EXTENSIONS OF D-OPTIMAL MINIMAL DESIGNS FOR MIXTURE MODELS

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by
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Dr. Pallavi Chitturi, Dr. Robert Krafty, Dr. Stan Altan (J&J R&D)

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ABSTRACT

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Dr. Jagbir Singh, Chair

The purpose of mixture experiments is to explore the optimum blends of mixture components, which will provide desirable response characteristics in finished products. D-Optimal minimal designs have been considered for a variety of mixture models, including Scheffé's linear, quadratic, and cubic models. Usually, these D-Optimal designs are minimally supported since they have just as many design points as the number of parameters. Thus, they lack the degrees of freedom to perform the Lack of Fit tests. Also, the majority of the design points in D-Optimal minimal designs are on the boundary: vertices, edges, or faces of the design simplex.

In this dissertation, extensions of the D-Optimal minimal designs are developed to allow additional interior points in the design space to enable prediction of the entire response surface. First, the extensions of the D-Optimal minimal designs for two commonly used second-degree mixture models are considered. Second, the methodology for adding interior points to general mixture models is generalized. Also a new strategy for adding multiple interior points for symmetric mixture models is proposed. When compared with the standard mixture designs, the proposed extended D-Optimal minimal design provides higher power for the Lack of Fit tests with comparable D-efficiency.

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To my family,

My Parents Taihua Li and Ruiying Ye, My Husband Bo Cheng, Daughter Emily Cheng and Son Jerry Cheng

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CHAPTER 1

INTRODUCTION

Many experiments are being conducted in industrial, agricultural, pharmaceutical, and other branches of science as a mixture of two or more components. Some examples are as follows:

1. Fruit punch is mixed by watermelon, pineapple, and orange juices. The flavor of fruit punch depends on the percentages of watermelon, pineapple, and orange juices that are present in the punch.

2. Chemical pesticides consist of four chemicals: vendex (x_1), omite (x_2), kelthane (x_3), and dibrom (x_4). The control of the mite population is related to the component proportions.

3. Pharmaceutical tablets (Anderson Cook et al, 2004) are formed by mixing a diluent (x_1) (used to better dissolve and disperse the active ingredient), a glidant (x_2) (used to avoid clumping during the manufacturing process), a disintegrant (x_3) (helpful for dissolving the tablet during digestion) and an active component fixed at 25% of the mixture. The hardness of tablet is a function of the percentages of diluents, glidant and disintegrant in the mixture.

4. The polymeric mucoadhesive formulation (Chu et al, 1991) consists of propylene glycol (x_1), glycerol formal (x_2), and water (x_3). The viscosity of the

formulation depends on the proportion of propylene glycol, glycerol formal, and water.

Mixture experiments consist of two primary features: factors that are the components of a mixture, and a response that depends only on the proportions of components (Myers and Montgometry, 1995) and not on the amount of the mixture. The purpose of mixing components together is to see whether there exist blends of two or more components with more desirable properties than the one obtained by single component. In particular, experiments are focused on predicting the entire response surface, and it is preferable to include interior design points inside the design space. The proportion of each component in the compound will influence the overall product characteristics. Consider a product formed by q components $(x_1, x_2, \dots, x_q)$ such that without loss of generality (WLOG),

$$\sum_{i=1}^{q} x_i = 1, \quad x_i \geq 0 \ \ \forall i. \tag{1.1}$$

These conditions are fundamental restrictions for mixture experiments. This means that the mixture composition will be formed by lending nonnegative quantities of various components, and the sum of nonnegative component proportions is fixed for all design points and taken as 1. The q-proportions can be expressed as a column vector $\mathbf{x} = (x_1, \dots, x_q)'$ in the $(q-1)$-dimensional design space.

$$(x_1, \dots, x_q)' \in [0,1]^q : x_1 + \dots + x_q = 1, x_i \geq 0, i = 1, \dots, q.$$

In this context, $(x_1, x_2, \dots, x_q)$ are called design points. Throughout this dissertation, we will use $x \leftrightarrow (x_1, x_2, \dots, x_q)$ to denote any permutation of $(x_1, x_2, \dots, x_q)$. In addition, we will use $C(n,k)$ to denote $n!/[k!(n-k)!]$, when $n \geq k \geq 0$ are integers.

In mixture experiments, the main considerations are:

1. A suitable design for collecting the observations to fit the model,

2. A test to judge the adequacy of the model to represent the response surface.

There are some commonly used mixture models in q components, where ϵ is the random error with mean zero and common variance σ^2.

I. Second-degree Mixture Model

$$y_{q,2}(x) = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i<j\le q} \beta_{ij} x_i x_j + \epsilon. \tag{1.2}$$

II. Special Cubic Mixture Model

$$y_{q,3}(x) = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i<j\le q} \beta_{ij} x_i x_j + \sum_{1\le i<j<k\le q} \beta_{ijk} x_i x_j x_k + \epsilon. \tag{1.3}$$

III. Special Quartic Mixture Model

$$y_{q,3(quartic)}(x) = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i<j\le q} \beta_{ij} x_i x_j + \sum_{m=1}^{q} \sum_{1\le i<j<k\le q} \beta_{ijkm} x_i x_j x_k x_m + \epsilon. \tag{1.4}$$

IV. Full Cubic Mixture Model

$$y_{q,3(full)}(x) = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i<j\le q} \beta_{ij} x_i x_j + \sum_{1\le i<j<k\le q} \beta_{ijk} x_i x_j x_k + \sum_{1\le i<j\le q} \gamma_{ij} x_i x_j (x_i - x_j) + \epsilon. \tag{1.5}$$

V. Additive Quadratic Mixture Model

$$y_{q,2(additive)}(x) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ii} x_i^2 + \epsilon. \tag{1.6}$$

In three components, equations (1.2),(1.3),(1.4),(1.5), and (1.6) respectively will appear as follows:

I. $y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \epsilon.$

II. $y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \epsilon.$

III. $y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{1123} x_1^2 x_2 x_3 + \beta_{1223} x_1 x_2^2 x_3 + \beta_{1233} x_1 x_2 x_3^2 + \epsilon.$

IV. $y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \gamma_{12} x_1 x_2 (x_1 - x_2) + \gamma_{13} x_1 x_3 (x_1 - x_3) + \gamma_{23} x_2 x_3 (x_2 - x_3) + \epsilon.$

V. $y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \epsilon.$

The mixture models can be written as

$$\mathbf{y} = \mathbf{X}\beta + \epsilon,$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}, \mathbf{X} = \begin{bmatrix} x_{11} & \dots & x_{1p} \\ x_{21} & \dots & x_{2p} \\ \vdots & \dots & \vdots \\ x_{n1} & \dots & x_{np} \end{bmatrix}, \beta = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_p \end{bmatrix}, \epsilon = \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \vdots \\ \epsilon_n \end{bmatrix}, \tag{1.7}$$

where n is the number of design points, and p is the number of parameters in the model. In this model, $\mathbf{y}$ represents the response vector, $\mathbf{X}$ is the design matrix, β is a vector of unknown parameters (or regression coefficients), and ϵ is a vector of random error terms, which are normally and independently distributed with mean zero and common variance σ^2. Assume $\mathbf{X'X}$ is a non-singular matrix, the least square estimator of β is $\hat{\beta} = (\mathbf{X'X})^{-\mathbf{1}}\mathbf{X'y}$ with dispersion matrix $\sigma^2(\mathbf{X'X})^{-\mathbf{1}}$, where $\mathbf{X'X}$ is the Fisher information matrix. Optimal designs have been developed for different mixture models. Kiefer and Wolfowitz (1959) established a theoretical framework for optimal design criteria. Silvey (1980), and Atkinson and Donev (1992) described the most commonly used design criteria.

Some popular criteria are:

a. A-*optimality*, which seeks to minimize the trace of $(\mathbf{X'X})^{-\mathbf{1}}$.

b. D-*optimality*, which seeks to maximize the determinant of $\mathbf{X'X}$, or equivalently minimizes the determinant of $(\mathbf{X'X})^{-\mathbf{1}}$. This criterion minimizes the variance of $\beta_{\mathbf{i}}$.

c. G-*optimality*, which seeks to minimize the maximum prediction variance over a specified set of design points.

d. V-*optimality*, which seems to minimize the average prediction variance over a specified set of design points.

Among those optimality criteria, D-*optimality* is the most widely used criterion and will be used in this dissertation.

1.1 Motivation to the Problem

Numerous design procedures have been developed to address the problem of model misspecification (too many regressors or too few regressors) for normal, logistic, and nonlinear models. Little work has been done to address the problem of model misspecification for mixture models. Usually the optimal designs for mixture models are minimally supported designs, where the number of design points is equal to the number of parameters in the model. In such designs, the Lack of Fit (LOF) test cannot be performed since there are no additional degrees of freedom available. In other words, minimal support designs lack the ability to check whether the model fits the data well and to estimate the parameters with greater precision. We need to add at least one additional design point to test for the LOF.

Most optimal design algorithms for mixture experiments select additional design points from a pre-generated candidate set. Also the majority of the design points are usually the boundary points (e.g., vertices, edges, faces) of the design space with one or more components equal to zero. However, more and more experiments are interested in predicting the entire response surface, and it is necessary and preferable to include more interior design points. The additional points are not replicates of the existing design points. They are inside the design space with all components greater than zero, and when used to test the adequacy of the model, they would enhance the power of the test.

1.2 Scope of this Dissertation

This dissertation focuses on the statistical methodology of adding interior points to the D-Optimal minimal designs for general mixture models, including a wide subclass of symmetric mixture models. There are a total of seven chapters.

Following the introduction in Chapter 1, the literature on D-Optimal minimal designs, standard designs for mixture experiment, and optimal designs for the LOF testing are reviewed in Chapter 2.

In the third chapter, we consider a special mixture model: second-degree mixture model with main effects and two factor interactions including one common factor. We begin with adding one additional interior point based on D-Optimal minimal design, and continue to add more points sequentially.

In Chapter 4, we extend the methodology to a widely used Scheffé's second-degree mixture model. The triangular association scheme is introduced to solve the additional interior points.

In Chapter 5, we generalize the methodology of adding interior points to D-Optimal minimal designs for general mixture models, and investigate multiple interior design points for symmetric mixture models. For commonly used symmetric mixture models, such as the second-degree mixture mode, additive quadratic model, and special cubic models, multiple interior points are provided for a practical useful range of factors.

In the sixth chapter, we explore the power of testing for LOF for various mixture models, and compare our proposed designs with standard designs by simulation. We also apply the methodology to mixture experiments with constraints on the component proportions.

Finally, we conclude with remarks and future research work in Chapter 7.

CHAPTER 2

LITERATURE REVIEW

2.1 D-Optimal Minimal Designs

Cost restrictions often make it desirable to use as few design points as possible for a particular problem. Then, the standard approach is to construct a D-Optimal minimal design. D-Optimal minimal design contains minimal support design points, that is, the number of design points is equal to the number of parameters in the model. Chan (2000) summarized known optimal designs for various mixture models. For example, Kiefer (1961) found that the $\{q, 2\}$ simplex-lattice design is the D-Optimal design for Scheffé's second-degree model (1.2); Kiefer (1961) proved that the $\{q, 3\}$ simplex-centroid design is the D-Optimal design for Scheffé's special cubic model (1.3). Since those designs are usually minimally supported, they do not have additional degrees of freedom to test for LOF.

2.2 Standard Designs for Mixture Experiments

In mixture experiments, the design space with q factors is a regular-sided hyperplane with q vertices in a $(q - 1)$-dimensional simplex space. There are a number of standard mixture designs. Scheffé (1958) first introduced the $\{q, m\}$ simplex-lattice design, which consists of points by the combination of the component proportions: the proportions by each component take the $(m+1)$ equally spaced values $x_i = 0, 1/m, 2/m, \ldots, 1$ for $i = 1, 2, \ldots, q$. All possible combinations of the components are used. For example, a $\{3, 2\}$ simplex-lattice design consists of six points. Each x_i may take three possible values $x_i = 0, 1/2, 1$ with six possible design points on the boundary of triangular space: $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$, and $(0, 1/2, 1/2)$. The number of points in the $\{q, m\}$ simplex-lattice design is $C(q+m-1, m)$. Another popular design is the simplex-centroid design (Scheffé, 1963). It consists all possible $2^q - 1$ points with q permutations of $x \leftrightarrow (1, 0, \ldots, 0)$, $C(q, 2)$ permutations of $x \leftrightarrow (1/2, 1/2, \ldots, 0)$, $\ldots$, and the overall centroid $(1/q, 1/q, \ldots, 1/q)$. For $q = 3$, the simplex-centroid design consists of seven points: $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$, $(0, 1/2, 1/2)$ and $(1/3, 1/3, 1/3)$. The $\{q, m\}$ simplex-lattice and q-component simplex-centroid designs are boundary (e.g., vertices, edges, faces) designs with the exception of the overall centroid. The points of these designs are positioned on the boundaries of the simplex factor space. Snee and Marquardt (1976) proposed simplex screening designs that contain $2q+1$ or $3q+1$ points. The $2q+1$ point design consists of q vertices of $x \leftrightarrow (1, 0, \ldots, 0)$, the overall centroid point $(1/q, 1/q, \ldots, 1/q)$, and the q interior points $x \leftrightarrow (\frac{q+1}{2q}, \frac{1}{2q}, \ldots, \frac{1}{2q})$. Sometimes it also includes q 'end effect' points $x \leftrightarrow (0, \frac{1}{q-1}, \ldots, \frac{1}{q-1})$. The inclusion of the end effect points results in a $(3q+1)$-point design. For $q = 3$, the $2q+1$ design contains seven design points: $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(1/3, 1/3, 1/3)$, $(2/3, 1/6, 1/6)$, $(1/6, 2/3, 1/6)$ and $(1/6, 1/6, 2/3)$. And $3q+1$ designs contains three additional design points: $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$. There are some other designs that contain $2q+1$ points; for example, one design containing q vertices of $x \leftrightarrow (1, 0, \ldots, 0)$, q interior points $x \leftrightarrow (\frac{1}{2q}, \frac{1}{2q(q-1)}, \ldots, \frac{1}{2q(q-1)})$, and overall centroid point $(1/q, 1/q, \ldots, 1/q)$; another design containing q vertices of $x \leftrightarrow (1, 0, \ldots, 0)$, q interior points $x \leftrightarrow (\frac{q+1}{2q}, \frac{1}{2q}, \ldots, \frac{1}{2q})$, and overall centroid point $(1/q, 1/q, \ldots, 1/q)$. When $q = 3$, the design points are $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(1/6, 5/12, 5/12)$, $(5/12, 1/6, 5/12)$, $(5/12, 5/12, 1/6)$, $(1/3, 1/3, 1/3)$, and $(1, 0, 0)$, $(0, 1, 0)$, $(0, 0, 1)$, $(1/6, 1/6, 2/3)$, $(1/6, 2/3, 1/6)$, $(2/3, 1/6, 1/6)$, $(1/3, 1/3, 1/3)$ respectively.

Draper and Lawrence (1965a,b) first suggested using appropriate designs that minimize both bias and variance in the fitted model over the simplex region. Kurotori (1966) and Crosier (1984) introduced pseudo components, a transformation from the original components for the upper and lower bounds constraints. pseudo components are often used to reduce the ill conditioning created by the restricted size of the experimental region. McLean and Anderson (1966) developed the extreme vertices design for mixture models with constraints on some or all component proportions. This design selects all the vertices and various centroids from the subregion of the constrained space. Cornell (1990, 2002) provided a comprehensive review of the literature on mixture experiments. Optimum designs for estimation of parameters of the response functions have also been studied (Galil and Kiefer, 1977; Liu and Neudecker, 1997; Pal and Mandal, 2006, 2007; Mandal and Pal, 2008, 2013). The question of extending D-Optimal minimal designs has not been addressed for mixture models.

2.3 Optimal Design to Test For LOF

One common problem in modeling the response in the mixture experiment is testing for LOF or inadequacy of a fitted model of the form $\mathbf{E}[\mathbf{y}] = \mathbf{X}\beta$. Shelton et al. (1983) summarized three general approaches for testing for LOF. The first approach is to have replicate observations at one or more existing design points for non minimal supported designs, and to partition the residual sum of square from the fitted model into sum of squares due to LOF and sum of squares due to Pure Error. The ratio of the mean square due to LOF to the mean square due to Pure Error provides a test for LOF. If the replicate observations are not available, then this approach for testing LOF cannot be used. The second approach proposed by Green (1971), Daniel and Wood (1971), and Shillington (1979) grouped values of the response at similar settings of the independent variables. A third approach is to use 'check points' method. In this method, a model is fitted to data at the design points and additional observations are collected at other points in the experimental region. These additional points besides the design points are called check points, and the observations at these check points are used for testing for LOF only. The check point method has been investigated by Scheffé (1958), Gorman and Hinman (1962), Kurotori (1966), and Snee (1971, 1977, 1979). Shelton et al.(1983) addressed the question of how to select check point locations so that the power of Scheffeś (1958) suggested F-test for LOF is maximized. Shelton's dissertation (1982) provided an example of Kurotori's rocket fuel. The elasticity (y) was expressed as a function of the proportion of three factors - binder (x_1), oxidizer (x_2) and fuel (x_3). Shelton started with $\{3, 2\}$ simplex-lattice design with second-degree mixture model. He wanted to find one powerful additional design point. Then he chose four additional check points $(1/3, 1/3, 1/3)$, $(2/3, 1/6, 1/6)$, $(1/6, 2/3, 1/6)$, and $(1/6, 1/6, 2/3)$ to test for LOF. He compared the power of the F-test by those check points and concluded that the observed value of the response at $(1/3, 1/3, 1/3)$ achieved the highest power and therefore considered it as optimal point. We are interested in the optimal design points for general second-order mixture model, as well as some other commonly used mixture models.

For nonlinear models, Lupinacci and Raghavarao (2000) proposed adding an extra point to D-Optimal design for two-parameter logistic model to test for LOF. Lupinacci and Raghavarao (2003) also proposed adding a third point midway between the minimal D-Optimal design for the two-parameter Michaelis-Menten model. Su and Raghavarao (2012) extended their work to more commonly used nonlinear models, including logistic, probit, and Gompertz models with two, three, and four parameters.

In practice, optimization problems may be difficult or impossible to solve analytically. Box and Hunter (1963, 1965) seemed to be the first to introduce computer-aided programs in tackling this problem for nonlinear models. Mitchell (1974a, 1974b) developed a computer algorithm called DETMAX to find D-Optimal designs. It required the user to list all possible design points for the experiment. This program seeks to maximize the determinant of $\mathbf{X}'\mathbf{X}$ by adding and deleting design points until a convergence criterion is satisfied. Galil and Kiefer (1980) developed useful modification to DETMAX, which reduced the amount of time to search for an optimal design and amount of computer space. Welch (1982) developed a branch-and-bound algorithm, which constructed all possible optimal designs for a given model and a specified set of possible design points. Welch (1984) generalized Mitchell's DETMAX algorithm and developed an efficient program for minimizing either the maximum variance or the average variance of the response estimator over the design region. Snee and Marquardt (1974) constructed the XVERT program to find extreme vertices of the design region and to calculate several optimality criteria for a variety of extreme vertex designs. Snee (1979) developed the CONSIM algorithm for finding extreme vertices and centroids of mixture design regions. David and William (1984) provided a review on the development in experimental design. Montgmomery and Voth (1994) discussed the impact of leverage, influential observations, and multicollinearity in mixture experiments and illustrated how those potential problems could be evaluated and considered in selecting mixture designs. In computer-generated designs, the constrained hyperpolyhedron regions could have very nonuniform distributions of leverage, and high levels of multicollinearity may be present.

One common feature of computer-aided algorithm is to use a candidate set of design points. Heredia-Langner et al (2003, 2004) presented a technique to generate D-efficient designs using genetic algorithm (GA). GA is an iterative optimization procedure that repeatedly applies mating, selection, and mutation operations to a group of solutions until some criterion of convergence has been met. This approach eliminated the need to explicitly consider a candidate set of points. However certain optimization problems cannot be solved by means of GA, and there is no absolute assurance of finding a global optimum. In a summary, most design points from computer algorithms are boundary points (e.g. vertices, edges, faces) or 'near-boundary' points. It is preferable to find distinct interior design points away from existing points. In this dissertation, we propose additional interior points based on D-Optimal minimal designs for analysis of general mixture models, including a wide subclass of symmetric mixture models for a practical useful range of factors.

CHAPTER 3

SPECIAL SECOND-DEGREE MIXTURE MODEL: MAIN EFFECTS AND TWO-FACTOR INTERACTIONS, INCLUDING ONE COMMON FACTOR

In this chapter, we consider adding one or more interior points to a special second-degree mixture model: main effects and two factor interactions with a common factor (WLOG, x_1). For example, consider a juice factory wanting to develop a watermelon-flavored fruit punch. The flavor depends on the percentages of watermelon, pineapple, and strawberry juices and mixed blends of watermelon with pineapple and strawberry.

Such model with q components could be expressed as:

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{j=2}^{q} \beta_{1j} x_1 x_j + \epsilon. \tag{3.1}$$

Since there are $(2q - 1)$ parameters in the model, at least $(2q - 1)$ design points are needed to estimate all of them.

3.1 D-Optimal Minimal Design

Let us consider a $(2q-1)$ by $(2q-1)$ design matrix $\mathbf{X}$, partitioned as

$$\mathbf{X} = \begin{bmatrix} \mathbf{P}_q & \mathbf{Q}_{q,q-1} \\ \mathbf{R}_{q-1,q} & \mathbf{S}_{q-1} \end{bmatrix},$$

where $\mathbf{P}$ is a q by q matrix, $\mathbf{S}$ is a $(q-1)$ by $(q-1)$ matrix, $\mathbf{Q}$ is a q by $(q-1)$ matrix, and $\mathbf{R}$ is a $(q-1)$ by q matrix. Then $|\mathbf{X}| = |\mathbf{P}||\mathbf{S} - \mathbf{R}\mathbf{P}^{-1}\mathbf{Q}| \leq |\mathbf{P}||\mathbf{S}|$. The determinant $|\mathbf{X}|$ is maximized when $\mathbf{P}$ and $\mathbf{S}$ are diagonal matrices of maximum determinant value. Considering the sum of nonnegative component proportions adding up to 1, we construct the following $(2q-1)$ design points for model (3.1), which include q vertex points:

$$\mathbf{x_1}' = \begin{bmatrix} 1 & 0 & \ldots & 0 \end{bmatrix},$$

$$\mathbf{x_2}' = \begin{bmatrix} 0 & 1 & \ldots & 0 \end{bmatrix},$$

$$\ldots$$

$$\mathbf{x_q}' = \begin{bmatrix} 0 & 0 & \ldots & 1 \end{bmatrix},$$

and $(q-1)$ points with one common factor x_1:

$$\mathbf{x_{q+1}}' = \begin{bmatrix} k_1 & 1-k_1 & \ldots & 0 \end{bmatrix},$$

$$\ldots$$

$$\mathbf{x_{2q-1}}' = \begin{bmatrix} k_{q-1} & 0 & \ldots & 1-k_{q-1} \end{bmatrix},$$

where $0 < k_i < 1$ for $i = 1, 2, \ldots, q-1$.

Then the design matrix $\mathbf{X}$ becomes

$$\begin{bmatrix} 1 & 0 & \dots & 0 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \dots & \dots & \dots & \dots & \dots & \vdots \\ 0 & 0 & \dots & 1 & 0 & \dots & 0 \\ k_1 & 1-k_1 & \dots & 0 & k_1(1-k_1) & \dots & 0 \\ \vdots & \dots & \dots & \dots & \dots & \dots & \vdots \\ k_{q-1} & 0 & \dots & 1-k_{q-1} & 0 & \dots & k_{q-1}(1-k_{q-1}) \end{bmatrix},$$

where $\mathbf{P}$ is an identity matrix of order q and $\mathbf{S}$ is a diagonal matrix of order $(q-1)$. The determinant of $\mathbf{X}$ is maximized when the determinant of the diagonal matrix $\mathbf{S}$ is maximized, which implies k_1=k_2=...=k_{q-1}=$\frac{1}{2}$. Since $\mathbf{X}$ is nonsingular, maximizing the determinant of $\mathbf{X}$ is equivalent to maximizing the determinant of $\mathbf{X}'\mathbf{X}$. Therefore the D-Optimal minimal mixture design for model (3.1) is $(2q-1)$ points described above with k_1=k_2=...=k_{q-1}=$\frac{1}{2}$. However, it has no degree of freedom left to test for LOF, and we need to add at least one additional design point to enable the LOF test.

3.2 One Additional Interior Point

Suppose $\mathbf{z}_1' = (\mathbf{v}_1', \mathbf{u}_1')$ is a new interior design point to be added, where

$$\mathbf{v}_1{}' = (x_1^z, ..., x_q^z), \quad \mathbf{u}_1' = (x_1^z x_2^z, \dots, x_1^z x_q^z). \tag{3.2}$$

This additional design point is located inside the design space. The new design matrix contains $2q$ distinct design points denoted by $\mathbf{X_1}$:

$$\mathbf{X_1} = \begin{bmatrix} 1 & 0 & \dots & 0 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \dots & \dots & \dots & \dots & \dots & \vdots \\ 0 & 0 & \dots & 1 & 0 & \dots & 0 \\ 1/2 & 1/2 & \dots & 0 & 1/4 & \dots & 0 \\ \vdots & \dots & \dots & \dots & \dots & \dots & \vdots \\ 1/2 & 0 & \dots & 1/2 & 0 & \dots & 1/4 \\ x_1^z & x_2^z & \dots & x_q^z & x_1^z x_2^z & \dots & x_1^z x_q^z \end{bmatrix} = \begin{bmatrix} \mathbf{X} \\ \mathbf{z_1'} \end{bmatrix}$$

We assume the responses are independent and the variance-covariance matrix for the response vector is $\mathbf{V} = \mathbf{I}_q\sigma^2$, where $\mathbf{I_q}$ is an identity matrix of order q.

The determinant of the information matrix of design matrix $\mathbf{X_1}$ ignoring σ^2 is

$$|\mathbf{X_1'}\mathbf{V^{-1}}\mathbf{X_1}| = |\mathbf{X_1'}\mathbf{X_1}| = |\mathbf{X'}\mathbf{X}|[1 + \mathbf{z_1}'(\mathbf{X'}\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}].$$

Thus, maximizing the determinant of $|\mathbf{X_1'}\mathbf{V^{-1}}\mathbf{X_1}|$ is equivalent to maximizing $\mathbf{z}_1'(\mathbf{X'}\mathbf{X})^{-\mathbf{1}}\mathbf{z}_1$.

