International Journal of Pure and Applied Mathematics
Volume 36 No. 3 2007, 373-390

ANALYZING MIXTURE EXPERIMENTS VIA GENERALIZED LINEAR MODELS

Kadri Ulaş Akay[1 §], Müjgân Tez[2]
[1,2]Department of Mathematics
Faculty of Arts and Sciences
University of Marmara
Göztepe-Kadıköy, Istanbul, 34722, TURKEY
[1]e-mail: kadriulas@marmara.edu.tr
[2]e-mail: mtez@marmara.edu.tr

Abstract: In the studies done till now, situations, where mixture experiments have a response with a normal distribution, have been taken into account. In case of having a response with a normal distribution, it would be sufficient to use Scheffé canonical polynomials and other mixture model forms for the analysis of the mixture experiments. However, as in many applications, there are situations when mixture experiments do not have a response with a normal distribution. In this paper, Generalized Linear Models (GLMs), which with a help of a link function takes advantage of natural distribution of the response, were used for the analysis of mixture experiments with a Gamma distribution. As a linear predictor, not only Scheffé models without a constant term were used but also mixture models with inverse terms were taken into account. The best subset models were obtained by using Gamma distribution together with canonical and non-canonical link functions. Then the proposed approach was examined on one example in literature.

AMS Subject Classification: 62K99, 62J12
Key Words: mixture experiments, generalized linear models, nonnormal response, Scheffé canonical polynomials, inverse terms in mixture models

Received: February 2, 2007

[§]Correspondence author

1. Introduction

In mixture experiments, the measured response is assumed to depend only on the proportions of the ingredients present in the mixture, not on the amount of the mixture. For example, the response might be the tensile strength of stainless steel, which is a mixture of iron, nickel, copper and chromium, or the octane rating of a blend of gasolines. The purpose of mixture experiments is to build an appropriate model that will relate the response(s) to the mixture components. The resulting models can be used to understand how the responses depend on the mixture components.

In a q-components mixture in which x_i represents the proportion of the i-th components present in mixture,

$$0 \leq x_i \leq 1\,, \quad i = 1, 2, ..., q\,, \; \sum_{i=1}^{q} x_i = 1\,. \tag{1}$$

The composition space of the q components takes the form of a regular $(q-1)-$ dimensional simplex. In modeling of mixture experiments, apart from using Scheffé canonical polynomials, mixture models with inverse terms, Becker homogenous mixture models and also models with slack variables are widely used (Cornell, [2]).

Mixture model forms, most commonly, used in fitting data are the canonical polynomials introduced by Scheffé [11] in the form,

$$E\left(Y\right) = \eta = \sum_{i=1}^{q} \beta_i x_i + \sum^{q}\sum_{i \leq j}^{q} \beta_{ij} x_i x_j + \sum^{q}\sum_{i \leq j \leq k}^{q}\sum^{q} \beta_{ijk} x_i x_j x_k\,. \tag{2}$$

For modeling well-behaved systems, generally the Scheffé polynomials are sufficient. For some situations, however, there are better modeling forms than Scheffé polynomials. For example, as an alternative to Scheffé mixture models, models with inverse term are used in order to model an extreme change in the response behavior as the value of one or more components tends to a boundary of the simplex region. The following, special cubic model including an inverse term was proposed by Draper and St. John [3],

$$E\left(Y\right) = \sum_{i=1}^{q} \beta_i x_i + \sum^{q}\sum_{i \leq j}^{q} \beta_{ij} x_i x_j + \sum^{q}\sum_{i \leq j \leq k}^{q}\sum^{q} \beta_{ijk} x_i x_j x_k + \sum_{i=1}^{q} \beta_{-i} x_i^{-1}\,. \tag{3}$$

The concerned response η, can be given as a function of x_i mixture components in the form,

$$\eta = f\left(x_1, x_2, ..., x_q\right) . \tag{4}$$

Therefore when the i-th experiment is performed,

$$y_i = \eta_i + \varepsilon_i . \tag{5}$$

In equation (5), if the values of $\varepsilon_i \sim NID\left(0, \sigma^2\right)$ and y_i are assumed to be the realization of a random variable, Y_i, then for the models (2) and (3), it is $Y_i \sim N\left(\mu_i, \sigma^2\right)$.

As usual we can represent the Scheffé canonical polynomial models and models with inverse term in a matrix form by

$$\mathbf{Y} = \mathbf{X}\beta + \varepsilon , \tag{6}$$

where $\mathbf{Y}$ is $n \times 1$ vector of observations on the response variable, $\mathbf{X}$ is $n \times p\,(\geq q)$ matrix, where p is number of the terms in the model, β is vector of parameters to be estimated and ε is $n \times 1$ vector of errors. It was assumed the errors have the property

$$E\left(\varepsilon\right) = 0, \quad E\left(\varepsilon\acute{\varepsilon}\right) = \sigma^2 \mathbf{I}_n , \tag{7}$$

where $\mathbf{I}_n$ is the identity matrix and σ^2 is the error variance. Hence $E\left(\mathbf{Y}\right) = \mu = \mathbf{X}\beta$, where μ is column vector of all expected responses. The expression $\mathbf{X}\beta$ is called the linear predictor and includes many special cases of the interest. The least squares estimator for β is $\mathbf{b} = \left(\acute{\mathbf{X}}\mathbf{X}\right)\acute{\mathbf{X}}\mathbf{y}$ and variance-covariance matrix of $\mathbf{b}$ is var($\mathbf{b}$) $= \left(\acute{\mathbf{X}}\mathbf{X}\right)^{-1}\sigma^2$. A comprehensive reference on the design and analysis of the mixture data is given by Cornell [2].

