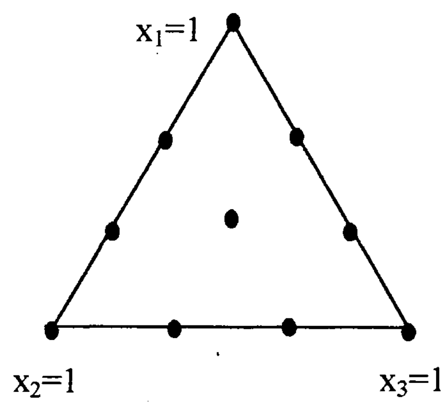


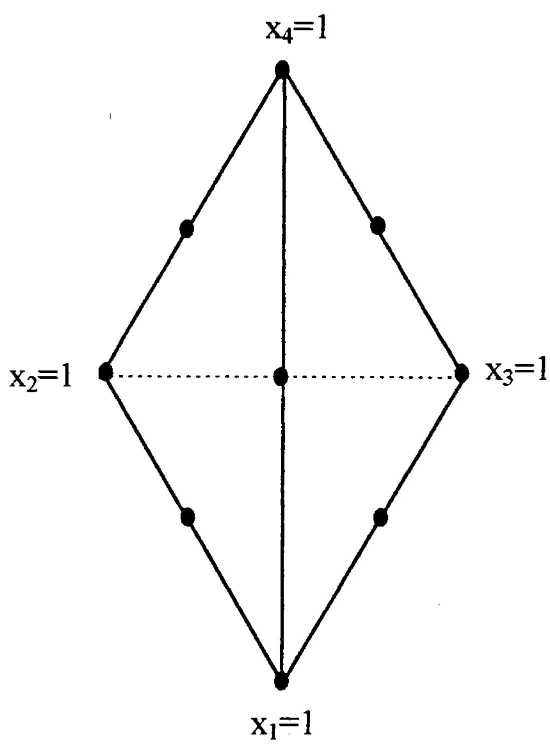
Figure 2.2 Simplex of Three Components



$\{3^l, 2\}$ Lattice



$\{3^l, 3\}$ Lattice



$\{4^l, 2\}$ Lattice

Figure 2.3 Some $\{q^l, m\}$ Lattices

$$\eta = \beta_0 + \sum_{i=1}^{q} \beta_i x_i. \tag{2.2}$$

Since the restriction $\sum_{i=1}^{q} x_i = 1$ applies , multiplying β_0 in equation (2.2) by $\sum_{i=1}^{q} x_i$, equation (2.2) becomes

$$\begin{aligned} \eta &= \beta_0 \sum_{i=1}^{q} x_i + \sum_{i=1}^{q} \beta_i x_i \\ &= \sum_{i=1}^{q} (\beta_0 + \beta_i) x_i \\ &= \sum_{i=1}^{q} \beta_i^* x_i. \end{aligned} \tag{2.3}$$

Equation (2.3) is then the first-degree canonical polynomial for design points on the {q, 1} simplex-lattice.

The general second-degree polynomial in q variables is

$$\eta = \beta_0 + \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ii} x_i^2 + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j. \tag{2.4}$$

Applying the identity $\sum_{i=1}^{q} x_i = 1$ and $x_i^2 = x_i(1 - \sum_{\substack{j=1 \\ j \neq i}}^{q} x_j)$, equation (2.4) becomes

$$\begin{aligned} \eta &= \beta_0 (\sum_{i=1}^{q} x_i) + \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ii} x_i (1 - \sum_{j \neq i}^{q} x_j) + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j \\ &= \sum_{i=1}^{q} (\beta_0 + \beta_i + \beta_{ii}) x_i - \sum_{i=1}^{q} \beta_{ii} x_i (\sum_{j \neq i}^{q} x_j) + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j \\ &= \sum_{i=1}^{q} \beta_i^* x_i + \sum_{i<j}\sum^{q} \beta_{ij}^* x_i x_j. \end{aligned} \tag{2.5}$$

Equation (2.5) is the second-degree canonical polynomial model for design points on the $\{q^{l}, 2\}$ simplex-lattice. Similarly, the cubic model for design points on $\{q^{l}, 3\}$ simplex-lattice can be shown to be

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j + \sum_{i<j<k}\sum\sum^{q} \beta_{ijk} x_i x_j x_k + \sum_{i<j}\sum^{q} \delta_{ij} x_i x_j (x_i - x_j). \tag{2.6}$$

A special case of equation (2.6) which is referred to as a "special cubic polynomial" is

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j + \sum_{i<j<k}\sum\sum^{q} \beta_{ijk} x_i x_j x_k .$$

Gorman and Hinman(1962) also derive the quartic canonical polynomial for mixture experiments.

The number of parameters in the {q^l, m} canonical polynomial is shown to be $\binom{q+m-1}{m}$ which is exactly the same number of the design points on the {q^l, m} simplex-lattice. If the observed mean responses of the design points in the {q^l, m} simplex-lattice are used to solve for the unknown parameters in the {q^l, m} canonical polynomial, the unknown parameters can be uniquely determined.

If x_i is set to 1, which forces x_j=0 for all j≠i, then $\eta = \beta_i$. The parameter β_i therefore represents the expected response to a pure component *i* and β_i is the height of the response surface above the simplex at the vertex where x_i=1 for i=1, 2, ..., q.

2.2 Simplex-Centroid Design and the Associated Model

Scheffe' (1963) proposes a new design for experiments with mixtures of q components consisting of $2^q - 1$ points. The points correspond to q permutations of (1, 0, 0, ..., 0), $\binom{q}{2}$ permutations of (1/2, 1/2, 0, ..., 0), $\binom{q}{3}$ permutations of (1/3, 1/3, 1/3, 0, ..., 0), ..., and so on, with the overall centroid point (1/q, 1/q, ..., 1/q). In other words, the design consists of all possible subsets of the q components, present in equal proportions. Such mixtures are located at the centroid of a (q-1)-dimensional simplex and the centroids of all lower-dimensional simplexes contained within the (q-1)-dimensional simplex. Figure 2.4 pictures the simplex-centroid designs for three components and four components.

The polynomial model associated with the q-component simplex-centroid design is

$$\eta=\sum_{i=1}^{q}\beta_i x_i+\sum_{i<j}\sum^{q}\beta_{ij}x_ix_j+\sum_{i<j}\sum_{<k}\sum^{q}\beta_{ijk}x_ix_jx_k+\ldots+\beta_{12\ldots q}x_1x_2\ldots x_q. \qquad (2.7)$$

The number of unknown parameters in equation (2.7) is 2^q-1 which is the same as the number of design points in the q-component simplex-centroid design. Thus, parameters in equation (2.7) can be uniquely determined while the measured mean responses of the design points are fitted to equation (2.7).

2.3 Axial Design

The $\{q^l, m\}$ simplex-lattice and q-component simplex-centroid designs have design points on the boundary of simplex, except at the overall centroid. Cornell (1975) suggests a new design consisting of points mainly inside the simplex. The axis of component i is defined to be the imaginary line extending from the base point x_i=0, x_j=1/(q-1), for all j≠i, to the vertex where x_i=1, x_j=0, for all j≠i. The base point is the centroid of the (q-2)-dimensional boundary which is opposite the vertex x_i=1, x_j=0, for all j≠i. The length of the axis is the shortest distance between the base point and vertex opposite to it. An axial design is a design where points are located only on the component axes. The simplest form of axial design is one whose points are positioned equidistant from the overall centroid (1/q, 1/q, ..., 1/q) toward each of the vertices. Figure 2.5 presents a picture of a three component design with 10 design points.

Data collected from an axial design would thus be fitted to Scheffe's

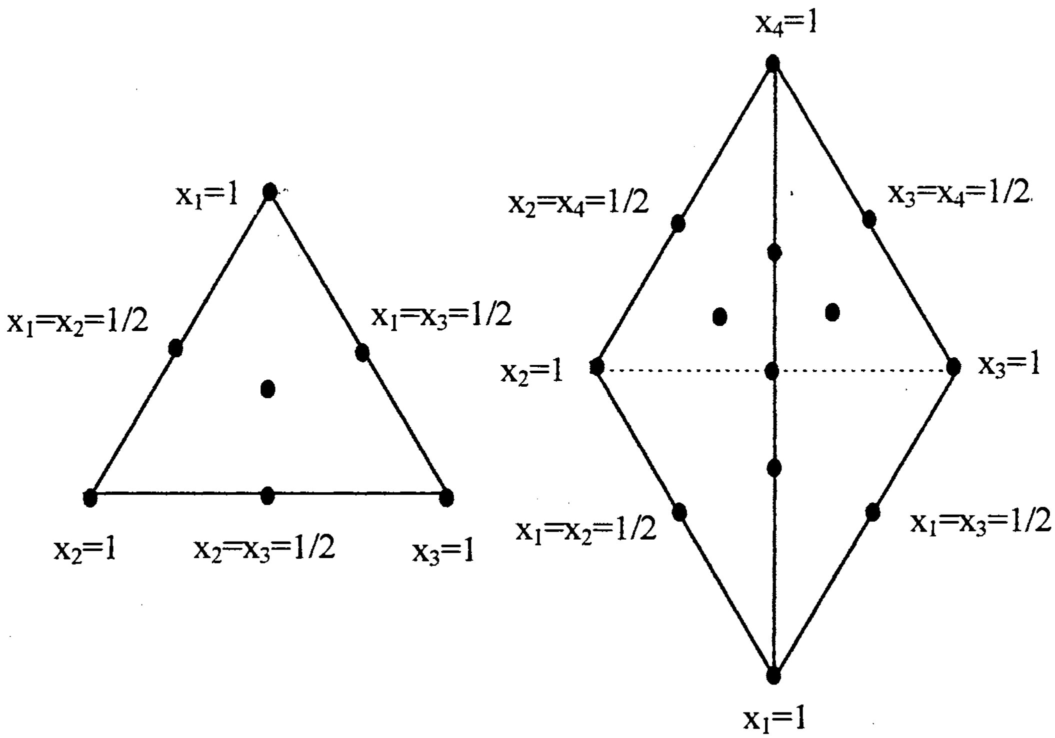
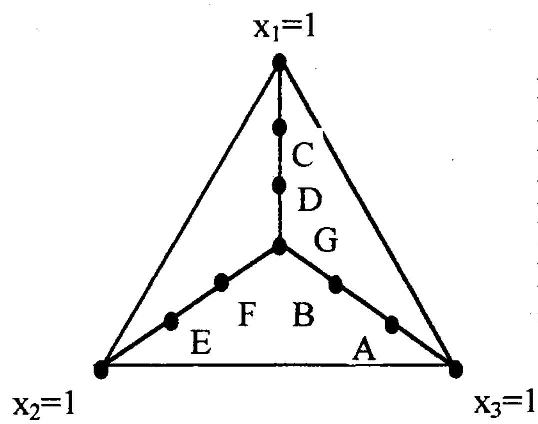


Figure 2.4 Simplex-Centroid Designs for 3 and 4 Components



A = (7/9, 1/9, 1/9)
B = (5/9, 2/9, 2/9)
C = (1/9, 7/9, 1/9)
D = (2/9, 5/9, 2/9)
E = (1/9, 1/9, 7/9)
F = (2/9, 2/9, 5/9)
G = (1/3, 1/3, 1/3)

Figure 2.5 Three-Component Axial Design with 10 Points canonical polynomial depending on the number of design points in the axial design. The least-squares method is used to obtain the estimates of parameters and the corresponding variance-covariance matrix.

The axial design is particularly useful in computing component effects and in screening experiments, especially when first-degree models are to be fitted.

2.4 Symmetric Simplex Design

Murty and Das (1968) develop a design which is the general case of the simplex-lattice and the simplex-centroid designs while symmetry conditions are imposed on the mixture variables. They define the symmetric simplex design as follows :

"Let the point (x_{1u}, x_{2u}, ..., x_{nu}) of a design, for a mixture experiment in n components where d of the $x_{iu's}$ are non-zero elements, be called a d^{th} ordered mixture and denoted by S_d. Further, let d_1 of the $x_{iu's}$ of S_d be each equal to q_1, d_2 of the $x_{iu's}$ equal to q_2, and so on, and d_h of the $x_{iu's}$ equal to q_h so that $d_1 + d_2 + ... + d_h = d$ and $d_1q_1 + d_2q_2 + ... + d_hq_h = 1$. Let all the d^{th} ordered mixtures S_d that are obtainable by permutation of the different fractions in the mixture over the n components be written in the form of a group called the group G_d, each mixture S_d forming a row of G_d and the i^{th} component being represented by the i^{th} column of G_d. Then it is seen that the number of rows in the group G_d is given by

$$W_d = \binom{n}{d_1}\binom{n-d_1}{d_2}\binom{n-(d_1+d_2)}{d_3}\cdots\binom{n-(d_1+d_2+...+d_{h-1})}{d_h}.$$

A symmetric simplex design for mixture experiments consists of some or all the group G_d, d=1, 2, ..., n, where every group G_d is obtained by permuting the different fractions over the n components in a d^{th} ordered mixture with d_1 components taking a proportion q_1, d_2 of them taking a proportion of q_2, and so on, d_h of them taking a proportion q_h such that $d_1 + d_2 + ... + d_h = d$ and $d_1 q_1 + d_2 q_2 + ... + d_h q_h = 1$."

It can be seen that given a point P of a group G_d, all such points on the simplex which are symmetrically placed as P with respect to every one of the n vertices are included in the group G_d, and hence in the designs.

Murty and Das also illustrate with examples to show that the simplex-lattice and simplex-centroid designs proposed by Scheffe' and the radial-lattice and radial-centroid designs proposed by Plackett (Scheffe' 1963) are just particular cases of symmetric simplex designs.

2.5 Mixture Experiments Using Ratios

In some mixture experimentations, one is likely to be interested in one or more of the components, not so much from the standpoint of their proportions in mixtures, but from their relationship to the other components in the mixtures in the form of their proportions. Kenworthy (1963) illustrates an example of experiments with mixtures using ratios. For the three component case, let x_1, x_2, and x_3 denote the proportions of the three components in the mixture. Transformation from the x_i variables to the ratio variables r_1 and r_2 can be

$$r_1 = \frac{x_2}{x_1}, \quad r_2 = \frac{x_3}{x_1}.$$

The number of ratios r_i should be one less than the number of components in the system and each ratio r_i contains at least one of the components used in the other ratios.

A simple first-degree model in r_1 and r_2 usually is

$$y = \alpha_0 + \alpha_1 r_1 + \alpha_2 r_2 + \varepsilon,$$

and a second-degree model in r_1 and r_2 generally is

$$y = \alpha_0 + \alpha_1 r_1 + \alpha_2 r_2 + \alpha_{11} r_1^2 + \alpha_{22} r_2^2 + \alpha_{12} r_1 r_2 + \varepsilon.$$

Note that the mixture variables x_i are mutually dependent since the restriction $\sum_{i=1}^{q} x_i = 1$. Standard orthogonal designs can be used with the ratio variables on the basis of staying within the experimental area. Equal spacing of ratio variables is desirable so that coding on ratio variables provides easier regression analysis.

2.6 Designs Using Mixture-Related Variables

Claringbold (1955) shows a method of orthogonal transformation from q mixture variables x_i to (q-1) mixture-related variables. He includes the following two-step procedures.

Step 1: Define the location of the origin of the new system to be at the centroid of the simplex by introducing the intermediate variables t_i where

$$t_i = q(x_i - \frac{1}{q}) = qx_i - 1.$$

Step 2: The axes of the original components are rotated so as to define the simplex using only q-1 variables, making the axis of variable q orthogonal to the simplex (variable q then is removed from further consideration).

If w_i are the q-1 variables by Claringbold's transformation from q mixture variables, a second-degree model on the q-1 mixture-related variables usually would be

$$y = \alpha_0 + \sum_{i=1}^{q-1} \alpha_i w_i + \sum_{i=1}^{q-1} \alpha_{ii} w_i^2 + \sum_{i}\sum_{<\, j} \alpha_{ij} w_i w_j + \varepsilon.$$

Standard designs such as factorial designs and central composite designs can be employed with mixture-related variables as long as all design points are within the simplex.

Draper and Lawrence (1965a and 1965b) perform another transformation to generate a system of (q-1) variables from the q-component system. The transformation produces a design region that is not necessarily centered at the centroid of the composite space. Thompson and Myers (1968) develop a technique using q-1 variables to fit a polynomial model over some ellipsoidal region of interest within the factor space. They also show that for the first and second order polynomial models, the estimation procedure can be simplified for the case of rotatable designs.

2.7 Designs and Models While Process Variables Are Also Considered to Be Factors

Process variables such as temperature, pressure, and amount of the mixture might also have an effect on the measured response to the mixture. Scheffe' (1963) introduces designs and regression equations including n process variables and the q mixture variables. He also introduces fractional replication of the designs in the case where the process variables are all at two levels. For a mixture problem involving three process variables each with I, J, and K levels respectively, a complete simplex-centroid by IJK experiment is one in which at each of the $2^q - 1$ points of the simplex-centroid design a complete IJK experiments are made with the process variables. If the process variables are denoted as z_i, i=1, 2, 3, the model associated with the complete simplex-centroid by IJK experiment where q=3 is

$$y = (\beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3) *$$

$$(\alpha_0 + \sum_i \alpha_i z_i + \sum_{i<j}\sum \alpha_{ij} z_i z_j + \sum_{i<j<k}\sum\sum^{q} \alpha_{ijk} z_i z_j z_k) + \varepsilon$$

$$
\begin{aligned}
&= \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i} \sum_{<j}^{q} \beta_{ij}^0 x_i x_j + \beta_{ijk}^0 x_i x_j x_k + \\
&\sum_{l=1}^{3} \Big(\sum_{i=1}^{q} \beta_i^l x_i + \sum_{i} \sum_{<j}^{q} \beta_{ij}^l x_i x_j + \beta_{ijk}^l x_i x_j x_k \Big) z_l + \\
&\sum_{l} \sum_{<m} \Big(\sum_{i=1}^{q} \beta_i^{lm} x_i + \sum_{i} \sum_{<j}^{q} \beta_{ij}^{lm} x_i x_j + \beta_{ijk}^{lm} x_i x_j x_k \Big) z_l z_m + \\
&\Big(\sum_{i=1}^{q} \beta_i^{123} x_i + \sum_{i} \sum_{<j}^{q} \beta_{ij}^{123} x_i x_j + \beta_{ijk}^{123} x_i x_j x_k \Big) z_1 z_2 z_3 + \varepsilon.
\end{aligned}
$$

Murty and Das (1968) illustrate a complete symmetric simplex X factorial design. Piepel and Cornell (1987) show D-optimal designs consisting of mixture variables and amount of the mixture.

Cornell and Gorman (1984) have a detailed discussion of fractional design plans for process variables in mixture experiments. A split-plot design approach where one could either embed the mixture blends in each of the processing conditions or embed the processing conditions within each of the mixture blends is shown by Cornell (1988).

2.8 The Mixture Problem for Categorized Components

Some mixture experiments involve two or more classes of components. Consider a reactor with two different kinds of incoming materials. One major category is a fluid type consisting of 2 components u_1 and u_2 (u_1 and u_2 represent proportions and $u_1 + u_2 = 1$). The other major category is a gas type consisting of 2 components v_1 and v_2 ($v_1 + v_2 = 1$). Each category has at least one member present in the mixture and each category contributes a fixed proportion present in the mixture. The mixture problem could be generalized into any number of major categories where each major category contributes a fixed proportion to the total mixture and is represented in every mixture by one or more of its member components.

Lambrakis (1968a) develops a theory called multiple-lattice design to empirically predict the response to any mixture of k major components. Assume two categories are considered in a mixture problem. Suppose one simplex-lattice from the first set of components $u_1, u_2, \ldots, u_p$ and another simplex-lattice from the second set of components $v_1, v_2, \ldots, v_q$. Also if all possible mixtures which can be produced by mixing each mixture from the first simplex-lattice with each mixture from the second simplex-lattice with proportions c_1 and c_2, respectively, then the design is called a double-lattice design. For example, the $\{p^l, 3\}$ simplex-lattice for the first category of components and the $\{q^l, 2\}$ simplex-lattice for the second category of components, will combine into the $\{p^l, q^l; 3, 2\}$ double lattice.

The canonical polynomial corresponding to the $\{p^l, 3\}$ simplex-lattice is

$$y = \sum_{i=1}^{p} \alpha_i u_i + \sum_{i} \sum_{< j}^{p} \alpha_{ij} u_i u_j + \sum_{i} \sum_{< j}^{p} \delta_{ij} u_i u_j (u_i - u_j) + \sum_{i} \sum_{< j} \sum_{< k}^{p} \alpha_{ijk} u_i u_j u_k + \varepsilon, \tag{2.8}$$

and the canonical polynomial corresponding to the $\{q^l, 2\}$ simplex-lattice is

$$y = \sum_{i=1}^{q} r_i v_i + \sum_{i} \sum_{< j}^{q} r_{ij} v_i v_j + \varepsilon. \tag{2.9}$$

Multiplying the right sides of the polynomials (2.8) and (2.9), and then replacing the products of the coefficient by a single coefficient, the regression function for the $\{p^l, q^l; 3, 2\}$ double lattice is

$$y = \sum_{i=1}^{p} \sum_{j=1}^{q} \alpha_{i,j} u_i v_j + \sum_{i=1}^{p} \sum_{j} \sum_{< k}^{q} \alpha_{i,jk} u_i v_j v_k + \sum_{i} \sum_{< j}^{p} \sum_{k=1}^{q} \alpha_{ij,k} u_i u_j v_k + \ldots +$$

$$\sum_{i<} \sum_{j<} \sum_{k}^{p} \sum_{l<} \sum_{m}^{q} \alpha_{ijk,lm} u_i u_j u_k v_l v_m + \varepsilon. \tag{2.10}$$

The number of design points required in the multiple simplex-lattice design with k categories becomes

$$\prod_{i=1}^{k}\binom{q_i + m_i - 1}{m_i},$$

where the $\{q_i^l, m_i\}$ simplex-lattice is used in the i^{th} category such that $q_1 + q_2 + ... + q_k = q$.

Cornell and Good (1970) perform a technique for mixture problems for categorized components where the factor space is an ellipsoid region. Mixture related variables which are obtained from the orthogonal transformation of mixture variables are used as design variables in the technique. Cornell (1971) also discusses the mixture problem with process variables for categorized components.

2.9 Computer-Aided Design

The model for mixture experiments can be written in matrix form as

$$\boldsymbol{Y}=\boldsymbol{X}\boldsymbol{\beta}+\boldsymbol{\varepsilon},$$

where $\boldsymbol{Y}$ is an Nx1 vector, the design matrix $\boldsymbol{X}$ is Nxp, $\boldsymbol{\beta}$ is a px1 vector, the error term $\boldsymbol{\varepsilon}$ is an Nx1 vector, N is the total number of observations in the mixture experiment and p is the number of parameters in the regression model. Then the least squares estimator of $\boldsymbol{\beta}$ and its variance-covariance matrix are given by

$$\hat{\boldsymbol{\beta}} = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{X}^{T}\boldsymbol{Y}, \quad \mathrm{Var}(\hat{\boldsymbol{\beta}}) = (\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\sigma^2.$$

The predicted response at some point $\boldsymbol{x}_0$ is $\hat{y}(\boldsymbol{x}_0)$ and

$$\mathrm{Var}[\hat{y}(\boldsymbol{x}_0)] = \boldsymbol{x}_0^{\mathrm{T}}(\boldsymbol{X}^{\mathrm{T}}\boldsymbol{X})^{-1}\boldsymbol{x}_0\sigma^2.$$

The design optimality criteria A-, D- ,G- ,V-optimality are each concerned with the choice of the elements in the matrix $\boldsymbol{X}$ that minimize various functions of $(\boldsymbol{X}^{T}\boldsymbol{X})^{-1}$. More specifically:

(1) A-optimality is when the trace of $(X^{T}X)^{-1}$ is minimized, in which case the average variance of the elements of $\hat{\beta}$ is minimized.

(2) D-optimality is when the determinant det($X^{T}X$) is maximized, or when $\det(X^{T}X)^{-1}$ is minimized, thereby minimizing the generalized variance of the elements of $\hat{\beta}$. If the errors are normally distributed, the D-optimal design minimizes the volume of the conference ellipsoid for the unknown parameter β.

(3) G-optimality seeks to minimize the maximum prediction variance, max $\{d = x_0^{T}(X^{T}X)^{-1}x_0\sigma^2\}$, over a specified set of design points.

(4) V-optimality seeks to minimize the average value d, d = $x_0^{T}(X^{T}X)^{-1}x_0\sigma^2$, over a specified set of design points.

The advantage of these four optimality criteria is that they can generate nearly optimal (as orthogonal as possible) designs based on the model using as few runs as possible. The assumption required for all optimal designs is that the model under consideration be true.