The matrix $\mathbf{X'}\mathbf{X}$ can be partitioned as $\begin{bmatrix} \mathbf{A_{11}} & \mathbf{A_{12}} \\ \mathbf{A_{21}} & \mathbf{A_{22}} \end{bmatrix}$, where $\mathbf{A_{11}} = \begin{bmatrix} \frac{q+3}{4} & \frac{1}{4}\mathbf{1}_{q-1}' \\ \frac{1}{4}\mathbf{1}_{q-1} & \frac{5}{4}\mathbf{I_{q-1}} \end{bmatrix}$, $\mathbf{A_{12}} = \mathbf{A_{21}'} = \begin{bmatrix} \frac{1}{8}\mathbf{1}_{q-1}' \\ \frac{1}{8}\mathbf{I_{q-1}} \end{bmatrix}$ and $\mathbf{A_{22}} = \frac{\mathbf{1}}{\mathbf{16}}\mathbf{I_{q-1}}$, and $\mathbf{1_{q-1}}$ is a column vector of $(q-1)$ ones. We note that $|\mathbf{X'}\mathbf{X}| = (\frac{1}{16})^{q-1}$, and the inverse matrix $(\mathbf{X'X})^{-\mathbf{1}}$ can be represented as

$$(\mathbf{X'X})^{-\mathbf{1}} = \begin{bmatrix} \mathbf{A} & \mathbf{B'} \\ \mathbf{B} & \mathbf{D} \end{bmatrix} \tag{3.3}$$

where $\mathbf{A} = \mathbf{I}_q$, $\mathbf{B}$ is a $(q-1) \times q$ matrix with $\mathbf{B} = \begin{bmatrix} -2\mathbf{1}_{q-1}' & -2\mathbf{I_{q-1}} \end{bmatrix}$ and $\mathbf{D} = 20\mathbf{I}_{q-1} + 4\mathbf{J}_{q-1}$. With one additional point $\mathbf{z}_1' = (\mathbf{v}_1', \mathbf{u}_1')$ for testing the LOF, we need to maximize $\mathbf{z}_1'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z}_1$ with constraints $\mathbf{v}_1'\mathbf{1} = 1$, where $\mathbf{1}$ is a column vector of ones.

In order to do that, we consider the following function:

$$L_1 = \begin{bmatrix} \mathbf{v}_1' & \mathbf{u}_1' \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} - 2\lambda(\mathbf{v}'{}_1 - 1), \tag{3.4}$$

where λ is the Lagrange multiplier.

Differentiating (3.4) with respect to (w.r.t) $\mathbf{v_1}$ and equating to zero, we get

$$\frac{\partial}{\partial \mathbf{v}_1}\{\begin{bmatrix} \mathbf{v_1}' & \mathbf{u}_1' \end{bmatrix}\}(\mathbf{X}'\mathbf{X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} = \lambda\mathbf{1}. \tag{3.5}$$

Let

$$\frac{\partial}{\partial \mathbf{v}_1}\{\begin{bmatrix} \mathbf{v_1}' & \mathbf{u_1}' \end{bmatrix}\} = \begin{bmatrix} \mathbf{I_q} & \mathbf{K_1} \end{bmatrix},$$

where $\mathbf{K}_1$ is a $q \times (q-1)$ matrix

$$\mathbf{K}_1 = \begin{bmatrix} x_2 & x_3 & \dots & x_q \\ x_1 & 0 & \dots & 0 \\ \vdots & \dots & \dots & \vdots \\ 0 & 0 & \dots & x_1 \end{bmatrix}.$$

Choose one $(q-1) \times q$ matrix $\mathbf{N}$, such that $\mathbf{N}\lambda\mathbf{1} = \mathbf{0}$,

$$\mathbf{N} = \begin{bmatrix} \text{-(q-1)} & 1 & 1 & \dots & 1 & 1 \\ 0 & 1 & -1 & \dots & 0 & 0 \\ \vdots & \dots & \dots & \dots & \dots & \vdots \\ 0 & 1 & 0 & \dots & 0 & -1 \end{bmatrix}.$$

Note that

$$\mathbf{N}\begin{bmatrix} \mathbf{I_q} & \mathbf{K}_1 \end{bmatrix} = \begin{bmatrix} \text{-(q-1)} & 1 & \dots & x_1 - (q-1)x_2 & \dots & x_1 - (q-1)x_q \\ 0 & 1 & \dots & x_1 & \dots & 0 \\ \vdots & \dots & \dots & \dots & \dots & \vdots \\ 0 & 1 & \dots & x_1 & \dots & -x_1 \end{bmatrix}, \tag{3.6}$$

and

$$(\mathbf{X}'\mathbf{X})^{-1}\begin{bmatrix}\mathbf{v_1}\\ \mathbf{u_1}\end{bmatrix} = \begin{bmatrix}\mathbf{v}-2\begin{pmatrix}x_1(1-x_1)\\ \mathbf{u}_1\end{pmatrix}\\ 2x_1(1-2x_1)\mathbf{1}_{q-1}-2(\mathbf{u_{11}}-10\mathbf{u_1})\end{bmatrix}, \tag{3.7}$$

where $\mathbf{u}_{11}' = (x_2^z, \ldots, x_q^z)$. Multiplying equation (3.5) by $\mathbf{N}$ on both sides and taking into account equations (3.6) and (3.7), we get

$$\begin{bmatrix} \text{-(q-1)} & 1 & 1 & \ldots & x_1-(q-1)x_2 & \ldots & x_1-(q-1)x_q \\ 0 & 1 & -1 & \ldots & x_1 & \ldots & 0 \\ \vdots & \ldots & \ldots & \ldots & \ldots & \ldots & \vdots \\ 0 & 1 & 0 & \ldots & x_1 & \ldots & -x_1 \end{bmatrix}(\mathbf{X}'\mathbf{X})^{-1}\begin{bmatrix}\mathbf{v_1}\\ \mathbf{u_1}\end{bmatrix} = \mathbf{0}.$$

It can be further simplified as

$$\begin{bmatrix} g \\ (1-4x_1+20x_1^2)\begin{pmatrix} x_2-x_3\\ x_2-x_4\\ \ldots\\ x_2-x_q\end{pmatrix}\end{bmatrix} = \mathbf{0}. \tag{3.8}$$

Since $1-4x_1+20x_1^2 > 0$ for any x_1, equations (3.8) imply that $x_2 = x_3 = \ldots = x_q$. Given the fact that $\mathbf{v}'\mathbf{1} = 1$, we have $x_2 = x_3 = \ldots = x_q = (1-x_1)/(q-1)$ and subsequently

$$g = (q-1)(1-2x_1)[4(q+4)x_1^2 - (q+22)x_1 + 3] = 0 \tag{3.9}$$

The solutions of equation (3.9) are as follows:

1. $x_1 = \frac{1}{2}$,
2. $x_1 = \frac{(q+22+\sqrt{q^2-4q+292})}{8(q+4)}$,
3. $x_1 = \frac{(q+22-\sqrt{q^2-4q+292})}{8(q+4)}$.

Therefore, the stationary solutions are

Solution IS: $(\frac{1}{2}, \frac{1}{2(q-1)}\mathbf{1}'_{q-1})$,

Solution IIS: $(\frac{q+22+\sqrt{q^2-4q+292}}{8(q+4)}, \frac{7q+10-\sqrt{q^2-4q+292}}{8(q+4)(q-1)}\mathbf{1}'_{q-1})$,

Solution $IIIS$: $(\frac{q+22-\sqrt{q^2-4q+292}}{8(q+4)}, \frac{7q+10+\sqrt{q^2-4q+292}}{8(q+4)(q-1)}\mathbf{1}'_{q-1})$.

Corresponding to these solutions, $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$ are:

Ia. $\frac{1}{q-1}$,

IIa. $\frac{1}{128(q-1)(q+4)^3}(q^4 + 120q^3 + 840q^2 + 8992q - 5040 + (q^3 - 6q^2 + 300q - 584)\sqrt{q^2 - 4q + 292})$,

IIIa. $\frac{1}{128(q-1)(q+4)^3}(q^4 + 120q^3 + 840q^2 + 8992q - 5040 - (q^3 - 6q^2 + 300q - 584)\sqrt{q^2 - 4q + 292})$.

When $q \leq 8$, Solution IS achieves the maximum value of $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$; when $q \geq 9$, Solution IIS gets the maximum value of $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$. Note that the difference of $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$ between solution IS and solution IIS is negligible when $q \geq 9$. Figure 3.1 sketches $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$ for three stationary solutions (IS, IIS and $IIIS$). For practical reasons, we recommend solution IS as the optimal interior design point, i.e. $(\frac{1}{2}, \frac{1}{2(q-1)}\mathbf{1}'_{q-1})$.

Let us denote

$$\mathbf{v_1'B'} + \mathbf{u_1'D} = \begin{bmatrix} w_{q+1} & w_{q+2} & \dots & w_{2q-1} \end{bmatrix},$$

where $\mathbf{B}$ and $\mathbf{D}$ are from (3.3). The Hessian matrix for stationary solutions becomes

$$\frac{\partial^2 f(\mathbf{x})}{\partial \mathbf{v} \partial \mathbf{v}'}|_{\mathbf{v}=v_1,\mathbf{u}=u_1} = 2\begin{bmatrix} \mathbf{I_q} & \mathbf{K}_1 \end{bmatrix}(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\frac{\partial}{\partial \mathbf{v}'}\{\begin{bmatrix} \mathbf{v} \\ \mathbf{u} \end{bmatrix}\} + \mathbf{2W}$$

where

$$\mathbf{W} = 2\begin{bmatrix} 0 & w_{q+1} & w_{q+2} & \dots & w_{2q-1} \\ w_{q+1} & 0 & 0 & \dots & 0 \\ w_{q+2} & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots \\ w_{2q-1} & 0 & 0 & \dots & 0 \end{bmatrix}. \tag{3.10}$$

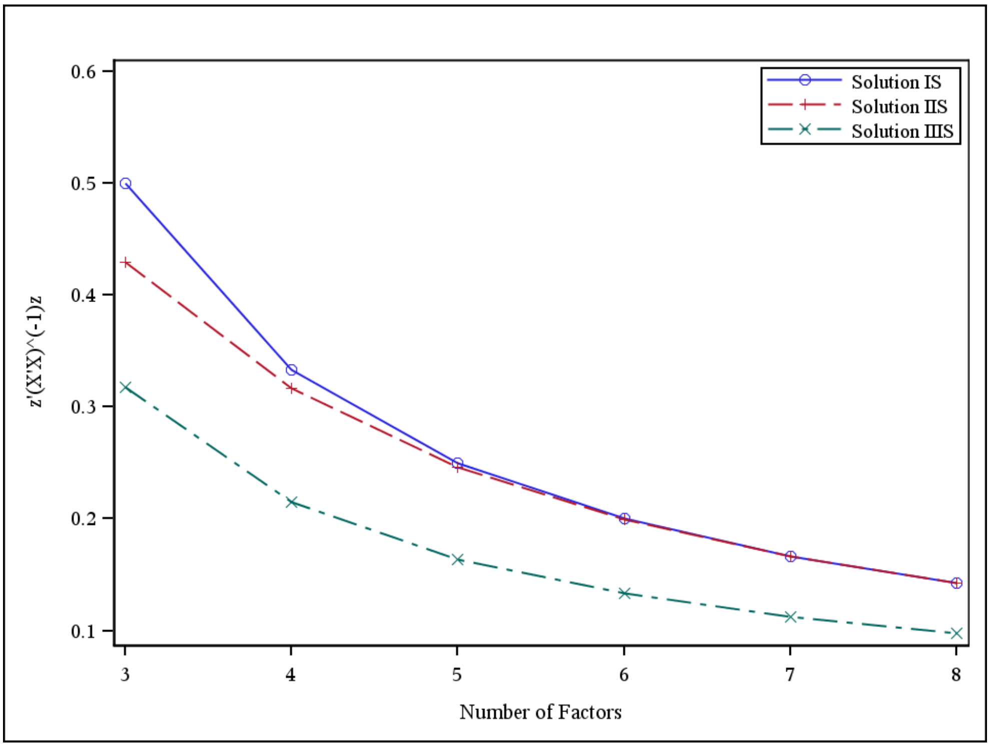

Figure 3.1: The $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$ of the Stationary Solutions for Special Second-degree Mixture Model

Since $x_2 = x_3 = \ldots = x_q$, the Hessian matrix is a function of x_1 and x_2,

$$2\begin{bmatrix} 1+4(1-x_1)(5x_2-x_1) & 2(2x_1-2x_2+20x_1x_2-4x_1^2)\mathbf{1_{q-1}}' \\ 2(2x_1-2x_2+20x_1x_2-4x_1^2)\mathbf{1_{q-1}} & (20x_1^2-4x_1+1)\mathbf{I_{q-1}}+4x_1^2\mathbf{J_{q-1}} \end{bmatrix}.$$

The Hessian matrix is not negative definite for all three stationary solutions, hence none of the stationary solutions maximizes the function $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$. In the absence of maximum values, we choose the stationary solution IS with the maximum values for $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$. Furthermore we generate the extended designs, also known as minimal plus one designs. Each design consists of one stationary interior point from solutions IS, IIS and $IIIS$, and $(2q-1)$ points from D-Optimal minimal designs. We denote those designs as IS_1, IIS_1 and $IIIS_1$, respectively. In addition, D-efficiency is calculated to compare the minimal plus one designs:

$$D_{efficiency} = 100 \times |\mathbf{X_1'X_1}|^{\mathbf{1/p}}/\mathbf{N},$$

where p is the number of parameters in the mixture model ($p = 2q - 1$), and N is the number of points used to fit the model ($N = 2q$). The ternary plots for three minimal plus one designs are displayed in Figure 3.2. Table 3.1 summarizes the stationary points and D-efficiencies for minimal plus one designs, denoted as D_1. Design IS_1 has the highest D-efficiency among these designs. We notice that the determinant of $|\mathbf{X_1'X_1}| = (\frac{1}{16})^{q-1}[1 + \mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}]$ decreases as the number of factor q increases. Thus, the difference of D-efficiency for three designs is relatively small.

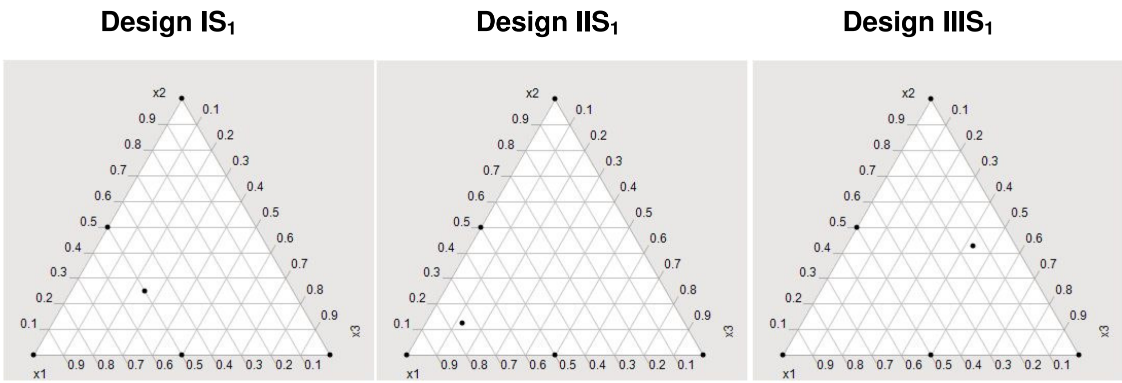

Figure 3.2: Ternary Plots for Minimal Plus One Designs for Special Second-degree Model

Table 3.1: Minimal Plus One Designs for Special Second-degree Mixture Model

Factors	Designs	One point added to D-Optimal minimal design	$\mathbf{z}_1'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z}_1$	D_1
3	IS_1	$x = (\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$	0.500	5.962*
	IIS_1	$x = (0.750, 0.125, 0.125)$	0.430	5.905
	$IIIS_1$	$x = (0.143, 0.429, 0.429)$	0.318	5.809
4	IS_1	$x = (\frac{1}{2}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6})$	0.333	3.969*
	IIS_1	$x = (0.673, 0.109, 0.109, 0.109)$	0.317	3.962
	$IIIS_1$	$x = (0, 139, 0.287, 0.287, 0.287)$	0.215	3.917
5	IS_1	$x = (\frac{1}{2}, \frac{1}{8}\mathbf{1_4'})$	0.250	2.990*
	IIS_1	$x = (0.614, 0.096\mathbf{1_4'})$	0.246	2.989
	$IIIS_1$	$x = (0.136, 0.216\mathbf{1_4'})$	0.164	2.966
6	IS_1	$x = (\frac{1}{2}, \frac{1}{10}\mathbf{1_5'})$	0.200	2.403*
	IIS_1	$x = (0.568, 0.086\mathbf{1_5'})$	0.199	2.403
	$IIIS_1$	$x = (0.132, 0.174\mathbf{1_5'})$	0.133	2.390
7	IS_1	$x = (\frac{1}{2}, \frac{1}{12}\mathbf{1_6'})$	0.167	2.010*
	IIS_1	$x = (0.531, 0.078\mathbf{1_6'})$	0.167	2.010
	$IIIS_1$	$x = (0.129, 0.145\mathbf{1_6'})$	0.112	2.003
8	IS_1	$x = (\frac{1}{2}, \frac{1}{14}\mathbf{1_7'})$	0.143	1.729*
	IIS_1	$x = (\frac{1}{2}, \frac{1}{14}\mathbf{1_7'})$	0.143	1.729
	$IIIS_1$	$x = (0.125, 0.125\mathbf{1_7'})$	0.098	1.724

Note: * Maximum D-efficiency for Designs IS_1, IIS_1, and $IIIS_1$.

3.3 Multiple Additional Interior Points

When we need more than one additional point, we add them sequentially, based on the previously added points. Denote the second additional point as $\mathbf{z_2'} = (x_1^z, x_2^z, \ldots, x_q^z, x_1^z x_2^z, \ldots, x_1^z x_q^z)$. The new design matrix becomes $\mathbf{X_2} = \begin{bmatrix} \mathbf{X_1} \\ \mathbf{z_2'} \end{bmatrix}$, where

$$\mathbf{X_1} = \begin{bmatrix} 1 & 0 & \ldots & 0 & 0 & \ldots & 0 \\ 0 & 1 & \ldots & 0 & 0 & \ldots & 0 \\ \vdots & \ldots & \ldots & \ldots & \ldots & \ldots & \vdots \\ 0 & 0 & \ldots & 1 & 0 & \ldots & 0 \\ 1/2 & 1/2 & \ldots & 0 & 1/4 & \ldots & 0 \\ \vdots & \ldots & \ldots & \ldots & \ldots & \ldots & \vdots \\ 1/2 & 0 & \ldots & 1/2 & 0 & \ldots & 1/4 \\ \frac{1}{2} & \frac{1}{2(q-1)} & \ldots & \frac{1}{2(q-1)} & \frac{1}{4(q-1)} & \ldots & \frac{1}{4(q-1)} \end{bmatrix}.$$

Similarly, maximizing the determinant of $|\mathbf{X_2'V^{-1}X_2}|$ is equivalent to maximizing $\mathbf{z}_2'(\mathbf{X_1'X_1})^{-\mathbf{1}}\mathbf{z}_2$. Since $(\mathbf{X_1'X_1}) = (\mathbf{X'X}) + \mathbf{z_1z_1'}$, and

$$(\mathbf{X_1'X_1})^{-\mathbf{1}} = (\mathbf{X'X})^{-\mathbf{1}}\{\mathbf{I} - \mathbf{z_1z_1'}(\mathbf{X'X})^{-\mathbf{1}}(\mathbf{1} + \mathbf{z_1'}(\mathbf{X'X})^{-\mathbf{1}}\mathbf{z_1})^{-\mathbf{1}}\}.$$

Recall

$$(\mathbf{X'X})^{-\mathbf{1}} = \begin{bmatrix} \mathbf{I_q} & \mathbf{M} \\ \mathbf{M'} & 20\mathbf{I_{q-1}} + 4\mathbf{J_{q-1}} \end{bmatrix},$$

where $\mathbf{M}$ is a $q \times (q-1)$ matrix with $\mathbf{M} = \begin{bmatrix} -2\mathbf{1}_{q-1}' \\ -2\mathbf{I_{q-1}} \end{bmatrix}$.

Also, we can see that

$$[1 + \mathbf{z_1'}(\mathbf{X'X})^{-\mathbf{1}}\mathbf{z_1}]^{-1} = (1 + \frac{1}{q-1})^{-1} = \frac{q-1}{q},$$

and

$$\mathbf{z_1z_1'}(\mathbf{X'X})^{-\mathbf{1}} = \begin{bmatrix} 0 & 0\mathbf{1}_{q-1}' & \frac{2}{q-1}\mathbf{1}_{q-1}' \\ 0\mathbf{1}_{q-1} & \mathbf{0_{q-1}} & \frac{2}{(q-1)^2}\mathbf{J_{q-1}} \\ 0\mathbf{1}_{q-1} & \mathbf{0_{q-1}} & \frac{1}{(q-1)^2}\mathbf{J_{q-1}} \end{bmatrix}. \tag{3.11}$$

Therefore,

$$(\mathbf{X_1'X_1})^{-1} = (\mathbf{X'X})^{-1} + \begin{bmatrix} \mathbf{0_q} & 0\mathbf{1_{q-1}}' \\ 0\mathbf{1_{q-1}} & -\frac{16}{q(q-1)}\mathbf{J_{q-1}} \end{bmatrix}$$

$$= \begin{bmatrix} \mathbf{I_q} & \mathbf{M} \\ \mathbf{M}' & 20\mathbf{I_{q-1}} + \frac{4(q^2-q-4)}{q(q-1)}\mathbf{J_{q-1}} \end{bmatrix}. \tag{3.12}$$

We want to maximize the determinant of $|\mathbf{X_2'V^{-1}X_2}|$, such that $\mathbf{v_2'1} = 1$,

$$\begin{bmatrix} \mathbf{v_2'} & \mathbf{u_2}' \end{bmatrix} (\mathbf{X_1'X_1})^{-1} \begin{bmatrix} \mathbf{v}_2 \\ \mathbf{u_2} \end{bmatrix} - 2\lambda(\mathbf{v_2'1} - 1), \tag{3.13}$$

where $\mathbf{v_2'}$=$(x_1^z, x_2^z, \ldots, x_q^z)$, $\mathbf{u_2}'$=$(x_1^z x_2^z, x_1^z x_3^z, \ldots, x_1^z x_q^z)$.
Differentiating (3.13) w.r.t $\mathbf{v_2}$ and combining the constraint $\mathbf{v_2}'\mathbf{1} = 1$, we get three stationary solutions:

1. $(\frac{1}{2}, \frac{1}{2(q-1)}\mathbf{1_{q-1}}')$,
2. $(\frac{q^2+22q-16+\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q^2+4q-4)}, \frac{7q^2+10q-16-\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q-1)(q^2+4q-4)}\mathbf{1_{q-1}}')$,
3. $(\frac{q^2+22q-16-\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q^2+4q-4)}, \frac{7q^2+10q-16+\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q-1)(q^2+4q-4)}\mathbf{1_{q-1}}')$.

with three corresponding $\mathbf{z}_2'(\mathbf{X_1'X_1})^{-1}\mathbf{z}_2$:

1. $\frac{1}{q}$,
2. $\frac{1}{128(q-1)(q^2+4q-4)^3}(q^7 + 120q^6 + 792q^5 + 6880q^4 - 25200q^3 + 26112q^2 - 8704q + \sqrt{q^4 - 4q^3 + 260q^2 - 512q + 256}(q^5 - 6q^4 + 268q^3 - 1032q^2 + 1280q - 512))$,
3. $\frac{1}{128(q-1)(q^2+4q-4)^3}(q^7 + 120q^6 + 792q^5 + 6880q^4 - 25200q^3 + 26112q^2 - 8704q - \sqrt{q^4 - 4q^3 + 260q^2 - 512q + 256}(q^5 - 6q^4 + 268q^3 - 1032q^2 + 1280q - 512))$.

Among them, stationary solution 1 achieves the maximum value of $\mathbf{z}_2'(\mathbf{X_1'X_1})^{-1}\mathbf{z}_2$ when $q \leq 7$, stationary solution 2 achieves the maximum value of $\mathbf{z}_2'(\mathbf{X_1'X_1})^{-1}\mathbf{z}_2$ when $q \geq 8$. Since stationary solution 1 is already one of the existing interior points, we could choose only solution 2 and 3.

Now we have the following minimal plus two designs. Each design consists of two additional interior points and $2q-1$ D-Optimal minimal design points. We represent them as designs IIS_2 and $IIIS_2$, respectively:

Design IIS_2:
$(\frac{q^2+22q-16+\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q^2+4q-4)}, \frac{7q^2+10q-16-\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q-1)(q^2+4q-4)}\mathbf{1_{q-1}}')$ and $(\frac{1}{2}, \frac{1}{2(q-1)}\mathbf{1}'_{q-1})$, plus D-Optimal minimal design points.
Design $IIIS_2$:
$(\frac{q^2+22q-16-\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q^2+4q-4)}, \frac{7q^2+10q-16+\sqrt{q^4-4q^3+260q^2-512q+256}}{8(q-1)(q^2+4q-4)}\mathbf{1_{q-1}}')$ and $(\frac{1}{2}, \frac{1}{2(q-1)}\mathbf{1}'_{q-1})$, plus D-Optimal minimal design points.

Table 3.2 summarizes the D-efficiency for minimal plus two designs. Design IIS_2 has larger D-efficiency than Design $IIIS_2$. The same methodology can be applied to include more than one additional design point into an existing design.

Table 3.2: Minimal Plus Two Designs for Special Second-degree Mixture Model

Factors	Designs	D_2
3	Design IIS_2 $(0.670, 0.165, 0.165)$ and $(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$	5.358^*
	Design $IIIS_2$ $(0.197, 0.401, 0.401)$ and $(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$	5.357
4	Design IIS_2 $(0.610, 0.130, 0.130, 0.130)$ and $(\frac{1}{2}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6})$	3.641^*
	Design $IIIS_2$ $(0, 176, 0.275, 0.275, 0.275)$ and $(\frac{1}{2}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6})$	3.618
5	Design IIS_2 $(0.563, 0.109\mathbf{1_4'})$ and $(\frac{1}{2}, \frac{1}{8}\mathbf{1_4'})$	2.773^*
	Design $IIIS_2$ $(0.162, 0.210\mathbf{1_4'})$ and $(\frac{1}{2}, \frac{1}{8}\mathbf{1_4'})$	2.761
6	Design IIS_2 $(0.526, 0.095\mathbf{1_5'})$ and $(\frac{1}{2}, \frac{1}{10}\mathbf{1_5'})$	2.249^*
	Design $IIIS_2$ $(0.153, 0.169\mathbf{1_5'})$ and $(\frac{1}{2}, \frac{1}{10}\mathbf{1_5'})$	2.242
7	Design IIS_2 $(0.495, 0.084\mathbf{1_6'})$ and $(\frac{1}{2}, \frac{1}{12}\mathbf{1_6'})$	1.896^*
	Design $IIIS_2$ $(0.145, 0.143\mathbf{1_5'})$ and $(\frac{1}{2}, \frac{1}{12}\mathbf{1_6'})$	1.891
8	Design IIS_2 $(0.470, 0.076\mathbf{1_7'})$ and $(\frac{1}{2}, \frac{1}{14}\mathbf{1_7'})$	1.640^*
	Design $IIIS_2$ $(0.139, 0.123\mathbf{1_5'})$ and $(\frac{1}{2}, \frac{1}{14}\mathbf{1_7'})$	1.637

Note: * Maximum D-efficiency for Designs IIS_2 and $IIIS_2$.

3.4 Example

Consider a juice production factory planning to develop a watermelon-flavored juice. There are three types of concentrated juice: watermelon (x_1), pineapple (x_2), and strawberry (x_3). The response of acceptance values is from scale 1 (extremely bad taste) to 9 (extremely good taste). Initially, five participants score each of the five concentrations listed as blend 1 to 5 in Table 3.3. These are the D-Optimal minimal design points for a special three-factor second-degree mixture model. To check the adequacy of the fitted model, we consider one additional interior point $(1/2, 1/4, 1/4)$. We take 6 more respondents in two groups, three of each. The responses are shown in Table 3.3 at blends 6 and 7.