In recent years, most of the interest has been focused on model building technology for situations in which model errors are nonnormal (Myers and Montgomery [8], Hamada and Nelder [4]). Applications with a nonnormal response like count of defects, proportions defective or times to failure have been taken into account in many experimental designs. These responses may follow Poisson, binomial and Gamma distributions, respectively. In each case, the variance is not a constant, but rather a function of the mean. For example, variance in Gamma distribution is the square of the mean. If the fitted linear model is correct, the least squares estimators will still be unbiased, but they will no longer possess the minimum variance property. This is because the optimality properties related with the least squares depend on the assumption of normality and homogenous variance. In this case, for the responses with binomial, Poisson and Gamma distribution, different methods from the least squares method should be used. One of these methods is the weighted least squares approach. The weighted least squares approach in mixture experiments was given by Cornell [1]. However, it is usually hard to decide the weights except from in some special situations. So, instead of determining the weights, a method which would iteratively determine them would be much more favorable. For this reason, Generalized Linear Models (GLMs) can be used in mixture experiments in order to obtain the parameter estimations with the help of iteratively reweighted least squares.

In this paper, mixture experiments with Gamma distribution will be examined. The purpose is to derive alternative models that can be used to explain the mixture system with different linear predictors and different link functions. Model control graphs and mixture surfaces will be drawn for the models that will be obtained. Interpretation of the mixture system will be done by using GLMs.

2. The Generalized Linear Models

GLMs offer a powerful alternative to data transformation (Lewis et al [5], [6]). Myers and Montgomery [8] and Hamada and Nelder [4] gave a comprehensive study on GLMs by the problems about the data transformation in response surface methods. Lewis et al [5] analyzed the five samples, which were analyzed before with response transformation in response surface methods, by using GLMs. Many potential problems related with the data transformation – the most practical method for obtaining the normality and the constant variance – have been mentioned in the literature (Hamada and Nelder [4]). The concepts underlying the use of GLMs allow one to fit models in the presence of natural non-homogenous variance and to work with parameter estimates that possess desirable properties rather than performing a transformation that would be expected to produce normality and homogenous variance simultaneously. Rather than transforming data to get an approximate normality, the class of allowed distributions for the untransformed response can be expanded. This wider class is called the exponential family.

All members of the exponential family of distributions have probability density functions for an observed response y that can be expressed in the form

$$f\left(y;\theta,\phi\right)=\exp\left\{\frac{y\theta-b\left(\theta\right)}{a\left(\phi\right)}+c\left(y,\phi\right)\right\}, \qquad (8)$$

where $a\left(\cdot\right), b\left(\cdot\right)$ and $c\left(\cdot\right)$ are specific functions. The parameter θ is a natural location parameter, and ϕ is often called a dispersion parameter. Members of exponential family include normal, binomial, Poisson, Gamma, inverse normal, geometric and negative binomial distributions. Gamma distribution in the form of (8) is

$$f(y;\mu,\phi) = \exp\left\{\left(y\left(-\frac{1}{\mu}\right) - \ln\mu\right)\nu + \nu\ln(\nu y) - \ln y - \ln\Gamma(\nu)\right\}, \qquad (9)$$

where $\theta = -\mu^{-1}$, $\phi = \nu^{-1}$, $a(\phi) = \phi$, $b(\theta) = -\ln(-\theta)$ and $c(y,\phi) = \nu\ln(\nu y) - \ln y - \ln\Gamma(\nu)$.

The mean and variance of Y in (8) are

$$E(Y) = b'(\theta), \quad \mathrm{var}(Y) = a(\phi)\, b'(\theta)\ . \qquad (10)$$

For Gamma distribution $E(Y) = \mu$ and $\mathrm{var}(Y) = \phi\mu^2$. Additional information on GLMs can be found McCullagh and Nelder [7], Myers et al [9] and Nelder and Wedderburn [10].

A GLM consists of three components: (1) the response distribution, which is a member of the exponential family; (2) a linear predictor, which is a linear combination of design variables, including main effects and interactions; and (3) a link function which relates the natural mean for specified exponential family member to linear predictor. The structure of GLMs for mixture experiments can be presented more clearly as follows.

2.1. The Linear Predictor (Systematic Structure)

In general, when GLMs are fitted, first and second-degree models are used as linear predictors. Scheffé canonical polynomials (2) and mixture models with inverse term (3) will be used for the systematic part including linear predictors. The best subset regression models (linear predictors) which obtained from the models (2) and (3) will be given in tables. In these models, linear mixture terms $(x_1, x_2, ..., x_q)$ are reserved in model and significant interaction and inverse terms are included to model. For the models for which the model control graphs are adequate, mixture surfaces on the experimental region will be obtained as well.