Mitchell (1974) develops an algorithm (DETMAX) for the construction of D-optimal experimental designs. Welch (1982, 1983, and 1984) develops a branch-and-bound searching algorithm (ACED) to construct a catalog of all A-, D-, G-, V-optimal n-point designs for a specified design region, linear model and number of observations. Both DETMAX and ACED algorithms can be employed on mixture and non-mixture problems. Piepel and Cornell (1987) obtain D-optimal designs for mixture-amount experiments using the DETMAX algorithm.

2.10 Other Important Designs and Models of Mixture Problem

There are other important designs and models which are indirectly related to the research but are worthwhile mentioning. Lambrakis (1968b) proposes a design where the proportion of each component in the mixture has to be greater than zero. Lambrakis (1969) proposes an alternative to the simplex-lattice design where extreme vertices of component i are replaced by $x_i = 0$, $x_j = \dfrac{1}{q-1}$, for all $j \neq i$. Kurotori (1966) develops experiments with mixtures of components having lower bounds. McLean and Anderson (1966) propose extreme vertex designs of mixture experiments for constrained components. Snee and Marquart (1974) propose extreme vertex designs for the linear mixture model. Snee (1975) develops experimental designs for quadratic models in constrained mixture spaces. For blocking designs, one could refer to Nigam (1970 and 1973), Saxena and Nigam (1973), Singh, Pratap, and Das (1982), John (1984), Czitrom (1988), and Draper, Prescott, Lewis, Dean, John, and Tuck (1993).

Draper and St. John (1977) propose a mixture model with inverse terms to model an extreme change in the response behavior as the value of one or more components tends to a boundary of the simplex region. Cornell and Gorman (1978) suggest an alternative model form for modeling the additive effect of one component in a multicomponent system. Becker (1968) proposes a homogeneous model of degree one for modeling the additive effect of one component and at the same time accommodating the curvilinear blending effects of the remaining two components. Cox (1971) proposes a mixture polynomial model for measuring component effects. Aitchison and Bacon-Shone (1984) develop a log contrast model for experiments with mixtures. Morris (1975) develops an interaction approach to gas modeling (octane blending models).

2.11 Summary

The literature survey presents the problems, contributions and needs to the objectives of the research. For a mixture problem with two three-component categories, a double-lattice design requires 100 design points and thus has 100 parameters in the corresponding model. This is sometimes infeasible to experimenters for economical reason. The disadvantage of orthogonal design using q-1 variables is that the experimental region of the design is not large compared to the simplex. Although the multiple simplex-lattice designs and rotatable designs using q-1 variables are developed in the literature, other alternative designs and models which are not shown in the literature could also be generated and used in the mixture problem for categorized components. The following subjects which are done in this research are the other alternative designs and models which are not available in the literature for the mixture problem with categorized components.

(1) Develop the simplex-lattice by simplex-centroid designs and the associated models.

(2) Develop multiple-centroid designs and the associated models.

(3) Develop designs and models using ratios of components as design variables.

(4) Obtain D-optimal designs and models.

(5) Develop designs and models using both mixture variables and mixture-related variables as design variables.

(6) Compare the performance among the multiple-lattice design, multiple-centroid design, design using ratios of components as design variables, D-optimal design, and the design using both mixture components and mixture-related variables as design variables.

CHAPTER 3

DESIGNS AND MODELS USING MIXTURE VARIABLES AS DESIGN VARIABLES

Lambrakis (1968a) develops the multiple-lattice design for mixture experiments with categorized components. In a multiple-lattice design, first, a simplex-lattice design is selected for each category based on all the minor components in each category. Then all the simplex-lattice designs are combined by factorial arrangement to form a multiple-lattice design. The total number of design points in a multiple-lattice design is the multiplication of the number of design points of the simplex-lattice design in each category. A multiple-centroid design and simplex-lattice by simplex-centroid design are developed in this chapter. Also their corresponding models are given and examples illustrate their use.

3.1 Introduction of the Mixture Problem with Categorized Components

Mixture experiments with components classified into categories while each category contributes a fixed proportion to the mixture is called the mixture problem with categorized components. Suppose q components are classified into k categories and each category contributes proportion c_i (i=1, 2, ..., k) to the mixture. Also assume each category consists of q_i (i=1, 2, ..., k) "minor" components such that $q_1 + q_2 + ... + q_k = q$. Let u_{ij} represent the j^{th} minor component in the i^{th} category and its corresponding proportion, then

$$\sum_{j=1}^{q_i} u_{ij} = c_i \quad \text{for i=1, 2, ..., k,} \tag{3.1}$$

and

$$\sum_{i=1}^{k} c_i = 1.$$

Divide both sides in equation (3.1) by c_i, then

$$\sum_{j=1}^{q_i} \frac{u_{ij}}{c_i} = 1 \quad \text{for i=1, 2, ..., k.} \tag{3.2}$$

Replace $\frac{u_{ij}}{c_i}$ by x_{ij}, then

$$\sum_{j=1}^{q_i} x_{ij} = 1 \quad \text{for i=1, 2, ..., k.} \tag{3.3}$$

From equation (3.3), one can think each category forms a sub-mixture with q_i components in the sub-mixture, and mixtures are formed by the k sub-mixtures. The x_{ij} is then the component and the proportion relative to the i^{th} sub-mixture assigned to the j^{th} minor component in the i^{th} category.

The mixture problem with categorized components could then be written as

$$\sum_{j=1}^{q_i} x_{ij} = 1 \quad \text{for i=1, 2, ..., k,}$$

and

$$\sum_{i=1}^{k} \sum_{j=1}^{q_i} c_i x_{ij} = 1, \tag{3.4}$$

where $0 \le x_{ij} \le 1$ (i=1, 2, ..., k ; j=1, 2, ..., q_i).

3.2 Multiple-Centroid Designs and Their Associated Models

Assume that the proportion of c_i contributed to the mixture for each category is fixed in advance and, for i=1, 2, ..., k, the proportion $(x_{i1}, x_{i2}, \ldots, x_{iq_i})$ as a vector can be values from the q_i permutations of (1, 0, 0, ..., 0), from the $\binom{q_i}{2}$ permutations of (1/2, 1/2, 0, ..., 0), from the $\binom{q_i}{3}$ permutations of (1/3, 1/3, 1/3, ..., 0), ..., and finally the value $(1/q_i, 1/q_i, \ldots, 1/q_i)$. In other words, the proportion x_{ij} can take values from the centroids of the $\{q_i^c, m_i\}$ simplex-centroid where m_i is the degree of the fitted regression equation on the design points to the i^{th} sub-mixture. Combining the centroids in each $\{q_i^c, m_i\}$ simplex-centroid for all categories by factorial arrangement establishes the $\{q_1^c, q_2^c, \ldots, q_k^c; m_1, m_2, \ldots, m_k\}$ multiple-centroid.

Since the number of design points of the $\{q_i^c, q_i\}$ simplex-centroid design is $2^{q_i} - 1$, the total number of design points of the $\{q_1^c, q_2^c, \ldots, q_k^c; m_1, m_2, \ldots, m_k\}$ multiple-centroid design then is

$$\prod_{i=1}^{k} (2^{q_i} - 1). \tag{3.5}$$

Let η_i be the expected response to the sub-mixture contributed by the minor components of the i^{th} category, the regression equation fitted to the $\{q_i^c, q_i\}$ simplex-centroid design is

$$\eta_i = \sum_{j=1}^{q_i} \beta_j^{(i)} x_{ij} + \sum_{1 \le j < k}^{q_i - 1} \sum^{q_i} \beta_{jk}^{(i)} x_{ij} x_{ik} + \ldots + \beta_{12\ldots q_i}^{(i)} x_{i1} x_{i2} \ldots x_{iq_i},$$

for i = 1, 2, 3, ... k, or

$$\eta_i = \sum_{r=1}^{q_i} \sum_{1 \le j_1 < j_2 < \ldots < j_r \le q_i} \beta_{j_1 j_2 \ldots j_r}^{(i)} x_{ij_1} x_{ij_2} \ldots x_{ij_r}, \tag{3.6}$$

for i = 1, 2, 3, ... k.

The number of parameters in equation (3.6) is $2^{q_i} - 1$ which is exactly the same as the number of design points of the $\{ q_i^c, q_i \}$ simplex-centroid design.

Suppose η is the overall expected response to the mixture with categorized components, the fitted regression equation to the mixture is the multiplication of the fitted regressions to the sub-mixtures. That is, the model for the $\{ q_1^c, q_2^c, \ldots, q_k^c; q_1, q_2, \ldots, q_k \}$ multiple-centroid design is

$$\eta = \prod_{i=1}^{k} \sum_{r=1}^{q_i} \sum_{1 \le j_1 < j_2 < \ldots < j_r \le q_i} \beta_{j_1 j_2 \ldots j_r}^{(i)} x_{ij_1} x_{ij_2} \ldots x_{ij_r} . \tag{3.7}$$

One would observe that the total number of parameters in equation (3.7) is exactly the same as the total number of design points of the $\{ q_1^c, q_2^c, \ldots, q_k^c; q_1, q_2, \ldots, q_k \}$ multiple-centroid design. Thus the parameters of equation (3.7) for the $\{ q_1^c, q_2^c, \ldots, q_k^c; q_1, q_2, \ldots, q_k \}$ multiple-centroid design can be determined uniquely.

The mixture problem with components in two categories using multiple-centroid design is illustrated in the next section. One might call it a double-centroid design.

3.3 Double-Centroid Design and the Associated Model

Suppose a $\{ q_1^c, m_1 \}$ simplex-centroid is from the first category of components $(x_{11}, x_{12}, \ldots, x_{1q_1})$ and another $\{ q_2^c, m_2 \}$ simplex-centroid is from the second category of components $(x_{21}, x_{22}, \ldots, x_{2q_2})$ and also all possible mixtures which can be produced by mixing each mixture from the first simplex-centroid with each mixture from the second simplex-centroid with proportions c_1 and c_2, respectively, then one has a double centroid. The double centroid is denoted by $\{ q_1^c, q_2^c; m_1, m_2 \}$.

The notation for the expected response to a mixture introduced by Scheffe' (1958) is used here. For example, from the $\{q_1^c, 3\}$ simplex-centroid for the first set of components and the $\{q_2^c, 2\}$ simplex-centroid for the second set of components, the $\{q_1^c, q_2^c; 3, 2\}$ double-centroid design is obtained. The $\{q_1^c, 3\}$ simplex-centroid contains q_1 pure mixtures η_i with proportions $x_{1i} = 1$, $\binom{q_1}{2}$ binary mixtures η_{ij} $(1 \le i < j \le q_1)$ with proportions $x_{1i} = x_{1j} = 1/2$, and $\binom{q_1}{3}$ ternary mixtures η_{ijk} $(1 \le i < j < k \le q_1)$ with proportions $x_{1i} = x_{1j} = x_{1k} = 1/3$. The $\{q_2^c, 2\}$ simplex-centroid contains q_2 pure mixtures η_i with proportions $x_{2i} = 1$, and $\binom{q_1}{2}$ binary mixtures η_{ij} $(1 \le i < j \le q_2)$ with proportions $x_{2i} = x_{2j} = 1/2$. Mixing each mixture from the $\{q_1^c, 3\}$ simplex-centroid with each mixture from the $\{q_2^c, 2\}$ simplex-centroid with proportions c_1 and c_2 respectively, the $\{q_1^c, q_2^c; 3, 2\}$ double-centroid is obtained and contains mixtures as shown in Table 3.1.

The polynomial model associated with the first category of components in the $\{q_1^c, q_2^c; 3, 2\}$ double lattice is

$$\eta_1 = \sum_{i=1}^{q_1} \beta_i^{(1)} x_{1i} + \sum_{1 \le i < j \le q_1} \sum \beta_{ij}^{(1)} x_{1i} x_{1j} + \beta_{ijk}^{(1)} x_{1i} x_{1j} x_{1k} \tag{3.8}$$

and the polynomial model associated to the second category of components is

$$\eta_2 = \sum_{i=1}^{q_2} \beta_i^{(2)} x_{2i} + \sum_{1 \le i < j \le q_2} \sum \beta_{ij}^{(2)} x_{2i} x_{2j}\,. \tag{3.9}$$

Since the mixtures in the $\{q_1^c, q_2^c; 3, 2\}$ double-centroid are obtained by mixing each mixture from the $\{q_1^c, 3\}$ simplex-centroid with each mixture from the $\{q_2^c, 2\}$ simplex-centroid, one will obtain the fitted regression model for the $\{q_1^c, q_2^c; 3, 2\}$ double-centroid by multiplying both the right sides of equations

Table 3.1 The $\{q_1^c, q_2^c;\ 3,\ 2\}$ Double-Centroid

Number of Mixtures	Response to Mixtures	Proportions of Components of Mixtures
$q_1 \cdot q_2$	$\eta_{i,j}(1 \le i \le q_1,\ 1 \le j \le q_2)$	$x_{1i} = 1, x_{2j} = 1$
$q_1 \cdot \binom{q_2}{2}$	$\eta_{i,jk}(1 \le i \le q_1,\ 1 \le j < k \le q_2)$	$x_{1i} = 1, x_{2j} = x_{2k} = 1/2$
$\binom{q_1}{2} \cdot q_2$	$\eta_{ij,k}(1 \le i < j \le q_1,\ 1 \le k \le q_2)$	$x_{1i} = x_{1j} = 1/2, x_{2k} = 1$
$\binom{q_1}{2} \cdot \binom{q_2}{2}$	$\eta_{ij,kl}(1 \le i < j \le q_1,\ 1 \le k < l \le q_2)$	$x_{1i} = x_{1j} = 1/2, x_{2k} = x_{2l} = 1/2$
$\binom{q_1}{3} \cdot q_2$	$\eta_{ijk,l}(1 \le i < j < k \le q_1,\ 1 \le l \le q_2)$	$x_{1i} = x_{1j} = x_{1k} = 1/3, x_{2l} = 1$
$\binom{q_1}{3} \cdot \binom{q_2}{2}$	$\eta_{ijk,lm}(1 \le i < j < k \le q_1,$ $1 \le l < m \le q_2)$	$x_{1i} = x_{1j} = x_{1k} = 1/3,$ $x_{2l} = x_{2m} = 1/2$

(3.8) and (3.9). Then the fitted model for the $\{ q_1^c,\ q_2^c;\ 3,\ 2 \}$ double-centroid design becomes

$$\eta = \Big(\sum_{i=1}^{q_1} \beta_i^{(1)} x_{1i} + \sum_{1 \le i < j \le q_1} \sum \beta_{ij}^{(1)} x_{1i} x_{1j} + \beta_{ijk}^{(1)} x_{1i} x_{1j} x_{1k}\Big) *$$

$$\Big(\sum_{i=1}^{q_2} \beta_i^{(2)} x_{2i} + \beta_{ij}^{(2)} x_{2i} x_{2j}\Big). \tag{3.10}$$

Multiplying the right side of equation (3.10) and replacing the coefficients by single coefficients, equation (3.10) becomes

$$\eta = \sum_{i=1}^{q_1} \sum_{j=1}^{q_2} \beta_{i,j} x_{1i} x_{2j} + \sum_{i=1}^{q_1} \sum_{1 \le j < k \le q_2} \sum \beta_{i,jk} x_{1i} x_{2j} x_{2k} + \sum_{1 \le i < j \le q_1} \sum \sum_{k=1}^{q_2} \beta_{ij,k} x_{1i} x_{1j} x_{2k} +$$

$$\sum_{1 \le i < j \le q_1} \sum \sum_{1 \le k < l \le q_2} \sum \beta_{ij,kl} x_{1i} x_{1j} x_{2k} x_{2l} + \sum_{1 \le i < j < k \le q_1} \sum \sum \sum_{l=1}^{q_2} \beta_{ijk,l} x_{1i} x_{1j} x_{1k} x_{2l} +$$

$$\sum_{1 \le i < j < k \le q_1} \sum \sum \sum_{1 \le l < m \le q_2} \sum \beta_{ijk,lm} x_{1i} x_{1j} x_{1k} x_{2l} x_{2m}. \tag{3.11}$$

For $q_1 = q_2 = 3$, the design points are obtained by the factorial arrangement of two simplex-centroids and are shown in Figure 3.1. The $\{3^c, 3^c; 3, 2\}$ double-centroid has 42 design points as shown in Table 3.2. The polynomial model for the $\{3^c, 3^c; 3, 2\}$ double-centroid design is

$$\eta = (\beta_1^{(1)} x_{11} + \beta_2^{(1)} x_{12} + \beta_3^{(1)} x_{13} + \beta_{12}^{(1)} x_{11} x_{12} + \beta_{13}^{(1)} x_{11} x_{13} + \beta_{23}^{(1)} x_{12} x_{13} + \beta_{123}^{(1)} x_{11} x_{12} x_{13}) *$$

$$(\beta_1^{(2)} x_{21} + \beta_2^{(2)} x_{22} + \beta_3^{(2)} x_{23} + \beta_{12}^{(2)} x_{21} x_{22} + \beta_{13}^{(2)} x_{21} x_{23} + \beta_{23}^{(2)} x_{22} x_{23})$$

$$= \beta_{1,1} x_{11} x_{21} + \beta_{1,2} x_{11} x_{22} + \beta_{1,3} x_{11} x_{23} + \ldots + \beta_{123,12} x_{11} x_{12} x_{13} x_{21} x_{22} +$$

$$\beta_{123,13} x_{11} x_{12} x_{13} x_{21} x_{23} + \beta_{123,23} x_{11} x_{12} x_{13} x_{22} x_{23}. \tag{3.12}$$

One can obtain the coefficient estimates of the fitted regression model for the $\{ q_1^c,\ q_2^c;\ m_1,\ m_2 \}$ double-centroid design by using the least-squares method. An example is shown in the next section on how to get and interpret the coefficient estimates of the fitted regression model for the multiple-centroid designs.

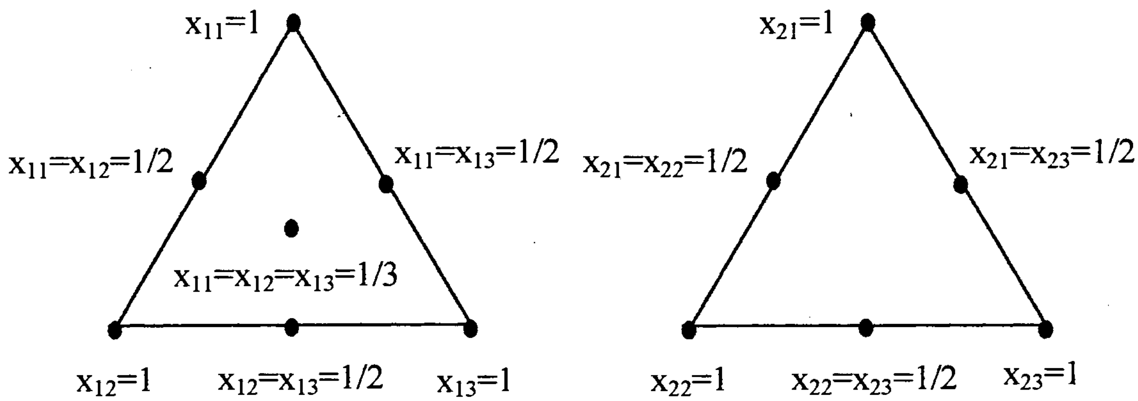


Figure 3.1 Constituent Points of the $\{3^c, 3^c; 3, 2\}$ Double-Centroid

Table 3.2 Design Points of the $\{3^c, 3^c; 3, 2\}$ Double-Centroid

Run No.	x_{11}	x_{12}	x_{13}	x_{21}	x_{22}	x_{23}
1	1	0	0	1	0	0
2	1	0	0	0	1	0
3	1	0	0	0	0	1
4	1	0	0	1/2	1/2	0
5	1	0	0	1/2	0	1/2
6	1	0	0	0	1/2	1/2
7	0	0	1	1	0	0
8	0	0	1	0	1	0
9	0	0	1	0	0	1
10	0	0	1	1/2	1/2	0
11	0	0	1	1/2	0	1/2
12	0	0	1	0	1/2	1/2
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.
37	1/3	1/3	1/3	1	0	0
38	1/3	1/3	1/3	0	1	0
39	1/3	1/3	1/3	0	0	1
40	1/3	1/3	1/3	1/2	1/2	0
41	1/3	1/3	1/3	1/2	0	1/2
42	1/3	1/3	1/3	0	1/2	1/2

3.4 Interpretation of the Coefficients in the Fitted Regression Model Associated with the Multiple-Centroid Design

One can interpret the coefficients of the fitted regression model in a multiple-centroid design. For ease in understanding the meaning of the coefficients, the $\{2^c, 2^c; 2, 2\}$ double-centroid design is illustrated. The design points of the $\{2^c, 2^c; 2, 2\}$ double-centroid are shown in Table 3.3.

The polynomial model associated with the $\{2^c, 2^c; 2, 2\}$ double-centroid design is

$$\eta = \beta_{1,1}x_{11}x_{21} + \beta_{1,2}x_{11}x_{22} + \beta_{1,12}x_{11}x_{21}x_{22} + \beta_{2,1}x_{12}x_{21} + \beta_{2,2}x_{12}x_{22} + \beta_{2,12}x_{12}x_{21}x_{22} + \beta_{12,1}x_{11}x_{12}x_{21} + \beta_{12,2}x_{11}x_{12}x_{22} + \beta_{12,12}x_{11}x_{12}x_{21}x_{22}. \quad (3.13)$$

Note that $x_{11} + x_{12} = 1$ and $x_{21} + x_{22} = 1$ are true for the $\{2^c, 2^c; 2, 2\}$ double-centroid design. Employing the design point in the first run and its associated mean response in Table 3.3 (i.e. $x_{11} = 1$, $x_{21} = 1$, and $\eta_{1,1}$) into equation (3.13), one obtains

$$\eta_{1,1} = \beta_{1,1}.$$

Let $\bar{\eta}$ denote the observed mean response to mixture and $\hat{\beta}$ the least-squares estimate of β, then

$$\hat{\beta}_{1,1} = \bar{\eta}_{1,1}. \quad (3.14)$$

Similarly, applying the values in the second, fourth, and fifth runs in Table 3.3 into equation (3.13), one has

$$\hat{\beta}_{1,2} = \bar{\eta}_{1,2}, \quad \hat{\beta}_{2,1} = \bar{\eta}_{2,1}$$

and

$$\hat{\beta}_{2,2} = \bar{\eta}_{2,2}. \quad (3.15)$$

Also assigning the values of the third run in Table 3.3 into equation (3.13), one obtains

Table 3.3 Design Points of the $\{2^c, 2^c; 2, 2\}$ Double-Centroid

Run No.	x_{11}	x_{12}	x_{21}	x_{22}	Mean Responses
1	1	0	1	0	$\eta_{1,1}$
2	1	0	0	1	$\eta_{1,2}$
3	1	0	1/2	1/2	$\eta_{1,12}$
4	0	1	1	0	$\eta_{2,1}$
5	0	1	0	1	$\eta_{2,2}$
6	0	1	1/2	1/2	$\eta_{2,12}$
7	1/2	1/2	1	0	$\eta_{12,1}$
8	1/2	1/2	0	1	$\eta_{12,2}$
9	1/2	1/2	1/2	1/2	$\eta_{12,12}$

$$\bar{\eta}_{1,12} = \frac{1}{2}(\hat{\beta}_{1,1} + \hat{\beta}_{1,2}) + \frac{1}{4}\hat{\beta}_{1,12}. \tag{3.16}$$

By substituting equations (3.14) and (3.15) into equation (3.16), one gets

$$\hat{\beta}_{1,12} = 4\,\bar{\eta}_{1,12} - 2(\bar{\eta}_{1,1} + \bar{\eta}_{1,2}). \tag{3.17}$$

Similar equations such as the following four equations could be obtained by applying the values of the last four runs in Table 3.3.

$$\hat{\beta}_{2,12} = 4\,\bar{\eta}_{2,12} - 2(\bar{\eta}_{2,1} + \bar{\eta}_{2,2}). \tag{3.18}$$

$$\hat{\beta}_{12,1} = 4\,\bar{\eta}_{12,1} - 2(\bar{\eta}_{1,1} + \bar{\eta}_{2,1}). \tag{3.19}$$

$$\hat{\beta}_{12,2} = 4\,\bar{\eta}_{12,2} - 2(\bar{\eta}_{1,2} + \bar{\eta}_{2,2}). \tag{3.20}$$

$$\hat{\beta}_{12,12} = 16\,\bar{\eta}_{12,12} - 8(\bar{\eta}_{1,12} + \bar{\eta}_{2,12} + \bar{\eta}_{12,1} + \bar{\eta}_{12,2}) + 4(\bar{\eta}_{1,1} + \bar{\eta}_{2,1} + \bar{\eta}_{1,2} + \bar{\eta}_{2,2}). \tag{3.21}$$

From equation (3.14) and (3.15), one would observe that the least-squares estimate of $\beta_{i,j}$ is the observed mean response to the mixture while the i^{th} component in the first category and the j^{th} component in the second category take the proportions of one relative to its corresponding sub-mixture.