Table 3.3: Fruit Punch Acceptance Rating Data

Blend	Watermelon x_1	Pineapple x_2	Strawberry x_3	General Acceptance y
1	1	0	0	4.6
2	0	1	0	5.8
3	0	0	1	6.9
4	1/2	1/2	0	7.0
5	1/2	0	1/2	6.5
Extra design points				
Group I				
6	1/2	1/4	1/4	6.3, 6.9, 7.6
Group II				
7	1/2	1/4	1/4	4.4, 3.6, 3.7

By using the first five blends $(1-5)$, the fitted model is:

$$\widehat{y}(\mathbf{x}) = 4.6x_1 + 5.8x_2 + 6.9x_3 + 7.2x_1x_2 + 3.0x_1x_3 \tag{3.14}$$

To check the adequacy of the fitted model, we use the additional point listed at blend 6. The model becomes

$$\widehat{y}(\mathbf{x}) = 4.60x_1 + 5.80x_2 + 6.90x_3 + 7.64x_1x_2 + 3.44x_1x_3, \tag{3.15}$$

where the estimated standard error of the main factor coefficients is 0.5438 and interaction terms is 2.3826 for x_1x_2 and x_1x_3. Since there are three replications at blend 6, the pure-error sum of squares (SSPE) is

$$SSPE = (6.3 - 6.93)^2 + (6.9 - 6.93)^2 + (7.6 - 6.93)^2 = 0.8467,$$

with 2 degrees of freedom. From model (3.15), the residual sum of squares (SSE) is 0.8870, so that LOF sum of squares ($SSLF$) is 0.0402 with 1 degree of freedom. Hence the F statistics to test LOF is

$$F = \frac{SSLF/1}{SSPE/2} = 0.095, \tag{3.16}$$

with p-value equals to 0.7871 and the LOF is not significant at the 0.05 level. Therefore, the mixture model for Group I indicates a good fit.

If we check the model using the additional point listed at blend 7, the fitted model is:

$$\widehat{y}(x) = 4.60x_1 + 5.80x_2 + 6.90x_3 + 0.36x_1x_2 - 3.84x_1x_3, \tag{3.17}$$

where the estimated standard error of the main factor coefficients is 1.827 and the interaction terms for x_1x_2 and x_1x_3 is 8.051. Similarly

$$SSPE = (4.4 - 3.9)^2 + (3.6 - 3.9)^2 + (3.7 - 3.9)^2 = 0.38,$$

and

$$SSLF = 10.127 - 0.380 = 9.747,$$
$$F = \frac{SSLF/1}{SSPE/2} = 51.3,$$

with p-value equals to 0.0189 and the LOF is significant at the 0.05 level for Group II. In this case, the model is inadequate, and one may fit a higher-order model or add more factors to the experiment.

CHAPTER 4

SECOND-DEGREE MIXTURE MODEL

In this chapter, we consider adding one interior point for a popular Scheffé's second-degree mixture model based on the D-Optimal minimal designs. In many cases, this model fits data well. The model is

$$y = \sum_{1 \le i \le q} \beta_i x_i + \sum_{1 \le i < j \le q} \beta_{ij} x_i x_j + \epsilon. \tag{4.1}$$

It has a total of $\frac{q(q+1)}{2}$ parameters, hence it requires at least $\frac{q(q+1)}{2}$ design points to estimate them all. We consider the models for any $q \ge 3$ to encompass most of the practical applications.

4.1 D-Optimal Minimal Design

Kiefer (1961) proved that the $(q, 2)$ simplex-lattice design is D-Optimal. The design assigns equal weight to each of the extreme vertices $x \leftrightarrow (1, 0, \ldots, 0)$ and the edge midpoints $x \leftrightarrow (\frac{1}{2}, \frac{1}{2}, 0, \ldots, 0)$. Consider the design matrix

$$\mathbf{X} = \begin{bmatrix} 1 & 0 & \ldots & 0 & 0 & \ldots & 0 \\ 0 & 1 & \ldots & 0 & 0 & \ldots & 0 \\ \vdots & \ldots & \ldots & \ldots & \ldots & \ldots & \vdots \\ 0 & 0 & \ldots & 1 & 0 & \ldots & 0 \\ 1/2 & 1/2 & \ldots & 0 & 1/4 & \ldots & 0 \\ \vdots & \ldots & \ldots & \ldots & \ldots & \ldots & \vdots \\ 0 & \ldots & 1/2 & 1/2 & 0 & \ldots & 1/4 \end{bmatrix} = \begin{bmatrix} \mathbf{I}_q & \mathbf{X_{12}} \\ \mathbf{X_{21}} & \frac{1}{4}\mathbf{I}_{\frac{\mathbf{q(q-1)}}{\mathbf{2}}} \end{bmatrix}, \tag{4.2}$$

where $\mathbf{X_{12}}$ is a zero matrix of $q \times \frac{q(q-1)}{2}$, and $\mathbf{X_{21}}$ is a $\frac{q(q-1)}{2} \times q$ matrix, such that

$$\mathbf{X_{21}} = (x_{ij,k}) = \begin{cases} \frac{1}{2} & \text{when } i = k \ \ or \ \ j = k, \\ 0 & \text{otherwise} \end{cases}$$

with ij representing all two factor interaction terms i and j, and k representing the column of $\mathbf{X_{21}}$, $i, j, k = 1, 2, \ldots, q$ and $i < j$.

4.2 One Additional Interior Point

In order to allow the LOF test, we consider the problem of adding one interior design point to the above D-Optimal minimal design. Let $\mathbf{z}_1' = (\mathbf{v}_1', \mathbf{u}_1')$ be a new interior design point to be added, where

$$\mathbf{v}_1^{'} = (x_1^z, ..., x_q^z), \quad \mathbf{u}_1^{'} = (x_1^z x_2^z, x_1^z x_3^z, \ldots, x_{q-1}^z x_q^z), \tag{4.3}$$

where $0 < x_1^z, ..., x_q^z < 1$ and $\mathbf{v}_1^{'}\mathbf{1} = 1$.

Further denote the new design matrix by $\mathbf{X_1}$,

$$\mathbf{X_1} = \begin{bmatrix} \mathbf{X} \\ \mathbf{z}_1^{'} \end{bmatrix}.$$

Maximizing the determinant $|\mathbf{X_1^{'}}\mathbf{V^{-1}}\mathbf{X_1}|$ is equivalent to maximizing $\mathbf{z}_1^{'}(\mathbf{X}^{'}\mathbf{X})^{-\mathbf{1}}\mathbf{z}_1$.

$$\mathbf{X}^{'}\mathbf{X} = \begin{bmatrix} \mathbf{A_{11}} & \mathbf{A_{12}} \\ \mathbf{A_{21}} & \mathbf{A_{22}} \end{bmatrix}, \tag{4.4}$$

where $\mathbf{A_{11}} = \frac{q+2}{4}\mathbf{I_q} + \frac{1}{4}\mathbf{J_q}$, $\mathbf{A_{22}} = \frac{1}{16}\mathbf{I_{\frac{q(q-1)}{2}}}$, and $\mathbf{A_{12}} = \mathbf{A_{21}}'$. $\mathbf{A_{12}} = (a_{k,ij})$ is a q by $\frac{q(q-1)}{2}$ matrix, such that, for $i, j, k = 1, 2, \ldots, q$ and $i < j$,

$$\mathbf{A_{12}} = (a_{k,ij}) = \begin{cases} \frac{1}{8} & \text{when } k = i \ \ or \ \ k = j, \\ 0 & \text{otherwise.} \end{cases}$$

Since $\mathbf{X'X}$ is nonsingular, we have

$$(\mathbf{X'X})^{-1} = \begin{bmatrix} \mathbf{A_{11}}^{-1}(\mathbf{I} + \mathbf{A_{12}}\mathbf{F}^{-1}\mathbf{A_{21}}\mathbf{A_{11}}^{-1}) & -\mathbf{A_{11}}^{-1}\mathbf{A_{12}}\mathbf{F}^{-1} \\ -\mathbf{F}^{-1}\mathbf{A_{21}}\mathbf{A_{11}}^{-1} & \mathbf{F}^{-1} \end{bmatrix},$$

with $\mathbf{F} = \mathbf{A_{22}} - \mathbf{A_{21}}\mathbf{A_{11}}^{-1}\mathbf{A_{12}}$ being a nonsingular matrix. It can be verified that

$$\mathbf{A_{11}}^{-1} = \frac{4}{q+2}\{\mathbf{I_q} - \frac{1}{2(q+1)}\mathbf{J_q}\},$$

$$\mathbf{A_{12}}\mathbf{A_{21}} = \frac{q-2}{64}\mathbf{I_q} + \frac{1}{64}\mathbf{J_q},$$

$$\mathbf{A_{21}}\mathbf{A_{12}} = (a_{jl,j'l'}) = \begin{cases} \frac{1}{32} & \text{when } j = j' \quad \text{and} \quad l = l' \\ \frac{1}{64} & \text{when } j = j' \quad \text{or} \quad j = l' \quad \text{or} \quad l = j' \quad \text{or} \quad l = l' \\ & \text{and } j \neq j' \quad \text{and} \quad l \neq l' \\ 0 & \text{otherwise} \end{cases}$$

where $j, j', l, l' = 1, 2, \ldots, q$, $j < l$ and $j' < l'$.

Next we introduce a triangular association scheme of order $\frac{q(q-1)}{2}$ (Raghavarao, 1971). It is an array of q rows and q columns with the following properties:

- The positions in the principal diagonal are blank.
- The $\frac{q(q-1)}{2}$ positions above the principal diagonal are filled by the numbers $1, 2, \ldots, \frac{q(q-1)}{2}$.
- The array is symmetric about the principal diagonal.
- The ones that lie in the same row and same column are treated as first associate, the others are treated as the second associate.

Thus, these association matrices of a triangular association scheme are indexed by pairs (i, j), $1 \leq j < l \leq q$ and defined as follows:

$$\mathbf{B_0} = \mathbf{I}_{\mathbf{\frac{q(q-1)}{2}}},$$

$$\mathbf{B_1} = b_{(jl,j'l')},$$

where $b_{(jl,j'l')} = \begin{cases} 1 & \text{if } (j = j' \text{ or } j = l' \text{ or } l = j' \text{ or } l = l') \text{ but not } (j = j' \text{ and } l = l') \\ 0 & \text{otherwise} \end{cases}$

$$\mathbf{B_2} = \mathbf{J}_{\mathbf{\frac{q(q-1)}{2}}} - \mathbf{B_0} - \mathbf{B_1}.$$

Note that

$$\mathbf{A_{21}A_{12}} = \frac{1}{32}\mathbf{B_0} + \frac{1}{64}\mathbf{B_1}.$$

From Raghavarao (1971), we have

$$\mathbf{B_1B_2} = (q-3)\mathbf{B_1} + (2q-8)\mathbf{B_2}, \tag{4.5}$$

$$\mathbf{B_1^2} = 2(q-2)\mathbf{B_0} + (q-2)\mathbf{B_1} + 4\mathbf{B_2}, \tag{4.6}$$

and

$$\mathbf{B_2^2} = \frac{(q-2)(q-3)}{2}\mathbf{B_0} + \frac{(q-3)(q-4)}{2}\mathbf{B_1} + \frac{(q-4)(q-5)}{2}\mathbf{B_2}. \tag{4.7}$$

We can express matrix $\mathbf{F}$ as:

$$\begin{aligned} \mathbf{F} &= \mathbf{A_{22}} - \mathbf{A_{21}A_{11}}^{-1}\mathbf{A_{12}} \\ &= \frac{1}{16}\mathbf{I}_{\mathbf{\frac{q(q-1)}{2}}} - \frac{4}{q+2}(\frac{1}{32}\mathbf{I}_{\mathbf{\frac{q(q-1)}{2}}} + \frac{1}{64}\mathbf{B_1}) + \frac{1}{8(q+1)(q+2)}\mathbf{J}_{\mathbf{\frac{q(q-1)}{2}}}. \end{aligned} \tag{4.8}$$

$\mathbf{F} = a_0\mathbf{B_0} + a_1\mathbf{B_1} + a_2\mathbf{B_2}$, where $a_0 = \frac{q^2+q+2}{16(q+1)(q+2)}$, $a_1 = -\frac{q-1}{16(q+1)(q+2)}$, and $a_2 = \frac{1}{8(q+1)(q+2)}$.

We note that $\mathbf{F^{-1}}$ can be expressed as:

$$\mathbf{F^{-1}} = (a_0\mathbf{B_0} + a_1\mathbf{B_1} + a_2\mathbf{B_2})^{-1} = b_0\mathbf{B_0} + b_1\mathbf{B_1} + b_2\mathbf{B_2}.$$

Solving the equations for b_0, b_1, b_2 in terms of a_0, a_1 and a_2, and taking into account (4.5) - (4.8), we obtain

$$b_0 = 24 \quad , \quad b_1 = 4 \quad , \quad b_2 = 0.$$

Hence $\mathbf{F^{-1}} = 24\mathbf{B_0} + 4\mathbf{B_1}$.
Since $\mathbf{B_1 A_{21}} = (q-4)\mathbf{A_{12}} + \frac{1}{4}\mathbf{J}_{\mathbf{q},\frac{\mathbf{q(q-1)}}{\mathbf{2}}}$, we have

$$\begin{aligned} -\mathbf{F^{-1}A_{21}A_{11}}^{-1} &= (24\mathbf{B_0} + 4\mathbf{B_1})\mathbf{A_{21}}\frac{-4}{q+2}(\mathbf{I_q} - \frac{1}{2(q+1)}\mathbf{J_q}) \\ &= \{\frac{2}{(q+1)} - \frac{4}{(q+2)} + \frac{2q}{(q+1)(q+2)}\}\mathbf{J}_{\mathbf{q},\frac{\mathbf{q(q-1)}}{\mathbf{2}}} - 16\mathbf{A_{21}} \\ &= -16\mathbf{A_{21}}, \end{aligned}$$

Finally,

$$\mathbf{A_{11}}^{-1}(\mathbf{I_q} + \mathbf{A_{12}F}^{-1}\mathbf{A_{21}A_{11}}^{-1}) = \mathbf{A_{11}}^{-1}(\frac{q+2}{4}\mathbf{I_q} + \frac{1}{4}\mathbf{J_q}) = \mathbf{I_q}.$$

Thus, we have

$$(\mathbf{X'X})^{-1} = \begin{bmatrix} \mathbf{I_q} & -\mathbf{16A_{12}} \\ -\mathbf{16A_{21}} & 24\mathbf{B_0} + 4\mathbf{B_1} \end{bmatrix}. \tag{4.9}$$

Let the matrix $\mathbf{X}$ in (4.5) be partitioned as $\mathbf{X} = \begin{bmatrix} \mathbf{V} & \mathbf{U} \end{bmatrix}$, with $\mathbf{V} = \begin{bmatrix} \mathbf{v_1} & \ldots & \mathbf{v}_{\frac{\mathbf{q(q+1)}}{\mathbf{2}}} \end{bmatrix}'$, where $\mathbf{v_i}' = [x_{i1}, ..., x_{iq}]$, and $\mathbf{U} = \begin{bmatrix} \mathbf{u_1} & \ldots & \mathbf{u}_{\frac{\mathbf{q(q+1)}}{\mathbf{2}}} \end{bmatrix}'$, where $\mathbf{u_i}' = \left[x_{i1}x_{i2}, ..., x_{i(q-1)}x_{iq}\right]$.
Then, we have

$$\mathbf{X}'\mathbf{X} = \begin{bmatrix} \mathbf{A_{11}} & \mathbf{A_{12}} \\ \mathbf{A_{21}} & \mathbf{A_{22}} \end{bmatrix} = \begin{bmatrix} \mathbf{V'V} & \mathbf{V'U} \\ \mathbf{U'V} & \mathbf{U'U} \end{bmatrix}. \tag{4.10}$$

By replacing $\mathbf{A_{12}}$ and $\mathbf{A_{21}}$ from (4.10), we get

$$(\mathbf{X'X})^{-1} = \begin{bmatrix} \mathbf{I_q} & -\mathbf{16V'U} \\ -\mathbf{16U'V} & 24\mathbf{B_0} + 4\mathbf{B_1} \end{bmatrix}. \tag{4.11}$$

We use the Lagrange multiplier to maximize $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$, such that $\mathbf{v_1}'\mathbf{1} = 1$.

$$L_1 = \begin{bmatrix} \mathbf{v_1'} & \mathbf{u_1'} \end{bmatrix} (\mathbf{X'X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{v_1} \\ \mathbf{u_1} \end{bmatrix} - \mathbf{2}\lambda(\mathbf{v_1'1} - \mathbf{1}), \tag{4.12}$$

where λ is the Lagrange multiplier.

Differentiating (4.12) w.r.t $\mathbf{v}_1$ and equating to zero, we get

$$\frac{\partial}{\partial \mathbf{v_1}}\{\begin{bmatrix} \mathbf{v_1^{'}} & \mathbf{u_1^{'}} \end{bmatrix}\} \begin{bmatrix} \mathbf{I_q} & -\mathbf{16V'U} \\ -\mathbf{16U'V} & 24\mathbf{B_0} + 4\mathbf{B_1} \end{bmatrix} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} = \lambda \mathbf{1}, \tag{4.13}$$

Let

$$\frac{\partial}{\partial \mathbf{v}_1}\{\begin{bmatrix} \mathbf{v_1^{'}} & \mathbf{u_1^{'}} \end{bmatrix}\} = \begin{bmatrix} \mathbf{I_q} & \mathbf{K}, \end{bmatrix}$$

where

$$\mathbf{K} = \frac{\partial \mathbf{u}_1^{'}}{\partial \mathbf{v}_1} = \begin{bmatrix} x_2 & x_3 & \dots & x_q & 0 & 0 & \dots & 0 \\ x_1 & 0 & \dots & 0 & x_3 & x_4 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \vdots \\ 0 & 0 & \dots & x_1 & 0 & 0 & \dots & x_{q-1} \end{bmatrix}$$

Let $\mathbf{N}$ be a $(q-1) \times q$ matrix, such that $\mathbf{N}\lambda\mathbf{1} = \mathbf{0}$,

$$\mathbf{N} = \begin{bmatrix} 1 & -1 & 0 & \dots & 0 \\ 1 & 0 & -1 & \dots & 0 \\ \vdots & \dots & \dots & \dots & \vdots \\ 1 & 0 & 0 & \dots & -1 \end{bmatrix}$$

Multiplying (4.13) by $\mathbf{L}$ on both sides, we get

$$\mathbf{N}\begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix} \begin{bmatrix} \mathbf{I_q} & -\mathbf{16V'U} \\ -\mathbf{16U'V} & 24\mathbf{B_0} + 4\mathbf{B_1} \end{bmatrix} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} = \mathbf{0}, \tag{4.14}$$

or equivalently,

$$\mathbf{N}(\mathbf{v}_1 - 16\mathbf{KU'Vv_1} - 16\mathbf{V'Uu_1} + 24\mathbf{Ku_1} + 4\mathbf{KB_1u_1}) = \mathbf{0}.$$

The $(2q+1)$ stationary points are obtained by solving the equations above. They are labeled as solutions IQ, IIQ and $IIIQ$, with lower labels representing solutions with shorter distance between the stationary solutions and the overall centroid point $(\frac{1}{q}, \dots, \frac{1}{q})$.

Solution IQ: $x = (\frac{1}{q}, \dots, \frac{1}{q})$, Solution IIQ: q points of $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = \frac{(5q+2+\sqrt{q^2-4q+76})}{8(q^2+q-3)}$,

Solution $IIIQ$: q points of $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = \frac{(5q+2-\sqrt{q^2-4q+76})}{8(q^2+q-3)}$.

The corresponding values of $\mathbf{z}_1^{'}(\mathbf{X}^{'}\mathbf{X})^{-1}\mathbf{z}_1$ for each solution group are listed below:

Ia. $\frac{q^2+4q-4}{q^3}$,

IIa. $\frac{1}{128(-3+q+q^2)^3}[q^6+115q^5+712q^4-772q^3-4648q^2+6088q-1664+\sqrt{76-4q+q^2}(q^5-3q^4+62q^3+124q^2-792q+608)]$,

IIIa. $\frac{1}{128(-3+q+q^2)^3}[q^6+115q^5+712q^4-772q^3-4648q^2+6088q-1664-\sqrt{76-4q+q^2}(q^5-3q^4+62q^3+124q^2-792q+608)]$.

Among them, solution IQ attains the maximum value of $\mathbf{z}_1^{'}(\mathbf{X}^{'}\mathbf{X})^{-\mathbf{1}}\mathbf{z}_1$ when $q=3$, solution IIQ has maximum value of $\mathbf{z}_1^{'}(\mathbf{X}^{'}\mathbf{X})^{-\mathbf{1}}\mathbf{z}_1$ when $q \geq 4$. Figure 4.1 shows $\mathbf{z_1}^{'}(\mathbf{X}^{'}\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$ for three stationary solutions (IQ, IIQ and $IIIQ$).

We rewrite $(\mathbf{X}'\mathbf{X})^{-\mathbf{1}} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix}$ and denote

$$\mathbf{v_1}'\mathbf{B}' + \mathbf{u_1}'\mathbf{D} = \begin{bmatrix} w_{q+1} & w_{q+2} & \ldots & w_{\frac{q(q+1)}{2}} \end{bmatrix}.$$

The Hessian matrix for the second-degree mixture model is given by

$$\frac{\partial^2 L_1}{\partial \mathbf{v}'\partial \mathbf{v}}|_{\mathbf{v}=v_1,\mathbf{u}=u_1} = \frac{\partial}{\partial \mathbf{v}'}\left[\frac{\partial}{\partial \mathbf{v}}L_1\right] = \frac{\partial}{\partial \mathbf{v}'}\left(2\begin{bmatrix} \mathbf{I}_q & \mathbf{K} \end{bmatrix}(\mathbf{X}'\mathbf{X})^{-1}\begin{bmatrix} \mathbf{v} \\ \mathbf{u} \end{bmatrix}\right)$$

$$= 2\begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix}(\mathbf{X}^{'}\mathbf{X})^{-1}\frac{\partial}{\partial \mathbf{v}'}\{\begin{bmatrix} \mathbf{v} \\ \mathbf{u} \end{bmatrix}\}+$$

$$2\begin{bmatrix} (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_1 \partial v_1} & \ldots & (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_1 \partial v_q} \\ \ldots & \ldots & \ldots \\ (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_q \partial v_1} & \ldots & (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_q \partial v_q} \end{bmatrix}. \tag{4.15}$$

Equivalently the Hessian matrix for second-degree mixture model can be expressed as

$$\frac{\partial^2 \mathbf{L}_1}{\partial \mathbf{v}\partial \mathbf{v}'}|_{\mathbf{v}=v_1,\mathbf{u}=u_1} = 2[\mathbf{I_q} - 16\mathbf{K}\mathbf{U}'\mathbf{V} - 16\mathbf{V}'\mathbf{U}\mathbf{K}^{'} + \mathbf{K}\mathbf{D}\mathbf{K}'] + \mathbf{W}$$

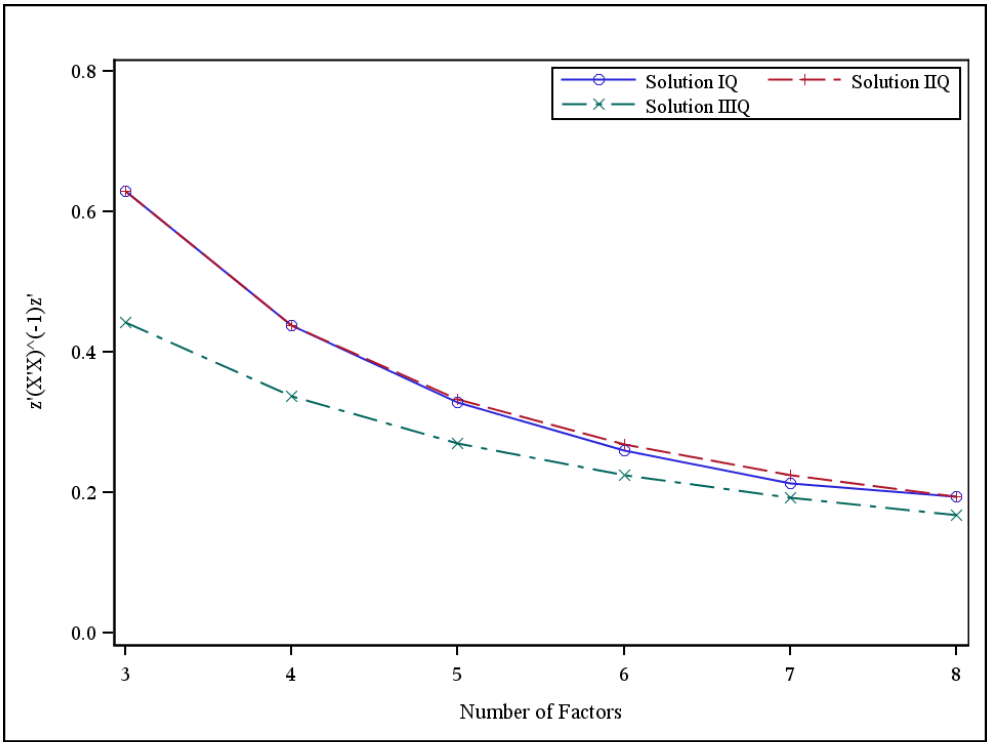

Figure 4.1: The $\mathbf{z_1'}(\mathbf{X'X})^{-\mathbf{1}}\mathbf{z_1}$ of the Stationary Solutions for Second-degree Mixture Model

where

$$\mathbf{W} = 2 \begin{bmatrix} 0 & w_{q+1} & w_{q+2} & \cdots & w_{2q-1} \\ w_{q+1} & 0 & w_{2q} & \cdots & w_{3q-3} \\ w_{q+2} & w_{2q} & 0 & \cdots & w_{4q-6} \\ \vdots & \cdots & \cdots & \cdots & \vdots \\ w_{2q-2} & w_{3q-4} & w_{4q-7} & \cdots & w_{\frac{q(q+1)}{2}} \\ w_{2q-1} & w_{3q-3} & w_{4q-6} & \cdots & 0 \end{bmatrix}. \tag{4.16}$$

The first part of this Hessian matrix is a nonnegative definite matrix. The second part, matrix $\mathbf{W}$, cannot be a negative definite matrix because $\mathbf{e_k'We_k} = 0$ for any canonical vector $\mathbf{e_k}$. Hence the Hessian matrix cannot be a negative definite matrix, and none of the interior stationary points can be a local maximum of $\mathbf{z_1'(X'X)^{-1}z_1}$. In the absence of a local maximum, we select an additional design point among the stationary interior points with the maximum value of $\mathbf{z_1}'\mathbf{(X'X)^{-1}z_1}$. Thus we choose solution IQ $x = (\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ when $q = 3$, and solution IIQ, $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$ when $q \geq 4$, where $\delta = \frac{(5q+2+\sqrt{q^2-4q+76})}{8(q^2+q-3)}$.
The three minimal plus one designs are listed below:

Design IQ_1: overall centroid $x = (\frac{1}{q}, \frac{1}{q}, \ldots, \frac{1}{q})$ plus D-Optimal minimal design points.