2.2. The Link Function

Unlike a transformation, a link function takes advantage of the natural distribution of the response. The model can be found with the help of a differentiable link function as

$$\eta_i = g(\mu_i)\ . \qquad (11)$$

Distribution	**Canonical Link**
Normal	$\eta_i = \mu_i$ (identity link)
Binomial	$\eta_i = \ln\left(\frac{p_i}{1-p_i}\right)$ (logistic link)
Poisson	$\eta_i = \ln(\mu_i)$ (log link)
Gamma	$\eta_i = \frac{1}{\mu_i}$ (reciprocal link)
Exponential	$\eta_i = \frac{1}{\mu_i}$ (reciprocal link)

Table 1: Canonical link for various exponential family members

There are many possible choices for link functions. If for (11) $\eta_i = \theta_i$, then η_i is a canonical link. Canonical link functions of some distributions are given in Table 1.

In this paper, alternative models which explain the mixture system in the best way will be defined by using different link functions.

2.3. The Random Component

For a GLM, the observations $y_1, y_2, ...y_n$ are assumed to be independent with means $\mu_1, \mu_2, ..., \mu_n$, respectively. We treat y_i as a realization of a random variable Y_i. If $Y_i \sim N\left(\mu, \sigma^2\right)$, the special case of GLM known as normal linear regression will be obtained. In this case, Scheffé canonical polynomials and models with inverse terms will be written as

$$\eta_i = \mu_i = \mathbf{x}_i'\beta, \quad i = 1, 2, ..., n\,. \tag{12}$$

The GLM framework provides an extension of normal linear model by considering alternative link functions.

Let the probability density function of the random variable Y_i have the Gamma distribution (9). When $\phi = 1$ is in function (9), the distribution is reduced to exponential distribution. Exponential and Gamma distributions have many applications in times to failure, reliability and survival time problems (Myers et al [9], McCullagh and Nelder [7]). For both distributions, the variance is equal to the square of the mean. As a result, one important feature for both distributions is that $\frac{\sigma_y}{\mu_y}$ is constant. This property is interpreted as constant coefficient of variation. The coefficient of variation (CV) for the Gamma distribution is

$$CV = \frac{\{\text{var }(Y)\}^{\frac{1}{2}}}{E\,(Y)} = \sqrt{\phi}\,. \tag{13}$$

The CV is a specific measure of variation which scales the standard deviation by the expectation. Thus, rather than having a constant variance, Gamma distribution imposes the constant coefficient of variation. Therefore, continuous data with skewed distribution and variation that increases with the mean can be modeled with a Gamma distribution.

As it is given in Table 1, the reciprocal link function is a canonical function of both the exponential and Gamma distribution. If the reciprocal function is taken as the link function, the model will be given as,

$$\mu_i = \frac{1}{\mathbf{x}_i' \beta}\,, \quad i = 1, 2, ..., n\,. \tag{14}$$

However, in many applications both the log and identity link may be useful.

Parameter estimation in GLMs is performed with the method of maximum likelihood. The computer package programs to support the fitting of GLMs are *SAS*, *S-PLUS*, *STATA* and *GENSTAT*. In this paper, parameter predictions were done by using the program, *GENSTAT*, after determining GLMs with the best subset linear predictors. The approaches taken for the use of GLMs in mixture experiments will be examined on the following part over the resistivity data set.

3. Example

Surface resistivity values for paper coatings were recorded for 10 different blends of three chemicals (A, B and C). The data are listed in Table 2. Blends 11, 12 and 13 are replicate formulations of blend 1. The constrained region defined by

$$0.75 \leq x_1 \leq 0.90, \quad 0.10 \leq x_2 \leq 0.25, \quad 0 \leq x_3 \leq 0.15 \tag{14}$$

is shown in Figure 1 (Cornell [2]).

The design in Figure 1 is augmented simplex-centroid design when the units are expressed in terms of L-pseudocomponent proportions.

Cornell gave results about the resistivity data set related with the use of Scheffé models and models with inverse terms. These results provided evidence that the mixture models including inverse terms are better than Scheffé models. This can be understood by looking at the resistivity data in Table 2: 12.2, 12.5, and 13.5 values appear around the border where x_3 the component is zero. In this case, mixture models with inverse term are more advantageous to use in order to model these changes than Scheffé models. In the modeling studies of Cornell, done by using real components, by taking into account that x_3

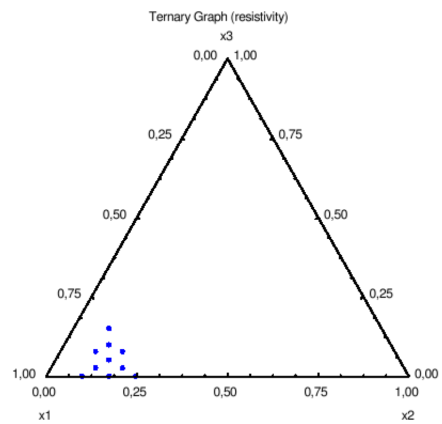

Figure 1: An augmented simplex-centroid design for the paper coatings arguments

	Chemical Proportions			
Blend No	*A* (x_1)	*B* (x_2)	*C* (x_3)	*Surface Resistivity (SR)*
1	0.800	0.150	0.050	10.4
2	0.825	0.100	0.075	10.8
3	0.850	0.125	0.025	11.1
4	0.750	0.250	0.000	12.2
5	0.750	0.100	0.150	9.9
6	0.825	0.175	0.000	12.5
7	0.775	0.125	0.100	9.9
8	0.900	0.100	0.000	13.5
9	0.775	0.200	0.025	10.4
10	0.750	0.175	0.075	9.7
11	0.800	0.150	0.050	10.5
12	0.800	0.150	0.050	10.4
13	0.800	0.150	0.050	10.3

Table 2: Resistivity values for the paper coating experment

component is zero for the model with inverse term, each component has been added $c = 0.01$. Cornell has offered two alternative models that can be used to model mixture system. Table 3 includes the alternative subset regression models which can be used for modeling the mixture system. The (X) symbol was used to show that the term used in the model is not meaningful.