The estimate of $\beta_{i,jk}$ in equation (3.17) and (3.18) measures the curvature between $x_{2j} = 1$ and $x_{2k} = 1$ at $x_{1i} = 1$. Similarly, the estimate of $\beta_{ij,k}$ in equation (3.19) and (3.20) measures the curvature between $x_{1i} = 1$ and $x_{1j} = 1$ at $x_{2k} = 1$. Also one finds that all the estimates of β are contrasts of the mean response vector η except $\beta_{i,j}$.

Similarly, one can expand the interpretation of the coefficient estimates in the fitted regression model associated with the multiple-centroid design by applying the values of the design points and the observed mean responses to the fitted regression equation.

3.5 Simplex-lattice by Simplex-centroid Design and the Associated Model

The multiple-lattice method (Lambrakis, 1968a) and the multiple-centroid method (Section 3.2) have been developed for the mixture problem with categorized components. Another method similar to these two methods can be developed. Suppose there are two categories of components, and a $\{q_1^l, m_1\}$ simplex-lattice design is selected from the first category of components $(x_{11}, x_{12}, x_{13}, ..., x_{1q_1})$ and a $\{q_2^c, m_2\}$ simplex-centroid design is selected from the second category of components $(x_{21}, x_{22}, x_{23}, ..., x_{2q_2})$. Also, all possible mixtures which can be produced by mixing each mixture from the first simplex-lattice with each mixture from the second simplex-centroid, with proportions c_1 and c_2, respectively, results in a <u>simplex-lattice by simplex-centroid design</u>.

For example, suppose two categories of components are considered in a mixture experiment with at least one non-zero component in each category. If one applies $\{q_1^l, 2\}$ simplex-lattice design on the first category of components and applies $\{q_2^c, 3\}$ simplex-centroid design on the second category of components, then combine the two designs in a factorial arrangement to be $\{q_1^l, q_2^c; 2, 3\}$ design or $\{q_1^l, 2\}$ simplex-lattice by $\{q_2^c, 3\}$ simplex-centroid design. The polynomial equation corresponding to the $\{q_1^l, q_2^c; 2, 3\}$ design is

$$\eta = \left(\sum_{i=1}^{q_1} \beta_i^{(1)} x_{1i} + \sum_{1 \le i < j \le q_1} \sum \beta_{ij}^{(1)} x_{1i} x_{1j}\right) * \left(\sum_{i=1}^{q_2} \beta_i^{(2)} x_{2i} + \sum_{1 \le i < j \le q_2} \sum \beta_{ij}^{(2)} x_{2i} x_{2j} + \right.$$

$$\left. \sum_{1 \le i < j < k \le q_2} \sum \sum \beta_{ijk}^{(2)} x_{2i} x_{2j} x_{2k}\right). \tag{3.22}$$

The number of design points in the $\{q_1^l, q_2^c; m_1, m_2\}$ design and the number of parameters in the associated model are equal to $\binom{q_1+m_1-1}{m_1}(2^{q_2}-1)$. This ensures that the estimates of parameters in the model can be determined uniquely.

For $q_1 = q_2 = 3$, the design points of the $\{3^l, 2\}$ simplex-lattice by $\{3^c, 3\}$ simplex-centroid design are shown in Table 3.4. The polynomial equation corresponding to the $\{3^l, 3^c; 2, 3\}$ design is

$$\eta = (\beta_1^{(1)}x_{11} + \beta_2^{(1)}x_{12} + \beta_3^{(1)}x_{13} + \beta_{12}^{(1)}x_{11}x_{12} + \beta_{13}^{(1)}x_{11}x_{13} + \beta_{23}^{(1)}x_{12}x_{13}) \; * \\ (\beta_1^{(2)}x_{21} + \beta_2^{(2)}x_{22} + \beta_3^{(2)}x_{23} + \beta_{12}^{(2)}x_{21}x_{22} + \beta_{13}^{(2)}x_{21}x_{23} + \beta_{23}^{(2)}x_{22}x_{23} + \\ \beta_{123}^{(2)}x_{21}x_{22}x_{23}). \tag{3.23}$$

Multiplying the right side of equation (3.23) and then replacing the products of the coefficients by single coefficients, equation (3.23) becomes

$$\eta = \beta_{1,1}x_{11}x_{21} + \beta_{1,2}x_{11}x_{22} + \beta_{1,3}x_{11}x_{23} + \ldots + \beta_{23,13}x_{12}x_{13}x_{21}x_{23} + \\ \beta_{23,23}x_{12}x_{13}x_{22}x_{23} + \beta_{23,123}x_{12}x_{13}x_{21}x_{22}x_{23}. \tag{3.24}$$

By substituting the component values at the design points of the $\{3^l, 3^c; 2, 3\}$ design and the measured response into equation (3.24), one can obtain the estimates of the coefficients in the model associated with the $\{3^l, 3^c; 2, 3\}$ design. This will be shown in the next section.

3.6 Coefficient Estimates of the Fitted Equation Associated with the $\{3^l, 2\}$ Simplex-Lattice by $\{3^c, 3\}$ Simplex-Centroid Design

By applying the component values at the design points of the $\{3^l, 2\}$ simplex-lattice by $\{3^c, 3\}$ simplex-centroid design in Table 3.4 into its corresponding model which is shown in equation (3.24), one obtains the estimates of coefficients in the model as

Table 3.4 $\{3^l, 2\}$ Simplex-Lattice by $\{3^c, 3\}$ Simplex-Centroid Design

Run No.	x_{11}	x_{12}	x_{13}	x_{21}	x_{22}	x_{23}	Mean Response
1	1	0	0	1	0	0	$\eta_{1,1}$
2	1	0	0	0	1	0	$\eta_{1,2}$
3	1	0	0	0	0	1	$\eta_{1,3}$
4	1	0	0	1/2	1/2	0	$\eta_{1,12}$
5	1	0	0	1/2	0	1/2	$\eta_{1,13}$
6	1	0	0	0	1/2	1/2	$\eta_{1,23}$
7	1	0	0	1/3	1/3	1/3	$\eta_{1,123}$
8	0	1	0	1	0	0	$\eta_{2,1}$
9	0	1	0	0	1	0	$\eta_{2,2}$
10	0	1	0	0	0	1	$\eta_{2,3}$
11	0	1	0	1/2	1/2	0	$\eta_{2,12}$
12	0	1	0	1/2	0	1/2	$\eta_{2,13}$
13	0	1	0	0	1/2	1/2	$\eta_{2,23}$
14	0	1	0	1/3	1/3	1/3	$\eta_{2,123}$
15	0	0	1	1	0	0	$\eta_{3,1}$
16	0	0	1	0	1	0	$\eta_{3,2}$
17	0	0	1	0	0	1	$\eta_{3,3}$
18	0	0	1	1/2	1/2	0	$\eta_{3,12}$
19	0	0	1	1/2	0	1/2	$\eta_{3,13}$
20	0	0	1	0	1/2	1/2	$\eta_{3,23}$
21	0	0	1	1/3	1/3	1/3	$\eta_{3,123}$
22	1/2	1/2	0	1	0	0	$\eta_{12,1}$
23	1/2	1/2	0	0	1	0	$\eta_{12,2}$
24	1/2	1/2	0	0	0	1	$\eta_{12,3}$
25	1/2	1/2	0	1/2	1/2	0	$\eta_{12,12}$

Table 3.4 (Continued) $\{3^l, 2\}$ Simplex-Lattice by $\{3^c, 3\}$ Simplex-Centroid Design

26	1/2	1/2	0	1/2	0	1/2	$\eta_{12,13}$
27	1/2	1/2	0	0	1/2	1/2	$\eta_{12,23}$
28	1/2	1/2	0	1/3	1/3	1/3	$\eta_{12,123}$
29	1/2	0	1/2	1	0	0	$\eta_{13,1}$
30	1/2	0	1/2	0	1	0	$\eta_{13,2}$
31	1/2	0	1/2	0	0	1	$\eta_{13,3}$
32	1/2	0	1/2	1/2	1/2	0	$\eta_{13,12}$
33	1/2	0	1/2	1/2	0	1/2	$\eta_{13,13}$
34	1/2	0	1/2	0	1/2	1/2	$\eta_{13,23}$
35	1/2	0	1/2	1/3	1/3	1/3	$\eta_{13,123}$
36	0	1/2	1/2	1	0	0	$\eta_{23,1}$
37	0	1/2	1/2	0	1	0	$\eta_{23,2}$
38	0	1/2	1/2	0	0	1	$\eta_{23,3}$
39	0	1/2	1/2	1/2	1/2	0	$\eta_{23,12}$
40	0	1/2	1/2	1/2	0	1/2	$\eta_{23,13}$
41	0	1/2	1/2	0	1/2	1/2	$\eta_{23,23}$
42	0	1/2	1/2	1/3	1/3	1/3	$\eta_{23,123}$

$$\hat{\beta}_{i,j} = \bar{\eta}_{i,j},$$

$$\hat{\beta}_{i,jk} = 4\bar{\eta}_{i,jk} - 2(\bar{\eta}_{i,j} + \bar{\eta}_{i,k}),$$

$$\hat{\beta}_{i,jkl} = 27\bar{\eta}_{i,jkl} - 12(\bar{\eta}_{i,jk} + \bar{\eta}_{i,jl} + \bar{\eta}_{i,kl}) + 3(\bar{\eta}_{i,j} + \bar{\eta}_{i,k} + \bar{\eta}_{i,l}),$$

$$\hat{\beta}_{ij,k} = 4\bar{\eta}_{ij,k} - 2(\bar{\eta}_{i,k} + \bar{\eta}_{j,k}),$$

$$\hat{\beta}_{ij,kl} = 16\bar{\eta}_{ij,kl} - 8(\bar{\eta}_{i,kl} + \bar{\eta}_{j,kl} + \bar{\eta}_{ij,k} + \bar{\eta}_{ij,l}) + 4(\bar{\eta}_{i,k} + \bar{\eta}_{i,l} + \bar{\eta}_{j,k} + \bar{\eta}_{j,l}),$$

and

$$\hat{\beta}_{ij,klm} = 108\bar{\eta}_{ij,klm} - 48(\bar{\eta}_{ij,kl} + \bar{\eta}_{ij,km} + \bar{\eta}_{ij,lm}) + 12(\bar{\eta}_{ij,k} + \bar{\eta}_{ij,l} + \bar{\eta}_{ij,m}) - 54(\bar{\eta}_{i,klm} + \bar{\eta}_{j,klm}) + 24(\bar{\eta}_{i,kl} + \bar{\eta}_{i,km} + \bar{\eta}_{i,lm} + \bar{\eta}_{j,kl} + \bar{\eta}_{j,km} + \bar{\eta}_{j,lm}) - 6(\bar{\eta}_{i,k} + \bar{\eta}_{i,l} + \bar{\eta}_{i,m} + \bar{\eta}_{j,k} + \bar{\eta}_{j,l} + \bar{\eta}_{j,m}). \tag{3.25}$$

One may observe from equation (3.24) that $\hat{\beta}_{i,jk}$, $\hat{\beta}_{i,jkl}$, $\hat{\beta}_{ij,k}$, $\hat{\beta}_{ij,kl}$, and $\hat{\beta}_{ij,klm}$ are contrasts of the measured mean response vector η. Also $\hat{\beta}_{i,j}$, $\hat{\beta}_{i,jk}$, $\hat{\beta}_{ij,k}$ and $\hat{\beta}_{ij,kl}$ have the same interpretation as those in the multiple-centroid design which is shown in Section 3.4.

3.7 Generalization of the Least-Squares Estimates of the Coefficients in the Regression Models Associated with the Multiple-Lattice, Multiple-Centroid, and Simplex-Lattice by Simplex-Centroid Designs

For a q-component design, let the response to pure component i be denoted by η_i, the response to a 1:1 binary mixture of components i and j by η_{ij} (i < j), the response to a 1:1:1 ternary mixture of components i, j, k by η_{ijk} (i < j< k), and the response to 2:1 and 1:2 binary mixtures of components i and j, respectively by η_{iij} and η_{ijj} (i < j).

The model corresponding to the $\{q^l, 2\}$ simplex-lattice design is

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}\sum^{q} \beta_{ij} x_i x_j . \tag{3.26}$$

The least-squares estimates (LSE) of the coefficients in equation (3.26) which can be obtained from Scheffe' (1958) are

$$\hat{\beta}_i = \bar{\eta}_i ,$$

and

$$\hat{\beta}_{ij} = 4\,\bar{\eta}_{ij} - 2(\bar{\eta}_i + \bar{\eta}_j). \tag{3.27}$$

The regression model corresponding to the $\{q^l,3\}$ simplex-lattice design is

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{1\le i<j}\sum^{q} \beta_{ij} x_i x_j + \sum_{1\le i<j}\sum^{q} \gamma_{ij} x_i x_j (x_i - x_j) + \sum_{1\le i<j<k}\sum\sum^{q} \beta_{ijk} x_i x_j x_k . \tag{3.28}$$

The LSE of the coefficients in equation (3.28) which can be obtained from Scheffe' (1958) are

$$\hat{\beta}_i = \bar{\eta}_i ,$$

$$\hat{\beta}_{ij} = \frac{9}{4}(\bar{\eta}_{iij} + \bar{\eta}_{ijj} - \bar{\eta}_i - \bar{\eta}_j),$$

$$\hat{\gamma}_{ij} = \frac{9}{4}(3\bar{\eta}_{iij} - 3\,\bar{\eta}_{ijj} - \bar{\eta}_i + \bar{\eta}_j),$$

and

$$\hat{\beta}_{ijk} = 27\,\bar{\eta}_{ijk} - \frac{27}{4}(\bar{\eta}_{iij} + \bar{\eta}_{ijj} + \bar{\eta}_{iik} + \bar{\eta}_{ikk} + \bar{\eta}_{jjk} + \bar{\eta}_{jkk}) + \frac{9}{2}(\bar{\eta}_i + \bar{\eta}_j + \bar{\eta}_k). \tag{3.29}$$

The regression model corresponding to a q-component simplex-centroid design is

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{1\le i<j}\sum^{q} \beta_{ij} x_i x_j + \sum_{1\le i<j<k}\sum\sum^{q} \beta_{ijk} x_i x_j x_k + \ldots + \beta_{123\ldots q} x_1 x_2 \ldots x_q . \tag{3.30}$$

The LSE of the coefficients in equation (3.30) which can be obtained from Scheffe' (1963) are

$$\hat{\beta}_i = \bar{\eta}_i ,$$

$$\hat{\beta}_{ij} = 4\,\bar{\eta}_{ij} - 2(\bar{\eta}_i + \bar{\eta}_j),$$

$$\hat{\beta}_{ijk} = 27\,\bar{\eta}_{ijk} - 12(\bar{\eta}_{ij} + \bar{\eta}_{ik} + \bar{\eta}_{jk}) + 3(\bar{\eta}_i + \bar{\eta}_j + \bar{\eta}_k),$$

and

$$\hat{\beta}_{ijkm} = 256_{ijkm} - 108(\bar{\eta}_{ijk} + \bar{\eta}_{ijm} + \bar{\eta}_{ikm} + \bar{\eta}_{jkm}) + 32(\bar{\eta}_{ij} + \bar{\eta}_{ik} + \bar{\eta}_{im} + \bar{\eta}_{jk} + \bar{\eta}_{jm} + \bar{\eta}_{km}) - 4(\bar{\eta}_i + \bar{\eta}_j + \bar{\eta}_k + \bar{\eta}_m). \tag{3.31}$$

The general formula for the LSE of the coefficients in equation (3.30) is given in Scheffe' (1963).

Lambrakis (1968a) illustrates the $\{p^l, q^l; 3, 2\}$ double-lattice and obtains the LSE of the coefficients in the corresponding regression model. In Section 3.3, the $\{q_1^c, q_2^c; 3, 2\}$ double-centroid design is illustrated and the LSE of the coefficients in the corresponding regression model are also obtained. In Section 3.5, the $\{3^l, 2\}$ simplex-lattice by $\{3^c, 3\}$ simplex-centroid design is illustrated and the LSE of the coefficients in the corresponding model are obtained in Section 3.6.

From the LSE of the coefficients in the corresponding models of multiple-lattice, multiple-centroid, and simplex-lattice by simplex-centroid designs, one can observe that the LSE of the coefficients of any of the three models are equal to the product of the LSE of the coefficients in the individual models associated with the simplex designs. One might conjecture that the above statement is also true for the expanded designs and models in the mixture problem with more than two categories of components.

For example, suppose (x_1, x_2, x_3), (x_4, x_5, x_6), and (x_7, x_8, x_9) are 3 categories with 3 components each in a mixture problem. One would like to perform the $\{3^c, 3\}$ simplex-centroid by $\{3^l, 3\}$ simplex-lattice by $\{3^c, 2\}$ simplex-centroid design (i.e. $\{3^c, 3^l, 3^c; 3, 3, 2\}$ design) on the 9 components. There will be

$(2^3-1)\binom{3+3-1}{3}(2^3-2)$ = 420 design points in the $\{3^c, 3^l, 3^c; 3, 3, 2\}$ design and the corresponding model of the design is

$$\begin{aligned}
\eta = &(\sum_{i=1}^{3}\beta_i x_i + \sum_{1\le i<}\sum_{j}^{3}\beta_{ij}x_i x_j + \beta_{123}x_1x_2x_3)*\\
&(\sum_{k=4}^{6}\beta_k x_k + \sum_{4\le k<}\sum_{l}^{6}\beta_{kl}x_k x_l + \sum_{4\le k<}\sum_{l}^{6}\gamma_{kl}x_k x_l(x_k - x_l) + \beta_{456}x_4x_5x_6)*\\
&(\sum_{m=7}^{9}\beta_m x_m + \sum_{7\le m<}\sum_{n}^{9}\beta_{mn}x_m x_n)\\
= &\sum_{i=1}^{3}\sum_{k=4}^{6}\sum_{m=7}^{9}\beta_i\beta_k\beta_m x_i x_k x_m + \ldots +\\
&\sum_{1\le i<}\sum_{j}^{3}\sum_{4\le k<}\sum_{l}^{6}\sum_{7\le m<}\sum_{n}^{9}\beta_{ij}\gamma_{kl}\beta_{mn}x_i x_j x_k x_l(x_k - x_l)x_m x_n + \ldots\\
= &\sum_{i=1}^{3}\sum_{k=4}^{6}\sum_{m=7}^{9}\beta_{i,k,m}x_i x_k x_m + \ldots +\\
&\sum_{1\le i<}\sum_{j}^{3}\sum_{4\le k<}\sum_{l}^{6}\sum_{7\le m<}\sum_{n}^{9}\beta_{ij,kl,mn}x_i x_j x_k x_l(x_k - x_l)x_m x_n + \ldots
\end{aligned} \tag{3.32}$$

Then, the estimates for $\hat{\beta}_{ij,kl,mn}$ would be

$\hat{\beta}_{ij,kl,mn}$ = ($\hat{\beta}_{ij}$ of the model associated with the $\{3^c, 3\}$ simplex-centroid design)

* ($\hat{\gamma}_{kl}$ of the model associated with the $\{3^l, 3\}$ simplex-lattice design)

* ($\hat{\beta}_{mn}$ of the model associated with the $\{3^c, 2\}$ simplex-centroid design)

$$= [4\bar{\eta}_{ij} - 2(\bar{\eta}_i + \bar{\eta}_j)]*[\frac{9}{4}(3\bar{\eta}_{kkl} - 3\bar{\eta}_{kll} - \bar{\eta}_k + \bar{\eta}_l)]*[4\bar{\eta}_{mn} - 2(\bar{\eta}_m + \bar{\eta}_n)]$$

$$= 108(\bar{\eta}_{ij,kkl,mn} - \bar{\eta}_{ij,kll,mn}) - 54(\bar{\eta}_{ij,kkl,m} + \bar{\eta}_{ij,kkl,n} - \bar{\eta}_{ij,kll,m} - \bar{\eta}_{ij,kll,n})$$

$$- 36(\bar{\eta}_{ij,k,mn} - \bar{\eta}_{ij,l,mn}) + 18(\bar{\eta}_{ij,k,m} + \bar{\eta}_{ij,k,n} - \bar{\eta}_{ij,l,m} - \bar{\eta}_{ij,l,n}) - 54(\bar{\eta}_{i,kkl,mn}$$

$$+ \bar{\eta}_{j,kkl,mn} - \bar{\eta}_{i,kll,mn} - \bar{\eta}_{j,kll,mn}) + 18(\bar{\eta}_{i,k,mn} + \bar{\eta}_{j,k,mn} - \bar{\eta}_{i,l,mn} - \bar{\eta}_{j,l,mn})$$

$$+ 27(\bar{\eta}_{i,kkl,m} + \bar{\eta}_{i,kkl,n} + \bar{\eta}_{j,kkl,m} + \bar{\eta}_{j,kkl,n} - \bar{\eta}_{i,kll,m} - \bar{\eta}_{i,kll,n} - \bar{\eta}_{j,kll,m}$$

$$- \bar{\eta}_{j,kll,n}) - 9(\bar{\eta}_{i,k,m} + \bar{\eta}_{i,k,n} + \bar{\eta}_{j,k,m} + \bar{\eta}_{j,k,n} - \bar{\eta}_{i,l,m} - \bar{\eta}_{i,l,n} - \bar{\eta}_{j,l,m} - \bar{\eta}_{j,l,n})$$

(3.33)

where $\bar{\eta}_{ij,kkl,mn}$ is the observed response at $x_i = 1/2, x_j = 1/2, x_k = 2/3, x_l = 1/3$, $x_m = 1/2$, and $x_n = 1/2$. Also the $\hat{\beta}_{ij,kl,mn}$ is a contrast of the measured mean response vector η.

3.8 Summary

The mixture problem with categorized components is introduced for the study. When the components in the mixture can be separated in groups by their nature, then the components in each group form an individual simplex mixture problem. The mixture problem in this case is called the mixture problem with categorized components.

The multiple-centroid design and simplex-lattice by simplex-centroid design are developed in this chapter. Since each category forms a simplex mixture problem, the multiple-centroid design is formed by the factorial arrangement of the design for each category while applying a simplex-centroid design to each category. The simplex-lattice design by simplex-centroid design is formed by applying a simplex-lattice design on the first category and a simplex-centroid design on the second category. Then a factorial arrangement is made on the two simplex designs to complete a simplex-lattice by simplex-centroid design.

The corresponding regression models for the multiple-centroid design and simplex-lattice by simplex-centroid design are also developed in the study. The number of distinct design points of the multiple-centroid design and simplex-lattice by simplex-centroid design are the same as the number of parameters in their corresponding regression models.

The interpretation of the coefficients in the fitted regression model associated with the multiple-centroid design are also performed in this chapter. One can apply similar logic to the interpretation of the coefficients in the fitted regression model associated with the simplex-lattice by simplex-centroid design.

The calculation of the coefficient estimates by the least-squares method is illustrated on the regression models associated with the multiple-centroid design and the simplex-lattice by simplex-centroid design. Finally, the generalization of the least-squares estimates of the coefficients in the regression models associated with the multiple-lattice, multiple-centroid, and simplex-lattice by simplex-centroid designs are also developed and illustrated.

The advantage of using either multiple-centroid design or simplex-lattice by simplex-centroid design is that the two designs require less design points than the multiple-lattice design. Also the two designs provide simpler models than that of the multiple-lattice design.

CHAPTER 4

DESIGNS AND MODELS USING RATIOS OF COMPONENTS AS DESIGN VARIABLES

The multiple-lattice design introduced by Lambrakis (1968a), the multiple-centroid design and simplex-lattice by simplex-centroid design developed in Chapter 3 are some methods used in the mixture problem with categorized components. Kenworthy (1963) illustrates an example of experiments with mixtures using ratios of components. By using a concept similar to that of Kenworthy, the method of ratios of components can also be applied to the mixture problem with components in categories. By using the ratio method, one is interested in one or more of the components, not so much from the standpoint of their proportions in mixtures (or sub-mixtures), but from their relationship to the other components in the mixtures (or sub-mixtures) in the form of their proportions. An example is used to illustrate how to use the ratios of components in the mixture problem with categorized components.