Design IIQ_1: one of $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = \frac{(5q+2+\sqrt{q^2-4q+76})}{8(q^2+q-3)}$ plus D-Optimal minimal design points.

Design $IIIQ_1$: one of $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = \frac{(5q+2-\sqrt{q^2-4q+76})}{8(q^2+q-3)}$ plus D-Optimal minimal design points.

Figure 4.2 displays the ternary plots for three designs. Table 4.1 summarizes the additional design point, the value of $\mathbf{z_1'(X'X)^{-1}z_1}$, and D-efficiencies for minimal plus one designs, denoted as D_1. It also includes the distance between each stationary point and the overall centroid point, defined as $dist = \sqrt{\sum_{i=1}^{q}(x_i - \frac{1}{q})^2}$. Design IIQ_1 has the maximum value of $\mathbf{z_1'(X'X)^{-1}z_1}$ and higher D-efficiency than the other two designs when $q \geq 4$, but the difference in D-efficiency is relatively small because the determinant of $\mathbf{X'X}$ decreases as the number of factor increases. We note that Design IIQ_1 includes the additional point with shorter nonzero distance to overall centroid point.

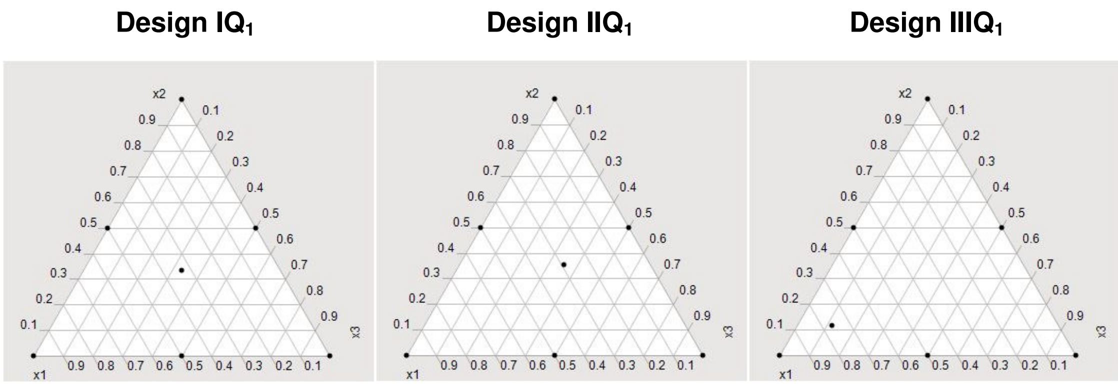

Figure 4.2: Ternary Plots for Minimal Plus One Stationary Designs for Second-degree Mixture Model

Table 4.1: Minimal Plus One Designs for Second-degree Mixture Model

Factors	One Additional Point	$\mathbf{z_1'}(\mathbf{X'X})^{\mathbf{-1}}\mathbf{z_1}$	Distance to Centroid	D_1
3	IQ_1 $x = (\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$	0.630	0	3.874*
	IIQ_2 One of $x \leftrightarrow (0.290, 0.355, 0.355)$	0.629	0.053	3.874
	$IIIQ_2$ One of $x \leftrightarrow (0.765, 0.117, 0.117)$	0.442	0.529	3.796
4	IQ_1 $x = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	0.438	0	1.786
	IIQ_1 One of $x \leftrightarrow (0.322, 0.226, 0.226, 0.226)$	0.439	0.084	1.786*
	$IIIQ_1$ One of $x \leftrightarrow (0, 707, 0.098, 0.098, 0.098)$	0.337	0.528	1.773
5	IQ_1 $x = (\frac{1}{5}\mathbf{1_5'})$	0.328	0	1.003
	IIQ_1 One of $x \leftrightarrow (\frac{1}{3}, \frac{1}{6}\mathbf{1_4'})$	0.333	0.149	1.003*
	$IIIQ_1$ One of $x \leftrightarrow (\frac{2}{3}, \frac{1}{12}\mathbf{1_4'})$	0.271	0.522	1.000
6	IQ_1 $x = (\frac{1}{6}\mathbf{1_6'})$	0.259	0	0.634
	IIQ_1 One of $x \leftrightarrow (0.337, 0.133\mathbf{1_5'})$	0.269	0.186	0.634*
	$IIIQ_1$ One of $x \leftrightarrow (0.638, 0.073\mathbf{1_5'})$	0.225	0.516	0.633
7	IQ_1 $x = (\frac{1}{7}\mathbf{1_7'})$	0.213	0	0.434
	IIQ_1 One of $x \leftrightarrow (0.337, 0.110\mathbf{1_6'})$	0.225	0.210	0.434*
	$IIIQ_1$ One of $x \leftrightarrow (0.616, 0.064\mathbf{1_6'})$	0.192	0.511	0.434
8	IQ_1 $x = (\frac{1}{8}\mathbf{1_8'})$	0.180	0	0.314
	IIQ_1 One of $x \leftrightarrow (0.336, 0.095\mathbf{1_7'})$	0.225	0.194	0.314*
	$IIIQ_1$ One of $x \leftrightarrow (0.599, 0.057\mathbf{1_7'})$	0.168	0.507	0.314

Note: * Maximum D-efficiency for Designs IQ_1, IIQ_1, and $IIIQ_1$.

CHAPTER 5

GENERAL MIXTURE MODELS

In this chapter, we consider extending D-Optimal minimal designs by adding interior points for general mixture models. A wide subclass of symmetric mixture models, which includes most of the commonly used mixture models are defined. In this class, the proposed strategy of adding one interior point yields multiple design points obtained by permuting the stationary points. Numeric solutions for one and multiple interior points are provided for two other commonly used models: the additive quadratic and the special cubic mixture models for a practically useful range of factors.

5.1 One Additional Interior Point for General Mixture Models

A general nth order q-factor mixture model is defined as

$$y = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i,j\le q} \beta_{ij} h_2(x_i, x_j) + \ldots + \sum_{1\le i_1,..,i_n\le q} \beta_{i_1,\ldots,i_n} h_n(x_{i_1}, \ldots, x_{i_n}) + \epsilon. \quad (5.1)$$

where $\sum_{i=1}^{q} x_i = 1$, $x_i \ge 0$ for all i. The most well known case of model (5.1) is the Scheffé's q-factor polynomial model of order n,

$$y = \sum_{1\le i\le q} \beta_i x_i + \sum_{1\le i<j\le q} \beta_{ij} x_i x_j + \ldots + \sum_{1\le i_1<\ldots<i_n\le q} \beta_{i_1,\ldots,i_n} x_{i_1} \ldots x_{i_n} + \epsilon. \quad (5.2)$$

Also, if $\sum_{1 \le i_1,..,i_n \le q} \beta_{i_1,...,i_k} x_{i_1} \ldots x_{i_k}$ reduces to $\sum_{1 \le i \le q} \beta_{i,...,i} x_i^k$ for $1 \le k \le n$, then model (5.1) becomes the q-factor additive polynomial model of order n,

$$y = \sum_{1 \le i \le q} \beta_i x_i + \sum_{1 \le i \le q} \beta_{ii} x_i^2 + \ldots + \sum_{1 \le i \le q} \beta_{i,...,i} x_i^n + \epsilon, \tag{5.3}$$

Polynomial mixture models are the most common, but other mixture models have also been studied and used (e.g., Becker, 1968,1978; Draper et.al, 1977a, 1977b; Zhang and Wong, 2013).

The D-Optimal minimal designs are known for a variety of mixture models. Let $\mathbf{X}$ be the given $M_n \times M_n$ D-Optimal minimal design matrix for model (5.1). For the nth order mixture model, the dimension of $(\mathbf{X}'\mathbf{X})^{-1}$ is $M_n \times M_n$, where $M_n \le C(q,1) + C(q,2) + \ldots + C(q,q) = 2^q - 1$. Scheffé's polynomial model (5.2) corresponds to $M_n = C(q+n-1,n)$, and general additive polynomial model (5.3) corresponds to $M_n = nq$. Then the nonsingular information matrix $(\mathbf{X}'\mathbf{X})$ is also known. The design matrix is constructed as

$$\mathbf{X} = \begin{bmatrix} x_{11} & ... & x_{1q} & h_2(x_{11}, x_{12}) & ... & h_n(x_{11}, ..., x_{1q}) \\ ... & ... & ... & ... & ... & ... \\ x_{M_n 1} & ... & x_{M_n q} & h_2(x_{M_n 1}, x_{M_n 2}) & ... & h_n(x_{M_n 1}, ..., x_{M_n q}) \end{bmatrix}$$

and is partitioned as $\mathbf{X} = \begin{bmatrix} \mathbf{V} & \mathbf{U} \end{bmatrix}$, with $M_n \times q$ matrix $\mathbf{V} = \begin{bmatrix} \mathbf{v_1} & ... & \mathbf{v_{M_n}} \end{bmatrix}'$, where $\mathbf{v_i'} = [x_{i1}, ..., x_{iq}]$, and $M_n \times (M_n - q)$ matrix $\mathbf{U} = \begin{bmatrix} \mathbf{u_1} & ... & \mathbf{u_{M_n}} \end{bmatrix}'$, where $\mathbf{u_i'} = [h_2(x_{i1}, x_{i2}), ..., h_n(x_{i1}, ..., x_{iq})]$. With this choice of partition, we have

$$\mathbf{X}'\mathbf{X} = \begin{bmatrix} \mathbf{V}' \\ \mathbf{U}' \end{bmatrix} \begin{bmatrix} \mathbf{V} & \mathbf{U} \end{bmatrix} = \begin{bmatrix} \mathbf{V}'\mathbf{V} & \mathbf{V}'\mathbf{U} \\ \mathbf{U}'\mathbf{V} & \mathbf{U}'\mathbf{U} \end{bmatrix}, \tag{5.4}$$

where $\mathbf{V}'\mathbf{V}$ is a $q \times q$ matrix and $\mathbf{U}'\mathbf{U}$ is a $(M_n - q) \times (M_n - q)$ matrix.

Let us further denote

$$\left(\mathbf{X}'\mathbf{X}\right)^{-1} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix}. \tag{5.5}$$

Using the Schur Complement,

$$\mathbf{A} = \left(\mathbf{V}'\mathbf{V} - \mathbf{V}'\mathbf{U}\left(\mathbf{U}'\mathbf{U}\right)^{-1}\mathbf{U}'\mathbf{V}\right)^{-1}$$

$$\mathbf{D} = \left(\mathbf{U}'\mathbf{U} - \mathbf{U}'\mathbf{V}\left(\mathbf{V}'\mathbf{V}\right)^{-1}\mathbf{V}'\mathbf{U}\right)^{-1}$$

$$\mathbf{B} = -\left[\mathbf{U}'\mathbf{U} - \mathbf{U}'\mathbf{V}\left(\mathbf{V}'\mathbf{V}\right)^{-1}\mathbf{V}'\mathbf{U}\right]^{-1}\mathbf{U}'\mathbf{V}\left(\mathbf{V}'\mathbf{V}\right)^{-1}.$$

First, consider the problem of adding one interior design point to the known minimal D-Optimal design. Let $\mathbf{z_1'} = (\mathbf{v}_1', \mathbf{u}_1')$ be the new interior design point to be added, where

$$\mathbf{v}_1{}' = (x_1^z, ..., x_q^z), \tag{5.6}$$

$$\mathbf{u}_1' = \mathbf{u}_1'\left(\mathbf{v}_1\right) = (h_2(x_1^z, x_2^z), \ldots, h_n(x_1^z, ..., x_q^z)), \tag{5.7}$$

with $0 < x_1^z, ..., x_q^z < 1$ and $\mathbf{v}_1' 1 = 1$. Further denote the new design matrix by $\mathbf{X_1}$, $\mathbf{X_1} = \begin{bmatrix} \mathbf{X} \\ \mathbf{z}_1' \end{bmatrix}$.

Theorem 1 *For the extended design* $\mathbf{X_1}$*,* $|\mathbf{X_1'}\mathbf{X_1}|$ *has a local maximum with respect to additional interior design point* $\mathbf{z}_1' = (\mathbf{v}_1', \mathbf{u}_1')$ *(with* $0 < x_1^z, ..., x_q^z < 1$ *and* $\mathbf{v}_1'\mathbf{1} = 1$*) if and only if* $\mathbf{v}_1$ *is a solution of the equations*

$$\begin{bmatrix} -\mathbf{1_{q-1}} & \mathbf{I_{q-1}} \end{bmatrix} \begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} = \mathbf{0} \tag{5.8}$$

where $\mathbf{K} = \frac{\partial \mathbf{u}'}{\partial \mathbf{v}}$ *. The Hessian matrix*

$$\mathbf{A} + \frac{\partial \mathbf{u}'}{\partial \mathbf{v}}\mathbf{B} + \mathbf{B}'\frac{\partial \mathbf{u}}{\partial \mathbf{v}'} + \frac{\partial \mathbf{u}'}{\partial \mathbf{v}}\mathbf{D}\frac{\partial \mathbf{u}}{\partial \mathbf{v}'} +$$

$$\begin{bmatrix} (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_1 \partial v_1} & ... & (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_1 \partial v_q} \\ ... & ... & ... \\ (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_q \partial v_1} & ... & (\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D})\frac{\partial^2 \mathbf{u}}{\partial v_q \partial v_q} \end{bmatrix} \tag{5.9}$$

is negative definite.

Proof: The generalization of the Sylvester's determinant theorem (Harville, 2008) implies that

$$|\mathbf{X}_1'\mathbf{X}_1| = |\mathbf{X}'\mathbf{X}|[1 + \mathbf{z}_1'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z}_1].$$

Since the determinant $|\mathbf{X}'\mathbf{X}|$ is already maximized by the definition of the D-Optimal minimal design $\mathbf{X}$, maximizing $|\mathbf{X}_1'\mathbf{X}_1|$ is equivalent to maximizing $f(\mathbf{v}) = \mathbf{z}_1'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z}_1$ subject to constraint $\mathbf{v}_1'\mathbf{1} = 1$. The general approach is to use the Lagrange multiplier and maximize

$$L_1 = [\mathbf{v}_1' \;\; \mathbf{u}_1'] \, (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} - 2\lambda(\mathbf{v}_1'\mathbf{1} - 1).$$

where $(M_n - q) \times 1$ vector $\mathbf{u}_1' = \left[h_2\left(x_1^z, x_2^z\right), ..., h_n(x_1^z, ..., x_q^z)\right]$. Then $q \times 1$ vector is

$$\frac{\partial}{\partial \mathbf{v}} L_1 = 2 \begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} - 2\lambda \mathbf{1}, \tag{5.10}$$

where $(M_n - q) \times q$ matrix $\mathbf{K} = \frac{\partial \mathbf{u}_1'}{\partial \mathbf{v}_1}$. Since $\left(\mathbf{I_{q-1}} \otimes \begin{bmatrix} 1 & -1 \end{bmatrix}\right) \mathbf{1} = \mathbf{0}$, (5.10) implies (5.8). Further,

$$\frac{\partial^2 L_1}{\partial \mathbf{v}' \partial \mathbf{v}} = \frac{\partial}{\partial \mathbf{v}'} \left[\frac{\partial}{\partial \mathbf{v}} L_1\right] = \frac{\partial}{\partial \mathbf{v}'} \left(2 \begin{bmatrix} \mathbf{I}_q & \mathbf{K} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix}\right). \tag{5.11}$$

Let us denote $f_k'(\mathbf{v}) = \begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix}_{k\cdot} = \begin{bmatrix} \mathbf{e_k}' & [\mathbf{K}]_{k\cdot} \end{bmatrix} = \begin{bmatrix} \mathbf{e_k}' & \frac{\partial \mathbf{u}'}{\partial v_k} \end{bmatrix}$, where $\mathbf{e_k}$ is the k^{th} canonical vector in R^q, and $h(\mathbf{v}) = (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix}$. Then the $1 \times q$ vector becomes (Vonesh and Chinchilli, 1997),

$$\begin{aligned} \frac{1}{2}\frac{\partial}{\partial \mathbf{v}'} \left[\frac{\partial}{\partial \mathbf{v}} L_1\right]_k |_{\mathbf{v}=\mathbf{v}_1, \mathbf{u}=\mathbf{u}_1} &= \frac{\partial}{\partial \mathbf{v}'} \left\{f_k'(\mathbf{v})\, h(\mathbf{v})\right\} \qquad (5.12) \\ &= f_k'(\mathbf{v}) (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{I_q} \\ \frac{\partial \mathbf{u}}{\partial \mathbf{v}'} \end{bmatrix} + [\mathbf{v}'\mathbf{u}'] (\mathbf{X}'\mathbf{X})^{-1} \frac{\partial}{\partial \mathbf{v}'} \begin{bmatrix} \mathbf{e}_k \\ \frac{\partial \mathbf{u}}{\partial v_k} \end{bmatrix} \\ &= \begin{bmatrix} \mathbf{e_k}' & [\mathbf{K}]_{k\cdot} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{I_q} \\ \mathbf{K}' \end{bmatrix} + [\mathbf{v}'\mathbf{u}'] (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{0_q} \\ \frac{\partial^2 \mathbf{u}}{\partial v_k \partial \mathbf{v}'} \end{bmatrix}, \end{aligned}$$

so that $\frac{1}{2}\frac{\partial}{\partial \mathbf{v}'}\left[\frac{\partial}{\partial \mathbf{v}}L_1\right]_k = \mathbf{a}'_{\mathbf{k}} + \mathbf{b}'_{\mathbf{k}}$,

where $a_k = \begin{bmatrix} \mathbf{e}'_{\mathbf{k}} & [\mathbf{K}]_{k\cdot} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{I_q} \\ \mathbf{K}' \end{bmatrix}$ and $\mathbf{b}'_{\mathbf{k}} = [\mathbf{v}'\mathbf{u}'] (\mathbf{X}'\mathbf{X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{0}_q \\ \frac{\partial^2 u}{\partial v_k \partial v'} \end{bmatrix}$.

Consequently, the Hessian is

$$\frac{\partial^2 L_1}{\partial \mathbf{v} \partial \mathbf{v}'} = \begin{bmatrix} \frac{\partial}{\partial \mathbf{v}'}\left[\frac{\partial}{\partial \mathbf{v}}L_1\right]_1 \\ \cdots \\ \frac{\partial}{\partial \mathbf{v}'}\left[\frac{\partial}{\partial \mathbf{v}}L_1\right]_q \end{bmatrix} = 2 \begin{bmatrix} \mathbf{a}'_{\mathbf{1}} \\ \cdots \\ \mathbf{a}'_{\mathbf{q}} \end{bmatrix} + 2 \begin{bmatrix} \mathbf{b}'_{\mathbf{1}} \\ \cdots \\ \mathbf{b}'_{\mathbf{q}} \end{bmatrix}.$$

It is straightforward that

$$\begin{bmatrix} \mathbf{a}'_{\mathbf{1}} \\ \cdots \\ \mathbf{a}'_{\mathbf{q}} \end{bmatrix} = \begin{bmatrix} \mathbf{I}_q & \mathbf{K} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{I}_q \\ \mathbf{K}' \end{bmatrix}.$$

Also, $\mathbf{b}'_{\mathbf{k}} = \mathbf{h}(\mathbf{v})' \mathbf{C}_{\mathbf{k}}$, where $\mathbf{C}_{\mathbf{k}} = \begin{bmatrix} \mathbf{0}_q \\ \frac{\partial^2 \mathbf{u}}{\partial v_k \partial v'} \end{bmatrix}$, and therefore,

$$\mathbf{b}'_{\mathbf{k}} = \left[\left(\mathbf{I_q} \otimes \mathbf{h}(\mathbf{v})^{\mathbf{T}}\right) \mathbf{Vec}(\mathbf{C_k})\right]^{\mathbf{T}} = \mathbf{Vec}(\mathbf{C_k})^{\mathbf{T}} (\mathbf{h}(\mathbf{v}) \otimes \mathbf{I_q}).$$

Let us denote $\mathbf{C} = \begin{bmatrix} Vec(C_1)^T \\ \cdots \\ Vec(C_q)^T \end{bmatrix}$, then

$$\begin{bmatrix} \mathbf{b}'_{\mathbf{1}} \\ \cdots \\ \mathbf{b}'_{\mathbf{q}} \end{bmatrix} = \begin{bmatrix} Vec(C_1)^T \\ \cdots \\ Vec(C_q)^T \end{bmatrix} (\mathbf{h}(\mathbf{v}) \otimes \mathbf{I_q}) = \mathbf{C}\left((\mathbf{X}'\mathbf{X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{v} \\ \mathbf{u} \end{bmatrix} \otimes \mathbf{I_q}\right). \tag{5.13}$$

Thus, the Hessian may be expressed as

$$\frac{\partial^2 L_1}{\partial \mathbf{v} \partial \mathbf{v}'}|_{\mathbf{v}=\mathbf{v_1}} = 2 \begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{I_q} \\ \mathbf{K}' \end{bmatrix} + 2\mathbf{C}\left((\mathbf{X}'\mathbf{X})^{-\mathbf{1}} \begin{bmatrix} \mathbf{v} \\ \mathbf{u} \end{bmatrix} \otimes \mathbf{I_q}\right) \tag{5.14}$$

Using (5.5), we can write

$$\begin{bmatrix} \mathbf{I_q} & \mathbf{K} \end{bmatrix} (\mathbf{X}'\mathbf{X})^{-1} \begin{bmatrix} \mathbf{I_q} \\ \mathbf{K}' \end{bmatrix} = \mathbf{A} + \frac{\partial \mathbf{u}'}{\partial \mathbf{v}}\mathbf{B} + \mathbf{B}'\frac{\partial \mathbf{u}}{\partial \mathbf{v}'} + \frac{\partial \mathbf{u}'}{\partial \mathbf{v}}\mathbf{D}\frac{\partial \mathbf{u}}{\partial \mathbf{v}'}. \tag{5.15}$$

Further, we have

$$\mathbf{b}_{\mathbf{k}}' = [\mathbf{v}'\mathbf{u}'] \left(\mathbf{X}'\mathbf{X}\right)^{-\mathbf{1}} \begin{bmatrix} \mathbf{0}_q \\ \frac{\partial^2 \mathbf{u}}{\partial v_k \partial v'} \end{bmatrix} = [\mathbf{v}'\mathbf{u}'] \begin{bmatrix} \mathbf{A}_q & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix} \begin{bmatrix} \mathbf{0}_q \\ \frac{\partial^2 \mathbf{u}}{\partial v_k \partial v'} \end{bmatrix} = \left(\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D}\right) \frac{\partial^2 \mathbf{u}}{\partial \mathbf{v_k} \partial \mathbf{v}'}, \tag{5.16}$$

Combining (5.15) and (5.16), we obtain (5.9). □

5.2 One Additional Interior Point for Other Mixture Models

5.2.1 Additive Quadratic Mixture Model

The additive quadratic mixture model is defined as

$$y = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{ii} x_i^2 + \epsilon. \tag{5.17}$$

There are $2q$ parameters in the model, and at least $2q$ design points are needed to estimate all parameters. Here we consider additive quadratic models with $q \geq 3$. Chan et al (1995, 1998) proved that the D-Optimal saturated axial design for model (5.17) contains the points $x \leftrightarrow (1, 0, \ldots, 0)$, and $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = 1/(q-1)$ when $3 \leq q \leq 6$, and $\delta = ((5q-1) - \sqrt{(9q^2 - 10q + 1)})/(4q^2)$ when $q \geq 7$. The last expression for δ is asymptotically $1/2$ when $q \to \infty$.
Let

$$\left(\mathbf{X}'\mathbf{X}\right)^{-\mathbf{1}} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix},$$

where $\mathbf{A} = a_1(q,\delta)\mathbf{I}_q + a_2(q,\delta)\mathbf{J}_q$, $\mathbf{B} = b_1(q,\delta)\mathbf{I}_q + b_2(q,\delta)\mathbf{J}_q$ and $\mathbf{D} = d_1(q,\delta)\mathbf{I}_q + d_2(q,\delta)\mathbf{J}_q$.

$$a_1(q,\delta) = \frac{2 - 4(-1+q)\delta + 2(2-6q+3q^2)\delta^2 - 4q(2-3q+q^2)\delta^3 + (-2+q)^2 q^2 \delta^4}{(-2+q)^2 \delta^2 (-1+q\delta)^2};$$

$$a_2(q,\delta) = [2q^6\delta^5 - q^5\delta^4(11+8\delta) + 8(1+\delta+\delta^2) + 2q^4\delta^3(12+20\delta+5\delta^2) - q^3\delta^2(26+76\delta+45\delta^2+4\delta^3) + 2q^2\delta(8+33\delta+36\delta^2+8\delta^3) - 2q(3+14\delta+23\delta^2+10\delta^3)]/[(-2+q)^2(-1+q)^2\delta^2(-2+q\delta)^2(-1+q\delta)^2];$$

$$b_1(q,\delta) = \frac{(1+(1-q\delta)(-\delta^2+(1-(-1+q)\delta)^2))}{(2-2q\delta+q^2\delta^2)};$$

$$b_2(q,\delta) = [-q^6\delta^5 - 2q^5\delta^4(3+2\delta) - 2q(1+\delta)^2(3+5\delta) + 4(2+\delta+\delta^2) + q^4\delta^3(15+21\delta+5\delta^2) - q^3\delta^2(19+44\delta+23\delta^2+2\delta^3) + q^2\delta(14+43\delta+39\delta^2+8\delta^3)]/[(-2+q)^2(-1+q)^2\delta^2(-2+q\delta)^2(-1+q\delta)^2];$$

$$d_1(q,\delta) = \frac{2-2q\delta+q^2\delta^2}{(-2+q)^2\delta^2(-1+q\delta)^2};$$

$$d_2(q,\delta) = [(8 - q^5\delta^4 + 2q^4\delta^3(3+\delta) - q^3\delta^2(12+12\delta+\delta^2) - 2q(3+8\delta+3\delta^2) + 2q^2\delta(6+10\delta+3\delta^2))]/[(-2+q)^2(-1+q)^2\delta^2(-2+q\delta)^2(-1+q\delta)^2].$$

More specifically, when $3 \le q \le 6$, $\delta = 1/(q-1)$, they could be simplified as:

$$\mathbf{A} = \frac{q^4-4q^3+6q^2-4q+2}{(q-2)^2}\mathbf{I}_q - \frac{(q-1)^2}{q-2}\mathbf{J}_q,$$

$$\mathbf{B} = \frac{-q(q^2-3q+3)(q-1)}{(q-2)^2}\mathbf{I}_q + \frac{(q-1)^2}{q-2}\mathbf{J}_q,$$

and

$$\mathbf{D} = \frac{(q-1)^2(q^2-2q+2)}{(q-2)^2}\mathbf{I}_q - \frac{(q-1)^2}{q-2}\mathbf{J}_q.$$

When $q \ge 7$, let $\delta = ((5q-1) - \sqrt{(9q^2-10q+1)})/(4q^2) \approx 1/(2q)$. We get

$$\mathbf{A} = \frac{17q^2+4q+4}{(q-2)^2}\mathbf{I}_q - \frac{8(17q^3-26q^2+8q-3)}{9(q^2-3q+2)^2}\mathbf{J}_q,$$

$$\mathbf{B} = \frac{-2q(9q+2)}{(q-2)^2}\mathbf{I}_q + \frac{2(71q^3 - 110q^2 + 29q - 6)}{9(q^2 - 3q + 2)^2}\mathbf{J}_q,$$

and

$$\mathbf{D} = \frac{20q^2}{(q-2)^2}\mathbf{I}_q - \frac{4q(37q^2 - 58q + 13)}{9(q^2 - 3q + 2)^2}\mathbf{J}_q.$$

By solving the equation of

$$\frac{\partial}{\partial \mathbf{v}_1}\{\begin{bmatrix} \mathbf{v}_1' & \mathbf{u}_1' \end{bmatrix}\}(\mathbf{X}'\mathbf{X})^{-1}\begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} = \lambda\mathbf{1},$$

we get $(2q+1)$ stationary points grouped as solution IA, IIA and $IIIA$ except for $q = 4$. When $q = 4$, there is only one stationary solution (overall centroid point). Figure 5.1 shows the value of $\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z_1}$ for three stationary solutions. Furthermore, the Hessian matrix can be expressed as

$$\frac{\partial^2 f(\mathbf{v})}{\partial \mathbf{v}\partial \mathbf{v}'} = 2[\mathbf{A} + \mathbf{KB} + (\mathbf{KB})' + \mathbf{KDK}'] + \mathbf{W},$$

where

$$\mathbf{W} = 4\begin{bmatrix} w_{q+1} & 0 & \dots & 0 \\ 0 & w_{q+2} & \dots & 0 \\ \vdots & \dots & \dots & \vdots \\ 0 & 0 & \dots & w_{2q} \end{bmatrix}, \tag{5.18}$$

and

$$\mathbf{v}'\mathbf{B}' + \mathbf{u}'\mathbf{D} = \begin{bmatrix} w_{q+1} & w_{q+2} & \dots & w_{2q} \end{bmatrix}.$$

For any canonical vector $\mathbf{e_k} = (1, 0, \dots, 0)$, $\mathbf{e_k}'\mathbf{W}\mathbf{e_k} = b_1 + b_2 + d_1 + d_2 = \frac{3+\delta+q^2\delta-2q(1+\delta)}{\delta(q-2)(q-1)(q\delta-2)}$ is greater than 0 when $\delta = 1/(q-1)$ $(3 \leq q \leq 6)$ and $\delta = ((5q-1) - \sqrt{(9q^2 - 10q + 1)})/(4q^2)$ $(q \geq 7)$. Hence, the Hessian matrix cannot be a negative definite matrix, and the stationary points for additive quadratic model are either local minimal points or saddle points. We choose the stationary solution with maximum information as the additional interior design point.