Models	*Best subsets with 1 terms*							*Best subsets with 2 terms*				*Best subsets with 3 terms*	
No	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
x_1	11.786 (0.254)	13.258 (0.662)	0.67 (3.63)	13.085 (0.764)	−85.1 (39.2)	8.198 (0.802)	−58.5 (23.3)	−71.3 (23.8)	14.068 (0.594)	2.8 (3.1)	13.977 (0.664)	13.576 (0.546)	13.668 (0.57)
x_2	2.008 (0.999)	8.11 (3.15)	30.32 (7.93)	8.39 (3.66)	−249 (101)	10.21 (1.89)	−176.5 (60.1)	−208.5 (61.2)	5.33 (2.65)	25.25 (6.82)	5.49 (2.97)	43.7 (12.4)	43.8 (13.0)
x_3	4.33 (1.52)	25.8 (10.1)	−24.22 (4.85)	23.8 (11.9)	−264 (101)	−1.93 (1.62)	−163.9 (62.1)	−196.5 (62.6)	18.86 (8.2)	110.4 (57.5)	178 (56.6)	4.86 (2.75)	4.78 (2.91)
x_1x_2	X	X	X	X	X	X	X	X	X	X	X	−59.6 (18.2)	−59.7 (19.1)
x_1x_3	X	X	X	X	X	X	X	X	X	−176.7 (75.3)	−207.5 (75.2)	X	X
x_2x_3	X	X	X	−305.2 (98.6)	X	X	X	−271.1 (65.9)	1187 (445)	X	−285.1 (75.2)	−71.4 (22.8)	X
$x_1x_2x_3$	X	−428 (111)	X	X	X	X	−361.2 (82.2)	X	−1922 (566)	X	X	X	−98.3 (34.3)
$(x_1+0.01)^{-1}$	X	X	X	X	104.7 (41.6)	X	76.1 (24.7)	89.6 (25.3)	X	X	X	X	X
$(x_2+0.01)^{-1}$	X	X	1.055 (0.291)	X	X	0.3153 (0.0694)	X	X	X	0.941 (0.242)	X	X	X
$(x_3+0.01)^{-1}$	0.02658 (0.00186)	X	X	X	X	0.0225 (0.00138)	X	X	X	X	X	0.02257 (0.00151)	0.02189 (0.00178)
R_A^2	98.16	83.64	82.27	78.88	74.42	99.42	91.56	90.76	90.27	88.19	87.83	99.35	99.28
MSE	0.02423	0.2150	0.2330	0.2775	0.3361	0.0076	0.1108	0.1214	0.1279	0.1552	0.1600	0.00856	0.009426

Table 3: The best subset regression models obtained for Scheff and Models with inverse terms

The models 2, 4, 9, and 11 in Table 3 are Scheffé canonical polynomials and the others are models with inverse term. It can be seen by looking at the model control graphs that the models 6, 10, and 13 are sufficient. As these models include different interactions and inverse terms, they provide an advantage to the researcher in interpreting the mixture system, so that the researcher can choose any desired model. For example, the model control graphs for model 13 in Table 3 are given in Figure 2.

x_1 and x_3 components are more effective on the response than x_2 in Figure 3. Especially with the increase in the value of x_1, the value of the response is increasing and with the increase in x_3, the value of the response is decreasing. The terms x_1x_2 and $x_1x_2x_3$, has a negative effect on the result. The large values of $(x_3 + 0.01)^{-1}$ are also more effective on the response than its small

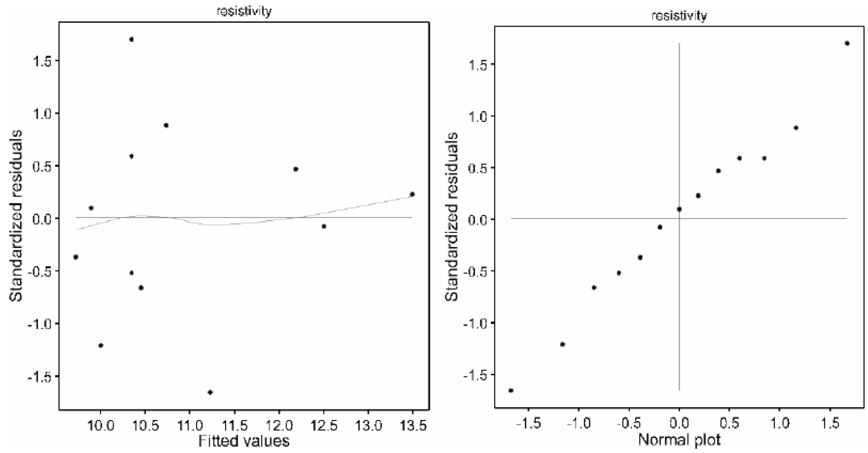

Figure 2: Model control graphs of model 13 with inverse term

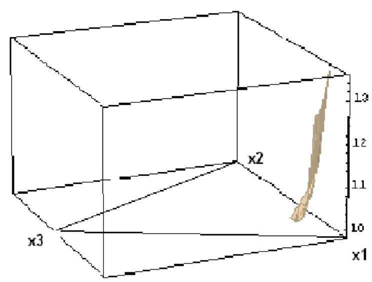

Figure 3: The mixture surface on experimental region for the model 13

values. The response take its maximum value from the upper limit of x_1 and lower limits of x_2 and x_3.