4.1 Example of Two Categories with Three Components in Each Category

The use of ratios of components can be treated in a variety of ways. Let x_{ij} be the j^{th} (j=1, 2, ..., q_i) component in the i^{th} category. For three components in the first category whose proportions are denoted by x_{11}, x_{12}, and x_{13}, several possible sets of transformations from the x_{1i} (i=1, 2 and 3) variables to the ratio variables r_1 and r_2 include

$$\begin{aligned}
&\text{Set I} \quad r_1 = \frac{x_{13}}{x_{11}},\ r_2 = \frac{x_{13}}{x_{12}} \\
&\text{Set II} \quad r_1 = \frac{x_{11}}{x_{12}},\ r_2 = \frac{x_{12}}{x_{13}} \\
&\text{Set III} \quad r_1 = \frac{x_{11}}{x_{12} + x_{13}},\ r_2 = \frac{x_{12}}{x_{13}}
\end{aligned} \tag{4.1}$$

In each set of ratios, each ratio r_i, i=1 or 2, contains at least one of the components used in the other ratio of the same set. The number of ratios r_i in each set should be one less than the number of components in the category. If the number of ratios in a set is equal to the number of components q_i in i^{th} category, the ratios form a redundant set because the sum of the component proportions is unity. Note that any type of ratio can be used in a set as long as there is a tie-in with a component in one of the other ratios in the same set.

Suppose r_1 and r_2 are the ratios transformed from the first 3-component category, and r_3 and r_4 are the ratios transformed from the second 3-component category in a mixture problem where

$$\begin{aligned}
&r_1 = \frac{x_{13}}{x_{11}},\ r_2 = \frac{x_{13}}{x_{12}}, \\
&r_3 = \frac{x_{21}}{x_{22}},\ r_4 = \frac{x_{21}}{x_{23}}.
\end{aligned} \tag{4.2}$$

A simple first-degree model in r_1, r_2, r_3 and r_4 is

$$y = \alpha_0 + \alpha_1 r_1 + \alpha_2 r_2 + \alpha_3 r_3 + \alpha_4 r_4 + \varepsilon$$

which becomes, in terms of x_{11}, x_{12}, x_{13}, x_{21}, x_{22} and x_{23},

$$y = \alpha_0 + \alpha_1 \frac{x_{13}}{x_{11}} + \alpha_2 \frac{x_{13}}{x_{12}} + \alpha_3 \frac{x_{21}}{x_{22}} + \alpha_4 \frac{x_{21}}{x_{23}} + \varepsilon. \tag{4.3}$$

The model is fitted to the data collected at design points chosen using the r_i. The coefficients α_i (i=0, 1, 2, 3 and 4) in the first-degree model then can be determined.

Suppose the four ratio variables are defined as in equation (4.2). The paths of values for the ratio variables r_1 and r_2 are defined along the rays emanating from the vertex $x_{12}=1$ for r_1 and from the vertex $x_{11}=1$ for r_2. The paths of values for the ratio variables r_3 and r_4 are defined along the rays emanating from the vertex $x_{23}=1$ for r_3 and from the vertex $x_{22}=1$ for r_4. These rays are drawn in Figure 4.1.

Alternatively, one can construct an orthogonal design such as factorial or central-composite design on the ratios of components. Data collected at the design points of the factorial design are then fitted to the model. For example, suppose one set of values of r_1, 0.5 and 1.5, are combined with values of r_2, 1.0 and 2.0. Also let r_3 have the set of values 0.1 and 2.0 in combination with values of r_4 equal to 0.1 and 2.0. The factorial design on the uncoded and coded ratio variables and the actual component values are displayed in Table 4.1.

A second-degree model using uncoded ratio variables can be expressed as

$$\begin{aligned} y = {} & \alpha_0 + \alpha_1 r_1 + \alpha_2 r_2 + \alpha_3 r_3 + \alpha_4 r_4 + \alpha_{11} r_1^2 + \alpha_{22} r_2^2 + \alpha_{33} r_3^2 + \\ & \alpha_{44} r_4^2 + \alpha_{12} r_1 r_2 + \alpha_{13} r_1 r_3 + \alpha_{14} r_1 r_4 + \alpha_{23} r_2 r_3 + \alpha_{24} r_2 r_4 + \\ & \alpha_{34} r_3 r_4 + \varepsilon. \end{aligned} \tag{4.4}$$

Data collected from the 16 design points can be fitted to equation (4.4) and least-squares estimates of α can then be determined.

Also a second-degree model using coded ratio variables of the form

$$\begin{aligned} y = {} & \alpha_0' + \alpha_1' r_1' + \alpha_2' r_2' + \alpha_3' r_3' + \alpha_4' r_4' + \alpha_{12}' r_1' r_2' + \alpha_{13}' r_1' r_3' + \\ & \alpha_{14}' r_1' r_4' + \alpha_{23}' r_2' r_3' + \alpha_{24}' r_2' r_4' + \alpha_{34}' r_3' r_4' + \varepsilon \end{aligned} \tag{4.5}$$

can be fitted to the observations collected at the 16 design points.

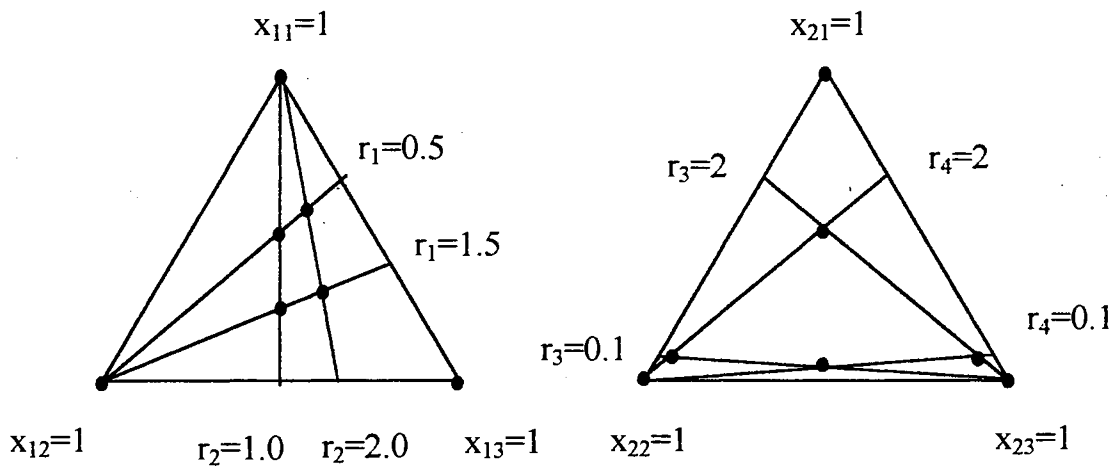


Figure 4.1 Rays Defined by the Ratios $r_1 = \frac{x_{13}}{x_{11}}$, $r_2 = \frac{x_{13}}{x_{12}}$, $r_3 = \frac{x_{21}}{x_{22}}$, and $r_4 = \frac{x_{21}}{x_{23}}$

Table 4.1 Design Points of 2^4 Factorial Design Based on the Ratios of Components

Run	Uncoded Ratio Variables				Coded Ratio Variables				Component Proportions						
	r_1	r_2	r_3	r_4	r_1'	r_2'	r_3'	r_4'	x_{11}	x_{12}	x_{13}	x_{21}	x_{22}	x_{23}	y
1	0.5	1.0	0.1	0.1	-1	-1	-1	-1	0.5	0.25	0.25	0.048	0.476	0.476	12.75
2	0.5	1.0	0.1	2.0	-1	-1	-1	1	0.5	0.25	0.25	0.087	0.87	0.043	8.76
3	0.5	1.0	2.0	0.1	-1	-1	1	-1	0.5	0.25	0.25	0.087	0.043	0.87	8.21
4	0.5	1.0	2.0	2.0	-1	-1	1	1	0.5	0.25	0.25	0.5	0.25	0.25	8.01
5	0.5	2.0	0.1	0.1	-1	1	-1	-1	0.571	0.143	0.286	0.048	0.476	0.476	8.96
6	0.5	2.0	0.1	2.0	-1	1	-1	1	0.571	0.143	0.286	0.087	0.87	0.043	8.72
7	0.5	2.0	2.0	0.1	-1	1	1	-1	0.571	0.143	0.286	0.087	0.043	0.87	8.51
8	0.5	2.0	2.0	2.0	-1	1	1	1	0.571	0.143	0.286	0.5	0.25	0.25	12.54
9	1.5	1.0	0.1	0.1	1	-1	-1	-1	0.25	0.375	0.375	0.048	0.476	0.476	8.73
10	1.5	1.0	0.1	2.0	1	-1	-1	1	0.25	0.375	0.375	0.087	0.87	0.043	8.64
11	1.5	1.0	2.0	0.1	1	-1	1	-1	0.25	0.375	0.375	0.087	0.043	0.87	8.24
12	1.5	1.0	2.0	2.0	1	-1	1	1	0.25	0.375	0.375	0.5	0.25	0.25	12.09
13	1.5	2.0	0.1	0.1	1	1	-1	-1	0.308	0.231	0.462	0.048	0.476	0.476	8.88
14	1.5	2.0	0.1	2.0	1	1	-1	1	0.308	0.231	0.462	0.087	0.87	0.043	12.58
15	1.5	2.0	2.0	0.1	1	1	1	-1	0.308	0.231	0.462	0.087	0.043	0.87	12.35
16	1.5	2.0	2.0	2.0	1	1	1	1	0.308	0.231	0.462	0.5	0.25	0.25	22.76

Note : $r_1' = \dfrac{r_1 - 1}{0.5}$, $r_2' = \dfrac{r_2 - 1.5}{0.5}$, $r_3' = \dfrac{r_3 - 1.05}{0.95}$, $r_4' = \dfrac{r_4 - 1.05}{0.95}$,

$$x_{11} = \frac{1}{1 + r_1 + r_1 / r_2}, \quad x_{12} = x_{11} r_1 / r_2, \quad x_{13} = r_1 x_{11},$$

$$x_{22} = \frac{1}{1 + r_3 + r_3 / r_4}, \quad x_{21} = r_3 x_{22}, \quad x_{23} = x_{22} r_3 / r_4 .$$

While equations (4.4) and (4.5) both seem to be useful models for the factorial design, equation (4.5) is better than equation (4.4) since the variables $r_i^{'}$ and $r_i^{'}r_j^{'}$ in equation (4.5) are mutually orthogonal.

To illustrate how to analyze the collected data from physical experiments and predict the mean response at any point inside experimental region. Suppose the actual response observed at each design point is as shown in Table 4.1. By applying the observed responses and coded ratio values in equation (4.5), the second-degree model for predicting the response y is

$$\hat{y} = 10.67 + 1.11r_1^{'} + 1.24r_2^{'} + 0.92r_3^{'} + 1.09r_4^{'} + 1.11r_1^{'}r_2^{'} + 1.16r_1^{'}r_3^{'} + 1.14r_1^{'}r_4^{'} + 1.21r_2^{'}r_3^{'} + 1.15r_2^{'}r_4^{'} + 1.17r_3^{'}r_4^{'}. \tag{4.6}$$

Suppose one wishes to estimate the mean response at point x_{11}=0.45, x_{12}=0.25, x_{13}=0.30, x_{21}=0.25, x_{22}=0.50, and x_{23}=0.25. One transforms the x_{ij} (i=1, 2 ; j=1, 2, 3) values into their corresponding uncoded ratio values which are

$$r_1 = \frac{x_{13}}{x_{11}} = \frac{0.30}{0.45} = \frac{2}{3},\ r_2 = \frac{x_{13}}{x_{12}} = \frac{0.30}{0.25} = \frac{6}{5},$$
$$r_3 = \frac{x_{21}}{x_{22}} = \frac{0.25}{0.50} = \frac{1}{2},\ r_4 = \frac{x_{21}}{x_{23}} = \frac{0.25}{0.25} = 1.$$

The next step is to transform the uncoded ratio values into their corresponding coded ratio values which are

$$r_1^{'} = \frac{r_1 - 1}{0.5} = \frac{\frac{2}{3} - 1}{0.5} = -0.666,$$
$$r_2^{'} = \frac{r_2 - 1.5}{0.5} = \frac{1.2 - 1.5}{0.5} = -0.6,$$
$$r_3^{'} = \frac{r_3 - 1.05}{0.95} = \frac{0.5 - 1.05}{0.95} = -0.579,$$

$$r_4^{'} = \frac{r_4 - 1.05}{0.95} = \frac{1 - 1.05}{0.95} = -0.0526.$$

Finally one substitutes the coded ratio values into equation (4.6) and which results in $\hat{y}(x) = 0.4168$.

4.2 Summary

This chapter illustrates the method of ratios of components to design and model the mixture problem with categorized components. The ratios of components can be in any form as long as there is a tie-in with a component in one of the other ratios in the same category. There are no ties among the ratios of different categories. The number of ratios in a category should be one less than the number of components in the category.

After the ratios of components in all categories have been carefully defined, the level values for each ratio are assigned based on the region of interest in each category. With equal spaced ratio values, one will then standardize the uncoded ratios into coded ratios which will make the coded ratio variables become mutually orthogonal. A classical design such as factorial design or central-composite design can be applied to the coded ratio variables. Data collected at the design points are fitted into the regression model corresponding to the design and then the estimates of the coefficients in the model are then determined.

The ratio method provides an alternative way to explore the surface of the mixture problem with categorized components. Orthogonal designs can be employed by using the ratio method while multiple-lattice, multiple-centroid, and simplex-lattice by simplex-centroid designs can't.

CHAPTER 5

COMPUTER-AIDED D-OPTIMAL DESIGNS AND THEIR CORRESPONDING MODELS

The multiple-lattice design developed by Lambrakis (1968a), the multiple-centroid design, and the simplex-lattice by simplex-centroid design developed in Chapter 3 require a large number of design points which quite often make these designs infeasible or uneconomical. The ratio method developed and illustrated in Chapter 4, however can use orthogonal designs such as factorial or central-composite designs. Unfortunately, the experimental region defined by the ratio method cannot cover the extreme vertices defined by the original mixture problem. As such, it is not always a feasible method to experimenters when the extreme vertices are required to be in the experimental region. In this chapter, D-optimal designs for the mixture problem with categorized components are developed and illustrated. By using the approach developed in this chapter, one can find at least one design which has minimum generalized variance of the estimates of the coefficients in a specified model, assuming that the relationship between the response of interest and the components in the mixture is correctly described by the model.

5.1 A, D, G, V-Optimality and G-Efficiency

A, D, G, V-optimality are described in Section 2.9 where these optimalities are all variance-minimizing criteria. For example, D-optimal design points are obtained by selecting design points from candidate design points so as to maximize the determinant $|X^T X|$, where X is the design matrix expanded in the form of the model believed to adequately represent the relationship between the design variables and the response of interest. In this chapter, the DETMAX algorithm by Mitchell (1974) is used to find D-optimal or near D-optimal designs. The DETMAX algorithm uses an exchange-of-point scheme. The DETMAX algorithm does not guarantee that a D-optimal design is generated in any one "try". The MIXSOFT software by Piepel (1994) is used to find D-optimal or near D-optimal designs for the mixture problem with categorized components where 20 tries are performed in the search of each D-optimal design. The MIXSOFT software is useful for both mixture and nonmixture problems. From the result of the 20 tries, one might be sure to obtain D-optimal designs when the maximum determinant value among the 20 tries is repeated many times in the 20 tries.

Design properties such as the maximum and average values of $d = x_0(X^T X)^{-1} x_0$ over all points x_0 in the candidate set, trace$(X^T X)^{-1}$ and % G-efficiency are also calculated after obtaining the D-optimal or near D-optimal design in each try. The % G-efficiency is defined as $100\frac{p}{n}$, where p is the number of parameters in the assumed model form and n is the number of distinct design points in the design.

5.2 Example of the Mixture Problem with Two Three-Component Categories

Designs containing exactly N points and obtained using D-optimality criteria are called D_N-optimal designs. The D-optimal designs offer alternative designs to experimenters where smaller number of design points can be used than are required by multiple-lattice, multiple-centroid, and simplex-lattice by simplex-centroid designs.

Suppose there are two categories in a mixture problem with three components in each category. The three components in the first category are denoted by x_1, x_2 and x_3 and the other three components in the second category are denoted by x_4, x_5 and x_6. Then the restrictions hold:

$$\begin{aligned} x_1 + x_2 + x_3 &= 1, \\ x_4 + x_5 + x_6 &= 1, \end{aligned} \tag{5.1}$$

and $x_i \geq 0$, i=1, 2, ..., 6.

Equation (5.1) can be written as

$$\begin{aligned} x_1 + x_2 &\leq 1, \\ x_4 + x_5 &\leq 1, \end{aligned} \tag{5.2}$$

and $x_i \geq 0$, i=1, 2, 4, 5.

The first-degree model for the mixture problem in x_1, x_2, x_4, and x_5 is written as

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_4 x_4 + \beta_5 x_5 + \varepsilon, \tag{5.3}$$

where $x_1 + x_2 \leq 1$, $x_4 + x_5 \leq 1$, and $x_i \geq 0$ (i=1, 2, 4, 5).

The model with linear plus cross product terms for the mixture problem is written as

$$\begin{aligned} y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_4 x_4 + \beta_5 x_5 + \beta_{12} x_1 x_2 + \beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \\ \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{45} x_4 x_5 + \varepsilon, \end{aligned} \tag{5.4}$$

where $x_1 + x_2 \leq 1$, $x_4 + x_5 \leq 1$, and $x_i \geq 0$ (i=1, 2, 4, 5).

The quadratic model for the mixture problem can be

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_4 x_4 + \beta_5 x_5 + \beta_{12} x_1 x_2 + \beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{45} x_4 x_5 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{44} x_4^2 + \beta_{55} x_5^2 + \varepsilon, \quad (5.5)$$

where $x_1 + x_2 \le 1$, $x_4 + x_5 \le 1$, and $x_i \ge 0$ (i=1, 2, 4, 5).

When the entire experimental region is to be explored, the factor space or design region is said to be unconstrained. With an unconstrained region in a single simplex mixture problem, one generally uses candidate points which depend on the type of the model assumed. For a linear model in a single simplex mixture problem, the candidate points generally are extreme vertices of the simplex. If the fitted model is quadratic, one generally uses extreme vertices and midpoints of edges as the candidate points. Although the candidate design points for single simplex experimental region are generally selected according to the model to be fitted, in this study, a set of candidate design points for obtaining D-optimal designs in the mixture problem with categorized components are not generated in the same way as those for single simplex experimental region. First, the constituent points for each category are selected and then the final candidate design points are obtained by the factorial arrangement of the constituent points in one category with the constituent points in the other categories. For a q-component category, the constituent points in the category are selected as the union of the $\{q^l, m\}$ simplex-lattice designs ($m \le q$). For example, in a three-component category, the constituent points of the category are the union of a $\{3^l, 1\}$ simplex-lattice design, a $\{3^l, 2\}$ simplex-lattice design, a $\{3^l, 3\}$ simplex-lattice design. They are pictured in Figure 5.1 and shown in Table 5.1.

The overall candidate design points for obtaining D-optimal design of the mixture problem with two 3-component categories are the factorial arrangement of the two sets of the constituent points corresponding to the two categories. Thus the number of candidate design points for the mixture problem is 169, regardless of

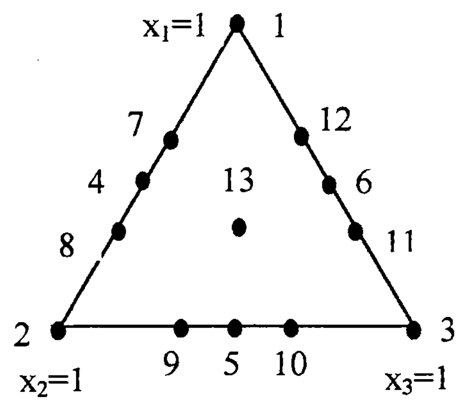


Figure 5.1 Constituent Points of A Three-Component Category

Table 5.1 Constituent Points of Two Three-Component Categories for Constructing Candidate Design Points

Number	x_1	x_2	x_3
1	1	0	0
2	0	1	0
3	0	0	1
4	1/2	1/2	0
5	0	1/2	1/2
6	1/2	0	1/2
7	2/3	1/3	0
8	1/3	2/3	0
9	0	2/3	1/3
10	0	1/3	2/3
11	1/3	0	2/3
12	2/3	0	1/3
13	1/3	1/3	1/3

Number	x_4	x_5	x_6
1	1	0	0
2	0	1	0
3	0	0	1
4	1/2	1/2	0
5	0	1/2	1/2
6	1/2	0	1/2
7	2/3	1/3	0
8	1/3	2/3	0
9	0	2/3	1/3
10	0	1/3	2/3
11	1/3	0	2/3
12	2/3	0	1/3
13	1/3	1/3	1/3

the model to be fitted. The purpose of using the new candidate design points which are different from those suggested in a single simplex experimental region is to check if the previous suggestion is still valid for D-optimal design in the mixture problem with categorized components where the experimental region is constructed by multiple simplexes. The overall candidate points are partially shown in Table 5.2.

Candidate design points are denoted as (i, j) where i and j are the numbers in Table 5.1 and i is the constituent point from the first category and j is the constituent point from the second category. For example, the candidate design point (2, 5) is equivalent to $x_1 = 0,\ x_2 = 1,\ x_3 = 0,\ x_4 = 0,\ x_5 = 1/2,$ and $x_6 = 1/2$. The values of x_1, x_2, x_4 and x_5 are substituted into equations (5.3), (5.4), and (5.5) to obtain the matrix $\boldsymbol{X}$ and the determinant value of ($\boldsymbol{X}^T\boldsymbol{X}$) is calculated. Finally, the D_N-optimal design for each assumed model is obtained.

Computer software MIXSOFT is used to obtain D_N-optimal designs for the three models by selecting a fraction of the 169 candidate design points which has the maximum determinant value of ($\boldsymbol{X}^T\boldsymbol{X}$). Note that the D_N-optimal design can have design points which are replicated.

5.3 Results of the Example

Three models are selected to find their corresponding D_N-optimal designs. The three models are linear, linear plus cross product terms, and quadratic which correspond to equations (5.3), (5.4), and (5.5), respectively. There are 169 candidate design points for each model. Tables 5.3, 5.4 and 5.5 show the D_N-optimal designs for the three models in the order of the number of design points N.