Now we generate minimal plus one designs based on one stationary point from solutions (IA, IIA, $IIIA$), and $2q$ points from D-Optimal minimal designs. We name them as Design IA_1, IIA_1, and $IIIA_1$, respectively. When $q = 3$, stationary

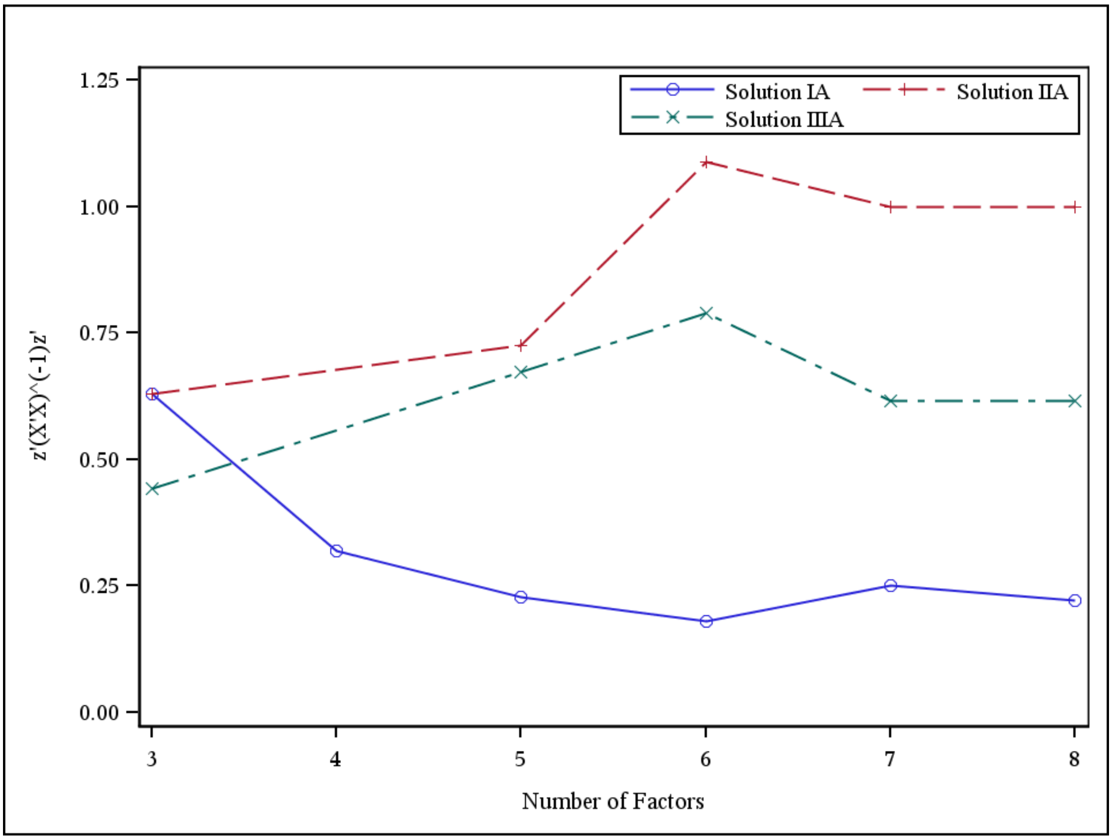

Figure 5.1: The $\mathbf{z_1'}(\mathbf{X'X})^{-1}\mathbf{z_1}$ of the Stationary Solutions for Additive Quadratic Model

solutions and D-Optimal minimal design points are the same for the second-degree mixture model and the additive quadratic model. The ternary plots for three-factor additive quadratic model is displayed as Figure 4.2. Table 5.1 summarizes the additional design point, the value of $\mathbf{z_1'}(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z_1}$, D-efficiencies, and the distance between each stationary point and the overall centroid point. There is only one stationary point when $q = 4$. We note that Design IIA_1 has the highest D-efficiency when $q \geq 5$, and Design IA_1 has the highest D-efficiency when $q = 3$, although the difference between Design IA_1 and IIA_1 is negligible. The higher D-efficiency of the extended design with the additional point is generally associated with a shorter nonzero distance to overall centroid point.

Table 5.1: Minimal Plus One Designs for Additive Quadratic Mixture Model

Factors	One Additional Point	$\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z_1}$	Distance to Centroid	D_1
3	IA_1 $x = (\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$	0.630	0	4.881*
	IIA_1 One of $x \leftrightarrow (0.290, 0.355, 0.355)$	0.629	0.053	4.881
	$IIIA_1$ One of $x \leftrightarrow (0.765, 0.117, 0.117)$	0.442	0.529	4.783
4	IA_1 $x = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	0.320	0	3.364
5	IA_1 $x = (\frac{1}{5}\mathbf{1_5'})$	0.228	0	2.296
	IIA_1 One of $x \leftrightarrow (0.635, 0.091\mathbf{1_4'})$	0.725	0.486	2.375*
	$IIIA_1$ One of $x \leftrightarrow (0.821, 0.045\mathbf{1_4'})$	0.674	0.694	2.368
6	IA_1 $x = (\frac{1}{6}\mathbf{1_6'})$	0.181	0	1.632
	IIA_1 One of $x \leftrightarrow (0.605, 0.079\mathbf{1_5'})$	1.088	0.480	1.711*
	$IIIA_1$ One of $x \leftrightarrow (0.893, 0.021\mathbf{1_5'})$	0.790	0.796	1.689
7	IA_1 $x = (\frac{1}{7}\mathbf{1_7'})$	0.250	0	1.456
	IIA_1 One of $x \leftrightarrow (0.550, 0.075\mathbf{1_6'})$	1.000	0.440	1.506*
	$IIIA_1$ One of $x \leftrightarrow (0.866, 0.022\mathbf{1_6'})$	0.617	0.781	1.483
8	IA_1 $x = (\frac{1}{8}\mathbf{1_8'})$	0.221	0	1.256
	IIA_1 One of $x \leftrightarrow (0.543, 0.065\mathbf{1_7'})$	1.000	0.447	1.293*
	$IIIA_1$ One of $x \leftrightarrow (0.864, 0.020\mathbf{1_7'})$	0.617	0.790	1.269

Note: * Maximum D-efficiency for Designs IA_1, IIA_1 and $IIIA_1$.

5.2.2 Special Cubic Mixture Model

Another commonly used mixture model is the Scheffé's special cubic model. It is defined as:

$$y = \sum_{1\leq i\leq q} \beta_i x_i + \sum_{1\leq i<j\leq q} \beta_{ij} x_i x_j + \sum_{1\leq i<j<k\leq q} \beta_{ijk} x_i x_j x_k + \epsilon. \tag{5.19}$$

Lim (1990) proved that the D-Optimal minimal design contains x $\leftrightarrow (1, 0, \ldots, 0)$, x $\leftrightarrow (\frac{1}{2}, \frac{1}{2}, 0, \ldots, 0)$,and x $\leftrightarrow (\frac{1}{3}, \frac{1}{3}, \frac{1}{3}, 0, \ldots, 0)$. There are $M = C(q,1) + C(q,2) + C(q,3) = \frac{q^3+5q}{6}$ parameters in the model.
Let

$$(\mathbf{X}'\mathbf{X})^{-1} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix},$$

where $\mathbf{A} = \mathbf{I}_q$, $\mathbf{B} = \begin{bmatrix} -16\mathbf{U}'\mathbf{V} \\ \mathbf{E}_1' \end{bmatrix}$ and $\mathbf{D} = \begin{bmatrix} 24\mathbf{B_0} + 4\mathbf{B_1} & \mathbf{E_2} \\ \mathbf{E}_2' & \mathbf{D_{22}} \end{bmatrix}$, where $\mathbf{U}'\mathbf{V}$, $\mathbf{B_0}$ and $\mathbf{B_1}$ are from the second-degree mixture model in Section 4.2, and $\mathbf{D_{22}}$ is the matrix of order $C(q,3)$,

$$\mathbf{D_{22}} = (x_{ijk,i'j'k'}) = \begin{cases} 1188 & \text{when } i = i' \text{ and } j = j' \text{ and } k = k', \\ 162 & \text{when } ijk \text{ and } i'j'k' \text{ have two factors in common,} \\ 9 & \text{when } ijk \text{ and } i'j'k' \text{ have one factor in common,} \\ 0 & \text{when } i \neq i' \text{ and } j \neq j' \text{ and } k \neq k'. \end{cases}$$

with ijk, $i'j'k'$ representing all three factor interaction terms i, j, k and i', j', k'. Also, $C(q,1) \times C(q,3)$ matrix $\mathbf{E_1}$,

$$\mathbf{E_1} = (x_{i,i'j'k'}) = \begin{cases} 3 & \text{when } i = i' \text{ or } i = j' \text{ or } j = k', \\ 0 & \text{otherwise.} \end{cases}$$

and $C(q,2) \times C(q,3)$ matrix $\mathbf{E_2}$,

$$\mathbf{E_2} = (x_{ij,i'j'k'}) = \begin{cases} -60 & \text{when } ij \text{ and } i'j'k' \text{ have two factors in common,} \\ -6 & \text{when } ij \text{ and } i'j'k' \text{ have one factor in common,} \\ 0 & \text{otherwise.} \end{cases}$$

with i, j, k representing the rows, ij and ijk representing two factor and three factor interactions, respectively.
By solving the equation of

$$\frac{\partial}{\partial \mathbf{v}_1}\{\begin{bmatrix} \mathbf{v_1}' & \mathbf{u}_1' \end{bmatrix}\}(\mathbf{X}'\mathbf{X})^{-1}\begin{bmatrix} \mathbf{v}_1 \\ \mathbf{u}_1 \end{bmatrix} = \lambda\mathbf{1},$$

we get the stationary interior points listed in Table 5.2. The number of stationary solutions varies with the number of factors.
Let us denote $\mathbf{v}_1'\mathbf{B}' + \mathbf{u}_1'\mathbf{D} = \begin{bmatrix} w_{q+1} & w_{q+2} & \dots & w_{\frac{q^3+5q}{6}} \end{bmatrix}$. Then the Hessian matrix could be expressed as

$$\frac{\partial^2 f(\mathbf{v})}{\partial \mathbf{v}\partial \mathbf{v}'} = 2[\mathbf{A} + \mathbf{KB} + (\mathbf{KB})' + \mathbf{KDK}'] + \mathbf{W},$$

and

$$\mathbf{W} = 2\begin{bmatrix} \mathbf{a_1}' \\ \mathbf{a_2}' \\ \dots \\ \mathbf{a_q}' \end{bmatrix}, \tag{5.20}$$

where

$$\mathbf{a_1}' = [0, \dots, w_{2q-1} + x_2 a_{l+q-2} + \dots + x_q a_{l+C(q-1,2)}]$$

$$\mathbf{a_2}' = [w_{q+1} + \sum_{i=3}^{q} x_i w_{l+i-2}, \dots, w_{3q-3} + x_1 a_{l+q-2} + \dots + x_{q-1} a_{M-C(q-2,3)}],$$

and

$$\mathbf{a_q}' = [w_{2q-1} + x_2 a_{l+q-2} + \dots + x_q a_{l+C(q-1,2)}, \dots, 0],$$

with $l = C(q+1, 2)$, $M = \frac{q^3+5q}{6}$, and $C(q-2, 3) = 0$ when $q < 5$.

The zero-diagonal symmetric matrix $\mathbf{W}$ cannot be negative definite, and the same arguments as in section 5.1 imply that the stationary points are either saddle points or points of local minimum. Similarly we generate minimal plus one designs based on one of the stationary solutions and D-Optimal minimal design points.

We label the proposed designs as Design IIC, $IIIC$, $\ldots$, with lower design labels representing designs with shorter distances between the stationary solutions and the overall centroid. For stationary solutions containing more than q additional points, we choose q out of all permuted points for comparisons. We also include the overall centroid point for all designs. Table 5.2 summarizes the additional points, the value of $\mathbf{z}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z}$, the distance to the overall centroid point, and D-efficiency. When $q = 3$, overall centroid point is one of the stationary solutions and also one of D-Optimal minimal design points, and hence it is not included in the table. Either Design IC_1 or IIC_1 provides higher D-efficiency, although the D-efficiency of all designs are very close. Figure 5.2 displays the location of the design points for a three-factor special cubic model.

Table 5.2: Minimal Plus One Designs for Special Cubic Model

Factors	One Additional Point	$\mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}$	Distance to Centroid	D_1
3	IIC_1 One of $x \leftrightarrow (0.090, 0.455, 0.455)$	0.626	0.298	1.592*
	$IIIC_1$ One of $x \leftrightarrow (0.751, 0.124, 0.124)$	0.391	0.512	1.557
4	IC_1 $x = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	0.807	0	0.322*
	IIC_1 One of $x \leftrightarrow (0.108, 0.297, 0.297, 0.297)$	0.752	0.164	0.322
	$IIIC_1$ One of $x \leftrightarrow (0.070, 0.070, 0.430, 0.430)$	0.451	0.360	0.317
	IVC_1 One of $x \leftrightarrow (0.699, 0.100, 0.100, 0.100)$	0.276	0.518	0.314
5	IC_1 $x = (\frac{1}{5}\mathbf{1_5}')$	0.633	0	0.093
	IIC_1 One of $x \leftrightarrow (0.126, 0.218\mathbf{1_4}')$	0.665	0.083	0.093*
	$IIIC_1$ One of $x \leftrightarrow (0.099\mathbf{1_2}', 0.268\mathbf{1_3}')$	0.598	0.184	0.093
	IVC_1 One of $x \leftrightarrow (0.413\mathbf{1_2}', 0.058\mathbf{1_3}')$	0.351	0.389	0.092
	VC_1 One of $x \leftrightarrow (0.665, 0.084\mathbf{1_4}')$	0.213	0.520	0.092
6	IC_1 $x = (\frac{1}{6}\mathbf{1_6}')$	0.502	0	0.035*
	IIC_1 One of $x \leftrightarrow (0.142, 0.172\mathbf{1_5}')$	0.502	0.027	0.035
	$IIIC_1$ One of $x \leftrightarrow (0.131\mathbf{1_2}', 0.185\mathbf{1_4}')$	0.501	0.062	0.035
	IVC_1 One of $x \leftrightarrow (0.097\mathbf{1_3}', 0.237\mathbf{1_3}')$	0.491	0.171	0.035
	VC_1 One of $x \leftrightarrow (0.401\mathbf{1_2}', 0.049\mathbf{1_4}')$	0.287	0.406	0.035
	VIC_1 One of $x \leftrightarrow (0.640, 0.072\mathbf{1_5}')$	0.174	0.519	0.035

Note: * Maximum D-efficiency for each factor.

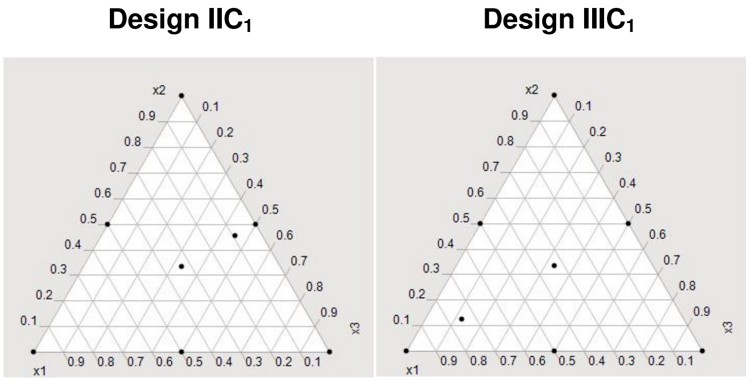

Figure 5.2: Ternary Plots for Minimal Plus one Designs for Three-factor Special Cubic Model

5.3 Symmetric Mixture Models

We consider model (5.1) to be a symmetric mixture model if all functions

$$H_k(x_1, x_2, \ldots, x_q) = \sum_{1 \le i_1 \le, \ldots \le, i_k \le q} h_k(x_{i_1}, \ldots, x_{i_k}),\ 2 \le k \le n, \tag{5.21}$$

with $\sum_{1\le i\le q} h_1(x_{i_1}, \ldots, x_{i_k}) \stackrel{def}{=} \sum_{1\le i\le q} x_i$, are symmetric functions of q arguments $x_1, \ldots, x_q$. Most of the commonly used mixture models are symmetric, including Scheffé's linear, second-degree, special cubic, and additive mixture models. From the proof of Theorem 1, it is straightforward to obtain proposition 1.

Proposition 1 *Let model (5.1) be symmetric and* $f(\mathbf{v}) = \mathbf{z}_1'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z}_1$ *be a symmetric function of* q *variables* $x_1^z, ..., x_q^z$. *The extended minimal design with one added point* $\mathbf{v}_1$ *has the same D-efficiency as the extended minimal design with one added point* $\mathbf{v}_2$ *if* $\mathbf{v}_2 \leftrightarrow \mathbf{v}_1$.

Thus, for symmetric mixture models, each stationary point except for the overall centroid provides at least q distinct additional design points. Proposition 2 gives a sufficient condition for $f(\mathbf{v})$ to be a symmetric function.

Proposition 2 *Let* $(\mathbf{X}'\mathbf{X})^{-1}$*be partitioned as in* (5.5). *If matrices* $\mathbf{A}$, $\mathbf{B}$ *and* $\mathbf{D}$ are such that functions $\mathbf{v}_1'\mathbf{A}\mathbf{v}_1$, $\mathbf{u}_1'\mathbf{B}\mathbf{v}_1$, and $\mathbf{u}_1'\mathbf{D}\mathbf{u}_1$ *are invariant with respect to a transposition of any* i^{th} *and* j^{th} *coordinates of vector* $\mathbf{v}_1$ $(1 \le i \le j \le q)$, *then* $f(\mathbf{v}) = \mathbf{z}_1' (\mathbf{X}'\mathbf{X})^{-1} \mathbf{z}_1$ *is a symmetric function of* q *arguments* $x_1^z, ..., x_q^z$.

Proof: Since any permutation can be expressed as a composition of a sequence of transpositions, it is sufficient to show that function $f(\mathbf{v}_1) = \mathbf{z}_1' (\mathbf{X}'\mathbf{X})^{-1} \mathbf{z}_1$ is invariant with respect to any transposition of arguments (a permutation of any two coordinates x_i^z and x_j^z in the independent subvector $\mathbf{v}' = (x_1^z, \ldots, x_q^z)$). Using (5.5), $f(\mathbf{v}_1) = \mathbf{z}_1' (\mathbf{X}'\mathbf{X})^{-1} \mathbf{z}_1 = \mathbf{v}_1'\mathbf{A}\mathbf{v}_1 + 2\mathbf{u}_1'\mathbf{B}\mathbf{v}_1 + \mathbf{u}_1'\mathbf{D}\mathbf{u}_1$, then $f(\mathbf{v}_1)$ is invariant with respect to a permutation of any two coordinates x_i^z and x_j^z by the assumptions. □

5.4 Multiple Additional Interior Points for Commonly Used Symmetric Mixture Models

5.4.1 Second-degree Mixture Model

Since $f(\mathbf{v}) = \mathbf{z}_1'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{z}_1 = \mathbf{v}_1'\mathbf{A}\mathbf{v}_1 + 2\mathbf{u}_1'\mathbf{B}\mathbf{v}_1 + \mathbf{u}_1'\mathbf{D}\mathbf{u}_1$, where

$$(\mathbf{X}'\mathbf{X})^{-1} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix} = \begin{bmatrix} \mathbf{I_q} & -\mathbf{16V'U} \\ -\mathbf{16U'V} & 24\mathbf{B_0} + 4\mathbf{B_1} \end{bmatrix}, \tag{5.22}$$

from section 4.2. Note that $\mathbf{v}_1'\mathbf{A}\mathbf{v}_1 = \sum_{i=1}^{q} x_i^{z2}$, $\mathbf{u}_1'\mathbf{B}\mathbf{v}_1 = -2\sum_{i=1}^{q} x_i^{z2}(1-x_i^z)$ and $\mathbf{u}_1'\mathbf{D}\mathbf{u}_1 = 24\mathbf{u}_1'\mathbf{u}_1 + 4\mathbf{u}_1'\mathbf{B_1}\mathbf{u}_1 = 24\sum_{1\le i<j\le q}^{q}(x_i^z x_j^z)^2 + 4\sum_{1\le i<j\le q}^{q} x_i^z x_j^z(x_i^z + x_j^z)(1 - x_i^z - x_j^z)$ are invariant with respect to a permutation of any two coordinates x_i^z and x_j^z. The conditions of proposition 2 are satisfied. Hence, the conditions of proposition 1 are satisfied, and all permutations of a stationary point result in the same determinant of the information matrix. Thus, we can use permutation of any stationary point except the overall centroid to get at least q additional interior points.

We propose the following two designs based on solutions IIQ and $IIIQ$, augmented with the overall centroid point.

Design IIQ_{q+1}: q points of $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = \frac{(5q+2+\sqrt{q^2-4q+76})}{8(q^2+q-3)}$, overall centroid and D-Optimal minimal points.

Desugn $IIIQ_{q+1}$: q points of $x \leftrightarrow (1-(q-1)\delta, \delta, \ldots, \delta)$, where $\delta = \frac{(5q+2-\sqrt{q^2-4q+76})}{8(q^2+q-3)}$, overall centroid and D-Optimal minimal points.

The proposed designs are compared with the following three commonly used designs described in section 2.2.

Design IV: q points of $x \leftrightarrow (\frac{q+1}{2q}, \frac{1}{2q}, \ldots, \frac{1}{2q})$, overall centroid and D-Optimal minimal points.

Design V: q points of $x \leftrightarrow (\frac{1}{2}, \frac{1}{2(q-1)}, \ldots, \frac{1}{2(q-1)})$, overall centroid and D-Optimal minimal points.

Design VI: q points of $x \leftrightarrow (\frac{1}{2q}, \frac{2q-1}{2q(q-1)}, \ldots, \frac{2q-1}{2q(q-1)})$, overall centroid and D-Optimal minimal points.

Each design contains $(q+1)$ additional interior points and $C(q,2)$ D-Optimal minimal points. Figure 5.4 displays the ternary plots for all considered designs when $q = 3$. Table 5.3 summarizes the additional design points and D-efficiency (denoted as D_{q+1}) for all designs. In general, Design III_{q+1} has the highest D-efficiency among all designs except for $q = 3$, and Design VI has the highest D-efficiency when $q = 3$. Design II_{q+1} provides comparable D-efficiency compared with standard designs.