Draper and St. John [3] brought forward that the extreme changes in the response have been accompanied with non-homogenous error variance and therefore the transformations that could stabilize the variance would be suitable. In this paper, apart from the transformations that could stabilize the variance, an alternative analysis will be done by using GLMs which takes the advantage of natural distribution of the response. Because resistivity is well known to have a distribution with a heavy right tail, and thus a Gamma distribution may indeed be appropriate (Myers et al [9]). For this reason, the resistivity data for the paper layers will be analyzed with GLMs with Gamma distribution. As a linear predictor, the special cubic Scheffé model will be used. The parameter predictions and the standard errors for the different link functions of GLMs

Link Function	*Reciprocal*			*Log*				*Identity*			
Linear Predictors	*Best subsets with 1 terms*		*Best subsets with 2terms*	*Best subsets with 1 terms*		*Best subsets with 2 terms*		*Best subsets with 1 terms*		*Best subsets with 2 terms*	
No	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
x_1	0.07351 (0.0182)	0.07471 (0.00451)	0.07046 (0.00386)	2.5891 (0.0522)	2.5738 (0.061)	2.6482 (0.0487)	2.6408 (0.0543)	13.051 (0.694)	12.871 (0.798)	13.987 (0.669)	13.861 (0.75)
x_2	0.113 (0.0182)	0.1105 (0.0218)	0.1243 (0.0178)	2.162 (0.249)	2.19 (0.293)	1.959 (0.217)	1.973 (0.243)	8.61 (3.3)	8.89 (3.82)	5.44 (2.89)	5.69 (3.27)
x_3	−0.0363 (0.068)	−0.025 (0.0829)	−0.998 (0.386)	3.711 (0.796)	3.573 (0.95)	3.21 (0.673)	15.52 (4.63)	24.3 (9.18)	22.7 (10.7)	18.22 (7.67)	166.3 (55.6)
x_1x_2	X	X	X	X	X	X	X	X	X	X	X
x_1x_3	X	X	1.302 (0.51)	X	X	X	−16.05 (6.15)	X	X	X	−193.5 (74.2)
x_2x_3	X	2.638 (0.684)	2.493 (0.536)	X	−27.48 (7.88)	88.6 (36.5)	−26.04 (6.15)	X	−282.5 (89.2)	1115 (433)	−270 (70.1)
$x_1x_2x_3$	3.596 (0.737)	X	X	−38.01 (8.72)	X	−149.7 (46.4)	X	−396 (101)	X	−1815 (555)	X
Deviance	0.00927	0.01267	0.00697	0.01204	0.01594	0.00688	0.00855	0.01518	0.01946	0.00814	0.01035
MeanDev.	0.00103	0.0014	0.00087	0.00133	0.00177	0.00086	0.00106	0.00168	0.00216	0.00101	0.00129

Table 4: GLM with Gamma distribution obtained with different link functions

with Gamma distribution are given in Table 4.

Alternative models were obtained for the different link functions in Table 4, however when these models were examined with model control graphs, it was seen that they were not sufficient. For this reason, mixture models with inverse term will be used as alternative linear predictors. The parameter predictions together with the standard errors for the subset regression models obtained for reciprocal, log and identity link functions are given in Tables 5-7 respectively.

As the model control graphs of the models in Table 5 were examined, it was seen that the models 6, 9, 10, 11, and 13 were sufficient. Especially if model 13 is chosen, the model control graphs for this model given in Figure 4.

The mixture surface obtained on the experimental region for model 13 in Table 5 is given Figure 5.

From the examination of model control graphs for the models in Table 6, it was determined that only models 9 and 10 were sufficient. For example, in case of having model 9, the model control graphs are given in Figure 6.

The mixture surface obtained for GLM with log link is given in Figure 7.