For D_N-optimal designs, N points out of all candidate design points are selected based on a certain model such that the determinant of ($\boldsymbol{X}^T\boldsymbol{X}$) is

Table 5.2 Candidate Design Points of the Mixture Problem with Two Three-Component Categories for Obtaining D-Optimal Designs

Number	Candidate Points	x_1	x_2	x_3	x_4	x_5	x_6
1	(1, 1)	1	0	0	1	0	0
2	(1, 2)	1	0	0	0	1	0
3	(1, 3)	1	0	0	0	0	1
4	(1, 4)	1	0	0	1/2	1/2	0
5	(1, 5)	1	0	0	0	1/2	1/2
6	(1, 6)	1	0	0	1/2	0	1/2
7	(1, 7)	1	0	0	2/3	1/3	0
8	(1,8)	1	0	0	1/3	2/3	0
9	(1, 9)	1	0	0	0	2/3	1/3
10	(1, 10)	1	0	0	0	1/3	2/3
11	(1, 11)	1	0	0	1/3	0	2/3
12	(1, 12)	1	0	0	2/3	0	1/3
13	(1, 13)	1	0	0	1/3	1/3	1/3
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.
157	(13, 1)	1/3	1/3	1/3	1	0	0
158	(13, 2)	1/3	1/3	1/3	0	1	0
159	(13, 3)	1/3	1/3	1/3	0	0	1
160	(13, 4)	1/3	1/3	1/3	1/2	1/2	0
161	(13, 5)	1/3	1/3	1/3	0	1/2	1/2
162	(13, 6)	1/3	1/3	1/3	1/2	0	1/2
163	(13, 7)	1/3	1/3	1/3	2/3	1/3	0
164	(13, 8)	1/3	1/3	1/3	1/3	2/3	0
165	(13, 9)	1/3	1/3	1/3	0	2/3	1/3
166	(13, 10)	1/3	1/3	1/3	0	1/3	2/3
167	(13, 11)	1/3	1/3	1/3	1/3	0	2/3
168	(13, 12)	1/3	1/3	1/3	2/3	0	1/3
169	(13, 13)	1/3	1/3	1/3	1/3	1/3	1/3

Table 5.3 D_N-Optimal Designs for the Mixture Problem with Two Three-Component Categories While Model Is Linear

N	Preference Order	Design Points
6	1	(1, 1), (1, 2), (2, 2), (2, 3), (3, 1), (3, 3)
7	1	(1, 1), (1, 3), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3)
8	1	(1, 1), (1, 2), (1, 3), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3)
9	1	(1, 1), (1, 2), (1, 3), (2, 1), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3)
10	1	(1, 1), (1, 2), (1, 3), (2, 1), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3), (3, 3)
11	1	(1, 1), (1, 2), (1, 3), (2, 1), (2, 2), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3), (3, 3)
12	1	(1, 1), (1, 1), (1, 2), (1, 3), (2, 1), (2, 2), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3), (3, 3)
13	1	(1, 1), (1, 1), (1, 2), (1, 2), (1, 3), (2, 1), (2, 2), (2, 3), (2, 3), (3, 1), (3, 2), (3, 3), (3, 3)
13	1	(1, 1), (1, 2), (1, 2), (1, 3), (2, 1), (2, 2), (2, 2), (2, 3), (3, 1), (3, 1), (3, 2), (3, 3), (3, 3)
13	1	(1, 1), (1, 2), (1, 3), (1, 3), (2, 1), (2, 1), (2, 2), (2, 2), (2, 3), (3, 1), (3, 2), (3, 3), (3, 3)
14	1	(1, 1), (1, 2), (1, 2), (1, 3), (1, 3), (2, 1), (2, 1), (2, 2), (2, 3), (3, 1), (3, 1), (3, 2), (3, 3), (3, 3)
14	1	(1, 1), (1, 2), (1, 2), (1, 3), (2, 1), (2, 1), (2, 2), (2, 3), (2, 3), (3, 1), (3, 2), (3, 2), (3, 3), (3, 3)

Table 5.4 D_N-Optimal Designs for the Mixture Problem with Two Three-Component Categories While Model Is Linear Plus Cross Product Terms

N	Preference Order	Design Points
12	1	Base Points + (3, 4), (4, 3), (4, 4)
13	1	Base Points + (3, 4), (4, 1), (4, 3), (4, 4)
13	1	Base Points + (2, 4), (3, 4), (4, 3), (4, 4)
13	1	Base Points + (1, 4), (3, 4), (4, 3), (4, 4)
14	1	Base Points + (1, 4), (3, 4), (4, 2), (4, 3), (4, 4)
14	1	Base Points + (1, 4), (3, 4), (4, 1), (4, 3), (4, 4)
15	1	Base Points + (1, 4), (2, 4), (3, 4), (4, 1), (4, 2), (4, 3)
16	1	Base Points + (1, 4), (2, 4), (3, 3), (3, 4), (4, 1), (4, 2), (4, 3)
17	1	Base Points + (1, 4), (2, 4), (3, 2), (3, 3), (3, 4), (4, 1), (4, 2), (4, 3)
17	1	Base Points + (1, 4), (2, 4), (3, 1), (3, 3), (3, 4), (4, 1), (4, 2), (4, 3)
18	1	Base Points + (1,3), (1, 4), (2, 3), (2, 4), (3, 3), (3, 4), (4, 1), (4, 2), (4, 4)
18	1	Base Points + (1, 4), (2, 4), (3, 1), (3, 2), (3, 3), (4, 1), (4, 2), (4, 3), (4, 4)
19	1	Base Points + (1, 3), (1, 4), (2, 3), (2, 4), (3, 1), (3, 2), (3, 3), (4, 1), (4, 2), (4, 4)
20	1	Base Points + (1, 2), (1, 3), (1, 4), (2, 3), (2, 4), (3, 1), (3, 2), (3, 3), (4, 1), (4, 2), (4, 4)
20	1	Base Points + (1, 3), (1, 4), (2, 1), (2, 3), (2, 4), (3, 1), (3, 2), (3, 3), (4, 1), (4, 2), (4, 4)
20	1	Base Points + (1, 3), (1, 4), (2, 2), (2, 3), (2, 4), (3, 1), (3, 2), (3, 3), (4, 1), (4, 2), (4, 4)

Table 5.5 D_N-Optimal Designs for the Mixture Problem with Two Three-Component Categories While Model Is Quadratic

N	Preference Order	Design Points
16	1	Base Points + (4, 4), (4, 5), (5, 4), (5, 6), (6, 5), (6, 6), (13, 3)
16	1	Base Points + (3, 13), (4, 4), (4, 5), (5, 4), (5, 6), (6, 5), (6, 6)
17	1	Base Points + (2, 6), (4, 3), (4, 4), (5, 1), (5, 5), (6, 4), (6, 5), (6, 6)
17	1	Base Points + (2, 5), (3, 4), (4, 4), (4, 6), (5, 2), (5, 6), (6, 5), (6, 6)
17	1	Base Points + (1, 6), (3, 4), (4, 1), (4, 5), (5, 5), (5, 6), (6, 4), (6, 5)
18	1	Base Points + (1, 6), (2, 5), (4, 3), (4, 4), (5, 2), (5, 6), (6, 4), (6, 5), (6, 6)
19	1	Base Points + (2, 5), (3, 6), (4, 4), (4, 5), (4, 6), (5, 3), (5, 4), (6, 1), (6, 4), (6, 5)
19	1	Base Points + (1, 5), (3, 6), (4, 4), (4, 5), (4, 6), (5, 1), (5, 4), (5, 5), (6, 3), (6, 4)
19	1	Base Points + (2, 6), (3, 5), (4, 4), (4, 5), (4, 6), (5, 3), (5, 4), (6, 2), (6, 4), (6, 6)
20	1	Base Points + (1, 6), (3, 5), (4, 1), (4, 4), (4, 5), (5, 4), (5, 5), (5, 6), (6, 3), (6, 4), (6, 6)
20	1	Base Points + (1, 5), (3, 6), (4, 2), (4, 4), (4, 6), (5, 4), (5, 5), (5, 6), (6, 3), (6, 4), (6, 5)
20	1	Base Points + (1, 4), (3, 6), (4, 4), (4, 5), (4, 6), (5, 3), (5, 4), (5, 5), (6, 1), (6, 5), (6, 6)
20	1	Base Points + (2, 4), (3, 6), (4, 4), (4, 5), (4, 6), (5, 1), (5, 5), (5, 6), (6, 3), (6, 4), (6, 5)
21	1	Base Points + (1, 6), (2, 4), (3, 5), (4, 1), (4, 4), (4, 5), (5, 2), (5, 5), (5, 6), (6, 3), (6, 4), (6, 6)
21	1	Base Points + (1, 4), (2, 6), (3, 5), (4, 1), (4, 4), (4, 5), (5, 3), (5, 4), (5, 6), (6, 2), (6, 5), (6, 6)
21	1	Base Points + (1, 5), (2, 4), (3, 6), (4, 2), (4, 5), (4, 6), (5, 1), (5, 4), (5, 5), (6, 3), (6, 4), (6, 6)

Table 5.5 (Continued) D_N -Optimal Designs for the Mixture Problem with Two Three-Component Categories While Model Is Quadratic

N	Preference Order	Design Points
22	1	Base Points + (1, 6), (2, 5), (3, 3), (3, 4), (4, 3), (4, 4), (4, 6), (5, 2), (5, 5), (5, 6), (6, 1), (6, 4), (6, 5)
23	1	Base Points + (1, 6), (2, 1), (2, 5), (3, 3), (3, 4), (4, 3), (4, 4), (4, 6), (5, 2), (5, 5), (5, 6), (6, 1), (6, 4), (6, 5)
23	1	Base Points + (1, 2), (1, 6), (2, 5), (3, 3), (3, 4), (4, 3), (4, 4), (4, 6), (5, 2), (5, 5), (5, 6), (6, 1), (6, 4), (6, 5)
24	1	Base Points + (1, 1), (1, 5), (2, 2), (2, 6), (3, 3), (3, 4), (4, 3), (4, 4), (4, 6), (5, 1), (5, 4), (5, 5), (6, 2), (6, 5), (6, 6)
24	1	Base Points + (1, 1), (1, 5), (2, 2), (2, 6), (3, 3), (3, 4), (4, 3), (4, 4), (4, 5), (5, 1), (5, 5), (5, 6), (6, 2), (6, 4), (6, 6)

maximized. The D_N-optimal design generally is not unique for each specified model. In the case that there are several D_N-optimal designs which have the same det($X^T X$) values, then the D_N-optimal designs listed in the three tables are displayed in preference order based on other criteria such as the maximum and average values of d, $d = x_0(X^T X)^{-1} x_0$, % G-efficiency and trace $(X^T X)^{-1}$. If different designs have the same values for all criteria, then they are all listed in tables.

For the model which is linear, one can observe from Table 5.3 that the D_N-optimal ($6 \leq N \leq 14$) designs consist of constituent points which are the extreme vertices of the two categories. This result matches the previous suggestion on the candidate design points for single simplex experimental region assuming that the model is linear. As expected, the D_9-optimal design for the linear model is unique, and consists of the factorial arrangement of all the extreme vertices of the two categories. They are (1, 1), (1, 2), (1, 3), (2, 1), (2, 2), (2, 3), (3, 1), (3, 2), and (3, 3). One will call these 9 points **"base points"**.

For the model with linear plus cross product terms, Table 5.4 shows that the D_N-optimal designs ($12 \leq N \leq 20$) consist of constituent points which are the extreme vertices and the midpoints of two extreme vertices in the two categories. This result also matches the previous suggestion on the candidate design points for single simplex experimental region assuming that the model is quadratic. One also observes that the "base points" are always included in all D_N-optimal designs for the model with linear plus cross product terms.

For the model which is quadratic, Table 5.5 shows that the D_N-optimal ($17 \leq N \leq 24$) designs contain constituent points which are the extreme vertices and the midpoints of edges. However this is not true when N is 16. This discovery shows that one needs face centroids as the candidate points for D-optimal designs when the model is quadratic in the mixture problem with categorized components.

5.4 Summary

Sometimes multiple-lattice designs, multiple-centroid designs and simplex-lattice by simplex-centroid designs are not feasible due to the large number of design points required. The D-optimal designs offer a much smaller number of design points than the above three designs. Methods for constructing models and candidate design points and for searching D-optimal designs are developed for the mixture problem with categorized components. A mixture problem with two three-component categories is illustrated; the D-optimal designs for linear, linear plus cross product terms, and quadratic models are obtained.

The D_N-optimal design can be nonunique for a certain model. The research also finds that face centroids need to be considered in the set of candidate points for D-optimal designs in the mixture problem with categorized components. For D_N-optimal designs other than the above three models, one can use the same approach to obtain them based on personal interest. The purpose of the research is to develop the methods to establish the models and candidate design points in order to find the D-optimal designs. The research is not intended to obtain D_N-optimal designs for every possible model and any value of N.

CHAPTER 6

DESIGNS AND MODELS USING BOTH MIXTURE COMPONENTS AND MIXTURE-RELATED VARIABLES AS DESIGN VARIABLES

Process variables are factors in an experiment that will not form any proportion of the mixture but can affect the blending properties of the components when their values are changed. Thus, the settings of process variables can be independent of each other and independent of the components in the mixtures.

For the q-component ($x_1, x_2, \ldots, x_q$) mixture experiment, the sum of the proportions of the q components is unity. This restriction makes the settings of the components in the mixture be dependent. If one transforms the q components into (q-1) variables ($w_1, w_2, \ldots, w_{q-1}$), then the (q-1) variables can be set values the same way as process variables. The (q-1) variables transformed from the q components in the mixture are called <u>mixture-related variables (MRVs)</u>.

In this chapter, designs and models using both mixture components and mixture-related variables are shown. Sections 6.1, 6.2 and 6.3 will review several transformation and design methods which are already available in the literature. Then, Section 6.4 shows the methods reviewed in these sections are applied to the mixture problem with categorized components.

6.1 Transformation from Component Variables to Mixture-Related Variables for Classical Designs

In order to apply classical designs such as factorial designs or central-composite designs on the q component variables in the mixture problem, one first has to transform the q components in the mixture into (q-1) mixture-related variables. To achieve this, the region of interest is either ellipsoidal or cuboidal inside the simplex constructed by the q components in the mixture. In the general q-component situation, an ellipsoidal region is expressible as

$$\sum_{i=1}^{q}\left(\frac{x_i - x_{0i}}{h_i}\right)^2 \le 1 \qquad (6.1)$$

where x_{0i} is the center of the interval of interest for component i and $2h_i$ represents the range of the symmetrical interval of interest for component i. Denote the vector $\boldsymbol{x_0} = (x_{01}, x_{02}, \ldots, x_{0q})$ as the center of the ellipsoidal region. Note that the centroid of the ellipsoidal region can be the centroid of the simplex. Also $x_{01} + x_{02} + \ldots + x_{0q} = 1$ is always true since $x_1 + x_2 + \ldots + x_q = 1$.

One can redefine the ellipsoidal region as a unit spherical region in another system of variables since it is much easier to work with a sphere than an ellipsoid. To obtain the unit sphere, one defines the intermediate variables v_i,

$$v_i = \frac{x_i - x_{0i}}{h_i}, \quad \text{i=1, 2, ..., q} \qquad (6.2)$$

such that the ellipsoidal region in equation (6.1) becomes a unit spherical region defined in v_i and centered at $v_i = 0,\ 1 \le i \le q$. The unit spherical region now is expressible as

$$\sum_{i=1}^{q} v_i^2 \le 1 \qquad (6.3)$$

and one has the condition that

$$\sum_{i=1}^{q} h_i v_i = 0 \tag{6.4}$$

since $\sum_{i=1}^{q}(x_i - x_{0i}) = 0$.

Equation (6.2) can be expressed in matrix notation as

$$\boldsymbol{v} = \boldsymbol{H}^{-1}(\boldsymbol{x} - \boldsymbol{x}_0) \tag{6.5}$$

where $\boldsymbol{v} = (v_1, v_2, \ldots, v_q)^T$, $\boldsymbol{x_0} = (x_{01}, x_{02}, \ldots, x_{0q})^T$ and $\boldsymbol{H}$ is the diagonal matrix $\boldsymbol{H}$ = diagonal ($h_1, h_2, \ldots, h_q$). For an experiment with N design points, let $\boldsymbol{V}$ be the N x q matrix whose u^{th} row is $\boldsymbol{v_u^T}$ where

$$\boldsymbol{v_u^T} = (\boldsymbol{x_u} - \boldsymbol{x_0})^T \boldsymbol{H}^{-1} \tag{6.6}$$

and let $\boldsymbol{X_c}$ be the N x q matrix whose u^{th} row is $(\boldsymbol{x_u} - \boldsymbol{x_0})^T$. The $\boldsymbol{X_c}$ will become

$$\boldsymbol{V} = \boldsymbol{X_c H}^{-1} \text{ or } \boldsymbol{X_c} = \boldsymbol{VH} \tag{6.7}$$

The $\boldsymbol{X_c}$ is an N x q matrix of rank q-1 since the sum of each row in $\boldsymbol{X_c}$ is zero. The rank of $\boldsymbol{V}$ is also q-1 since $\boldsymbol{H}$ is of full rank. Because the rank of the matrix $\boldsymbol{V}$ is q-1 there exists the single linear relation among the q columns of $\boldsymbol{V}$ of the form $\boldsymbol{VH1_q} = \boldsymbol{0_N}$. One can choose a q x q orthogonal matrix $\boldsymbol{T}$ (see Appendix A for a derivation of the form of $\boldsymbol{T}$) such that

$$\boldsymbol{VT} = [\boldsymbol{W}, \boldsymbol{0}] \tag{6.8}$$

where $\boldsymbol{W}$ is an N x (q-1) matrix of rank q-1, and $\boldsymbol{0}$ is an N x 1 vector of zeros. To figure out that this is possible, note that

$$\sum_{i=1}^{q}(x_i - x_{0i}) = \sum_{i=1}^{q} h_i v_i = 0$$

defines a (q-1)-dimensional linear manifold in q-space. The transformation in equation (6.8) is a rotation of the intermediate variables about the origin $\boldsymbol{v} = \boldsymbol{0}$. The rotation by $\boldsymbol{T}$ is chosen so that the constraint on the v's is expressed in the form $w_{uq} = 0$, $(1 \le u \le N)$. By ignoring this zero coordinate, one is actually projecting the q-dimensional unit sphere onto the (q-1)-dimensional manifold, producing again a unit sphere that is centered at $\boldsymbol{w} = \boldsymbol{0}$ where $\boldsymbol{w} = (w_1, w_2, \ldots, w_{q-1})$. Hence the region of interest is now a (q-1)-dimensional unit spherical region. The w_i (i=1, 2, ..., q-1) will be used to construct classical designs such as factorial designs or central-composite designs.

One can enlarge the ellipsoidal region to its maximum as long as the ellipsoidal region is inside the boundaries of the simplex. To obtain the maximum ellipsoidal region inside the simplex, one has to calculate the radius of the largest sphere centered at $\boldsymbol{w} = \boldsymbol{0}$ (which is also $\boldsymbol{v} = \boldsymbol{0}$) that will fit inside the simplex in the region space and by comparing it with $\rho = 1$, where $\rho = 1$ is the radius of the unit spherical region of interest. In order to determine the radius of the largest (q-1)-dimensional sphere, define ρ_i as the distance, measured in the w_i metric, from $\boldsymbol{w} = \boldsymbol{0}$ or $\boldsymbol{x} = \boldsymbol{x_0}$ to the closest (q-2)-dimensional face opposite the vertex where $x_i = 1$. Then, since $h_i \le x_{0i}$ define

$$\rho_i = x_{0i}\left\{\frac{1}{h_i^2} + \frac{1}{a - h_i^2}\right\}^{1/2}, \quad i=1, 2, \ldots, q \tag{6.9}$$

where $a = \sum_{i=1}^{q} h_i^2$. If

$$\rho^* = \min\{\rho_i,\ 1 \le i \le q\} \tag{6.10}$$

then ρ^* is the radius of the largest sphere. The largest sphere may be called the extended region of interest in the design space.

Once the component variables (x_i, i=1, 2, ..., q) are transformed into mixture-related variables (w_i, i=1, 2, ..., q-1) and the extended region of interest is set, one can set classical designs on the mixture-related variables. One can refer to Cornell and Good (1970) for the details of this section.

6.2 Factorial Design on Mixture-Related Variables with Ellipsoidal Region of Interest

In the q component mixture experiment, the factorial design on the q-1 mixture-related variables w_i (i=1, 2, ... q-1) is

$$
\boldsymbol{D_w} = c \begin{bmatrix} -1 & -1 & -1 & & & \\ 1 & -1 & -1 & & & \\ -1 & 1 & -1 & & & \\ 1 & 1 & -1 & & & \\ -1 & -1 & 1 & . & . & . \\ 1 & -1 & 1 & & & \\ -1 & 1 & 1 & & & \\ 1 & 1 & 1 & & & \\ . & . & . & & & \\ . & . & . & & & \\ . & . & . & & & \end{bmatrix}
$$

$$= c\ \{\boldsymbol{W} + \text{interaction terms}\} \tag{6.11}$$

where c is a scalar quantity that is called the radius multiplier. The $\boldsymbol{W}$ is a 2^{q-1} x (q-1) matrix with the elements the same as those of the first (q-1) columns of the 2^{q-1} factorial design. That is, the (q-1) columns of the $\boldsymbol{W}$ matrix are contrasts of the observed mean responses for calculating the main effects of w_i, i = 1, 2, ..., q-1. The design points according to the design matrix $\boldsymbol{D_w}$ lie on a sphere of radius $\sqrt{q-1}$. The design points are positioned symmetrically about the center $\boldsymbol{w}$ = $(w_1, w_2, \ldots, w_{q-1}) = (0, 0, \ldots, 0)$.

The size of the design in terms of the spread of the points depends on the values of the radius multiplier c. If the largest sphere inside the simplex is desired, Cornell and Good (1970) show that the radius multiplier c is

$$c = \frac{\rho^*}{\sqrt{q-1}} \tag{6.12}$$

where ρ^* is the radius of the largest sphere introduced in equation (6.10).

In Section 6.1, transformation from the q mixture components to q-1 mixture-related variables is reviewed. In order to have a factorial design on the mixture-related variables, one also has to obtain the settings of the components in the mixtures for physical experiments and which are transformed from the settings of the mixture-related variables.

Suppose $\boldsymbol{W}$ is a 2^{q-1}x (q-1) matrix with elements the same as those of the first (q-1) columns of the 2^{q-1} factorial design. That is, $\boldsymbol{W}$ is the same as $\boldsymbol{W}$ in equation (6.11) and can be the $\boldsymbol{W}$ matrix in equation (6.8). Substituting $\boldsymbol{V}$ in equation (6.7) into equation (6.8), results in

$$\boldsymbol{X_c} = [\boldsymbol{W},\ \boldsymbol{0}]\boldsymbol{T}'\boldsymbol{H} \tag{6.13}$$

where $\boldsymbol{X_c}$ is an N x q matrix of the form

$$\boldsymbol{X_c} = \begin{bmatrix} \boldsymbol{x_1} \\ \boldsymbol{x_2} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{x_N} \end{bmatrix} - \begin{bmatrix} \boldsymbol{x_0} \\ \boldsymbol{x_0} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{x_0} \end{bmatrix} \tag{6.14}$$

and $\boldsymbol{x_i}$ (i=1, 2, ..., N) is a 1 x q vector. Then applying equation (6.14) into equation (6.13), the settings of the components corresponding to the design $\boldsymbol{W}$ are

$$\begin{bmatrix} \boldsymbol{x_1} \\ \boldsymbol{x_2} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{x_N} \end{bmatrix} = \begin{bmatrix} \boldsymbol{x_0} \\ \boldsymbol{x_0} \\ \cdot \\ \cdot \\ \cdot \\ \boldsymbol{x_0} \end{bmatrix} + [\boldsymbol{W},\ \boldsymbol{0}]\boldsymbol{T}'\boldsymbol{H} \tag{6.15}$$

If one would like to perform a design with the largest sphere inside the simplex, the designed component values are

$$\begin{bmatrix} x_1 \\ x_2 \\ \cdot \\ \cdot \\ \cdot \\ x_N \end{bmatrix} = \begin{bmatrix} x_0 \\ x_0 \\ \cdot \\ \cdot \\ \cdot \\ x_0 \end{bmatrix} + c[\boldsymbol{W},\ \mathbf{0}]\boldsymbol{T}'\boldsymbol{H}$$

$$= \begin{bmatrix} x_0 \\ x_0 \\ \cdot \\ \cdot \\ \cdot \\ x_0 \end{bmatrix} + \frac{\rho^*}{\sqrt{q-1}}[\boldsymbol{W},\ \mathbf{0}]\boldsymbol{T}'\boldsymbol{H} \tag{6.16}$$

where ρ^* is shown in equation (6.10).

For example, suppose one would like to use the largest sphere inside the 3-component simplex with factorial design on the design variables w_1 and w_2 centered at $(x_1, x_2, x_3) = (1/3, 1/3, 1/3)$. The settings of the components for physical experiments are

$$\begin{bmatrix} x_{11} & x_{12} & x_{13} \\ x_{21} & x_{22} & x_{23} \\ x_{31} & x_{32} & x_{33} \\ x_{41} & x_{42} & x_{43} \end{bmatrix} = \begin{bmatrix} 1/3 & 1/3 & 1/3 \\ 1/3 & 1/3 & 1/3 \\ 1/3 & 1/3 & 1/3 \\ 1/3 & 1/3 & 1/3 \end{bmatrix} + \frac{\rho^*}{\sqrt{2}} \begin{bmatrix} -1 & -1 & 0 \\ -1 & 1 & 0 \\ 1 & -1 & 0 \\ 1 & 1 & 0 \end{bmatrix} *$$

$$\begin{bmatrix} -0.7071 & -0.40825 & 0.57735 \\ 0.7071 & -0.40825 & 0.57735 \\ 0 & 0.81650 & 0.57735 \end{bmatrix} * \begin{bmatrix} 1/6 & 0 & 0 \\ 0 & 1/6 & 0 \\ 0 & 0 & 1/6 \end{bmatrix} \tag{6.17}$$

where $\boldsymbol{T}$ is obtained through the method in Appendix A and $\boldsymbol{H}$ is assumed to be

$$\begin{bmatrix} 1/6 & 0 & 0 \\ 0 & 1/6 & 0 \\ 0 & 0 & 1/6 \end{bmatrix}$$

as long as the initial ellipsoid constructed by the constraints $\sum_{i=1}^{q}\left(\frac{x_i - x_{0i}}{h_i}\right)^2 \leq 1$ on the components is inside the simplex. The ρ_i (i=1, 2, 3) are calculated by equation (6.9) as

$$\rho_i = \frac{1}{3}\left\{\frac{1}{1/36} + \frac{1}{2/36}\right\}^{1/2} = \sqrt{6}, \quad \text{i=1, 2, 3.}$$

Then the value of ρ^* is

$$\rho^* = \min\{\rho_1, \rho_2, \rho_3\} = \sqrt{6}$$

By applying the value of ρ^* into equation (6.17), one obtains the settings of the components as

$$\begin{bmatrix} x_{11} & x_{12} & x_{13} \\ x_{21} & x_{22} & x_{23} \\ x_{31} & x_{32} & x_{33} \\ x_{41} & x_{42} & x_{43} \end{bmatrix} = \begin{bmatrix} 0.6553 & 0.2471 & 0.0976 \\ 0.4196 & 0.0114 & 0.5690 \\ 0.2471 & 0.6553 & 0.0976 \\ 0.0114 & 0.4196 & 0.5690 \end{bmatrix}$$

6.3 Factorial Arrangement on Components of Mixtures and Process Variables

Scheffe' (1963) introduces designs and regression equations including n process variables and q mixture variables. Suppose a mixture problem with 2 process variables each with 2 levels are denoted by $z_l = -1$ and $z_l = +1$ (l=1, 2). Also assume 3 components are considered in the mixture. Setting up design configurations in the process variables and mixture components involves setting up a mixture design at each point of a configuration in the process variables. For example, one may choose a simplex-centroid design for fitting the special cubic model in the mixture components

$$\eta_{sc} = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3. \quad (6.18)$$

For the two process variables with 2 levels each, a factorial arrangement is employed for fitting the model in the two process variables:

$$\eta_{pv} = \alpha_0 + \alpha_1 z_1 + \alpha_2 z_2 + \alpha_1 z_1 z_2. \quad (6.19)$$

Note that the subscript *SC* and *PV* in equations (6.18) and (6.19) are used to denote special cubic and process variables, respectively. The combined design denoted by a $2^2(z)$ by 3-component simplex-centroid is shown in Figure 6.1 and the design values are shown in Table 6.1.