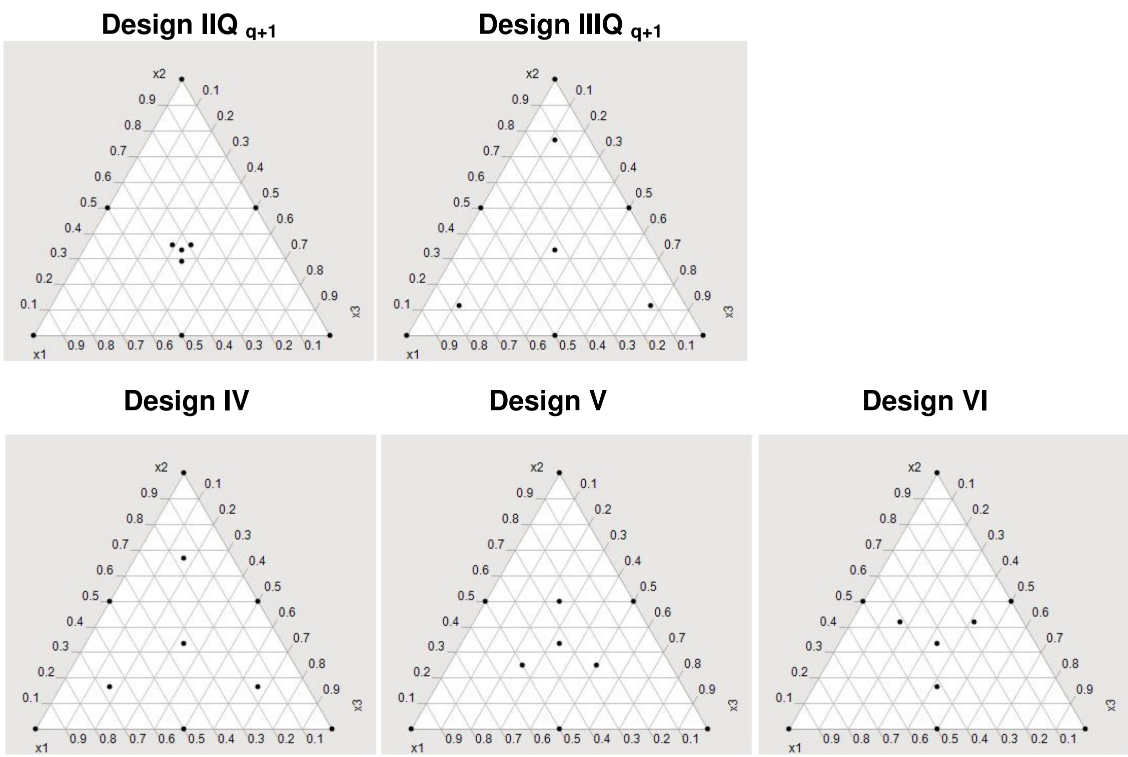

Figure 5.3: The Minimal Plus $(q+1)$ Points Designs for Three-factor Second-degree Mixture Model

Table 5.3: Minimal Plus $(q+1)$ Designs for Second-degree Mixture Model

Factors	Designs	$(q+1)$ Additional Points	D_{q+1}
3	IIQ_{q+1}	$x \leftrightarrow (0.290, 0.355, 0.355)$ and $(1/3\mathbf{1}_{\mathbf{3}}^{'})$	3.089
	$IIIQ_{q+1}$	$x \leftrightarrow (0.765, 0.117, 0.117)$ and $(1/3\mathbf{1}_{\mathbf{3}}^{'})$	3.184
	IV	$x \leftrightarrow (2/3, 1/6, 1/6)$ and $(1/3\mathbf{1}_{\mathbf{3}}^{'})$	3.148
	V	$x \leftrightarrow (1/2, 1/4, 1/4)$ and $(1/3\mathbf{1}_{\mathbf{3}}^{'})$	3.121
	VI	$x \leftrightarrow (1/6, 5/12, 1/12)$ and $(1/3\mathbf{1}_{\mathbf{3}}^{'})$	3.212*
4	IIQ_{q+1}	$x \leftrightarrow (0.322, 0.226, 0.226, 0.226)$ and $(1/4\mathbf{1}_{\mathbf{4}}^{'})$	1.423
	$IIIQ_{q+1}$	$x \leftrightarrow (0, 707, 0.098, 0.098, 0.098)$ and $(1/4\mathbf{1}_{\mathbf{4}}^{'})$	1.454*
	IIV	$x \leftrightarrow (5/8, 1/8, 1/8, 1/8)$ and $(1/4\mathbf{1}_{\mathbf{4}}^{'})$	1.447
	V	$x \leftrightarrow (1/2, 1/6, 1/6, 1/6)$ and $(1/4\mathbf{1}_{\mathbf{4}}^{'})$	1.442
	VI	$x \leftrightarrow (1/8, 7/24, 7/24, 7/24)$ and $(1/4\mathbf{1}_{\mathbf{4}}^{'})$	1.444
5	IIQ_{q+1}	$x \leftrightarrow (1/3, 1/6\mathbf{1}_{\mathbf{4}}^{'})$ and $(1/5\mathbf{1}_{\mathbf{5}}^{'})$	0.812
	$IIIQ_{q+1}$	$x \leftrightarrow (2/3, 1/12\mathbf{1}_{\mathbf{4}}^{'})$ and $(1/5\mathbf{1}_{\mathbf{5}}^{'})$	0.822*
	IV	$x \leftrightarrow (3/5, 1/10\mathbf{1}_{\mathbf{4}}^{'})$ and $(1/5\mathbf{1}_{\mathbf{5}}^{'})$	0.820
	V	$x \leftrightarrow (1/2, 1/8\mathbf{1}_{\mathbf{4}}^{'})$ and $(1/5\mathbf{1}_{\mathbf{5}}^{'})$	0.819
	VI	$x \leftrightarrow (1/10, 9/40\mathbf{1}_{\mathbf{4}}^{'})$ and $(1/5\mathbf{1}_{\mathbf{5}}^{'})$	0.814
6	IIQ_{q+1}	$x \leftrightarrow (0.337, 0.133\mathbf{1}_{\mathbf{5}}^{'})$ and $(1/6\mathbf{1}_{\mathbf{6}}^{'})$	0.522
	$IIIQ_{q+1}$	$x \leftrightarrow (0.638, 0.073\mathbf{1}_{\mathbf{5}}^{'})$ and $(1/6\mathbf{1}_{\mathbf{6}}^{'})$	0.526*
	IV	$x \leftrightarrow (7/12, 1/12\mathbf{1}_{\mathbf{5}}^{'})$ and $(1/6\mathbf{1}_{\mathbf{6}}^{'})$	0.525
	V	$x \leftrightarrow (1/2, 1/10\mathbf{1}_{\mathbf{5}}^{'})$ and $(1/6\mathbf{1}_{\mathbf{6}}^{'})$	0.525
	VI	$x \leftrightarrow (1/12, 11/60\mathbf{1}_{\mathbf{5}}^{'})$ and $(1/6\mathbf{1}_{\mathbf{6}}^{'})$	0.520
7	IIQ_{q+1}	$x \leftrightarrow (0.337, 0.110\mathbf{1}_{\mathbf{6}}^{'})$ and $(1/7\mathbf{1}_{\mathbf{7}}^{'})$	0.363
	$IIIQ_{q+1}$	$x \leftrightarrow (0.616, 0.064\mathbf{1}_{\mathbf{6}}^{'})$ and $(1/7\mathbf{1}_{\mathbf{7}}^{'})$	0.364*
	IV	$x \leftrightarrow (4/7, 1/14\mathbf{1}_{\mathbf{6}}^{'})$ and $(1/7\mathbf{1}_{\mathbf{7}}^{'})$	0.364
	V	$x \leftrightarrow (1/2, 1/12\mathbf{1}_{\mathbf{6}}^{'})$ and $(1/7\mathbf{1}_{\mathbf{7}}^{'})$	0.364
	VI	$x \leftrightarrow (1/14, 13/84\mathbf{1}_{\mathbf{6}}^{'})$ and $(1/7\mathbf{1}_{\mathbf{7}}^{'})$	0.361
8	IIQ_{q+1}	$x \leftrightarrow (0.336, 0.095\mathbf{1}_{\mathbf{7}}^{'})$ and $(1/8\mathbf{1}_{\mathbf{8}}^{'})$	0.266
	$IIIQ_{q+1}$	$x \leftrightarrow (0.599, 0.057\mathbf{1}_{\mathbf{7}}^{'})$ and $(1/8\mathbf{1}_{\mathbf{8}}^{'})$	0.267*
	IV	$x \leftrightarrow (9/16, 1/16\mathbf{1}_{\mathbf{7}}^{'})$ and $(1/8\mathbf{1}_{\mathbf{8}}^{'})$	0.267
	V	$x \leftrightarrow (1/2, 1/14\mathbf{1}_{\mathbf{7}}^{'})$ and $(1/8\mathbf{1}_{\mathbf{8}}^{'})$	0.267
	VI	$x \leftrightarrow (1/16, 15/112\mathbf{1}_{\mathbf{7}}^{'})$ and $(1/8\mathbf{1}_{\mathbf{8}}^{'})$	0.265

Note: * Maximum D-efficiency for each factor.

5.4.2 Additive Quadratic Mixture Model

Recall the inverse of the information matrix for additive quadratic model from section 5.2.1:

$$(\mathbf{X}'\mathbf{X})^{-1} = \begin{bmatrix} \mathbf{A} & \mathbf{B}' \\ \mathbf{B} & \mathbf{D} \end{bmatrix},$$

where $\mathbf{A} = a_1(q,\delta)\mathbf{I}_q + a_2(q,\delta)\mathbf{J}_q$, $\mathbf{B} = b_1(q,\delta)\mathbf{I}_q + b_2(q,\delta)\mathbf{J}_q$ and $\mathbf{D} = d_1(q,\delta)\mathbf{I}_q + d_2(q,\delta)\mathbf{J}_q$.

Since the blocks of $(\mathbf{X}'\mathbf{X})^{-1}$ are the linear combinations of $\mathbf{I_q}$ and $\mathbf{J_q}$, it is straightforward that conditions of Proposition 2 are satisfied. Thus, conditions of proposition 1 are satisfied and we can use permutations of any stationary point except the overall centroid to obtain at least q additional interior points. Then we propose two designs, consisting of q permuted points from solution IIA or $IIIA$, one overall centroid and $2q$ D-Optimal minimal design points. We name them as Design IIA_{q+1} and $IIIA_{q+1}$ respectively. The ternary plot is the same as second-degree mixture model when $q = 3$. Table 5.4 summarizes the D-efficiencies for all designs. Note that there is only one stationary solution (overall centroid point) when $q = 4$, and Designs IIA_{q+1} and $IIIA_{q+1}$ are not available when $q = 4$. In summary, Design IIA_{q+1} has the highest efficiency among all the designs except for $q = 3$, where Design VI has the highest efficiency.

Table 5.4: Minimal Plus $(q+1)$ Designs for Additive Quadratic Mixture Model

Factors	Designs	$(q+1)$ Additional Points	D_{q+1}
3	IIA_{q+1}	$x \leftrightarrow (0.290, 0.355, 0.355)$ and $(1/3\mathbf{1_3'})$	3.892
	$IIIA_{q+1}$	$x \leftrightarrow (0.765, 0.117, 0.117)$ and $(1/3\mathbf{1_3'})$	4.012
	IV	$x \leftrightarrow (2/3, 1/6, 1/6)$ and $(1/3\mathbf{1_3'})$	3.966
	V	$x \leftrightarrow (1/2, 1/4, 1/4)$ and $(1/3\mathbf{1_3'})$	3.932
	VI	$x \leftrightarrow (1/6, 5/12, 1/12)$ and $(1/3\mathbf{1_3'})$	4.047*
4	IV	$x \leftrightarrow (5/8, 1/8, 1/8, 1/8)$ and $(1/4\mathbf{1_4'})$	2.807*
	V	$x \leftrightarrow (1/2, 1/6, 1/6, 1/6)$ and $(1/4\mathbf{1_4'})$	2.741
	VI	$x \leftrightarrow (1/8, 7/24, 7/24, 7/24)$ and $(1/4\mathbf{1_4'})$	2.698
5	IIA_{q+1}	$x \leftrightarrow (0.635, 0.091\mathbf{1_4'})$ and $(1/5\mathbf{1_5'})$	2.059*
	$IIIA_{q+1}$	$x \leftrightarrow (0.821, 0.045\mathbf{1_4'})$ and $(1/5\mathbf{1_5'})$	2.037
	IV	$x \leftrightarrow (3/5, 1/10\mathbf{1_4'})$ and $(1/5\mathbf{1_5'})$	2.055
	V	$x \leftrightarrow (1/2, 1/8\mathbf{1_4'})$ and $(1/5\mathbf{1_5'})$	2.007
	VI	$x \leftrightarrow (1/10, 9/40\mathbf{1_4'})$ and $(1/5\mathbf{1_5'})$	1.812
6	IIA_{q+1}	$x \leftrightarrow (0.605, 0.079\mathbf{1_5'})$ and $(1/6\mathbf{1_6'})$	1.602*
	$IIIA_{q+1}$	$x \leftrightarrow (0.893, 0.021\mathbf{1_5'})$ and $(1/6\mathbf{1_6'})$	1.493
	IV	$x \leftrightarrow (7/12, 1/12\mathbf{1_5'})$ and $(1/6\mathbf{1_6'})$	1.601
	V	$x \leftrightarrow (1/2, 1/10\mathbf{1_5'})$ and $(1/6\mathbf{1_6'})$	1.568
	VI	$x \leftrightarrow (1/12, 11/60\mathbf{1_5'})$ and $(1/6\mathbf{1_6'})$	1.275
7	IIA_{q+1}	$x \leftrightarrow (0.550, 0.075\mathbf{1_6'})$ and $(1/7\mathbf{1_7'})$	1.394*
	$IIIA_{q+1}$	$x \leftrightarrow (0.866, 0.022\mathbf{1_6'})$ and $(1/7\mathbf{1_7'})$	1.262
	IV	$x \leftrightarrow (4/7, 1/14\mathbf{1_6'})$ and $(1/7\mathbf{1_7'})$	1.393
	V	$x \leftrightarrow (1/2, 1/12\mathbf{1_6'})$ and $(1/7\mathbf{1_7'})$	1.385
	VI	$x \leftrightarrow (1/14, 13/84\mathbf{1_6'})$ and $(1/7\mathbf{1_7'})$	1.117
8	IIA_{q+1}	$x \leftrightarrow (0.543, 0.065\mathbf{1_7'})$ and $(1/8\mathbf{1_8'})$	1.231*
	$IIIA_{q+1}$	$x \leftrightarrow (0.864, 0.020\mathbf{1_7'})$ and $(1/8\mathbf{1_8'})$	1.067
	IV	$x \leftrightarrow (9/16, 1/16\mathbf{1_7'})$ and $(1/8\mathbf{1_8'})$	1.228
	V	$x \leftrightarrow (1/2, 1/14\mathbf{1_7'})$ and $(1/8\mathbf{1_8'})$	1.229
	VI	$x \leftrightarrow (1/16, 15/112\mathbf{1_7'})$ and $(1/8\mathbf{1_8'})$	0.958

Note: * Maximum D-efficiency for each factor.

5.4.3 Special Cubic Mixture Model

Using the expression for $(\mathbf{X}'\mathbf{X})^{-1}$ provided in section 5.2.2, it is straightforward to show that function $f(\mathbf{v}_1) = \mathbf{z}_1' (\mathbf{X}'\mathbf{X})^{-1} \mathbf{z}_1$ is invariant with respect to any transposition of x_i^z and x_j^z. Therefore, we can use permutations of any stationary point to get multiple additional points using propositions 1 and 2. The number of stationary solutions varies with the number of factors. For stationary solutions containing more than q additional points, we choose q out of all permuted points for comparisons. We also include the overall centroid point for all designs. The corresponding proposed designs are labeled as Design $IIC_{q+1}, IIIC_{q+1}, \ldots$, and so forth. Figure 5.2 displays the locations of design points for three-factor special cubic model. Table 5.5 summarizes the additional design points and D-efficiency. In summary, the proposed designs have either larger or similar D-efficiency compared with standard designs.

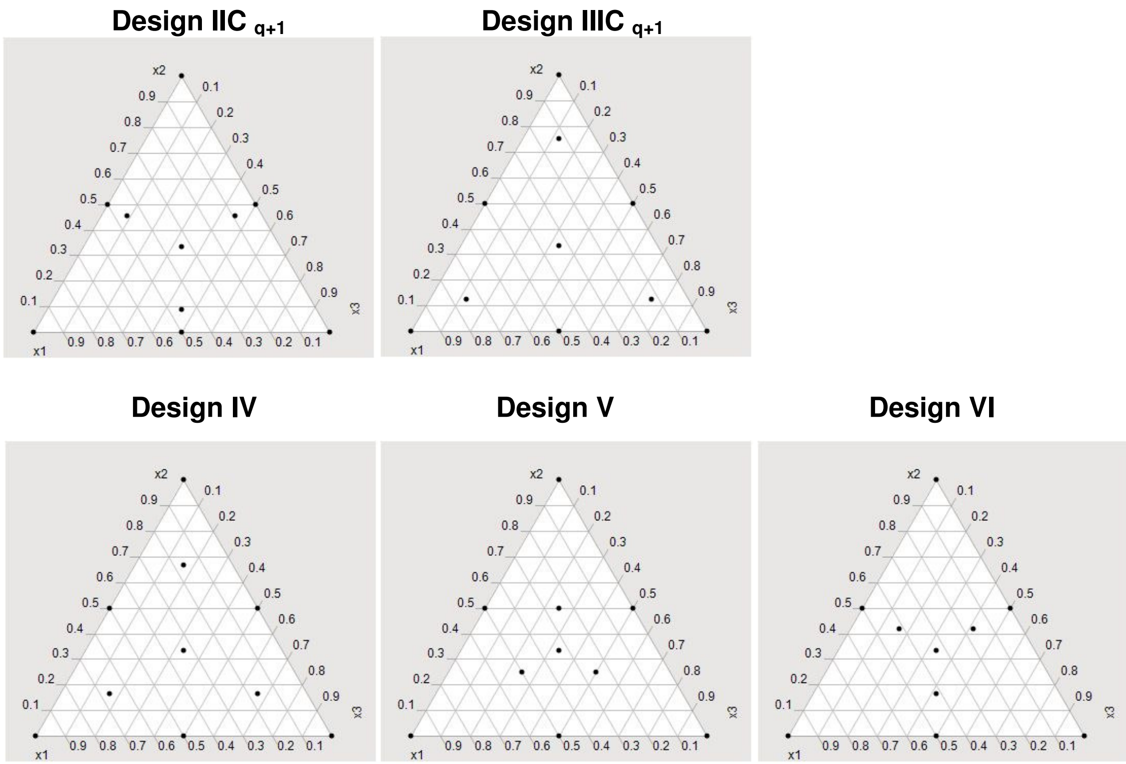

Figure 5.4: Ternary Plots for Minimal Plus $(q + 1)$ Designs for the Three-factor Special Cubic Model

Table 5.5: Minimal Plus $(q+1)$ Designs for Special Cubic Model

Factors	Designs	(q+1) Additional Points	D_{q+1}
3	IIC_{q+1}	$x \leftrightarrow (0.090, 0.455, 0.455)$ and $(1/3\mathbf{1}_\mathbf{3}^{'})$	1.418*
	$IIIC_{q+1}$	$x \leftrightarrow (0.751, 0.124, 0.124)$ and $(1/3\mathbf{1}_\mathbf{3}^{'})$	1.353
	IV	$x \leftrightarrow (2/3, 1/6, 1/6)$ and $(1/3\mathbf{1}_\mathbf{3}^{'})$	1.340
	V	$x \leftrightarrow (1/2, 1/4, 1/4)$ and $(1/3\mathbf{1}_\mathbf{3}^{'})$	1.354
	VI	$x \leftrightarrow (1/6, 5/12, 1/12)$ and $(1/3\mathbf{1}_\mathbf{3}^{'})$	1.375
4	IIC_{q+1}	$x \leftrightarrow (0.108, 0.297, 0.297, 0.297)$ and $(1/4\mathbf{1}_\mathbf{4}^{'})$	0.281*
	$IIIC_{q+1}$	$x \leftrightarrow (0.070, 0.070, 0.430, 0.430)$ and $(1/4\mathbf{1}_\mathbf{4}^{'})$	0.280
	IVC_{q+1}	$x \leftrightarrow (0.699, 0.100, 0.100, 0.100)$ and $(1/4\mathbf{1}_\mathbf{4}^{'})$	0.271
	IV	$x \leftrightarrow (5/8, 1/8, 1/8, 1/8)$ and $(1/4\mathbf{1}_\mathbf{4}^{'})$	0.270
	V	$x \leftrightarrow (1/2, 1/6, 1/6, 1/6)$ and $(1/4\mathbf{1}_\mathbf{4}^{'})$	0.273
	VI	$x \leftrightarrow (1/8, 7/24, 7/24, 7/24)$ and $(1/4\mathbf{1}_\mathbf{4}^{'})$	0.279
5	IIC_{q+1}	$x \leftrightarrow (0.126, 0.218\mathbf{1}_\mathbf{4}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.082
	$IIIC_{q+1}$	$x \leftrightarrow (0.099\mathbf{1}_\mathbf{2}^{'}, 0.267\mathbf{1}_\mathbf{3}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.083*
	IVC_{q+1}	$x \leftrightarrow (0.413\mathbf{1}_\mathbf{2}^{'}, 0.058\mathbf{1}_\mathbf{3}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.082
	VC_{q+1}	$x \leftrightarrow (0.665, 0.084\mathbf{1}_\mathbf{4}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.081
	IV	$x \leftrightarrow (3/5, 1/10\mathbf{1}_\mathbf{4}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.080
	V	$x \leftrightarrow (1/2, 1/8\mathbf{1}_\mathbf{4}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.081
	VI	$x \leftrightarrow (1/10, 9/40\mathbf{1}_\mathbf{4}^{'})$ and $(1/5\mathbf{1}_\mathbf{5}^{'})$	0.082
6	IIC_{q+1}	$x \leftrightarrow (0.142, 0.172\mathbf{1}_\mathbf{5}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.031
	$IIIC_{q+1}$	$x \leftrightarrow (0.131\mathbf{1}_\mathbf{2}^{'}, 0.185\mathbf{1}_\mathbf{4}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.032
	IVC_{q+1}.	$x \leftrightarrow (0.097\mathbf{1}_\mathbf{3}^{'}, 0.237\mathbf{1}_\mathbf{3}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.032*
	VC_{q+1} .	$x \leftrightarrow (0.401\mathbf{1}_\mathbf{2}^{'}, 0.049\mathbf{1}_\mathbf{4}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.032
	VIC_{q+1}	$x \leftrightarrow (0.640, 0.072\mathbf{1}_\mathbf{5}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.031
	IV	$x \leftrightarrow (7/12, 1/12\mathbf{1}_\mathbf{5}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.031
	V	$x \leftrightarrow (1/2, 1/10\mathbf{1}_\mathbf{5}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.031
	VI	$x \leftrightarrow (1/12, 11/60\mathbf{1}_\mathbf{5}^{'})$ and $(1/6\mathbf{1}_\mathbf{6}^{'})$	0.032

Note: * Maximum D-efficiency for each factor.

CHAPTER 6

SIMULATION AND APPLICATION

We have extended D-Optimal minimal designs by adding one or multiple interior points for general mixture models, including commonly used symmetric mixture models. In summary, our proposed designs show a higher or comparable D-efficiency than standard designs. However, the differences are relatively small because the determinant of the D-Optimal minimal information matrix $\mathbf{X}'\mathbf{X}$ decreases as the number of factors increases. Recall $|\mathbf{X_1'X_1}| = |\mathbf{X}'\mathbf{X}|[1 + \mathbf{z_1}'(\mathbf{X}'\mathbf{X})^{-\mathbf{1}}\mathbf{z_1}]$, and D-efficiency $= 100 \times |\mathbf{X_1'X_1}|^{\mathbf{1/p}}/N$, where $\mathbf{X}$ is the D-Optimal minimal design matrix and $\mathbf{z_1}$ is the new added design point.

In this chapter, we explore the power of the LOF test using the minimal plus $(q+1)$ designs for three mixture models in section 5.4 by simulation. LOF describes how the model fits a set of observations by summarizing the discrepancy between the observed values and the expected values under the fitted model. We also apply the proposed designs to mixture experiments with constraints on the component proportions.

6.1 Power of the LOF Test

To test for LOF, the residual sum of squares is partitioned into the sum of squares due to pure error ($SSPE$) and the sum of squares due to Lack of Fit ($SSLF$) as follows:

$$\sum_{j=1}^{c}\sum_{i=1}^{n_j}\widehat{\varepsilon}_{ij}^2 = \sum_{j=1}^{c}\sum_{i=1}^{n_j}\left(Y_{ij}-\widehat{Y}_j\right)^2 \tag{6.1}$$

$$= \underbrace{\sum_{j=1}^{c}\sum_{i=1}^{n_j}\left(Y_{ij}-\overline{Y}_{j\bullet}\right)^2}_{\text{(sum of squares due to pure error)}} + \underbrace{\sum_{j=1}^{c} n_j\left(\overline{Y}_{j\bullet}-\widehat{Y}_j\right)^2}_{\text{(sum of squares due to Lack of Fit)}}, \tag{6.2}$$

where $i = 1, 2, 3, \ldots, n_j$ and $j = 1, 2, \ldots, c$. Y_{ij} denotes the ith observation at the jth design point, $\overline{Y}_{j\bullet}$ is the average of the n_j observations at the jth design point, and $\widehat{Y}_j$ is the fitted value at jth design point. Under the assumptions of normally distributed errors, the $SSPE$ and $SSLF$ have chi-square distributions with corresponding degrees of freedom. The degree of freedom associated with $SSPE$ is $N-c$, where N is the total number of observations and c is the number of the design points. The degree of freedom for SSE is $N-p$, where p is the number of parameters in the mixture model. The SSLF is calculated as follows:

$$SSLF = SSE - SSPE$$

with the degree of freedom $c-p$. The LOF test statistics,

$$F^* = \frac{SSLF/(c-p)}{SSPE/(N-c)}, \tag{6.3}$$

has distribution with degrees of freedom $c-p$ and $N-c$. If $F^* \leq F(1-\alpha; c-p, N-c)$, then the LOF is not significant at α level and indicates a good fit. If $F^* > F(1-\alpha; c-p, N-c)$, then the LOF is significant at α level, showing the model is inadequate, and we may need to add higher order model or add more factors to the model.

In the simulation, we assume the true models to be the commonly used mixture models, such as special cubic model, special quartic models, full cubic model, etc.

The LOF is tested for the assumed simpler mixture models nested within the true models. We also assume that the errors are independent and identically normally distributed with mean zero and a common variance $\sigma^2 = 0.1$, $\epsilon \sim N(0, 0.1)$. There are 2000 datasets simulated for each design, with two to five replicates for each design point. The LOF power is calculated based on the 2000 simulated datasets.

6.1.1 Three-factor and four-factor Second-degree Mixture Model

Here we assume the true models to be special cubic and special quartic models, while the fitted models are the second-degree mixture models. If the tail probability of the LOF test statistic computed for the fitted model is less than 0.05, then the LOF is detected.

Three-factor Second-degree Mixture Model

We simulate the responses from two models: model 11 (special cubic model) and model 12 (special quartic model) in table 6.1. Three-factor second-degree designs in table 5.3 are used. Each design contains 10 points, in which six of them are D-Optimal minimal points and four of them are interior design points including the overall centroid point. Two to five replicates are used for each design point. We denote our proposed designs as Design IIQ and Design $IIIQ$. For the robustness of the results, we allow different coefficient (α) for the additional terms in the true models. The coefficients vary from 2, 4, 6 to 8 for both models. Tables 6.2 and 6.3, and figures 6.1 and 6.2 summarize the empirical rejection rates for LOF test. These results suggest that Design IIQ consistently provides the highest power to detect LOF among all designs.