The model control graphs for models in Table 7 provided evidence that only

Linear Predictors	*Best subsets with 1 terms*		*Best subsets with 2 terms*					*Best subsets with 3 terms*				*Best subsets with 4 terms*
No	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
x_1	0.08579 (0.002)	0.166 (0.02)	0.08409 (0.001)	0.08297 (0.001)	0.1172 (0.01)	0.09093 (0.002)	0.473 (0.1)	0.575 (0.1)	-0.1049 (0.06)	0.0737 (0.004)	0.10439 (0.008)	-0.364 (0.1)	0.2895 (0.07)
x_2	0.15343 (0.009)	-0.0502 (0.05)	0.13946 (0.007)	0.13969 (0.007)	0.082 (0.02)	0.14823 (0.007)	1.133 (0.3)	1.389 (0.4)	-0.543 (0.1)	-0.1089 (0.09)	0.0984 (0.01)	-1.625 (0.6)	0.651 (0.2)
x_3	0.1542 (0.01)	0.3686 (0.03)	0.0639 (0.02)	0.0653 (0.02)	0.209 (0.02)	0.762 (0.2)	1.017 (0.4)	1.277 (0.4)	-0.387 (0.1)	0.0958 (0.02)	0.1242 (0.03)	-0.852 (0.4)	0.585 (0.2)
x_1x_2	X	X	X	X	X	X	X	X	X	0.364 (0.1)	X	1.032 (0.3)	X
x_1x_3	X	X	X	X	X	-0.83 (0.3)	X	X	X	X	X	X	X
x_2x_3	X	X	0.999 (0.2)	X	X	X	X	2.378 (0.4)	X	1.046 (0.2)	0.715 (0.2)	X	5.70 (1.8)
$x_1x_2x_3$	X	X	X	1.366 (0.4)	X	X	3.155 (0.5)	X	X	X	X	X	-6.42 (2.57)
$(x_1+0.01)^{-1}$	X	X	X	X	X	X	-0.422 (0.1)	-0.53 (0.1)	0.2494 (0.07)	X	X	0.448 (0.1)	-0.2135 (0.08)
$(x_2+0.01)^{-1}$	X	-0.0076 (0.002)	X	X	-0.00276 (0.0008)	X	X	X	-0.0038 (0.0006)	X	-0.00174 (0.0007)	X	X
$(x_3+0.01)^{-1}$	-0.00018 (0.00001)	X	-0.00015 (0.00001)	-0.00014 (0.00001)	-0.00015 (0.00001)	-0.00022 (0.00002)	X	X	-0.00016 (0.00001)	-0.00014 (0.00001)	-0.00013 (0.00001)	-0.00021 (0.00002)	-0.00016 (0.00002)
Deviance	0.00289	0.01344	0.00106	0.00122	0.01298	0.00156	0.00504	0.00566	0.00051	0.00055	0.00057	0.00139	0.000436
MeanDev.	0.00032	0.00149	0.00013	0.00015	0.00016	0.00019	0.00063	0.00070	0.00007	0.00007	0.00008	0.00019	0.000072

Table 5: The parameter predictions of best subset linear predictors obtained for the reciprocal link functions from the models including inverse term

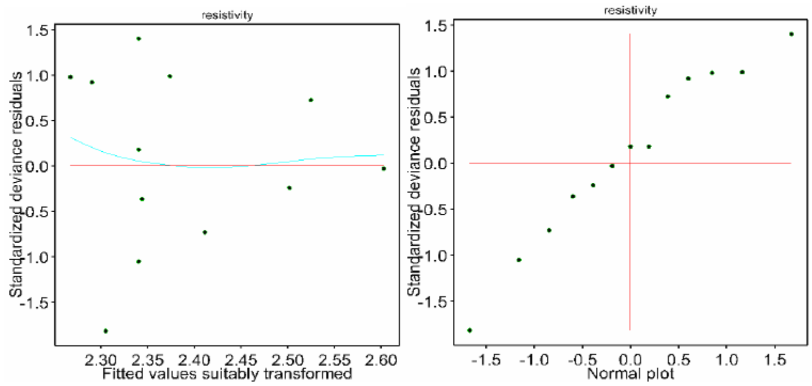

Figure 4: Model control graphs for GLM with reciprocal link

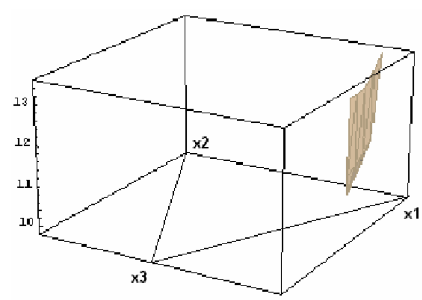

Figure 5: Mixture surface for GLM with reciprocal link

models 4 and 9 were sufficient. For example the model control graphs for model 9 are given in Figure 8.

GLMs with different interactions and inverse terms were obtained in Tables 5-7. Mixture surfaces on the experimental region were given for those models with sufficient model control graphs. The surfaces obtained on the experimental region in Figures 5, 7 and 9 are almost the same. As a result x_1 and x_3 components are more effective on the response than x_2. While x_1 has a positive effect on the response in the range $(0.75, 0.9)$, x_3 has a negative effect in the range $(0, 0.15)$. On the other hand, x_2 causes the response to decrease in a small degree in the range $(0.1, 0.15)$ and then increase in the range $(0.15, 0.25)$.