The combined model for both components and process variables is

$$\eta(x,z) = \beta_1(z)x_1 + \beta_2(z)x_2 + \beta_3(z)x_3 + \beta_{12}(z)x_1x_2 + \beta_{13}(z)x_1x_3 + \beta_{23}(z)x_2x_3 + \beta_{123}(z)x_1x_2x_3 \quad (6.20)$$

where $\beta_i(z)$, $\beta_{ij}(z)$ and $\beta_{123}(z)$, i, j = 1, 2, 3, i < j, indicates they are functions of the settings of the two process variables.

Then

$$\begin{aligned}
\eta(x,z) &= \sum_{i=1}^{3}[\gamma_i^0 + \sum_{l=1}^{2}\gamma_i^l z_l + \gamma_i^{12} z_1 z_2]x_i \\
&\quad + \sum\sum_{i<j}^{3}[\gamma_{ij}^0 + \sum_{l=1}^{2}\gamma_{ij}^l z_l + \gamma_{ij}^{12} z_1 z_2]x_i x_j \\
&\quad + [\gamma_{123}^0 + \sum_{l=1}^{2}\gamma_{123}^l z_l + \gamma_{123}^{12} z_1 z_2]x_1 x_2 x_3 \\
&= \sum_{i=1}^{3}\gamma_i^0 x_i + \sum\sum_{i<j}^{3}\gamma_{ij}^0 x_i x_j + \gamma_{123}^0 x_1 x_2 x_3 \\
&\quad + \sum_{l=1}^{2}[\sum_{i=1}^{3}\gamma_i^l x_i + \sum\sum_{i<j}^{3}\gamma_{ij}^l x_i x_j + \gamma_{123}^l x_1 x_2 x_3]z_l
\end{aligned}$$

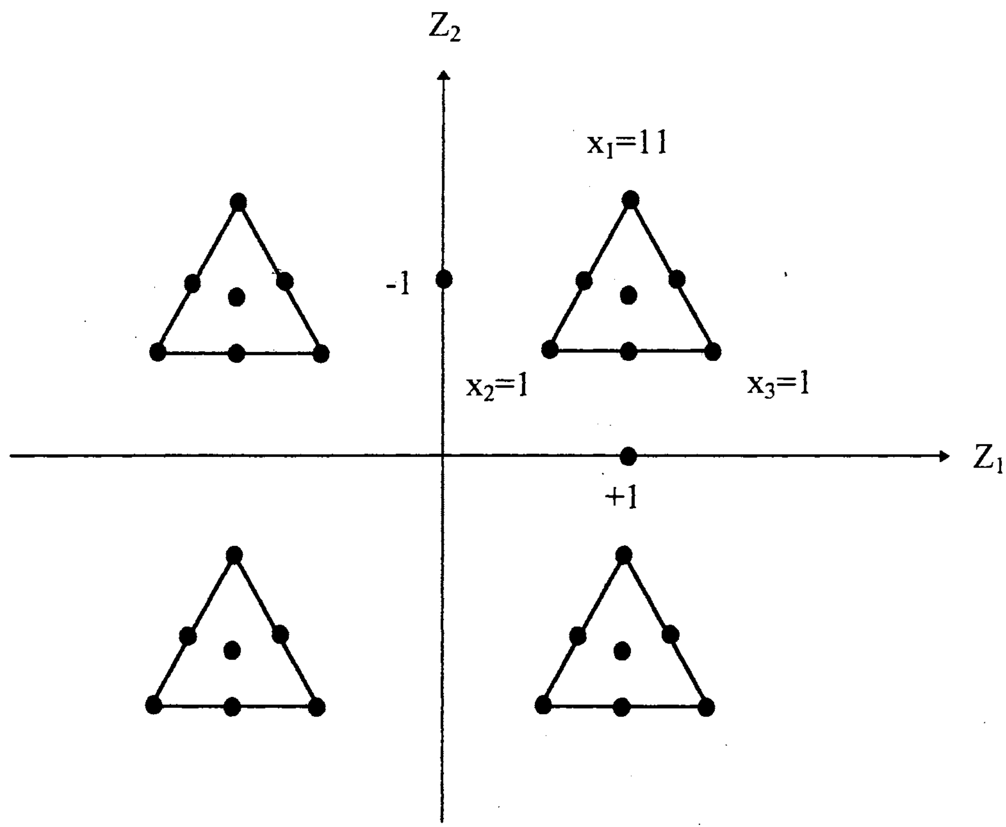


Figure 6.1. The 2^2 (z) by Three-Component Simplex-Centroid Design

Table 6.1 The $2^2(z)$ by Three-Component Simplex-Centroid Design

Run	Process Variables		Component Variables		
	z_1	z_2	x_1	x_2	x_3
1	-1	-1	1	0	0
2	-1	-1	0	1	0
3	-1	-1	0	0	1
4	-1	-1	1/2	1/2	0
5	-1	-1	1/2	0	1/2
6	-1	-1	0	1/2	1/2
7	-1	-1	1/3	1/3	1/3
8	-1	1	1	0	0
9	-1	1	0	1	0
10	-1	1	0	0	1
11	-1	1	1/2	1/2	0
12	-1	1	1/2	0	1/2
13	-1	1	0	1/2	1/2
14	-1	1	1/3	1/3	1/3
15	1	-1	1	0	0
16	1	-1	0	1	0
17	1	-1	0	0	1
18	1	-1	1/2	1/2	0
19	1	-1	1/2	0	1/2
20	1	-1	0	1/2	1/2
21	1	-1	1/3	1/3	1/3
22	1	1	1	0	0
23	1	1	0	1	0
24	1	1	0	0	1
25	1	1	1/2	1/2	0
26	1	1	1/2	0	1/2
27	1	1	0	1/2	1/2
28	1	1	1/3	1/3	1/3

$$+[\sum_{i=1}^{3}\gamma_i^{12}x_i+\sum_{i<j}^{3}\sum\gamma_{ij}^{12}x_ix_j+\gamma_{123}^{12}x_1x_2x_3]z_1z_2. \quad (6.21)$$

One observes that the number of parameters in the combined model is the same as the number of design points. Thus the estimates of the parameters can be uniquely determined by the least-squares method.

The first seven terms on the right-hand side of equation (6.21) are the linear and nonlinear blending portions of the model since these terms include the component proportions only. The remaining 21 terms represent the effects of changing the process conditions on the linear and nonlinear blending properties of mixture components. More specifically, $\sum_{i=1}^{3}\gamma_i^0 x_i$ is the linear blending proportion of the model and γ_i^0 is the expected response to component i averaged over all combinations of the levels of z_1 and z_2. The terms

$$\sum_{i<j}^{3}\sum\gamma_{ij}^0 x_ix_j+\gamma_{123}^0 x_1x_2x_3$$

are the nonlinear blending proportion of the model and γ_{ij}^0 is a measure of the nonlinear blending between components i and j averaged over all combinations of the levels of z_1 and z_2. The terms

$$[\sum_{i=1}^{3}\gamma_i^l x_i+\sum_{i<j}^{3}\sum\gamma_{ij}^l x_ix_j+\gamma_{123}^l x_1x_2x_3]z_l, \quad l=1,2$$

measure the effect of changing the level of process variable l on the linear and nonlinear blending properties of the components. Term γ_i^l measures the change in the expected response to component i for a 1-unit change in z_l, while γ_{ij}^l measures the change of nonlinear blending of components i and j for a 1-unit change in z_l. The terms

$$[\sum_{i=1}^{3}\gamma_i^{12}x_i+\sum_{i<j}^{3}\sum\gamma_{ij}^{12}x_ix_j+\gamma_{123}^{12}x_1x_2x_3]z_1z_2$$

measure the interaction effect of the two process variables on the linear and nonlinear blending properties of the three components.

Based on the methods described in Sections 6.1, 6.2 and 6.3, application of the available methods to the mixture problem with categorized components is presented in the next section.

6.4 Designs and Models Using Both Mixture Components and Mixture-Related Variables as Design Variables

In Section 6.1, transformation from components to mixture-related variables is shown. By defining an ellipsoidal region of interest inside the simplex, one sets a classical design such as a factorial design or central-composite design on the mixture-related variables. Then the corresponding component values for physical experiments are obtained through the transformation of the mixture-related variables. These are shown in Section 6.2. Also the factorial arrangement on the components of mixtures and process variables is shown in Section 6.3. The designs and models using both mixture components and mixture-related variables as design variables are developed by applying the above available methods.

In the mixture problem with categorized components, one chooses the components in any one category and transforms the components into mixture-related variables. Suppose q_1 components (x_{11}, x_{12}, ..., x_{1q}) in the first category are chosen to be transformed into q_1-1 mixture-related variables (w_{11}, w_{12}, ..., w_{1q_1-1}). Since the q_1-1 mixture-related variables are independent of the components in the other categories, they are set (or designed) independently. One can then apply any classical orthogonal design on the q_1-1 mixture-related variables. The corresponding component values of the classical design on the mixture-related variables are obtained through equation (6.15).

If there are two categories in the mixture and the components of the first category are transformed into mixture-related variables, one can apply the simplex-lattice or simplex-centroid designs on the components of the second category. If there are three or more categories in the mixture and the components of the first category are transformed into mixture-related variables, the components in the other categories form another mixture problem with categorized components. One can thus employ any available designs for the multiple-category mixture problem discussed in Chapters 3, 4 and 5 to design the components in these categories.

For example, suppose the mixture problem with two categories of 3 components is considered. The components (x_{11}, x_{12} and x_{13}) of the first category are transformed into 2 mixture-related variables (w_1 and w_2). The components in the second category are denoted by (x_{21}, x_{22}, x_{23}) and the simplex-centroid is chosen. Suppose one chooses a 2^2 factorial design on w_1 and w_2 with the largest ellipsoidal region of interest. Also, a factorial arrangement on the first group variables (w_1 and w_2) and the second group variables (x_{21}, x_{22}, x_{23}) is used. Then the combined design is denoted as a $2^2(w)$ by 3-component simplex-centroid design and is shown in Table 6.2. The model according to the illustration in Section 6.3 is

$$\begin{aligned}\eta = &\sum_{i=1}^{3}\gamma_i^0 x_{2i} + \sum_{i<j}^{3}\sum \gamma_{ij}^0 x_{2i}x_{2j} + \gamma_{123}^0 x_{21}x_{22}x_{23} \\ &+\sum_{l=1}^{2}[\sum_{i=1}^{3}\gamma_i^l x_{2i} + \sum_{i<j}^{3}\sum \gamma_{ij}^l x_{2i}x_{2j} + \gamma_{123}^l x_{21}x_{22}x_{23}]w_l \\ &+[\sum_{i=1}^{3}\gamma_i^{12} x_{2i} + \sum_{i<j}^{3}\sum \gamma_{ij}^{12} x_{2i}x_{2j} + \gamma_{123}^{12} x_{21}x_{22}x_{23}]w_1 w_2. \qquad (6.22)\end{aligned}$$

Table 6.2 The $2^2(w)$ by Three-Component Simplex-Centroid Design

Run	Mixture-Related Variables		Component Variables			Component Variables		
	w_1	w_2	x_{11}	x_{12}	x_{13}	x_{21}	x_{22}	x_{23}
1	-1	-1	0.6553	0.2471	0.0976	1	0	0
2	-1	-1	0.6553	0.2471	0.0976	0	1	0
3	-1	-1	0.6553	0.2471	0.0976	0	0	1
4	-1	-1	0.6553	0.2471	0.0976	1/2	1/2	0
5	-1	-1	0.6553	0.2471	0.0976	1/2	0	1/2
6	-1	-1	0.6553	0.2471	0.0976	0	1/2	1/2
7	-1	-1	0.6553	0.2471	0.0976	1/3	1/3	1/3
8	-1	1	0.4196	0.0114	0.5690	1	0	0
9	-1	1	0.4196	0.0114	0.5690	0	1	0
10	-1	1	0.4196	0.0114	0.5690	0	0	1
11	-1	1	0.4196	0.0114	0.5690	1/2	1/2	0
12	-1	1	0.4196	0.0114	0.5690	1/2	0	1/2
13	-1	1	0.4196	0.0114	0.5690	0	1/2	1/2
14	-1	1	0.4196	0.0114	0.5690	1/3	1/3	1/3
15	1	-1	0.2471	0.6553	0.0976	1	0	0
16	1	-1	0.2471	0.6553	0.0976	0	1	0
17	1	-1	0.2471	0.6553	0.0976	0	0	1
18	1	-1	0.2471	0.6553	0.0976	1/2	1/2	0
19	1	-1	0.2471	0.6553	0.0976	1/2	0	1/2
20	1	-1	0.2471	0.6553	0.0976	0	1/2	1/2
21	1	-1	0.2471	0.6553	0.0976	1/3	1/3	1/3
22	1	1	0.0114	0.4196	0.5690	1	0	0
23	1	1	0.0114	0.4196	0.5690	0	1	0
24	1	1	0.0114	0.4196	0.5690	0	0	1
25	1	1	0.0114	0.4196	0.5690	1/2	1/2	0
26	1	1	0.0114	0.4196	0.5690	1/2	0	1/2
27	1	1	0.0114	0.4196	0.5690	0	1/2	1/2
28	1	1	0.0114	0.4196	0.5690	1/3	1/3	1/3

Suppose a third category with 2 components is added to the above example and the $\{3^c, 2^c; 3, 2\}$ multiple-centroid design is used on the components of the second and third categories. Then the combined design is denoted by $2^2(w)$ by $\{3^c, 2^c; 3, 2\}$ and is shown in Table 6.3. The model corresponding to the design becomes

$$\begin{aligned}\eta = {} & (a_0 + a_1 w_1 + a_{21} w_2 + a_{12} w_1 w_2)* \\ & (b_1 x_{21} + b_2 x_{22} + b_3 x_{23} + b_{12} x_{21} x_{22} + b_{13} x_{21} x_{23} + b_{23} x_{22} x_{23} + b_{123} x_{21} x_{22} x_{23})* \\ & (c_1 x_{31} + c_2 x_{32} + c_{12} x_{31} x_{32}). \end{aligned} \tag{6.23}$$

The model in equation (6.23) has 84 parameters which is the same as the number of design points in Table 6.3. Thus, the parameters in equation (6.23) can be uniquely determined by the least-squares method.

The interpretations of the parameters in equation (6.22) have to be carefully stated. For example, the term γ_i^0 is the expected response to component x_{2i} averaged over all combinations of the levels of w_1 and w_2. The component blending properties in the second category which are represented by the last 21 terms in equation (6.22) are affected by the changes of the values of w_1 and w_2 rather than by the changes of the values of the process variables z_1 and z_2.

This section on the factorial arrangement of mixture components and mixture-related variables is used to illustrate how one can apply available mixture designs and models involving process variables to the mixture problem with categorized components. Other mixture designs and models involving process variables such as the split-plot design approach (Cornell, 1988), the use of fractional designs in the process variables (Cornell and Gorman, 1984), and mixture-amount experiment (Piepel and Cornell, 1985 and 1987) can also be applied to the mixture problem with categorized components as long as one transforms the components of one category into mixture-related variables.

Table 6.3 The $2^2(w)$ by $\{3^c, 3^c\,; 3, 2\}$ Design

Run	Mixture-Related Variables		Component Variables			Component Variables			Component Variables	
	w_1	w_2	x_{11}	x_{12}	x_{13}	x_{21}	x_{22}	x_{23}	x_{31}	x_{32}
1	-1	-1	0.6553	0.2471	0.0976	1	0	0	1	0
2	-1	-1	0.6553	0.2471	0.0976	1	0	0	0	1
3	-1	-1	0.6553	0.2471	0.0976	1	0	0	1/2	1/2
4	-1	-1	0.6553	0.2471	0.0976	0	1	0	1	0
5	-1	-1	0.6553	0.2471	0.0976	0	1	0	0	1
6	-1	-1	0.6553	0.2471	0.0976	0	1	0	1/2	1/2
7	-1	-1	0.6553	0.2471	0.0976	0	0	1	1	0
8	-1	-1	0.6553	0.2471	0.0976	0	0	1	0	1
9	-1	-1	0.6553	0.2471	0.0976	0	0	1	1/2	1/2
10	-1	-1	0.6553	0.2471	0.0976	1/2	1/2	0	1	0
11	-1	-1	0.6553	0.2471	0.0976	1/2	1/2	0	0	1
12	-1	-1	0.6553	0.2471	0.0976	1/2	1/2	0	1/2	1/2
13	-1	-1	0.6553	0.2471	0.0976	1/2	0	1/2	1	0
14	-1	-1	0.6553	0.2471	0.0976	1/2	0	1/2	0	1
15	-1	-1	0.6553	0.2471	0.0976	1/2	0	1/2	1/2	1/2
16	-1	-1	0.6553	0.2471	0.0976	0	1/2	1/2	1	0
17	-1	-1	0.6553	0.2471	0.0976	0	1/2	1/2	0	1
18	-1	-1	0.6553	0.2471	0.0976	0	1/2	1/2	1/2	1/2
19	-1	-1	0.6553	0.2471	0.0976	1/3	1/3	1/3	1	0
20	-1	-1	0.6553	0.2471	0.0976	1/3	1/3	1/3	0	1
21	-1	-1	0.6553	0.2471	0.0976	1/3	1/3	1/3	1/2	1/2
22	-1	1	0.4196	0.0114	0.5690	1	0	0	1	0
23	-1	1	0.4196	0.0114	0.5690	1	0	0	0	1
24	-1	1	0.4196	0.0114	0.5690	1	0	0	1/2	1/2
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
84	1	1	0.0114	0.4196	0.5690	1/3	1/3	1/3	1/2	1/2

6.5 Summary

For the mixture problem with categorized components, one can transform the components of one category (for example, the i^{th} category) in the mixtures into $(q_i - 1)$ mixture-related variables. The $(q_i - 1)$ mixture-related variables then independent of the components in the other categories. Thus the designs for the mixture problem involving process variables can be applied to the $(q_i - 1)$ mixture-related variables and one just deigns the $(q_i - 1)$ mixture-related variables as process variables. Design of a factorial arrangement on mixture variables and mixture-related variables is illustrated. One can employ not only the design but also all other mixture designs involving process variables into the mixture problem with categorized components by transforming the components of one category into mixture-related variables.

CHAPTER 7

COMPARISON OF THE DESIGNS AND MODELS FOR THE MIXTURE PROBLEM WITH CATEGORIZED COMPONENTS

Lambrakis (1968a) introduces multiple-lattice designs for the mixture problem with categorized components. In Chapter 3, multiple-centroid designs and simplex-lattice by simplex-centroid designs are developed. A method of using ratios of components in the mixtures is developed in Chapter 4. D_N-optimal designs for two three-component categories are obtained and are shown in Chapter 5. Finally, designs and models using mixture components and mixture-related variables as design variables are developed in Chapter 6. One might question which design is better versus another in certain situations. Here one would like to investigate the differences among these methods and try, if possible, to find which design is better than another. The mixture problem with two categories, one with 3 components and the other with 2 components, is illustrated for comparison among these designs.

7.1 Review of Designs for the Mixture Problem with Categorized Components

In order to compare different designs and models for the mixture problem with categorized components, six designs are reviewed. A mixture problem with three and two components in the first and second categories respectively is used as an example for all designs. The designs described in this section are compared with each other in Section 7.2.

7.1.1 The Multiple-Lattice Designs and the Associated Models

The multiple-lattice design is the first design introduced in the literature for the mixture problem with categorized components. Suppose the mixture problem with two categories is considered. The first category contains three components (x_1, x_2 and x_3) and the second category consists of two components (x_4 and x_5). Then, for the $\{3^l, 2^l; 3, 2\}$ double-lattice design, it contains $\binom{3+3-1}{3-1}\binom{2+2-1}{2-1} =$ 30 distinct design points and the experimental region for the $\{3^l, 2^l; 3, 2\}$ design is pictured in Figure 7.1. The values of the design points are shown in Table 7.1.

The corresponding model for the $\{3^l, 2^l; 3, 2\}$ design expressed in terms of the mean response to the mixture is

$$\begin{aligned}\eta = &\{\alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_{12} x_1 x_2 + \alpha_{13} x_1 x_3 + \alpha_{23} x_2 x_3 + \alpha_{123} x_1 x_2 x_3 + \\ &\gamma_{12} x_1 x_2 (x_1 - x_2) + \gamma_{13} x_1 x_3 (x_1 - x_3) + \gamma_{23} x_2 x_3 (x_2 - x_3)\} * \\ &\{\alpha_4 x_4 + \alpha_5 x_5 + \alpha_{45} x_4 x_5\} \\ = &\beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{34} x_3 x_4 + \beta_{35} x_3 x_5 + \\ &\beta_{145} x_1 x_4 x_5 + \ldots + \beta_{2345} x_2 x_3 x_4 x_5 (x_2 - x_3).\end{aligned} \tag{7.1}$$

Equation (7.1) can be rewritten in terms of the response to the mixture as

$$\begin{aligned}y = &\{\alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_{12} x_1 x_2 + \alpha_{13} x_1 x_3 + \alpha_{23} x_2 x_3 + \alpha_{123} x_1 x_2 x_3 + \\ &\gamma_{12} x_1 x_2 (x_1 - x_2) + \gamma_{13} x_1 x_3 (x_1 - x_3) + \gamma_{23} x_2 x_3 (x_2 - x_3)\} * \\ &\{\alpha_4 x_4 + \alpha_5 x_5 + \alpha_{45} x_4 x_5\} + \varepsilon \\ = &\beta_{14} x_1 x_4 + \beta_{15} x_1 x_5 + \beta_{24} x_2 x_4 + \beta_{25} x_2 x_5 + \beta_{34} x_3 x_4 + \beta_{35} x_3 x_5 + \\ &\beta_{145} x_1 x_4 x_5 + \ldots + \beta_{2345} x_2 x_3 x_4 x_5 (x_2 - x_3) + \varepsilon\end{aligned} \tag{7.2}$$

where ε is random error.

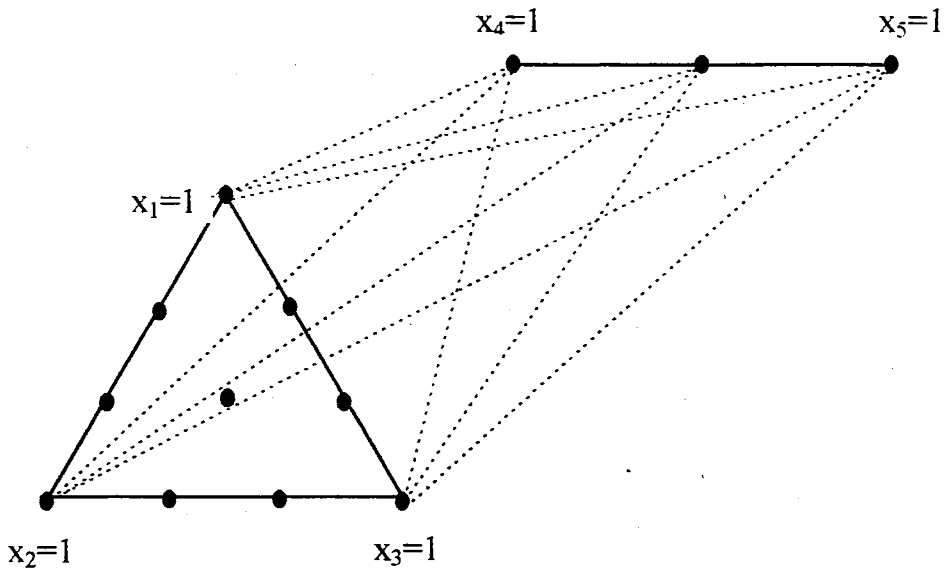


Figure 7.1 The Experimental Region of the $\{3^{l}, 2^{l}; 3, 2\}$ Design Where Each Point of the 10 Points in the First Category Is Combined with Each Point of the 3 Points in the Second Category

Table 7.1 The Design Points of the $\{3^l, 2^l; 3, 2\}$ Design

Run	Component Values			Component Values	
	x_1	x_2	x_3	x_4	x_5
1	1	0	0	1	0
2	1	0	0	0	1
3	1	0	0	1/2	1/2
4	0	1	0	1	0
5	0	1	0	0	1
6	0	1	0	1/2	1/2
7	0	0	1	1	0
8	0	0	1	0	1
9	0	0	1	1/2	1/2
10	2/3	1/3	0	1	0
11	2/3	1/3	0	0	1
12	2/3	1/3	0	1/2	1/2
13	2/3	0	1/3	1	0
14	2/3	0	1/3	0	1
15	2/3	0	1/3	1/2	1/2
16	1/3	2/3	0	1	0
17	1/3	2/3	0	0	1
18	1/3	2/3	0	1/2	1/2
19	1/3	0	2/3	1	0
20	1/3	0	2/3	0	1
21	1/3	0	2/3	1/2	1/2
22	0	2/3	1/3	1	0
23	0	2/3	1/3	0	1
24	0	2/3	1/3	1/2	1/2
25	0	1/3	2/3	1	0
26	0	1/3	2/3	0	1
27	0	1/3	2/3	1/2	1/2
28	1/3	1/3	1/3	1	0
29	1/3	1/3	1/3	0	1
30	1/3	1/3	1/3	1/2	1/2

The right side of the model in equation (7.1) contains 30 variables which is the same as the number of the distinct design points in the $\{3^l, 2^l; 3, 2\}$ design. The details for this method is shown in Section 2.8.