Table 6.1: True Models for Three-factor Mixture Models

True Model 11:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + 0.5(x_1x_2 + x_1x_3 + x_2x_3)$
(Special Cubic Model)	$+\alpha x_1x_2x_3 + \epsilon$
	α: $2, 4, 6, 8.$
True Model 12:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + 0.5(x_1x_2 + x_1x_3 + x_2x_3)$
(Special Quartic Model)	$+\alpha x_1^2x_2x_3 + (\alpha - 0.5)x_1x_2^2x_3$
	$+(\alpha - 1)x_1x_2x_3^2 + \epsilon$
	α: $2, 4, 6, 8.$

Table 6.2: The LOF Power when the True Model is Model 11

Replicates	Design	$\alpha = 2$	$\alpha = 4$	$\alpha = 6$	$\alpha = 8$
2	Design IIQ	9.30	25.65	52.35	80.75
2	Design IIIQ	7.05	15.95	32.85	54.80
2	Design IV	7.20	17.35	34.40	58.85
2	Design V	9.05	21.55	48.70	75.20
2	Design VI	7.40	20.75	43.60	71.05
3	Design IIQ	13.80	46.50	84.60	98.25
3	Design IIIQ	10.70	28.75	56.35	85.05
3	Design IV	9.15	30.05	62.05	89.25
3	Design V	12.20	41.15	77.15	96.75
3	Design VI	12.05	38.15	71.75	94.50
4	Design IIQ	18.00	62.25	95.30	99.95
4	Design IIIQ	11.65	39.95	73.90	95.70
4	Design IV	11.90	41.30	79.70	96.45
4	Design V	16.25	56.20	91.60	99.50
4	Design VI	14.55	52.35	89.05	99.35
5	Design IIQ	22.60	76.15	98.85	100.00
5	Design IIIQ	12.90	48.85	86.90	98.90
5	Design IV	15.50	53.45	91.05	99.40
5	Design V	19.00	68.65	97.30	100.00
5	Design VI	18.30	63.40	95.50	99.85

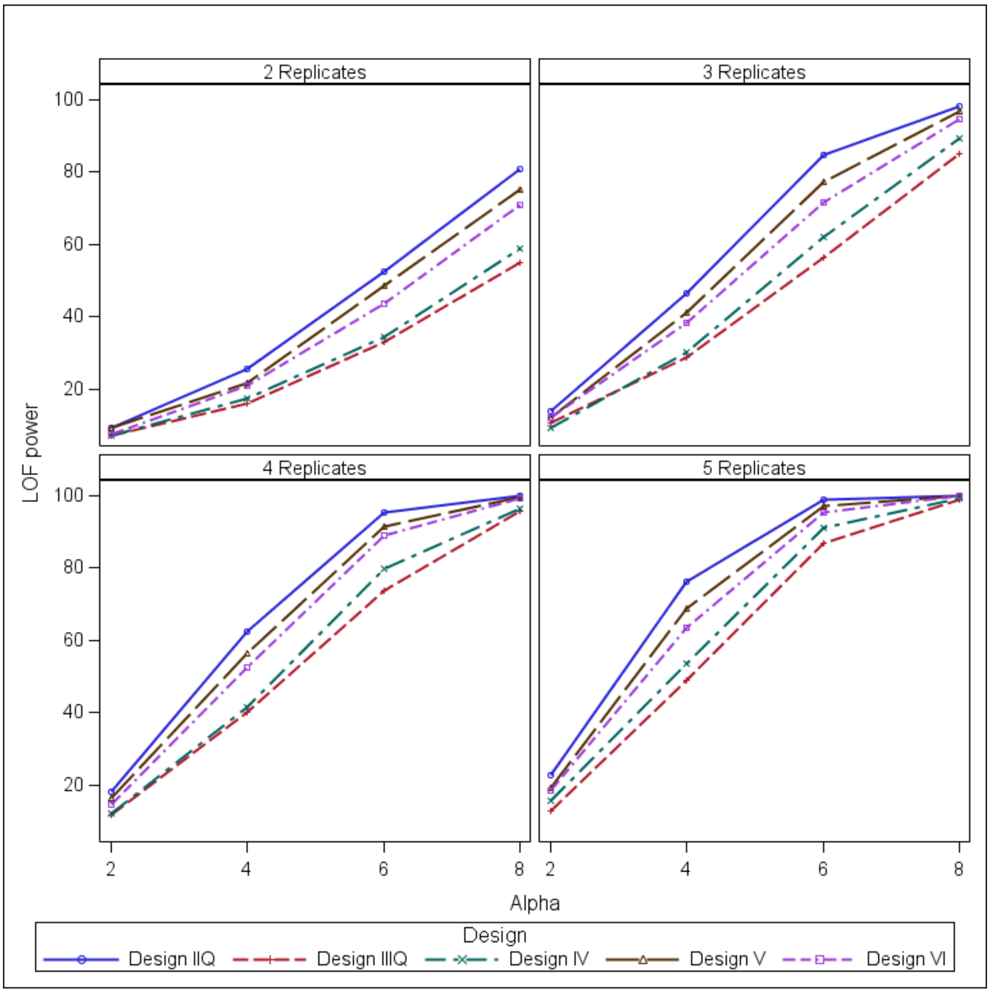

Figure 6.1: The LOF Power when the True Model is Model 11 and the Test Model is Three-factor Second-degree Model

Table 6.3: The LOF Power when the True Model is Model 12

Replicate	Design	$\alpha = 2$	$\alpha = 4$	$\alpha = 6$	$\alpha = 8$
2	Design IIQ	7.25	20.65	47.50	75.30
2	Design IIIQ	6.40	13.50	29.00	48.00
2	Design IV	6.00	14.05	31.35	54.40
2	Design V	7.25	18.20	40.80	69.60
2	Design VI	7.85	16.10	37.05	65.30
3	Design IIQ	9.55	34.15	77.50	96.75
3	Design IIIQ	8.05	21.70	49.15	78.40
3	Design IV	6.90	23.15	53.85	82.75
3	Design V	8.95	29.95	68.45	92.75
3	Design VI	7.75	28.90	64.50	91.20
4	Design IIQ	12.75	51.00	90.35	99.75
4	Design IIIQ	9.00	28.80	66.40	91.85
4	Design IV	8.65	33.15	71.60	95.35
4	Design V	10.40	44.20	84.55	99.10
4	Design VI	10.20	40.30	82.25	98.35
5	Design IIQ	13.85	63.85	96.85	99.95
5	Design IIIQ	10.65	37.25	79.05	97.85
5	Design IV	10.10	44.75	83.25	98.75
5	Design V	12.45	55.40	94.20	99.65
5	Design VI	11.45	50.70	92.35	99.55

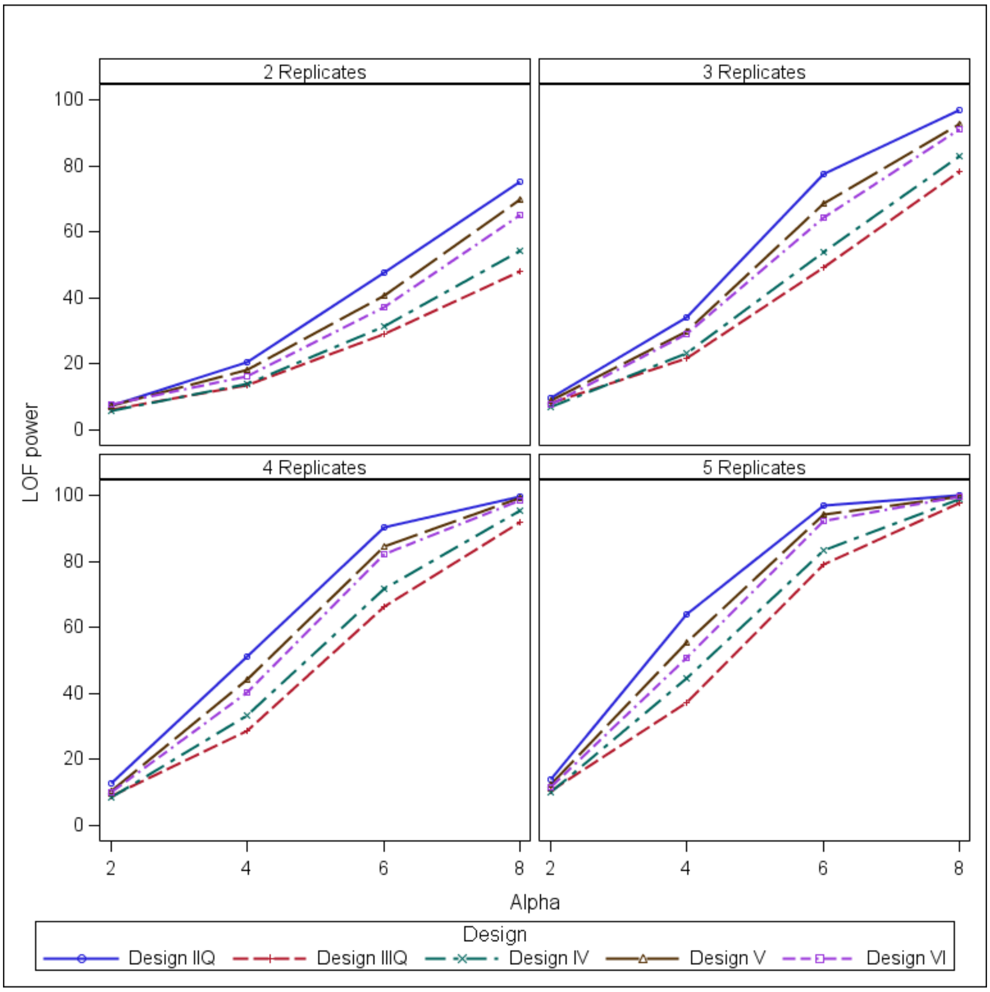

Figure 6.2: The LOF Power when the True Model is Model 12 and the Test Model is Three-factor Second-degree Model

Four-factor Second-degree Mixture Model

We simulate the responses using the models listed in table 6.4. The four-factor second-degree mixture model is used to test the adequacy of the model. Tables 6.5 and 6.6, and figures 6.3 and 6.4 summarize the empirical rejection rates for LOF test. The coefficients are 1, 2, 4, 6 for model 21 and 2, 4, 6 and 8 for model 22. Similarly, Design IIQ provides consistently higher power to detect LOF among all designs.

Table 6.4: True Models for Four-factor Mixture Models

True Model 21:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + 1.7x_4$
(Special Cubic Model)	$+0.5(x_1x_2 + x_1x_3 + x_1x_4 + x_2x_3 + x_2x_3 + x_2x_4 + x_3x_4)$
	$+\alpha(x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4) + \epsilon$
	α: $1, 2, 4, 6.$
True Model 22:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + 1.7x_4$
(Special Quartic Model)	$+0.5(x_1x_2 + x_1x_3 + x_1x_4 + x_2x_3 + x_2x_3 + x_2x_4 + x_3x_4)$
	$+\alpha x_1(x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4)$
	$+(\alpha - 0.5)x_2(x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4)$
	$+(\alpha - 1)x_3(x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4)$
	$+(\alpha - 1.5)x_4(x_1x_2x_3 + x_1x_2x_4 + x_1x_3x_4 + x_2x_3x_4) + \epsilon$
	α: $2, 4, 6, 8.$

Table 6.5: The LOF Power when the True Model is Model 21

Replicate	Design	$\alpha = 1$	$\alpha = 2$	$\alpha = 4$	$\alpha = 6$
2	Design IIQ	9.30	25.85	81.65	99.55
2	Design IIIQ	7.10	14.65	51.20	88.00
2	Design IV	7.85	15.15	56.50	91.80
2	Design V	6.35	19.60	68.30	97.25
2	Design VI	8.55	19.55	71.00	97.60
3	Design IIQ	11.45	44.10	97.55	100.00
3	Design IIIQ	8.95	24.25	77.15	99.30
3	Design IV	8.20	26.00	85.85	99.65
3	Design V	11.30	34.75	92.70	99.95
3	Design VI	10.60	34.30	93.15	99.95
4	Design IIQ	16.50	59.45	99.90	100.00
4	Design IIIQ	10.55	31.85	92.65	99.95
4	Design IV	11.20	36.30	95.10	100.00
4	Design V	13.90	47.95	98.90	100.00
4	Design VI	13.45	48.10	99.05	100.00
5	Design IIQ	20.90	70.60	100.00	100.00
5	Design IIIQ	12.00	40.10	97.15	100.00
5	Design IV	12.65	46.15	98.70	100.00
5	Design V	16.30	60.25	99.90	100.00
5	Design VI	16.90	59.75	99.85	100.00

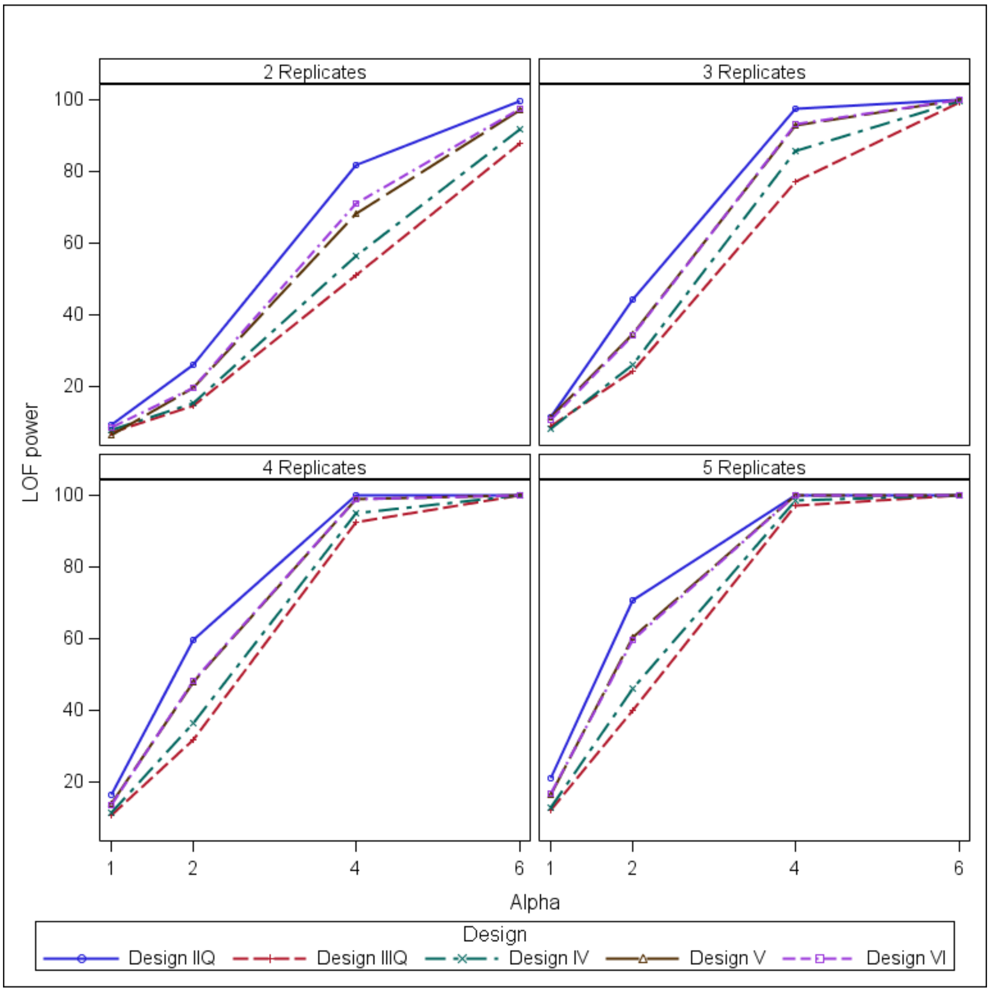

Figure 6.3: The LOF Power when the True Model is Model 21 and the Test Model is Four-factor Second-degree Model

Table 6.6: The LOF Power when the True Model is Model 22

Replicate	Design	$\alpha = 2$	$\alpha = 4$	$\alpha = 6$	$\alpha = 8$
2	Design IIQ	11.50	61.70	96.60	100.00
2	Design IIIQ	8.30	34.05	78.10	97.45
2	Design IV	8.95	41.75	82.50	98.45
2	Design V	10.55	50.20	91.95	99.90
2	Design VI	11.05	55.60	95.80	99.90
3	Design IIQ	19.25	87.85	100.00	100.00
3	Design IIIQ	10.70	57.15	96.15	100.00
3	Design IV	12.05	67.00	98.60	99.95
3	Design V	15.30	78.25	99.30	100.00
3	Design VI	15.45	83.10	99.90	100.00
4	Design IIQ	25.15	98.05	100.00	100.00
4	Design IIIQ	13.00	74.30	99.50	100.00
4	Design IV	16.35	81.85	100.00	100.00
4	Design V	19.60	92.55	100.00	100.00
4	Design VI	21.35	94.25	100.00	100.00
5	Design IIQ	31.20	99.20	100.00	100.00
5	Design IIIQ	18.85	87.00	100.00	100.00
5	Design IV	20.45	90.70	100.00	100.00
5	Design V	25.45	96.95	100.00	100.00
5	Design VI	25.15	98.60	100.00	100.00

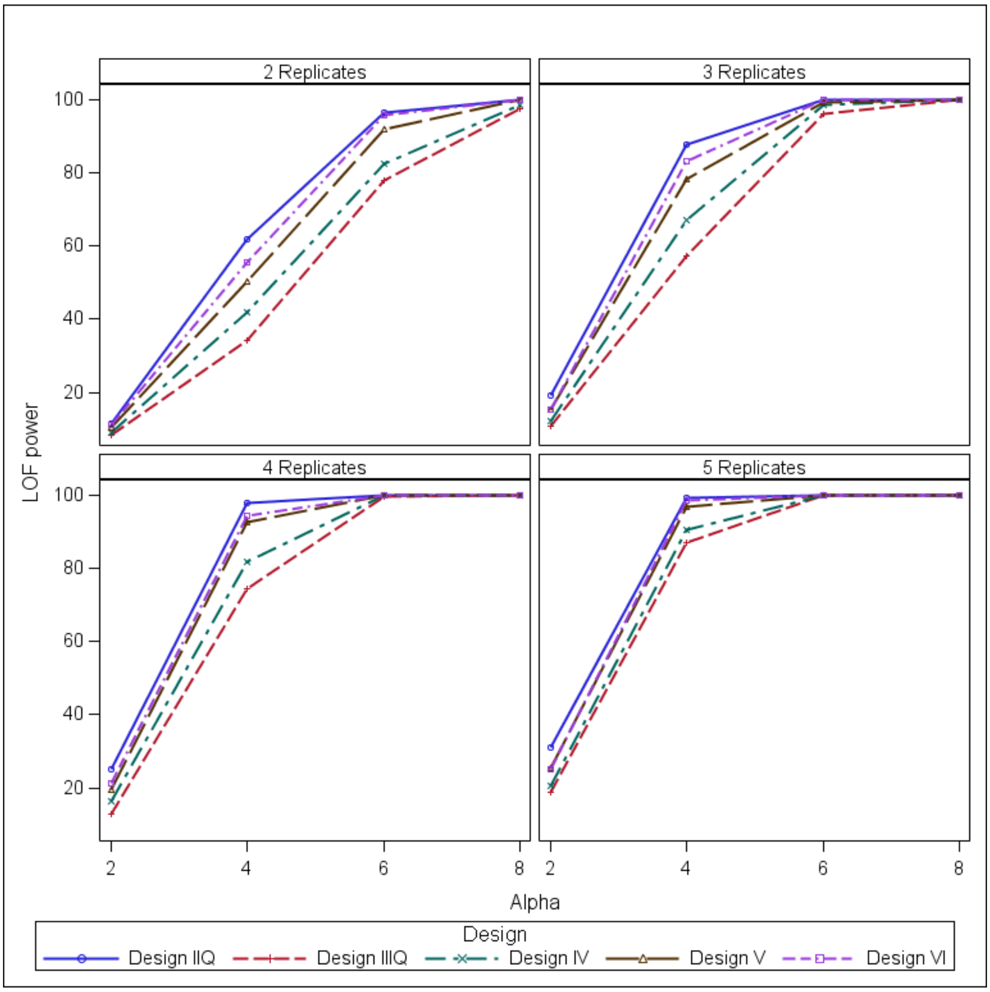

Figure 6.4: The LOF Power when the True Model is Model 22 and the Test Model is Four-factor Second-degree Model

6.1.2 Three-factor Additive Quadratic Model

Model 31 and model 32 in table 6.7 are used to simulate the responses. The three-factor minimal plus $(q + 1)$ designs from table 5.4 are used to fit the data and test for the LOF. The proposed designs are denoted as Design IIA and $IIIA$ respectively. Tables 6.8 and 6.9, Figures 6.5 and 6.6 summarize the empirical rejection rates for LOF test. In summary, Design IIA consistently provides the highest power to detect LOF among all designs.

Table 6.7: True Models for Three-factor Additive Quadratic Models

True Model 31:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + (x_1^2 + x_2^2 + x_3^2)$
	$+\alpha(x_1^3 + x_2^3 + x_3^3) + \epsilon$
	α: $0.5, 1, 2, 4.$
True Model 32:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + (x_1^2 + x_2^2 + x_3^2)$
	$+\alpha(x_1x_2x_3) + \epsilon$
	α: $2, 5, 8, 10.$

Table 6.8: The LOF Power when the True Model is Model 31

Replicate	Design	$\alpha = 0.5$	$\alpha = 1$	$\alpha = 2$	$\alpha = 4$
2	Design IIA	7.65	15.55	53.85	99.50
2	Design IIIA	6.25	11.20	31.20	89.75
2	Design IV	5.90	11.75	36.10	93.10
2	Design V	8.05	15.15	46.60	98.25
2	Design VI	6.70	13.05	43.40	97.70
3	Design IIA	8.70	26.50	83.65	100.00
3	Design IIIA	7.70	16.35	55.60	99.85
3	Design IV	7.50	18.70	62.95	99.95
3	Design V	8.80	23.75	79.25	100.00
3	Design VI	8.45	22.15	73.90	99.95
4	Design IIA	11.95	37.15	95.50	100.00
4	Design IIIA	8.80	22.75	74.40	100.00
4	Design IV	9.40	25.00	78.20	100.00
4	Design V	10.85	32.35	90.90	100.00
4	Design VI	10.70	30.15	89.20	100.00
5	Design IIA	13.50	48.15	99.00	100.00
5	Design IIIA	9.65	28.60	86.40	100.00
5	Design IV	10.65	31.20	90.75	100.00
5	Design V	12.80	41.20	96.85	100.00
5	Design VI	11.45	38.95	96.10	100.00

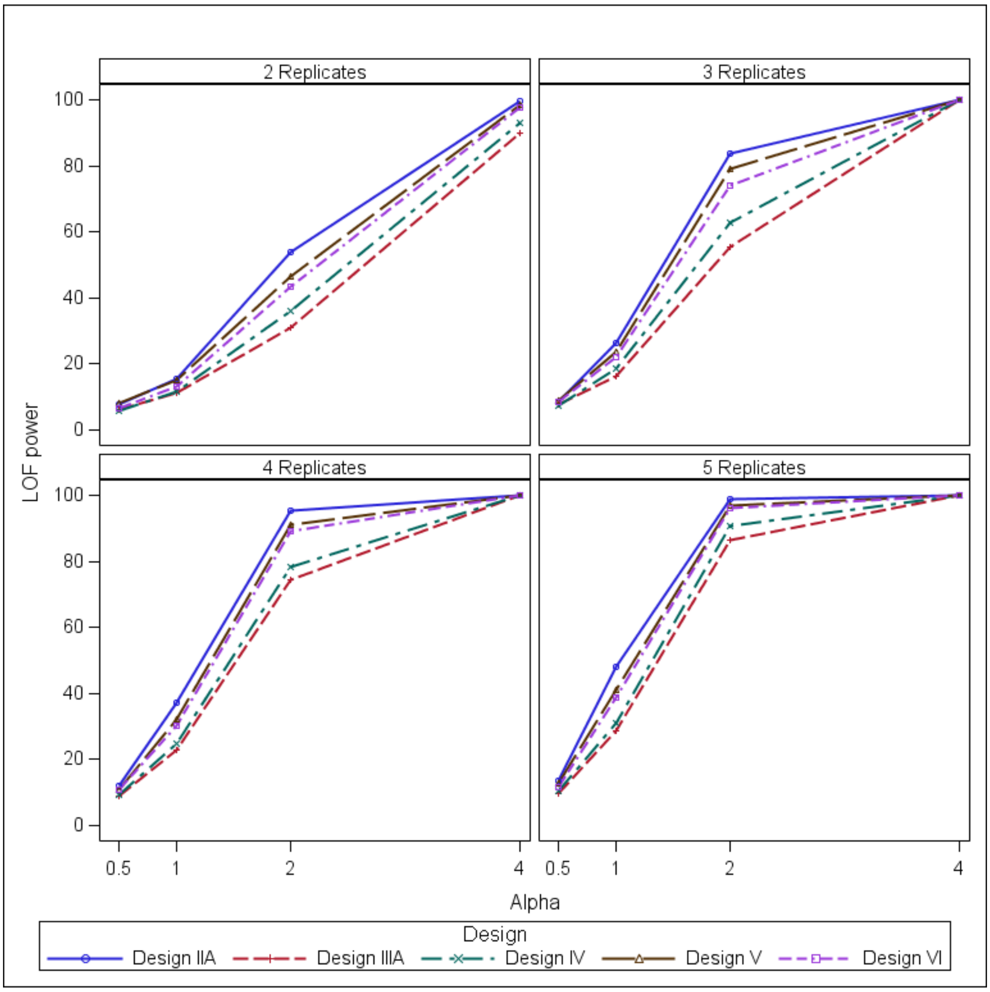

Figure 6.5: The LOF Power when the True Model is Model 31 and the Test Model is Three-factor Additive Quadratic Model

Table 6.9: The LOF Power when the True Model is Model 32

Replicate	Design	$\alpha = 2$	$\alpha = 5$	$\alpha = 8$	$\alpha = 10$
2	Design IIA	7.90	37.05	81.20	94.60
2	Design IIIA	8.10	21.25	55.35	76.95
2	Design IV	7.20	25.05	58.60	79.90
2	Design V	9.25	34.25	73.35	93.50
2	Design VI	10.20	28.85	72.40	89.85
3	Design IIA	13.20	66.90	98.65	99.80
3	Design IIIA	9.60	40.65	84.70	96.80
3	Design IV	10.25	46.35	89.25	98.10
3	Design V	12.65	60.45	96.55	99.75
3	Design VI	10.90	53.20	93.95	99.60
4	Design IIA	19.05	84.55	99.95	100.00
4	Design IIIA	11.05	56.25	95.05	99.80
4	Design IV	12.05	62.60	96.95	100.00
4	Design V	15.55	77.95	99.65	100.00
4	Design VI	13.85	73.10	99.50	99.95
5	Design IIA	22.60	93.50	100.00	100.00
5	Design IIIA	14.15	68.85	99.25	100.00
5	Design IV	16.05	75.40	99.65	100.00
5	Design V	20.35	86.10	100.00	100.00
5	Design VI	18.35	86.20	99.95	100.00

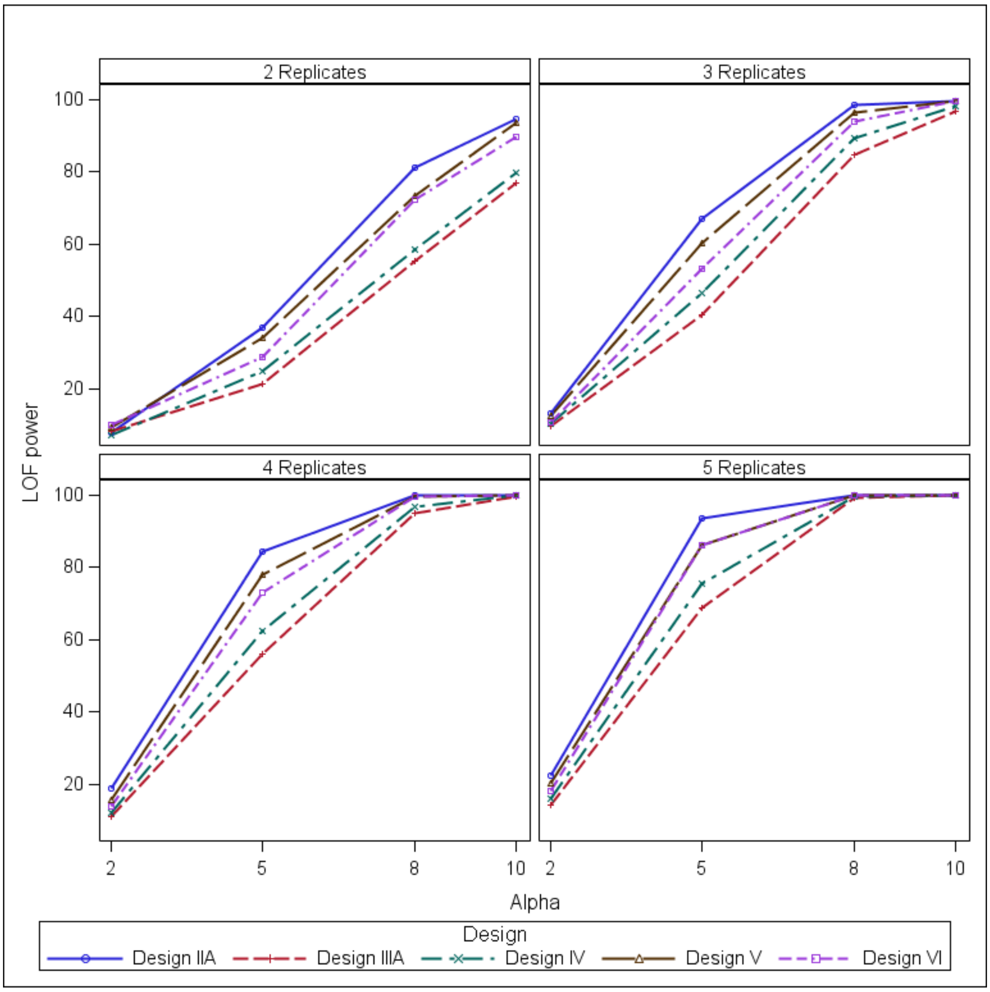

Figure 6.6: The LOF Power when the True Model is Model 32 and the Test Model is Three-factor Additive Quadratic Model

6.1.3 Three-factor Special Cubic Model

In this section, we use model 41 and model 42 listed in table 6.10 to simulate the responses. The three-factor minimal plus $(q + 1)$ designs in table 5.5 are used to fit the response and test for the LOF. We denote the proposed designs as Design IIC and $IIIC$, respectively. Tables 6.11 and 6.12, and figures 6.7 and 6.8 summarize the empirical rejection rates for LOF test. When the true model is model 41, Design IIC provides higher power to detect LOF compared with other designs. When the true model is model 42 (full cubic model), both Design IIC and Design IV have higher power to detect LOF than other designs.