Linear Predictors	*Best subsets with 1 terms*				*Best subsets with 2 terms*				*Best subsets with 3 terms*	
No	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
x_1	2.4642 (0.02)	1.5 (0.3)	−5.32 (3.5)	2.119 (0.09)	2.4737 (0.01)	2.4839 (0.02)	−2.82 (1.9)	−3.99 (1.9)	2.6088 (0.05)	2.6204 (0.05)
x_2	1.631 (0.1)	4.077 (0.6)	−18.55 (8.9)	2.42 (0.2)	1.7795 (0.09)	1.7742 (0.09)	−11.76 (4.9)	−14.67 (5.03)	4.97 (1.1)	4.97 (1.2)
x_3	1.744 (0.1)	−0.702 (0.4)	−19.92 (8.9)	1.14 (0.1)	2.502 (0.2)	2.487 (0.3)	−10.59 (5.09)	−13.54 (5.1)	2.095 (0.2)	2.084 (0.2)
x_1x_2	X	X	X	X	X	X	X	X	−4.68 (1.7)	−4.7 (1.8)
x_1x_3	X	X	X	X	X	X	X	X	X	X
x_2x_3	X	X	X	X	−8.36 (2.8)	X	X	−24.97 (5.4)	−9.02 (2.1)	X
$x_1x_2x_3$	X	X	X	X	X	−11.43 (4.2)	−33.13 (6.74)	X	X	−12.43 (3.3)
$(x_1+0.01)^{-1}$	X	X	8.42 (3.7)	X	X	X	5.74 (2.03)	6.96 (2.07)	X	X
$(x_2+0.01)^{-1}$	X	0.0912 (0.02)	X	0.03035 (0.007)	X	X	X	X	X	X
$(x_3+0.01)^{-1}$	0.00225 (0.0001)	X	X	0.001856 (0.0001)	0.001904 (0.0001)	0.001828 (0.0002)	X	X	0.001792 (0.0001)	0.001707 (0.0001)
Deviance	0.002265	0.01477	0.02403	0.000803	0.001099	0.001200	0.005965	0.006552	0.0005304	0.0006281
MeanDev.	0.000251	0.00164	0.00267	0.000100	0.000137	0.000150	0.000745	0.000819	0.0000757	0.0000897

Table 6: The best subset linear predictors obtained for the log link functions from the models with inverse term

4. Concluding Comments

In the studies done till now, it was assumed that the response has a normal distribution in mixture experiments. Therefore, first the analyses of mixture experiments were done in case of the response having a normal distribution. As an alternative way, a link function together with the GLMs which takes the advantage of the natural distribution of the response, were examined for the analysis of mixture experiments. Different subset regression models were obtained which could be used to model the mixture system in case of the variable