7.1.2 The Multiple-Centroid Designs and the Associated Models

For multiple-centroid designs developed in Chapter 3, the $\{3^c, 2^c; 3, 2\}$ design contains $(2^3-1)(2^2-1)=21$ distinct design points and the experimental region of the $\{3^c, 2^c; 3, 2\}$ design is plotted in Figure 7.2. The values of the distinct design points for the $\{3^c, 2^c; 3, 2\}$ design are shown in Table 7.2.

The model for the $\{3^c, 2^c; 3, 2\}$ design expressed in terms of the mean response to the mixture is

$$\begin{aligned}\eta &= (\alpha_1x_1+\alpha_2x_2+\alpha_3x_3+\alpha_{12}x_1x_2+\alpha_{13}x_1x_3+\alpha_{23}x_2x_3+\alpha_{123}x_1x_2x_3)*\\ &\quad(\alpha_4x_4+\alpha_5x_5+\alpha_{45}x_4x_5) \qquad (7.3)\\ &= \beta_{14}x_1x_4+\beta_{15}x_1x_5+\beta_{145}x_1x_4x_5+\ldots+\beta_{12345}x_1x_2x_3x_4x_5.\end{aligned}$$

Equation (7.3) can be rewritten in terms of the response to the mixture as

$$\begin{aligned}y &= (\alpha_1x_1+\alpha_2x_2+\alpha_3x_3+\alpha_{12}x_1x_2+\alpha_{13}x_1x_3+\alpha_{23}x_2x_3+\alpha_{123}x_1x_2x_3)*\\ &\quad(\alpha_4x_4+\alpha_5x_5+\alpha_{45}x_4x_5)+\varepsilon \qquad (7.4)\\ &= \beta_{14}x_1x_4+\beta_{15}x_1x_5+\beta_{145}x_1x_4x_5+\ldots+\beta_{12345}x_1x_2x_3x_4x_5+\varepsilon\end{aligned}$$

where ε represents random error. Sections 3.2, 3.3 and 3.4 show the details on this method.

7.1.3 The simplex-Lattice by Simplex-Centroid Designs and the Associated Models

By using the simplex-lattice by simplex-centroid design presented in Chapter 3, one finds the $\{3^l, 2^c; 3, 2\}$ design is in effect the same as the $\{3^l, 2^l; 3, 2\}$ design since the $\{2^l, 2\}$ simplex-lattice design is equivalent to the $\{2^c, 2\}$

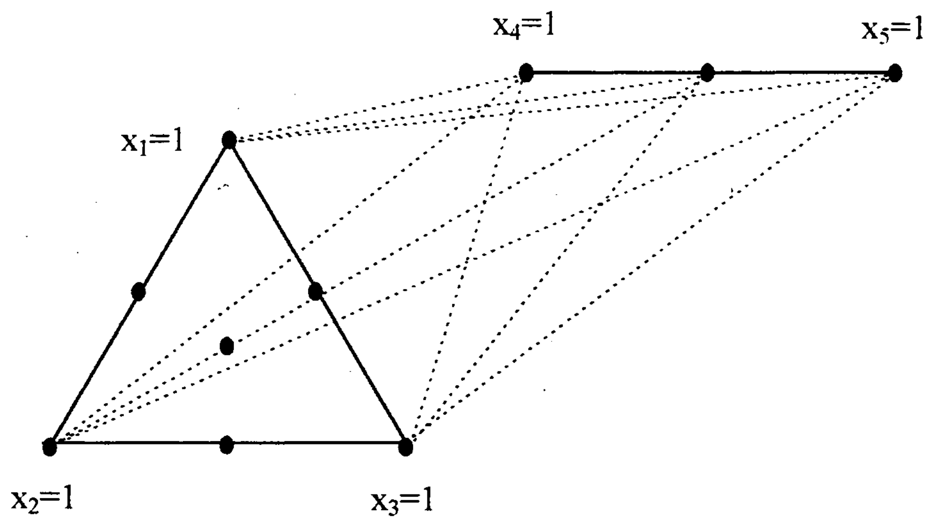


Figure 7.2 The Experimental Region of the $\{3^C, 2^C; 3, 2\}$ Design Where Each Point of the 7 Points in the First Category Is Combined with Each Point of the 3 Points in the Second Category

Table 7.2 The Design Points of the $\{3^c, 2^c; 3, 2\}$ Design

Run	Component Values			Component Values	
	x_1	x_2	x_3	x_4	x_5
1	1	0	0	1	0
2	1	0	0	0	1
3	1	0	0	1/2	1/2
4	0	1	0	1	0
5	0	1	0	0	1
6	0	1	0	1/2	1/2
7	0	0	1	1	0
8	0	0	1	0	1
9	0	0	1	1/2	1/2
10	1/2	1/2	0	1	0
11	1/2	1/2	0	0	1
12	1/2	1/2	0	1/2	1/2
13	1/2	0	1/2	1	0
14	1/2	0	1/2	0	1
15	1/2	0	1/2	1/2	1/2
16	0	1/2	1/2	1	0
17	0	1/2	1/2	0	1
18	0	1/2	1/2	1/2	1/2
19	1/3	1/3	1/3	1	0
20	1/3	1/3	1/3	0	1
21	1/3	1/3	1/3	1/2	1/2

simplex-centroid design. Also the $\{3^c, 2^l; 3, 2\}$ design is equivalent to the $\{3^c, 3^c; 3, 2\}$ design. One can refer to Section 3.5 for further details on this method.

7.1.4 The Designs Using Ratios of Components as Design Variables and the Associated Models

The method of using ratios of components as design variables is another alternative to the mixture problem with categorized components. For the mixture problem has three and two components in the first and second categories respectively, suppose the ratios are be defined as

$$r_1 = \frac{x_2}{x_1 + 0.01},\ r_2 = \frac{x_3}{x_1 + 0.01},\ r_3 = \frac{x_5}{x_4 + 0.01}. \tag{7.5}$$

The value 0.01 is used to avoid zero values in the denominator of the three ratios. One can use any small value such as 0.001. A 3^3 factorial design is then applied to the 3 ratios. The level values for each ratio are 0.1, 3.0 and 5.9 so that the experimental region is a little smaller than the multiple simplexes. One can use orthogonal design settings by letting $z_i = \frac{r_i - 3}{2.9}$, i=1, 2 and 3. Figure 7.3 shows the experimental region of the 3^3 design and Table 7.3 shows the values of the design points.

Assume a second-degree regression equation on variables z_i (i=1, 2, and 3) is fitted to the data collected at the design points of the 3^3 factorial design. Then, the second-degree regression equation is

$$\begin{aligned} y = {} & \beta_1 z_1 + \beta_2 z_2 + \beta_3 z_3 + \beta_{12} z_1 z_2 + \beta_{13} z_1 z_3 + \beta_{23} z_2 z_3 + \beta_{11} z_1^2 + \\ & \beta_{22} z_2^2 + \beta_{33} z_3^2 + \varepsilon \end{aligned} \tag{7.6}$$

where ε is random error. The details for this method are shown in Chapter 4.

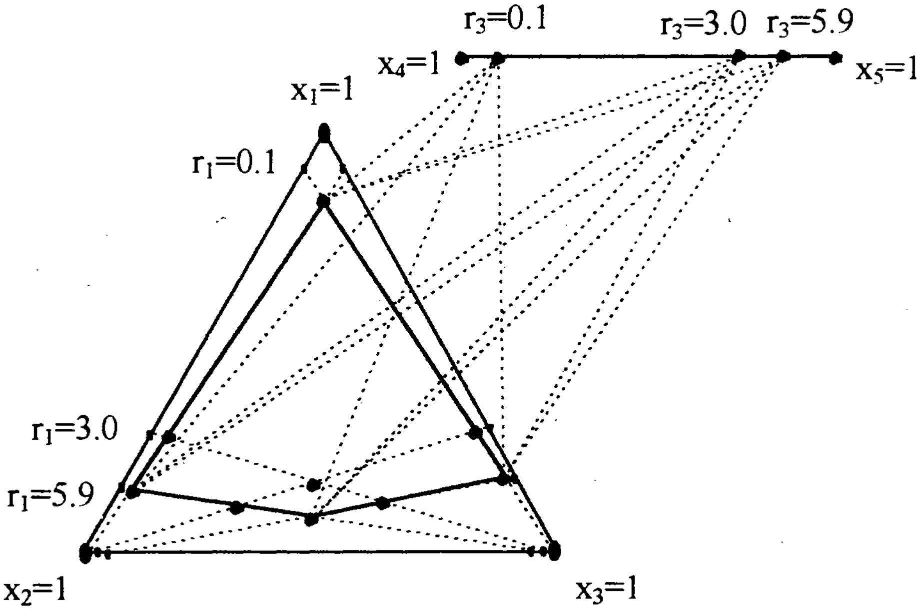


Figure 7.3 The Experimental Region of the 3^3 Factorial Design on r_1, r_2 and r_3 Defined in Equation (7.5) Where Level Values Are 0.1, 3.0 and 5.9 for Each r_i and Each Point of the 9 Points in the First Category Is Combined with Each Point of the 3 Points in the Second Category

Table 7.3 The Design Points of the 3^3 Factorial Design on Ratio Variables

Run	Ratio Values			Normalized Ratio Values			Component Values				
	r_1	r_2	r_3	z_1	z_2	z_3	x_1	x_2	x_3	x_4	x_5
1	0.1	0.1	0.1	-1	-1	-1	0.832	0.084	0.084	0.908	0.092
2	0.1	0.1	3	-1	-1	0	0.832	0.084	0.084	0.243	0.758
3	0.1	0.1	5.9	-1	-1	1	0.832	0.084	0.084	0.136	0.964
4	0.1	3	0.1	-1	0	-1	0.236	0.025	0.739	0.908	0.092
5	0.1	3	3	-1	0	0	0.236	0.025	0.739	0.243	0.758
6	0.1	3	5.9	-1	0	1	0.236	0.025	0.739	0.136	0.964
7	0.1	5.9	0.1	-1	1	-1	0.134	0.014	0.851	0.908	0.092
8	0.1	5.9	3	-1	1	0	0.134	0.014	0.851	0.243	0.758
9	0.1	5.9	5.9	-1	1	1	0.134	0.014	0.851	0.136	0.964
10	3	0.1	0.1	0	-1	-1	0.236	0.739	0.025	0.908	0.092
11	3	0.1	3	0	-1	0	0.236	0.739	0.025	0.243	0.758
12	3	0.1	5.9	0	-1	1	0.236	0.739	0.025	0.136	0.964
13	3	3	0.1	0	0	-1	0.134	0.433	0.433	0.908	0.092
14	3	3	3	0	0	0	0.134	0.433	0.433	0.243	0.758
15	3	3	5.9	0	0	1	0.134	0.433	0.433	0.136	0.964
16	3	5.9	0.1	0	1	-1	0.092	0.306	0.602	0.908	0.092
17	3	5.9	3	0	1	0	0.092	0.306	0.602	0.243	0.758
18	3	5.9	5.9	0	1	1	0.092	0.306	0.602	0.136	0.964
19	5.9	0.1	0.1	1	-1	-1	0.134	0.851	0.014	0.908	0.092
20	5.9	0.1	3	1	-1	0	0.134	0.851	0.014	0.243	0.758
21	5.9	0.1	5.9	1	-1	1	0.134	0.851	0.014	0.136	0.964
22	5.9	3	0.1	1	0	-1	0.092	0.602	0.306	0.908	0.092
23	5.9	3	3	1	0	0	0.092	0.602	0.306	0.243	0.758
24	5.9	3	5.9	1	0	1	0.092	0.602	0.306	0.136	0.964
25	5.9	5.9	0.1	1	1	-1	0.069	0.466	0.466	0.908	0.092
26	5.9	5.9	3	1	1	0	0.069	0.466	0.466	0.243	0.758
27	5.9	5.9	5.9		1	1	0.069	0.466	0.466	0.136	0.964

Note: $x_1 = \dfrac{1-0.01(r_1+r_2)}{1+r_1+r_2}$, $\quad x_2 = (x_1+0.01)r_1$, $\quad x_3 = (x_1+0.01)r_2$,

$x_4 = \dfrac{1-0.01r_3}{1+r_3}$, $\quad x_5 = (x_4+0.01)r_3$.

7.1.5 The D-optimal Designs and the Associated Models

D_N-optimal designs can also be applied to the mixture problem with categorized components. The candidate design points for the above case are shown in Table 7.4.

Assume a quadratic model on component variables is used to obtain D_N-optimal designs . The model is

$$\begin{aligned} y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{14} x_1 x_4 + \beta_{24} x_2 x_4 + \\ \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{44} x_4^2 + \varepsilon \end{aligned} \tag{7.7}$$

with the restriction that $0 \le x_1 + x_2 \le 1$ and $0 \le x_1, x_2, x_4 \le 1$. For further details on the construction of candidate design points and models, one can refer to Chapter 5.

The D_{24}-optimal, D_{42}-optimal, D_{54}-optimal and D_{60}-optimal designs for the quadratic model are obtained by the DETMAX algorithm through MIXSOFT software. These designs are used in comparison with other designs in the next section.

7.1.6 The Designs Using Mixture Components and Mixture-Related Variables as Design Variables and the Associated Models

The design using mixture components and mixture-related variables as design variables is developed in Chapter 6. Assume the three components (x_1, x_2 and x_3) of the first category are transformed into two mixture-related variables (w_1 and w_2) and a 2^2 factorial design is used on the variables w_i. Also, assume the simplex-centroid design is applied to the two components (x_4 and x_5)

Table 7.4 The Candidate Design Points for Obtaining D_N-Optimal Designs

Number	Component Values			Component Values	
	x_1	x_2	x_3	x_4	x_5
1	1	0	0	1	0
2	1	0	0	0	1
3	1	0	0	1/2	1/2
4	0	1	0	1	0
5	0	1	0	0	1
6	0	1	0	1/2	1/2
7	0	0	1	1	0
8	0	0	1	0	1
9	0	0	1	1/2	1/2
10	1/2	1/2	0	1	0
11	1/2	1/2	0	0	1
12	1/2	1/2	0	1/2	1/2
13	1/2	0	1/2	1	0
14	1/2	0	1/2	0	1
15	1/2	0	1/2	1/2	1/2
16	0	1/2	1/2	1	0
17	0	1/2	1/2	0	1
18	0	1/2	1/2	1/2	1/2
19	2/3	1/3	0	1	0
20	2/3	1/3	0	0	1
21	2/3	1/3	0	1/2	1/2
22	2/3	0	1/3	1	0
23	2/3	0	1/3	0	1
24	2/3	0	1/3	1/2	1/2
25	1/3	2/3	0	1	0
26	1/3	2/3	0	0	1
27	1/3	2/3	0	1/2	1/2
28	1/3	0	2/3	1	0
29	1/3	0	2/3	0	1
30	1/3	0	2/3	1/2	1/2
31	0	2/3	1/3	1	0
32	0	2/3	1/3	0	1
33	0	2/3	1/3	1/2	1/2
34	0	1/3	2/3	1	0
35	0	1/3	2/3	0	1
36	0	1/3	2/3	1/2	1/2
37	1/3	1/3	1/3	1	0
38	1/3	1/3	1/3	0	1
39	1/3	1/3	1/3	1/2	1/2

of the second category. A combined design on w_1, w_2, x_4 and x_5 pictured in Figure 7.4 is called a $2^2(w)$ by two-component simplex-centroid design and values of the design points are shown in Table 7.5.

The model corresponding to the $2^2(w)$ by two-component simplex-centroid design is

$$\begin{aligned} y = {} & (\gamma_4^0 x_4 + \gamma_5^0 x_5 + \gamma_{45}^0 x_4 x_5) + (\gamma_4^1 x_4 + \gamma_5^1 x_5 + \gamma_{45}^1 x_4 x_5) w_1 + \\ & (\gamma_4^2 x_4 + \gamma_5^2 x_5 + \gamma_{45}^2 x_4 x_5) w_2 + (\gamma_4^{12} x_4 + \gamma_5^{12} x_5 + \gamma_{45}^{12} x_4 x_5) w_1 w_2 + \varepsilon. \end{aligned} \tag{7.8}$$

Chapter 6 show all the details on the construction of the design and model.

The five designs and their corresponding models described above are compared with each other in the next section.

7.2 Comparison of the Five Designs for the Mixture Problem with Categorized Components

Responses for each design are generated by computer with the error term distributed as Normal (0, 1). For the $\{3^l, 2^l; 3, 2\}$ and $\{3^c, 2^c; 3, 2\}$ designs, two observations are generated at each distinct design point. Two replicates are also generated for the 3^3 factorial design on the ratios of components and the $2^2(w)$ x two-component simplex-centroid design. D_N-optimal designs, using N = 24, 42, 54 and 60, for the quadratic model on the component variables are obtained by MIXSOFT software. The number of distinct design points, the number of replicates, the total number of observations, and the degree of model in terms of x_i's for the five designs are summarized in Table 7.6.

From Table 7.6, one finds that the number of distinct design points are different for the five designs. The D_N-optimal designs are chosen such that the N values used are equal to the total number of observations in the other four designs.

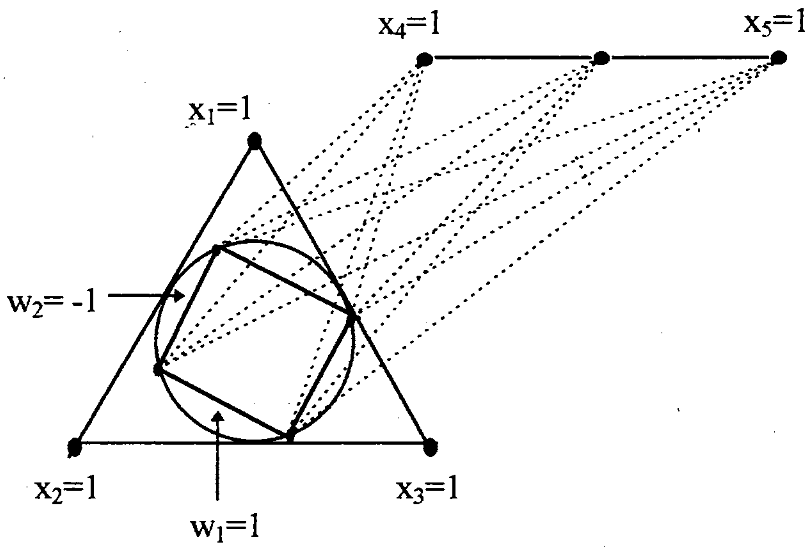


Figure 7.4 The Experimental Region of the $2^2(w)$ by Two-Component Simplex-Centroid Design Where Each Point of the 4 Points in the First Category Is Combined with Each Point of the 3 Points in the Second Category

Table 7.5 The Design Points of the $2^2(w)$ by Two-Component Simplex-Centroid Design

Run	Mixture-Related Variables		Component Values			Component Values	
	w_1	w_2	x_1	x_2	x_3	x_4	x_5
1	-1	-1	0.6553	0.2471	0.0976	1	0
2	-1	-1	0.6553	0.2471	0.0976	0	1
3	-1	-1	0.6553	0.2471	0.0976	1/2	1/2
4	-1	1	0.4196	0.0114	0.569	1	0
5	-1	1	0.4196	0.0114	0.569	0	1
6	-1	1	0.4196	0.0114	0.569	1/2	1/2
7	1	-1	0.2471	0.6553	0.0976	1	0
8	1	-1	0.2471	0.6553	0.0976	0	1
9	1	-1	0.2471	0.6553	0.0976	1/2	1/2
10	1	1	0.0114	0.4196	0.569	1	0
11	1	1	0.0114	0.4196	0.569	0	1
12	1	1	0.0114	0.4196	0.569	1/2	1/2

Table 7.6 Summary of the Five Designs Used for Comparison

Design	Number of Distinct Design Points	Number of Replicates	Total Number of Observations (N)	Degree of Model in Terms of x_i's
$\{3^l, 2^l; 3, 2\}$	30	2	60	5
$\{3^c, 2^c; 3, 2\}$	21	2	42	5
Design of Using Ratios	27	2	54	0
D_N-Optimal Designs	18	-------	24, 42, 54, 60	2
Designs of Using Components and MRVs	12	2	24	4

One observes that the corresponding models for the five designs are also different from each other. This makes it difficult to compare them with each other.

In order to compare the five designs, define

D_1 = The $\{3^l, 2^l; 3, 2\}$ design = Table 7.1

D_2 = The $\{3^c, 2^c; 3, 2\}$ design = Table 7.2

D_3 = The design using ratios = Table 7.3

D_4 = D_N-optimal designs (N = 24, 32, 54 and 60)

D_5 = The design using components and MRVs = Table 7.5

T_1 = Model corresponding to D_1 = Equation (7.2)

T_2 = Model corresponding to D_2 = Equation (7.4)

T_3 = Model corresponding to D_3 = Equation (7.6)

T_4 = Model corresponding to D_4 = Equation (7.7)

T_5 = Model corresponding to D_5 = Equation (7.8)

Now, for each model, responses are generated for each design based on one of the five models (T_1, T_2, T_3, T_4 and T_5). Then the responses generated are fitted to the regression equation corresponding to the assumed design and R_A^2 is calculated. For example, assume that T_2 is the true model to measure the relationship between response variable y and component variables (x_i's). Then, let observations be generated at the design points of the D_1 design based on the T_2 model. The responses generated are then fitted to the model (T_1) corresponding to the D_1 design and R_A^2 is calculated. One can observe the R_A^2 value when using the D_1 design while the true model is T_2 for a given set of parameter values (β) in the T_2 model. Thus, one can calculate R_A^2 by using design D_i (i = 1, 2, 3, 4 and 5) while assuming that model T_i (i =1, 2, 3, 4 and 5) is actually true. For simplicity, the parameter vector (β) is assumed to have equal element values in it and element values of 1, 3, 5, 10 and 50 are used for evaluation. The error term (ε) in the model is always assumed to be Normal (0, 1). The R_A^2 results for each β value are shown in Table 7.7.

From the R_A^2 results in Table 7.7, one observes that:

(1) In general, the larger the value of β for a given D_i (i=1, 2, 3, 4 and 5) design and Tj (j=1, 2, 3, 4 and 5) model, the larger the R_A^2 value. This is because the error term is relative small compared to the parameter values, while β is large, and thus the error term has little effect on the variation of responses.

(2) The D_1 design is always the best design among D_1, D_2, D_3 and D_4 designs for any one of the five models. Also the D_1 design is better than or equal to the D_5 design when the true model is either T_1, T_2, T_3 or T_4. However the D_1 design is not better than D_5 design when the true model is T_5. This is because the design points of the D_1 design are not inside the ellipsoidal experimental region of the D_5 design except at the point $(x_1, x_2, x_3) = (1/3, 1/3, 1/3)$.

(3) Although the D_1 design seems better than other designs in terms of R_A^2 value, one has to pay more to choose this design since it contains the maximum number of distinct design points (and total number of observations).

(4) The R_A^2 values using the D_1 or D_2 designs when the true model is either T_1 or T_2 are drastically affected by the size of the parameter values (β).

(5) The R_A^2 values using either the D_4 or D_5 design when the true model is either T_1 or T_2 can be negative when the parameter values in the true model are small. This is rarely seen in general regression cases. This is due to that the responses generated at the design points of D_4 and D_5 designs based on the model T_1 and T_2 when β is small have large variation. That is, the error term has very much effect on the responses when β is small. Another reason is that the actual model is far from the model corresponding to the design used.