Table 6.10: True Models for Three-factor Special Cubic Models

True Model 41:	$y = x_1 + 0.9x_2 + 0.8x_3 + 2(x_1x_2 + x_1x_3 + x_2x_3) + 3x_1x_2x_3$
	$+\alpha(x_1^2x_2^2 + x_1^2x_3^2 + x_2^2x_3^2) + \epsilon$
	α: $1, 5, 10, 15.$
True Model 42:	$y = 2x_1 + 1.9x_2 + 1.8x_3 + (x_1x_2 + x_1x_3 + x_2x_3) + 2x_1x_2x_3$
(Full Cubic Model)	$+\alpha x_1x_2(x_1 - x_2) + (\alpha - 0.5)x_1x_3(x_1 - x_3)$
	$+(\alpha - 1)x_2x_3(x_2 - x_3) + \epsilon$
	α: $0.5, 1, 1.5, 2.$

Table 6.11: The LOF Power when the True Model is Model 41

Replicate	Design	$\alpha = 1$	$\alpha = 5$	$\alpha = 10$	$\alpha = 15$
2	Design IIC	5.60	22.60	71.60	97.70
2	Design IIIC	4.35	4.70	6.00	7.65
2	Design IV	5.15	14.85	49.50	86.15
2	Design V	4.80	5.50	6.60	9.30
2	Design VI	5.70	5.45	4.65	5.90
3	Design IIC	5.65	37.80	93.30	100.00
3	Design IIIC	5.00	5.45	6.35	9.75
3	Design IV	5.50	24.15	74.20	98.25
3	Design V	5.65	5.80	8.60	13.15
3	Design VI	5.70	5.20	6.25	7.80
4	Design IIC	6.95	50.30	98.70	100.00
4	Design IIIC	4.70	4.40	7.65	11.80
4	Design IV	5.40	31.50	88.95	100.00
4	Design V	5.60	6.30	9.55	18.25
4	Design VI	4.60	4.40	6.90	7.95
5	Design IIC	6.35	61.35	99.90	100.00
5	Design IIIC	5.25	6.10	8.15	11.90
5	Design IV	6.55	37.70	95.80	100.00
5	Design V	5.55	6.35	12.45	20.85
5	Design VI	5.40	6.35	7.30	9.30

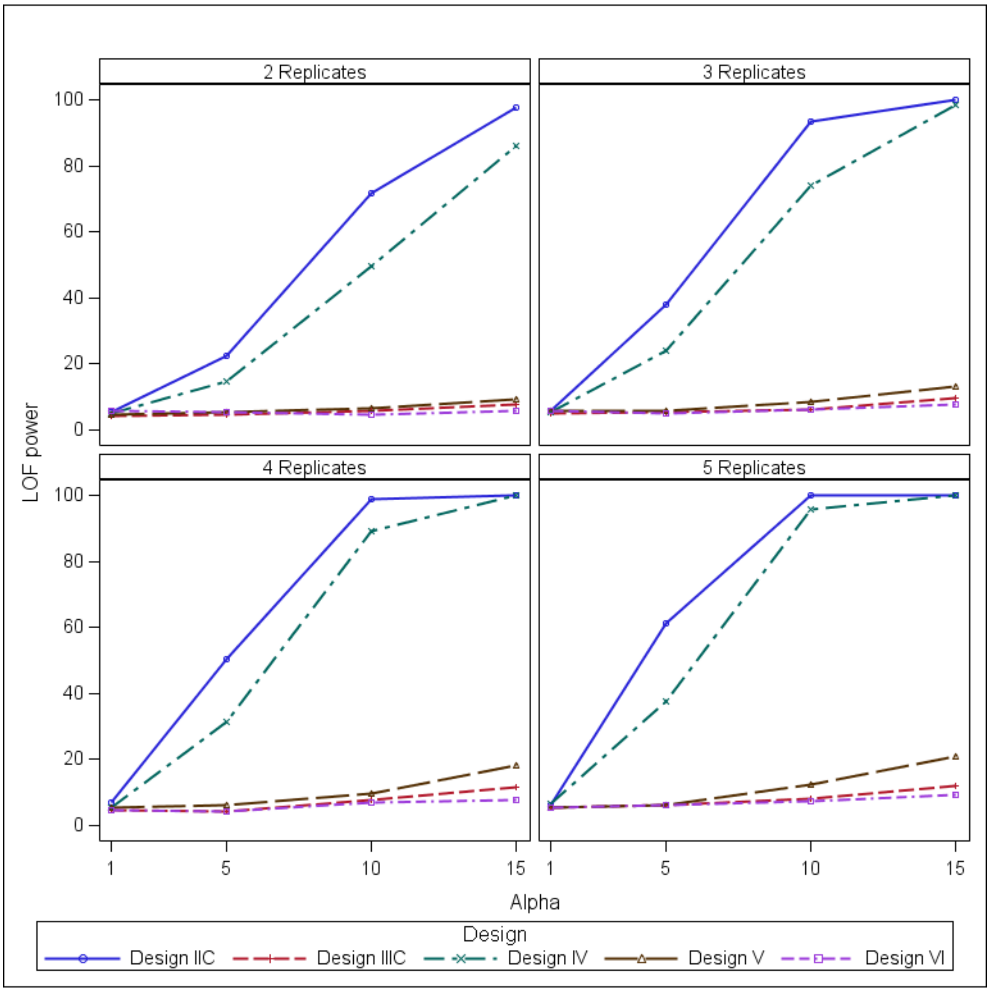

Figure 6.7: The LOF Power when the True Model is Model 41 and the Test Model is Three-factor Special Cubic Model

Table 6.12: The LOF Power when the True Model is Model 42

Replicate	Design	$\alpha = 0.5$	$\alpha = 1$	$\alpha = 1.5$	$\alpha = 2$
2	Design IIC	7.85	13.10	30.20	57.95
2	Design IIIC	5.35	5.95	6.10	8.85
2	Design IV	7.70	15.00	29.90	61.15
2	Design V	5.85	9.05	12.00	22.45
2	Design VI	6.35	5.75	7.90	10.50
3	Design IIC	10.85	21.05	52.75	85.05
3	Design IIIC	5.05	6.05	8.30	9.50
3	Design IV	11.10	21.90	51.00	85.00
3	Design V	6.70	10.10	21.75	40.60
3	Design VI	5.85	5.00	8.95	13.50
4	Design IIC	13.75	29.70	68.05	96.00
4	Design IIIC	4.85	5.95	8.40	11.75
4	Design IV	14.50	27.75	69.50	94.90
4	Design V	8.25	12.15	27.90	51.65
4	Design VI	5.45	7.80	11.10	18.10
5	Design IIC	16.25	35.70	80.85	98.70
5	Design IIIC	5.50	6.55	9.60	14.55
5	Design IV	16.10	37.65	79.90	98.95
5	Design V	8.95	14.70	36.30	66.55
5	Design VI	6.25	7.45	12.55	22.80

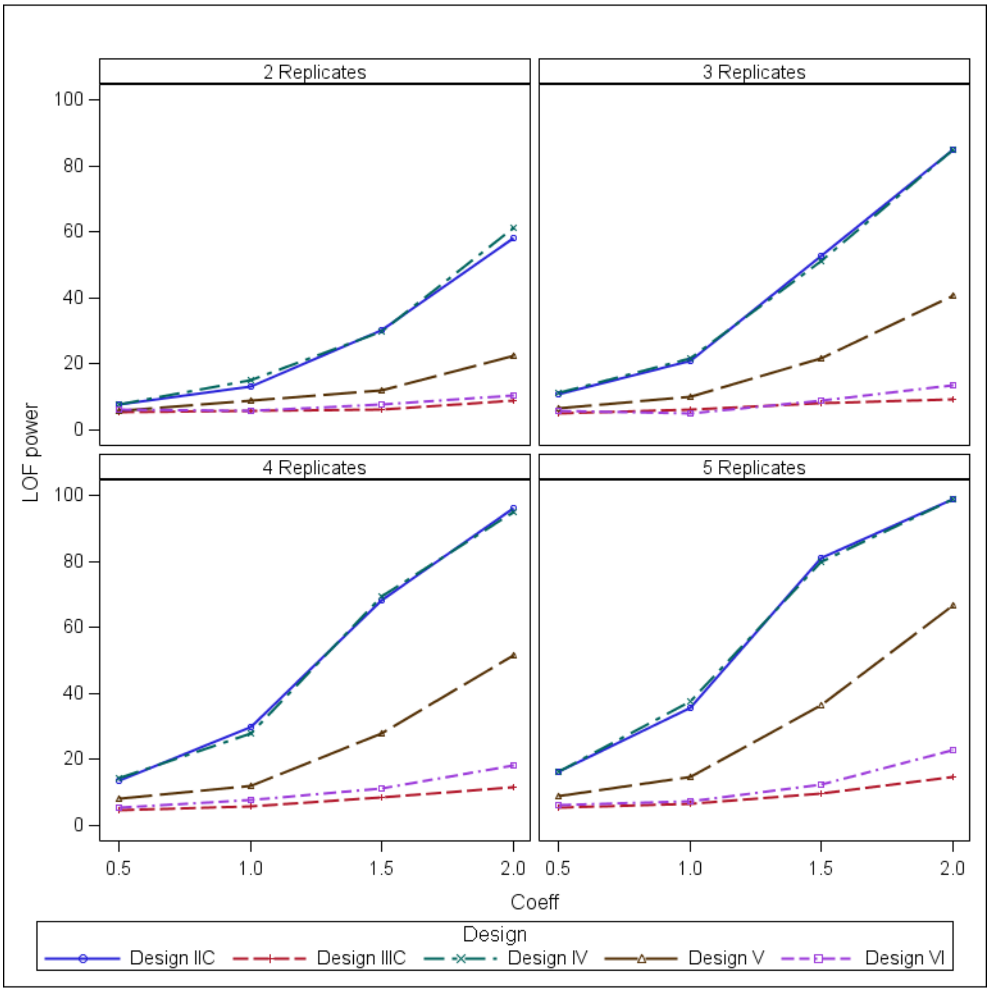

Figure 6.8: The LOF Power when the True Model is Model 42 and the Test Model is Three-factor Special Cubic Model

6.2 Application

In this section, we apply the methodology to mixture experiments with constraints on the component proportions. We continue to compare the proposed designs with standard designs in terms of D-efficiency and power of the LOF by simulation.

There are three constrained conditions:

1. Lower-bound restrictions are imposed on some or all of the component proportions, i.e. $0 \leq L_i \leq x_i$ for some or all i, $i = 1, 2, \ldots, q$.
   Kurotori (1966) introduced L-pseudocomponent transformation, defined as
   $$x_i^{'} = \frac{x_i - L_i}{1 - \sum_{1 \leq i \leq q} L_i}. \tag{6.4}$$
   The factor space in the L-pseudo components $x_i^{'}$ such that $\sum_{1 \leq i \leq q} x_i^{'} = 1$. The original component proportions could be transformed back as $x_i = L_i + (1 - \sum_{1 \leq i \leq q} L_i) x_i^{'}$.
   The linear bounds on the component proportions do not distort the shape of the subregion. It retains the shape of a regular simplex, called as L-simplex.

2. Upper-bound restrictions are imposed on some or all of the component proportions, that is, $x_i \leq U_i \leq 1$ for some or all i, $i = 1, 2, \ldots, q$.
   Crosier (1984) defined U-pseudocomponent as follows:
   $$u_i^{'} = \frac{U_i - x_i}{\sum_{1 \leq i \leq q} U_i - 1}. \tag{6.5}$$
   The original components could be transformed as $x_i = U_i - (\sum_{1 \leq i \leq q} U_i - 1) u_i^{'}$. The region of the U-pseudocomponents u_i is an inverted simplex, called U-simplex. The subregion is the interaction region of the original and the inverted simplex. The vertices of the U-simplex may extend beyond the boundaries of the original simplex, which implies the shape of the subregion might not be retained. If $\sum_{1 \leq i \leq q} U_i - min(U_1, \ldots, U_q) \leq 1$, the U-simplex lies entirely inside the original simplex.

3. Both upper and lower bounds are imposed on some or all of the component proportions, that is, $0 \leq L_i \leq x_i \leq U_i \leq 1$ for some or all i, $i = 1, 2, \ldots, q$. First we need to check the consistency of the upper and lower bounds. Let

$$R_L = 1 - \sum_{1 \leq i \leq q} L_i, \quad R_U = \sum_{1 \leq i \leq q} U_i - 1, \quad R_i = U_i - L_i.$$

If $R_i > R_L$ or $R_i > R_U$, that indicates an inconsistency lower bound L_i or upper bound U_i. Next the choice of using L-pseudocomponents or U-pseudocomponents transformation depends on the shape of the experimental region. If $R_L < R_U$, then the L-simplex is smaller than the U-simplex. Additionally if the L-simplex is completely inside the U-simplex, then L-pseudocomponent is used for transformation; otherwise U-pseudocomponent is used. If $R_L > R_U$, then the U-simplex is smaller than the L-simplex, and furthermore if U-simplex is entirely inside the L-simplex, then U-pseudocomponent is used; otherwise L-pseudocomponent is used. If neither simplex is inside the other or if $R_L = R_U$, then the experimental region is changed from simplex to hyperpolyhedron, and U-pseudocomponent is used.
When the shape of subregion has changed to hyperpolyhedron, it becomes complicated. Usually we need to first identify the number of vertices and higher-dimensional boundaries of the region. In general, the set of design points consists of at least q extreme vertices, the midpoints of at least $q(q-1)/2$ edges, and a subset of the face centroid. The procedure of adding interior points for hyperpolyhedron will not be discussed here.

We use the following example to illustrate pseudo transformation of the proposed designs, and explore the D-efficiency and power of the LOF test.

A tropical beverage was formulated by combining watermelon (x_1), orange (x_2), and pineapple (x_3) juices. It was decided to restrict the percentage of each components as follows: at least a proportion of 0.35 of watermelon is required to be present in each blend, combined with at least a proportion of 0.25 for orange, and 0.20 for pineapple. Thus, the surface of the simplex is defined by placing the lower bounds

$$x_1 \geq 0.35, \quad x_2 \geq 0.25, \quad x_3 \geq 0.20$$

Using L-pseudocomponent

$$x_i^{'} = \frac{x_i - L_i}{1 - \sum_{1 \leq i \leq q} L_i},$$

we have

$$x_1^{'} = \frac{x_1 - 0.35}{0.20}, \quad x_2^{'} = \frac{x_2 - 0.25}{0.20} \quad x_3^{'} = \frac{x_3 - 0.20}{0.20}.$$

It retains the shape of a regular simplex region.

Assume a three-factor second-degree mixture model is used to fit the data. Table 6.13 lists the original and peudocomponent settings for the proposed designs and standard designs. The first 7 points are the common design points for all designs, including 6 minimal D-Optimal points and one overall centroid point. The designs are denoted as Design IIQ and $IIIQ$ for proposed designs, Design IV-VI for standard designs. Figure 6.9 shows the ternary plots for the original settings for all designs. The D-efficiency of the original settings for Designs IIQ, $IIIQ$, IV-VI are $0.0423, 0.0436, 0.0431, 0.0427$, and 0.0440 respectively. The D-efficiency are comparable for all designs. To test for the LOF, the following two models (model 1 and 2) are used to simulate the responses, and the replicates of each design point are 2, 3, 4 and 5. The second-degree mixture models are used to fit the data and check the adequacy of the models.

Model 1: $y = 0.6x_1 + 0.9x_2 + 0.7x_3 + 0.5x_1x_2 + 0.5x_1x_3 + 0.5x_2x_3 + 1000x_1x_2x_3 + \epsilon$

Model 2: $y = 20.6x_1 + 0.9x_2 + 0.7x_3 + 0.5x_1x_2 + 0.5x_1x_3 + 0.5x_2x_3 + 600x_1^2x_2x_3$ $+550x_1x_2^2x_3 + 650x_1x_2x_3^2 + \epsilon$

Figure 6.10 plots the empirical rejection rate for the LOF test for all designs. Design IIQ consistently provides the highest LOF power among all designs. Thus, Design IIQ is recommended as it provides comparable D-efficiency but has substantially higher LOF power compared with other designs.

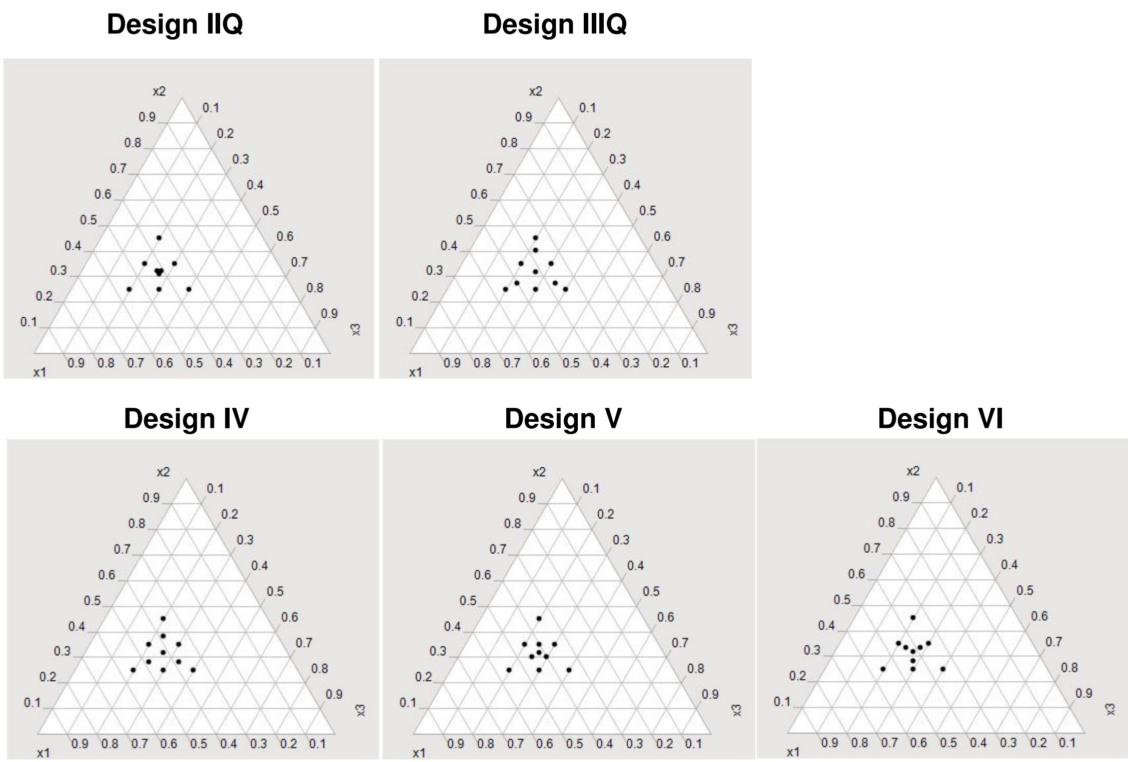

Figure 6.9: Ternary Plots for Juice Example

Table 6.13: Original and Pseudocomponents Settings for Juice Example

Designs		Pseudocomponent	Settings	Original	Component	Settings
	$x1'$	$x2'$	$x3'$	x1	x2	x3
1	1	0	0	0.55	0.25	0.2
2	0	1	0	0.35	0.45	0.2
3	0	0	1	0.35	0.25	0.4
4	0.5	0.5	0	0.45	0.35	0.2
5	0.5	0	0.5	0.45	0.25	0.3
6	0	0.5	0.5	0.35	0.35	0.3
7	0.333	0.333	0.333	0.417	0.317	0.267
IIQ	0.355	0.355	0.290	0.421	0.321	0.258
	0.355	0.290	0.355	0.421	0.308	0.271
	0.290	0.355	0.355	0.408	0.321	0.271
$IIIQ$	0.117	0.117	0.765	0.373	0.273	0.353
	0.765	0.117	0.117	0.503	0.273	0.223
	0.117	0.765	0.117	0.373	0.403	0.223
IV	0.667	0.167	0.167	0.483	0.283	0.233
	0.167	0.667	0.167	0.383	0.383	0.233
	0.167	0.167	0.667	0.383	0.283	0.333
V	0.500	0.250	0.250	0.450	0.300	0.250
	0.250	0.500	0.250	0.400	0.350	0.250
	0.250	0.250	0.500	0.400	0.300	0.300
VI	0.167	0.417	0.417	0.383	0.333	0.283
	0.417	0.167	0.417	0.433	0.283	0.283
	0.417	0.417	0.167	0.433	0.333	0.233

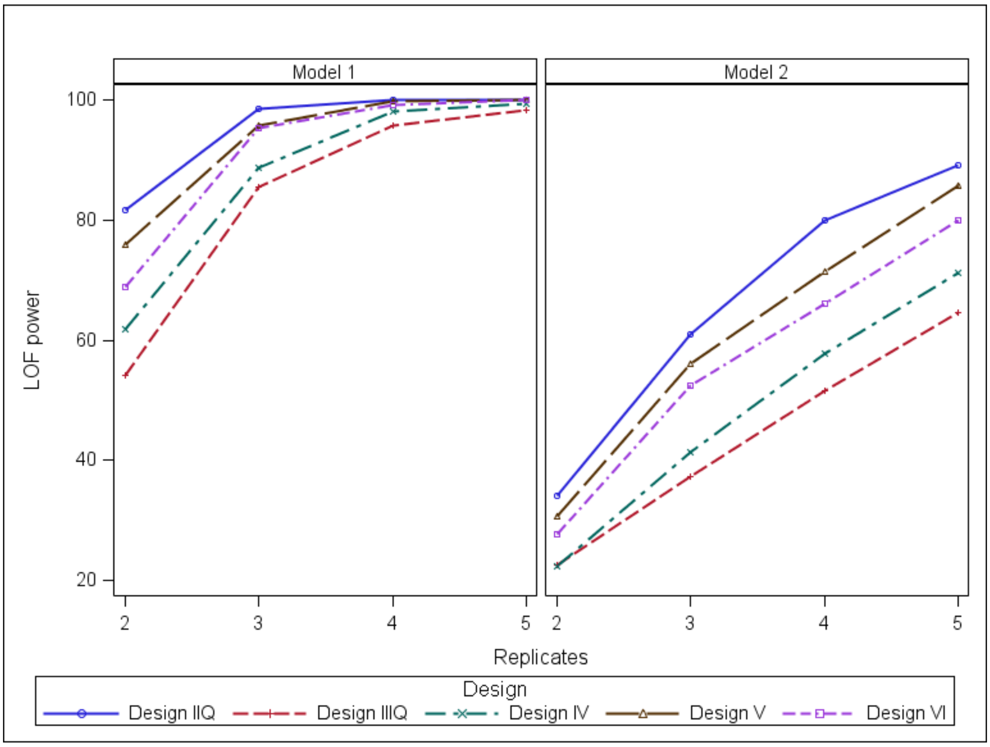

Figure 6.10: The LOF Power when the True Model is Model 1 and Model 2

CHAPTER 7

CONCLUSIONS AND FUTURE RESEARCH

In this dissertation, we investigate the problem of adding interior points to the D-Optimal minimal designs for mixture models. The proposed designs address the interest of predicting the interior design surface and enabling testing the LOF. The problem of adding one interior design point is considered initially for the special second-degree mixture model (chapter 3), then for the commonly used symmetric second-degree mixture model (chapter 4), and finally for a general mixture model with known D-Optimal minimal design (chapter 5).

It is proposed to find an additional design point as a solution to a suitable optimization problem, which is equivalent to maximizing the determinant of the information matrix of the extended design. When a local maximum does not exist in the interior of the design space, we select the stationary point with the maximum determinant of the extended information matrix as an additional point for the extended D-Optimal minimal design. The proposed designs and their D-efficiency are computed for the second-degree model, additive quadratic model, and special cubic model with a practically useful range of factors.

Furthermore, a wide subclass of symmetric mixture models is defined, which includes most of the commonly used mixture models. In this class, the proposed strategy of adding one interior design point yields multiple interior design points obtained by using permutations of the stationary point. The proposed designs are compared with the standard designs in terms of D-efficiency and power of the LOF test. The proposed designs yield higher or comparable D-efficiency among all designs, and the difference in D-efficiency is generally small. Nevertheless, the proposed designs with the shortest distance between additional interior design points and the overall centroid provide substantially higher LOF power than standard designs for commonly used and assumed mixture models.

In this concluding chapter, we outline two directions for further research. First, there are applications with mixture models with amount constraints. The D-Optimal minimal designs for such mixture models with amount constrains have been recently developed by Zhang and Wong (2013). It might be of interest to generalize the proposed methodology of extending D-Optimal minimal designs for a general constrained space.

The second direction is to consider the models that include process variables in the mixture experiment. Then the response depends not only on the proportion of the mixture components present in the mixture but also on the processing conditions. Process variables are factors in an experiment that do not form any portion of the mixture but whose levels could affect the blending properties of the components. The models involve both mixture variables and process variables. The methodology used to construct optimal designs involving process variables is a composition of two smaller designs, one being a mixture design for the mixture components only and the other being factorial/fractional factorial design for the process variables. For the data analysis, the mixed fractions are used for the process variables, where the matched fraction design consists of same fraction in the process variables at each and all mixture blends, and the mixed fraction design consists of different fractions in the process variables at various mixture blends. We are interested to incorporate the proposed extended D-Optimal minimal designs for mixture experiment with process variables.

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