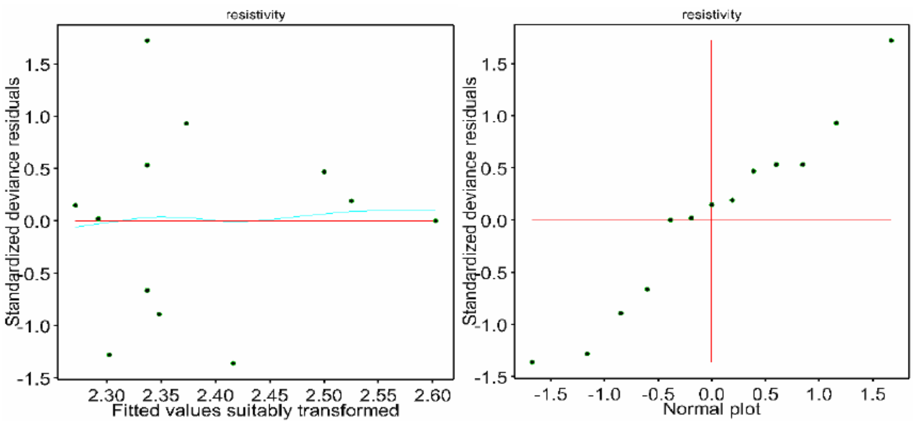

Figure 6: Model control graphs for GLM with log link

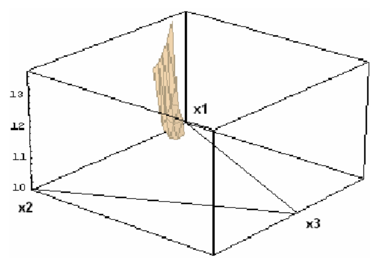

Figure 7: The mixture surface obtained for GLM with log link

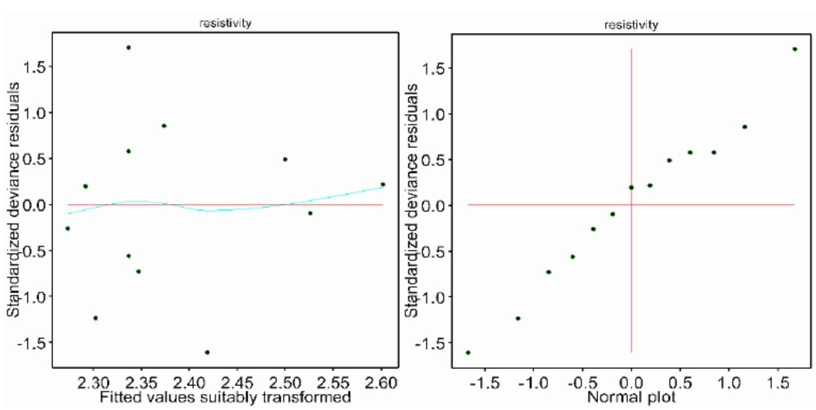

Figure 8: Model control graphs for GLM with identity link

Linear Predictors	*Best subsets with 1 terms*			*Best subsets with 2 terms*				*Best subsets with 3 terms*	
No	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
x_1	11.825 (0.2)	0.45 (3.6)	−87.4 (41.6)	8.245 (0.8)	−57.9 (23.7)	−70.9 (24.1)	2.77 (3.09)	13.550 (0.6)	13.654 (0.6)
x_2	1.80 (1.06)	30.70 (7.9)	−256 (108)	10.05 (2.09)	−175.0 (61.5)	−207.5 (62.4)	25.04 (6.9)	43.0 (14.2)	43.0 (14.9)
x_3	4.25 (1.4)	−23.37 (4.9)	−270 (108)	−1.99 (1.72)	−163.2 (63.2)	−196.1 (63.6)	106.5 (56.3)	5.08 (2.8)	4.97 (3.03)
x_1x_2	X	X	X	X	X	X	X	−58.4 (20.9)	−58.6 (21.8)
x_1x_3	X	X	X	X	X	X	−171.5 (74.3)	X	X
x_2x_3	X	X	X	X	X	−262.4 (60.4)	X	−73.2 (23.1)	X
$x_1x_2x_3$	X	X	X	X	−347.5 (76.1)	X	X	X	−101.0 (34.4)
$(x_1{+}0.01)^{-1}$	X	X	107.2 (44.3)	X	75.5 (25.2)	89.1 (25.6)	X	X	X
$(x_2{+}0.01)^{-1}$	X	1.066 (0.2)	X	0.3137 (0.07)	X	X	0.948 (0.2)	X	X
$(x_3{+}0.01)^{-1}$	0.02671 (0.001)	X	X	0.02249 (0.001)	X	X	X	0.02241 (0.001)	0.02171 (0.001)
Deviance	0.001760	0.01634	0.02509	0.0005586	0.006941	0.007475	0.009816	0.0005448	0.0005941
Mean Dev.	0.0001956	0.001815	0.002788	0.00006983	0.0008676	0.0009344	0.001227	0.00007783	0.0008487

Table 7: The best subset linear predictors obtained for the identity link functions from the models with inverse term

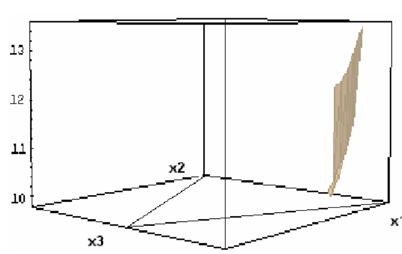

Figure 9: The mixture surface obtained for GLM with identity link

of the response usually having a normal and a Gamma distribution.

The best model can be determined by taking into account the mean deviance values of the models. Mean deviance value in linear regression is equal to *MSE*. However, this criterion should not be taken as basis because not only the model control graphs might be insufficient for the models with a small mean deviance value but also the predicted result values might not be suitable. In addition, the more meaningful interaction terms have the model, the more informative it becomes on the mixture system and the surface. However, this situation might lower the mean deviance value. Therefore, while choosing the models, model control graphs and the behavior of the mixture surface on the experimental region should be examined. From the models suitable for both situations, the researcher can use any of the models with the interactions and the inverse term. In this study, although different models which could be used in the modeling of the mixture system were determined, the surfaces formed on the experimental region were almost the same of each other as the constrained region was too small.

Now, let us compare the analysis results for the resistivity data set obtained by using normal and Gamma distributions. The *MSE* values of the models obtained with the assumption of the response having a normal distribution were greater than the values obtained by Gamma distribution. When the Gamma distribution is used, more subset regression models were also obtained. On the other hand, when an analysis was done with the reciprocal link function, the canonical link function of the Gamma distribution, it was seen that many of the models model control graphs were sufficient. Nevertheless, it should be observed that the identity linked models with normal and Gamma distributions were almost the same. In addition, in order to include the inverse terms into the model, to every component was added a small value of c like 0.01. In this part, subset regression models obtained for the values of c between 0.02 and 0.05 can be examined by taking into account the assumption of Draper and St. John [3]. On the other hand, in the modeling studies, pseudo-components can be used. For the modification of the inverse term including mixture models with pseudo-components, c value can also be examined between the values of 0.02 and 0.05. Alternative approaches can be investigated as well for measuring the effects of the components on the response with the help of GLMs on the constrained region.

References

[1] J.A. Cornell, Weighted versus unweighted estimates using Scheffé's mixture model for symmetrical error variance patterns, *Technometrics*, **19** (1977), 237-247.

[2] J.A. Cornell, *Experiments with Mixtures*, Wiley-Interscience, New York (2002).

[3] N.R. Draper, R.C.St. John, A mixtures model with inverse terms, *Technometrics*, **19** (1977), 37-46.

[4] M. Hamada, J.A. Nelder, Generalized linear models for quality-improvement experiments, *Journal of Quality Technology*, **29**, No. 3 (1997), 292-304.

[5] S.L. Lewis, D.C. Montgomery, R.H. Myers, Examples of designed experiments with nonnormal responses, *Journal of Quality Technology*, **33**, No. 3 (2001), 265-278.

[6] S.L. Lewis, D.C. Montgomery, R.H. Myers, Confidence interval coverage for designed experiments analyzed with GLMs, *Journal of Quality Technology*, **33**, No. 3 (2001), 279-292.

[7] P. McCullagh, J.A. Nelder, *Generalized Linear Models*, Second Edition, Chapman Hall (1989).

[8] R.H. Myers, D.C. Montgomery, A tutorial on generalized linear models, *Journal of Quality Technology*, **29**, No. 3 (1997), 274-291.

[9] R.H. Myers, D.C. Montgomery, G.G. Vining, *Generalized Linear Models*, Wiley-Interscience, New York (2001).

[10] J.A. Nelder, R.W.M. Wedderburn, Generalized linear models, *Journal of the Royal Statistical Society, Series A*, **135** (1972), 370-384.

[11] H. Scheffé, Experiments with mixtures, *Journal of the Royal Statistical Society, B*, **20** (1958), 344-360.