(6) The R_A^2 values using the D_2 design when the T1 model is true are always the

Table 7.7 R_A^2 Values Calculated by Using D_i (i=1, 2, 3, 4 and 5) Design to Generate Data Based on T_j (j=1, 2, 3, 4 and 5) Model and Data Are Fitted to T_i Model

β	N	Design	T_1	T_2	T_3	T_4	T_5
1	60	D_1	0.3072	0.3412	1.0000	0.7383	0.6778
1	42	D_2	0.0356	0.0356	1.0000	0.6312	0.6443
1	54	D_3	0.1781	0.1794	0.8268	0.6458	0.6240
1	*****	D_4	-0.0727	-0.1025	0.9816	*****	0.7368
1	24	D_5	-0.2500	-0.2436	1.0000	0.5051	0.9682
3	60	D_1	0.4818	0.5279	1.0000	0.9615	0.9582
3	42	D_2	0.2937	0.2937	1.0000	0.9421	0.9408
3	54	D_3	0.3045	0.2985	0.9766	0.9335	0.9239
3	*****	D_4	0.1857	0.0940	0.9816	*****	0.9440
3	24	D_5	-0.4201	-0.4608	1.0000	0.9290	0.9963
5	60	D_1	0.6542	0.6823	1.0000	0.9859	0.9853
5	42	D_2	0.5275	0.5275	1.0000	0.9785	0.9777
5	54	D_3	0.4297	0.4177	0.9914	0.9701	0.9675
5	*****	D_4	0.4482	0.3592	0.9816	*****	0.9694
5	24	D_5	-0.1930	-0.3296	1.0000	0.9746	0.9987
10	60	D_1	0.8645	0.8684	1.0000	0.9965	0.9964
10	42	D_2	0.8105	0.8105	1.0000	0.9946	0.9943
10	54	D_3	0.6374	0.6450	0.9987	0.9894	0.9877
10	*****	D_4	0.7785	0.7353	0.9816	*****	0.9807
10	24	D_5	0.5410	0.4251	1.0000	0.9938	0.9997
50	60	D_1	0.9934	0.9927	1.0000	0.9999	0.9999
50	42	D_2	0.9903	0.9903	1.0000	0.9998	0.9998
50	54	D_3	0.8184	0.9640	0.9999	0.9894	0.9943
50	*****	D_4	0.9854	0.9811	0.9816	*****	0.9839
50	24	D_5	0.9845	0.9807	1.0000	0.9998	1.0000

***** : See Table 7.7 Continued.

Table 7.7 (Continued) R_A^2 Values Calculated by Using the D_4 Design(True) to Generate Data Based on the T_4 Model with Data Are Fitted to the T_4 Model

β	N	R_A^2
1	24	0.6388
1	42	0.6708
1	54	0.6723
1	60	0.7233
3	24	0.9507
3	42	0.9509
3	54	0.9571
3	60	0.9519
5	24	0.9827
5	42	0.9818
5	54	0.9818
5	60	0.9836
10	24	0.9957
10	42	0.9954
10	54	0.9954
10	60	0.9959
50	24	0.9998
50	42	0.9998
50	54	0.9998
50	60	0.9998

same as the R_A^2 values using the D_2 design when the T_2 model is true for any equal parameter values. This is seen by applying the design points of the D_2 design to the T_1 and T_2 models.

The R_A^2 values in Table 7.7 are useful as a guide to show how the R_A^2 values vary from one design to another design for a set of parameter values, while assuming a certain model can really measure the relationship between the response and the components in the mixtures.

7.3 Summary

The multiple-lattice design introduced by Lambrakis (1968a), the multiple-centroid design, designs using ratios of components as design variables, D_N-optimal designs, and designs using mixture components and mixture-related variables as design variables are compared in this chapter. The mixture problem with three components in the first category and two components in the second category is used as an example for comparison for the five designs. The experimental region for each design is pictured, except for the D_N-optimal designs.

For each design, data are generated while assuming one of the five models is true. Then the data are fitted to the regression equation corresponding to the assumed design and R_A^2 is calculated. One can see how the R_A^2 values vary from one design to another. However, one cannot conclude that a design is better than another design since the number of distinct design points (and the total number of observations) are different from one design to another. One may choose a design based on the degree of the fitted regression equation required, the precision of forecasting, and the number of design points (and the total number of observations) that one can afford.

CHAPTER 8

SUMMARY, CONCLUSION AND FUTURE WORK

A mixture experiment is an experiment in which the response is assumed to depend only on the relative proportions of the components in the mixture and not on the total amount of the mixture. A mixture-amount experiment is an experiment where the total amount of the mixture varies as well, and the response depends not only on the relative proportions of the components but also on the total amount of the mixture. The mixture problem with categorized components is an experiment where the components in the mixture can be classified into several groups by their nature.

The purpose of a mixture experiment is to study the relationship between the response y and the components $\boldsymbol{x}$ in the mixture. A regression model is used to describe the relationship between the response y and the components $\boldsymbol{x}$ in the mixture. An efficient design is desired to collect data at design points and a regression model is fitted. Parameters in the model are estimated usually by the least-squares method. One can use the fitted regression model to estimate the response at any point inside the experimental region.

8.1 FIVE DESIGNS AND THEIR CORRESPONDING MODELS DEVELOPED IN THE STUDY

Lambrakis (1968a) introduces the mixture problem with categorized components. He develops the multiple-lattice design for this problem. One can think of the mixture problem with categorized components as an experiment where each category itself forms a mixture problem with a simplex region in it. In this study, five designs and their corresponding models are developed. They are:

(1) Multiple-centroid design: First, use a simplex-centroid design for the components in each category. Then, the final multiple-centroid design is formed by the factorial arrangement of the points of the simplex-centroid design in one category with the points of the simplex-centroid design in other categories. The combined regression model for the multiple-centroid design is the multiplication of the model corresponding to the simplex-centroid design for one category with the models corresponding to the simplex-centroid designs for other categories. The total number of distinct design points of the multiple-centroid design is the same as the number of parameters in its corresponding regression model.

(2) Simplex-lattice by simplex-centroid design: First, one chooses a simplex-lattice design for the components in the first category and a simplex-centroid design for the components in the second category. Then, the final simplex-lattice by simplex-centroid design is formed by the factorial arrangement of the points of the simplex-lattice design in the first category with the points of the simplex-centroid design in the second category. The combined regression model for the simplex-lattice by simplex-centroid design is the multiplication of the model corresponding to the simplex-lattice design for the first category with the model corresponding to the simplex-centroid design for the second category. The total number of distinct design points of the simplex-lattice by simplex-centroid design is the same as the number of parameters in its corresponding regression model.

(3) Design using ratios of components as design variables. First, formulate a set of ratios for the components in each category. The number of ratios in a

category should be one less than the number of components in the category. The ratios of components can be in any form as long as there is a tie-in with at least one component in one of the other ratios in the same category. There are no ties among the ratios of different categories. After the ratios of components in all categories have been carefully defined, the level values for each ratio are assigned based on the region of interest in each category. One then normalizes the uncoded ratios into coded ratio variables which makes the coded ratio variables mutually orthogonal. A classical design such as factorial design or central composite design and its corresponding model can be applied to the coded ratio variables. An example is also used to illustrate the ratios of design using components in the mixture.

(4) D_N-optimal design: First, one has to construct the constituent points for each category. For the i^{th} category with q_i components in it, the constituent points are the union of the points in the $\{q_i^l, m_i\}$ $(m_i \leq q_i)$ designs where m_i is the degree of the model corresponding to the lattice design. The final candidate design points are the factorial arrangement of the constituent points in one category with the constituent points in other categories. Then, one will choose a model which is assumed to correctly describe the relationship between the response and the components in the mixture. The D_N-optimal design is a design with exactly N points chosen from the set of candidate points which maximizes the det($X'X$) based on the assumed model. The D_N-optimal design can have points replicated many times in it such that the number of distinct design points in the D_N-optimal design is less than N. The D_N-optimal design can offer a smaller number of design points than other designs.

(5) Design using mixture components and mixture-related variables as design variables: First, one chooses the components of one category and transforms the components of the category into mixture-related variables. The

mixture-related variables can be designed as process variables. Then, one applies a simplex design or multiple-lattice design on the components in the other categories. Finally, one applies any design and its corresponding model involving process variables into the mixture components and mixture-related variables. An example of this design is illustrated.

8.2 ACHIEVEMENTS AND FINDINGS RELATED TO THE FIVE DESIGNS DEVELOPED IN THE STUDY

In addition to the five designs and their corresponding models developed in the study, the following achievements and findings are also realized.

(1) The interpretation of the coefficients in the fitted regression model associated with the multiple-centroid design is achieved. The same logic also applies to the interpretation of the fitted regression model associated with the simplex-lattice by simplex-centroid design.

(2) The calculation of the least-squares estimates of the coefficients in the regression models associated with the multiple-lattice, multiple-centroid, and simplex-lattice by simplex-centroid designs is generalized.

(3) Face centroids are required in the set of candidate design points for obtaining D_N-optimal designs when the model is assumed to be quadratic.

(4) The D_N-optimal designs are obtained for the mixture problem with two three-component categories while the models are linear, linear plus cross product terms, and quadratic.

(5) Comparison among multiple-lattice (D_1) design (and its corresponding model T_1), multiple-centroid (D_2) design (and its corresponding model T_2), design (D_3) using ratios of components as design variables (and its corresponding model T_3), D-optimal (D_4) design (and its corresponding model T_4), and design

(D_5) using both mixture components and mixture-related variables as design variables (and its corresponding model T_5) is made. For each model, responses are generated for each design based on one of the five models. Then the responses generated are fitted to the regression equation corresponding to the design and R_A^2 is calculated.

(6) The R_A^2 value using either the D_4 or D_5 design when the true model is either T_1 or T_2 can be negative when the parameter values in the true model are small.

(7) The R_A^2 values using the D_2 design when the T1 model is true are always the same as the R_A^2 values using the D_2 design when the T_2 model is true for any equal parameter values.

(8) Generally speaking, the multiple-lattice design is better than the other designs in terms of R_A^2 value. However, one has to pay more to this design since it contains the maximum number of distinct design points. One cannot conclude which design is better than another design since the number of design points are different from one design to another.

8.3 FUTURE WORK

In this study, five designs and their corresponding models are developed in addition to the multiple-lattice design and its corresponding model which is already available in the literature. One can extend the research to the following areas:

(1) Develop designs and models for the mixture problem with categorized components while lower-bound restrictions are placed on some or all of the components of one or more categories.

(2) Develop designs and models for the mixture problem with categorized components while upper-bound restrictions are placed on some or all of the components of one or more categories.

(3) Develop designs and models for the mixture problem with categorized components when both lower-bound and upper-bound restrictions are placed on some or all of the components of one or more categories.

(4) Develop designs and models for the mixture problem with categorized components when multicomponent constraints are placed on some or all of the components of one or more categories.

(5) Develop screening designs for the mixture problem with categorized components when the number of components in some categories is large.

(6) Develop block designs for the mixture problem with categorized components.

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Appendix A

A Form of the Orthogonal Matrix $\boldsymbol{T}$

In section 6.1, in order to produce a unit sphere centered at $\boldsymbol{w} = \boldsymbol{0}$ where $\boldsymbol{w} = (w_1, w_2, \ldots, w_{q-1})'$, the matrix $\boldsymbol{T}$ is used to rotate the axes of intermediate variables, the v_i, to project the (q-1)-dimensional unit sphere onto the (q-1)-dimensional linear manifold. The transformation is shown in equation (6.8) to be

$$\boldsymbol{VT} = [\boldsymbol{W}, \boldsymbol{0}] \tag{B.1}$$

where $\boldsymbol{W}$ is an N x (q-1) matrix of rank q-1 and $\boldsymbol{0}$ is an N x 1 vector of zeros.

In order to derive a form for the matrix $\boldsymbol{T}$, let $\boldsymbol{T}$ be partitioned as

$$\boldsymbol{T} = [\boldsymbol{T_1}, \boldsymbol{T_2}] \tag{B.2}$$

where $\boldsymbol{VT_1} = \boldsymbol{W}$ and $\boldsymbol{VT_2} = \boldsymbol{0}$. The matrix $\boldsymbol{T_1}$ is q x (q-1) and $\boldsymbol{T_2}$ is q x 1.

Sufficient conditions on the matrix $\boldsymbol{T}$ are that $\boldsymbol{T}$ is orthogonal and $\boldsymbol{VT_2} = \boldsymbol{0}$. One such matrix $\boldsymbol{T_2}$ can be obtained by using the relation $\sum_{i=1}^{q} h_i x_i = 0$ to find its elements. Let

$$k_i = \frac{h_i}{(\sum_{i=1}^{q} h_i^2)^{1/2}} \tag{B.3}$$

so that $\sum_{i=1}^{q} k_i x_i = 0$. The vector $\boldsymbol{T_2}$ can be defined simply as

$$T_2 = \begin{bmatrix} k_1 \\ k_2 \\ \cdot \\ \cdot \\ \cdot \\ k_q \end{bmatrix} \tag{B.4}$$

so that $VT_2 = \mathbf{0}$. Using the h_i $(1 \le i \le q)$, the elements of the (q-1) columns of the matrix T_1 can also be constructed. The only requirement is that the matrix T be orthogonal. One such T_1 can be obtained by letting

$$T_1^* = \begin{bmatrix} -h_2 & -h_1h_3 & -h_1h_4 & \\ h_1 & -h_2h_3 & -h_1h_4 & \\ 0 & h_1^2 + h_2^2 & -h_1h_4 & \\ 0 & 0 & h_1^2 + h_2^2 + h_3^2 & \\ \cdot & \cdot & 0 & \cdot \quad \cdot \quad \cdot \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ 0 & 0 & 0 & \end{bmatrix} \tag{B.5}$$

and then normalizing the columns in equation (B.5).

For example, suppose a 3-component mixture has restrictions on components like:

$$-\frac{1}{6} \le x_1 - \frac{1}{3} \le \frac{1}{6}$$
$$-\frac{1}{6} \le x_2 - \frac{1}{3} \le \frac{1}{6}$$
$$-\frac{1}{6} \le x_3 - \frac{1}{3} \le \frac{1}{6}$$

The matrix $\boldsymbol{H}$ is thus defined as

$$\boldsymbol{H}=\begin{bmatrix} 1/6 & 0 & 0 \\ 0 & 1/6 & 0 \\ 0 & 0 & 1/6 \end{bmatrix}$$

To obtain the elements of the vector $\boldsymbol{T_2}$ in equation (B.4), the quantity $(h_1^2+h_2^2+h_3^2)^{1/2}$ equals $\dfrac{\sqrt{3}}{6}$ and thus

$$\boldsymbol{T_2}=\begin{bmatrix} \dfrac{1}{\sqrt{3}} \\ \dfrac{1}{\sqrt{3}} \\ \dfrac{1}{\sqrt{3}} \end{bmatrix}=\begin{bmatrix} 0.57735 \\ 0.57735 \\ 0.57735 \end{bmatrix}$$

From equation (B.5), $\boldsymbol{T_1^*}$ is

$$\boldsymbol{T_1^*}=\begin{bmatrix} -\dfrac{1}{6} & -\dfrac{1}{36} \\ -\dfrac{1}{6} & -\dfrac{1}{36} \\ 0 & \dfrac{2}{36} \end{bmatrix}$$

By normalizing $\boldsymbol{T_1^*}$, one will get $\boldsymbol{T_1}$ as

$$\boldsymbol{T_1}=\begin{bmatrix} -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{6}} \\ -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{6}} \\ 0 & -\dfrac{2}{\sqrt{6}} \end{bmatrix}=\begin{bmatrix} -0.7071 & -0.40825 \\ 0.7071 & -0.40825 \\ 0 & 0.81650 \end{bmatrix}$$

Combining $\boldsymbol{T_1}$ and $\boldsymbol{T_2}$ to get $\boldsymbol{T}$ results in

$$\boldsymbol{T}=\begin{bmatrix} -0.7071 & -0.40825 & 0.57735 \\ 0.7071 & -0.40825 & 0.57735 \\ 0 & 0.81650 & 0.57735 \end{bmatrix}$$

One can check the orthogonality of $\boldsymbol{T}=[\boldsymbol{T_1},\boldsymbol{T_2}]$ by verifying that $\boldsymbol{TT'}=\boldsymbol{T'T}=\boldsymbol{I}$ where $\boldsymbol{I}$ is the identity matrix.

Appendix B.1

A SAS Program for Calculating R_A^2 Value

```
*************************************************************
```

This program generates data using the D1 (multiple-lattice) design assuming T1 (The model corresponding to the D1 design) is the true model. Data generated are then fitted into the T1 model. Then the parameters in the T1 model are estimated and R_A^2 value is calculated. The components x1, x2 and x3 are the components in the first category and x4 and x5 are the components in the second category.

```
*************************************************************
```

```
data;
input x1 x2 x3 x4 x5;
ran=rannor(12);
y=50*((x1+x2+x3+x1*x2+x1*x3+x2*x3+x1*x2*x3+x1*x2*(x1-x2)+
      x1*x3*(x1-x3)+x2*x3*(x2-x3))*(x4+x5+x4*x5))+ran;
a=x1*x4;
b=x1*x5;
c=x1*x4*x5;
d=x2*x4;
e=x2*x5;
f=x2*x4*x5;
g=x3*x4;
h=x3*x5;
```

```
i=x3*x4*x5;
j=x1*x2*x4;
k=x1*x2*x5;
l=x1*x2*x4*x5;
m=x1*x3*x4;
n=x1*x3*x5;
p=x1*x3*x4*x5;
q=x2*x3*x4;
r=x2*x3*x5;
s=x2*x3*x4*x5;
t=x1*x2*x3*x4;
u=x1*x2*x3*x5;
v=x1*x2*x3*x4*x5;
w=x1*x2*(x1-x2)*x4;
x=x1*x2*(x1-x2)*x5;
z=x1*x2*(x1-x2)*x4*x5;
aa=x1*x3*(x1-x3)*x4;
ab=x1*x3*(x1-x3)*x5;
ac=x1*x3*(x1-x3)*x4*x5;
ad=x2*x3*(x2-x3)*x4;
ae=x2*x3*(x2-x3)*x5;
af=x2*x3*(x2-x3)*x4*x5;
cards;
1 0 0 1 0
0 1 0 1 0
0 0 1 1 0
0.667 0.333 0 1 0
```

0.667 0 0.333 1 0

0.333 0.667 0 1 0

0.333 0 0.667 1 0

0 0.667 0.333 1 0

0 0.333 0.667 1 0

0.333 0.333 0.333 1 0

1 0 0 0 1

0 1 0 0 1

0 0 1 0 1

0.667 0.333 0 0 1

0.667 0 0.333 0 1

0.333 0.667 0 0 1

0.333 0 0.667 0 1

0 0.667 0.333 0 1

0 0.333 0.667 0 1

0.333 0.333 0.333 0 1

1 0 0 0.5 0.5

0 1 0 0.5 0.5

0 0 1 0.5 0.5

0.667 0.333 0 0.5 0.5

0.667 0 0.333 0.5 0.5

0.333 0.667 0 0.5 0.5

0.333 0 0.667 0.5 0.5

0 0.667 0.333 0.5 0.5

0 0.333 0.667 0.5 0.5

0.333 0.333 0.333 0.5 0.5

1 0 0 1 0

0 1 0 1 0

0 0 1 1 0

0.667 0.333 0 1 0

0.667 0 0.333 1 0

0.333 0.667 0 1 0

0.333 0 0.667 1 0

0 0.667 0.333 1 0

0 0.333 0.667 1 0

0.333 0.333 0.333 1 0

1 0 0 0 1

0 1 0 0 1

0 0 1 0 1

0.667 0.333 0 0 1

0.667 0 0.333 0 1

0.333 0.667 0 0 1

0.333 0 0.667 0 1

0 0.667 0.333 0 1

0 0.333 0.667 0 1

0.333 0.333 0.333 0 1

1 0 0 0.5 0.5

0 1 0 0.5 0.5

0 0 1 0.5 0.5

0.667 0.333 0 0.5 0.5

0.667 0 0.333 0.5 0.5

0.333 0.667 0 0.5 0.5

0.333 0 0.667 0.5 0.5

0 0.667 0.333 0.5 0.5

```
0 0.333 0.667 0.5 0.5
0.333 0.333 0.333 0.5 0.5
;
proc reg;
  model y = a b c d e f g h i j k l m n p q r s t u v w x z aa ab
        ac ad ae af/noint;
proc reg;
  model y = b c d e f g h i j k l m n p q r s t u v w x z
        aa ab ac ad ae af;
run;
```

Appendix B.2

A SAS Program for Calculating R_A^2 Value

****

This program generates data using the D2 (multiple-centroid) design assuming T1 (The model corresponding to the multiple-lattice design) is the true model. Data generated are then fitted into the T2 model (The model corresponding to the multiple-centroid design). Then the parameters in the T2 model are estimated and R_A^2 value is calculated. The components x1, x2 and x3 are the components in the first category and x4 and x5 are the components in the second category.

****

```
data;
input x1 x2 x3 x4 x5;
ran=rannor(12);
y=50*((x1+x2+x3+x1*x2+x1*x3+x2*x3+x1*x2*x3+x1*x2*(x1-x2)+
        x1*x3*(x1-x3)+x2*x3*(x2-x3))*(x4+x5+x4*x5))+ran;
a=x1*x4;
b=x1*x5;
c=x1*x4*x5;
d=x2*x4;
e=x2*x5;
f=x2*x4*x5;
g=x3*x4;
```

```
h=x3*x5;
i=x3*x4*x5;
j=x1*x2*x4;
k=x1*x2*x5;
l=x1*x2*x4*x5;
m=x1*x3*x4;
n=x1*x3*x5;
p=x1*x3*x4*x5;
q=x2*x3*x4;
r=x2*x3*x5;
s=x2*x3*x4*x5;
t=x1*x2*x3*x4;
u=x1*x2*x3*x5;
v=x1*x2*x3*x4*x5;
cards;
1 0 0 1 0
0 1 0 1 0
0 0 1 1 0
0.5 0.5 0 1 0
0.5 0 0.5 1 0
0 0.5 0.5 1 0
0.333 0.333 0.333 1 0
1 0 0 0.5 0.5
0 1 0 0.5 0.5
0 0 1 0.5 0.5
0.5 0.5 0 0.5 0.5
0.5 0 0.5 0.5 0.5
```

0 0.5 0.5 0.5 0.5

0.333 0.333 0.333 0.5 0.5

1 0 0 0 1

0 1 0 0 1

0 0 1 0 1

0.5 0.5 0 0 1

0.5 0 0.5 0 1

0 0.5 0.5 0 1

0.333 0.333 0.333 0 1

1 0 0 1 0

0 1 0 1 0

0 0 1 1 0

0.5 0.5 0 1 0

0.5 0 0.5 1 0

0 0.5 0.5 1 0

0.333 0.333 0.333 1 0

1 0 0 0.5 0.5

0 1 0 0.5 0.5

0 0 1 0.5 0.5

0.5 0.5 0 0.5 0.5

0.5 0 0.5 0.5 0.5

0 0.5 0.5 0.5 0.5

0.333 0.333 0.333 0.5 0.5

1 0 0 0 1

0 1 0 0 1

0 0 1 0 1

0.5 0.5 0 0 1

```
0.5 0 0.5 0 1
0 0.5 0.5 0 1
0.333 0.333 0.333 0 1
;
proc reg;
  model y = a b c d e f g h i j k l m n p q r s t u v/noint;
proc reg;
  model y = b c d e f g h i j k l m n p q r s t u v;
run;
```

2

VITA

Jengjung Fang

Candidate for the Degree of

Doctor of Philosophy

Thesis: DESIGNS AND MODELS FOR THE MIXTURE PROBLEM WITH CATEGORIZED COMPONENTS

Major Field: Industrial Engineering and Management

Biographical:

Personal data: Born in Kaoshiung, Taiwan, Republic of China, on January 26, 1961.

Education: Received Bachelor of Business degree in Industrial Management and Science from Cheng-Kung University, Tainan, Taiwan, Republic of China in June 1983. Received Master of Science in Industrial Engineering and Management from Oklahoma State University, Stillwater, Oklahoma in December 1989. Completed the requirements for the Doctor of Philosophy degree with a major in Industrial Engineering and Management in July 1995.

Experience: Employed as a teaching assistant; Oklahoma State University, Department of Industrial Engineering and Management, 1988 to 1989. Employed as an Industrial Engineer by Chinese Petroleum Corporation, Taiwan, Republic of China, 1989 to 1992. Employed as a teaching assistant; Oklahoma State University, Department of Industrial Engineering and Management, 1992 to 1995.

Professional Membership: National Engineering Honor Society, National Industrial Engineering Honor Society, American Society of Quality Control.