Design and Analysis of Experiments

Part X: Mixture Experiments
• Many products are made by mixing or blending two or more components or ingredients together
  – textile fiber blends
  – Explosives
  – Paints
  – Polymers
  – Ceramics
  – …
• In mixture experiments, the factors are the components of ingredients of a mixture, and consequently their levels are not independent

\[ 0 \leq x_i \leq 1 \quad i = 1, 2, \ldots, p \text{ components} \]

and \( x_1 + x_2 + \cdots + x_p = 1 \).

• If each component in the mixture can range from 0.0 to 100.0% of the total, a \( 2^3 \) factorial experiment would consist of all possible combinations of proportions 0.00 and 1.00 resulting in the corners of the cube:

the constraint \( x_1 + x_2 + x_3 = 1 \) reduces the three-dimensional experimental region to the two-dimensional shaded equilateral triangular plane.
Coordinate system for three-component mixture
Coordinate system for four-component mixture
Models and Designs

- Linear

\[ y = \sum_{i=1}^{p} \beta_i x_i \]

in a three-component mixture experiment

\[ y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \epsilon \]

and the constraint \( x_1 + x_2 + x_3 = 1 \) makes one of the four coefficients in this model redundant

\[ y = \beta_0^* + \beta_1^* x_1 + \beta_2^* x_2 + \epsilon \]

where \( x_3 = 1 - x_1 - x_2 \).

\( \beta_1^* \) and \( \beta_2^* \) do not represent the effects of components \( x_1 \) and \( x_2 \) as they would in a factorial experiment, but rather they represent the effects of \( x_1 \) and \( x_2 \) confounded with the opposite of the effect of the slack variable \( x_3 \).
**Scheffé Linear Model**

$\beta_0 = 1$ and by substituting $x_1 + x_2 + x_3$ for 1, the model can be written in the Scheffé form as

$$y = \beta_1^* x_1 + \beta_2^* x_2 + \beta_3^* x_3 + \epsilon$$

- the coefficients in the Scheffé form of the linear model do not represent the effects of the variables $x_1$, $x_2$, and $x_3$
  - a coefficient that is zero, or not significantly different from zero, does not mean that changing the corresponding mixture component will not affect product characteristics.
- Alternately, in the mixture model $\beta_i^*$ represents the predicted response at the vertex of the experimental region where $x_1 = 1$.
- the predicted response is a plane above the mixture experimental region ($\beta_i^* = \beta_i$).
If the response surface over the mixture region is nonlinear

General quadratic model in three variables:

\[ y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_1 x_1^2 + \beta_2 x_2^2 + \beta_3 x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \epsilon \]

Multiplying \( \beta_0 \) by \( x_1 + x_2 + x_3 \) and substituting \( x_1 \times (1 - x_2 - x_3) \) for \( x_1^2 \) and so forth

\[ y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \epsilon \]
For $p$ mixture components

$$y = \sum_{i=1}^{p} \beta_i x_i + \sum_{i<j}^{p} \beta_{ij} x_i x_j + \epsilon$$

The coefficients of the product terms $x_i x_j$ represent the quadratic curvature along an edge of the simplex experimental region.
• Experimental designs to fit Scheffé models
  – *Simplex-lattice designs* (SLD) are used to study the effects of the mixture components on the response variable
    • \( p \) components
    • \( m + 1 \) equally spaced values from 0 to 1
    • \( x_i = 0, \frac{1}{m}, \frac{2}{m}, ..., 1 \)
    • All possible combinations (mixtures) of the proportions are used
    • SLD\{\( p, m \}\)
**SLD{3,1}**

\[ x_i = 0, 1 \quad i = 1, 2, 3 \]

\[(x_1, x_2, x_3) = (1, 0, 0), (0, 1, 0), (0, 0, 1)\]

- Only the pure components are required for a linear design;
- The coefficients \( \beta_i \) in the linear model can be estimated as an average of all the response data at the pure component where \( x_i = 0 \);
- In the linear model, the effect of blending two or more components is assumed to be linear, and no intermediate points are necessary in the design.

**SLD{3, 2}**

\[ x_i = 0, \frac{1}{2}, 1 \quad i = 1, 2, 3 \]

Six runs:

\[(x_1, x_2, x_3) = (1, 0, 0), (0, 1, 0), (0, 0, 1), \left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(0, \frac{1}{2}, \frac{1}{2}\right)\]

- The 50/50 mixtures of each pair of components are required to estimate the coefficients \( \beta_{ij} \) of the quadratic blending effects in the model;
- The mixtures \( \left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right) \) and \( \left(0, \frac{1}{2}, \frac{1}{2}\right) \) are required in addition to the pure components for a quadratic design.
• In response surface experiments conducted with independent factors the experimental region can be restricted so that the general quadratic model is usually a good approximation to the true nonlinear model relating the response to the factor levels in the restricted region;

• In a mixture experiment, the experimental region consists of the full \((p-1)\) dimensional simplex or tetrahedron and cannot be restricted;
  – Higher order polynomial equations are sometimes necessary to approximate the true model over the entire simplex;
  – Full cubic model

\[
y = \sum_{i=1}^{p} \beta_i x_i + \sum_{i<j}^{p} \beta_{ij} x_i x_j + \sum_{i<j}^{p} \delta_{ij} x_i x_j (x_i - x_j) + \sum_{i<j<k} \beta_{ijk} x_i x_j x_k
\]

where the coefficients \(\delta_{ij}\) represent the cubic blending of binary mixtures along the edges of the simplex.

\[
\frac{3\delta_{ij}}{32} \quad \frac{-3\delta_{ij}}{32}
\]

[Diagram showing the cubic blending along the edges of the simplex.]

\[
x_i=1 \quad \frac{3}{4} \quad \frac{2}{4} \quad \frac{1}{4} \quad 0
\]

\[
x_j=0 \quad \frac{1}{4} \quad \frac{2}{4} \quad \frac{3}{4} \quad 1
\]
**SLD{3, 3}**

\[ x_i = 0, \frac{1}{3}, \frac{2}{3} \quad i = 1, 2, 3 \]

Ten runs:

\[ (x_1, x_2, x_3) = (1, 0, 0), (0, 1, 0), (0, 0, 1), \left(\frac{1}{3}, \frac{2}{3}, 0\right), \left(\frac{2}{3}, \frac{1}{3}, 0\right), \left(\frac{1}{3}, 0, \frac{2}{3}\right), \]

\[ \left(\frac{2}{3}, 0, \frac{1}{3}\right), \left(0, \frac{1}{3}, \frac{2}{3}\right), \left(0, \frac{2}{3}, \frac{1}{3}\right), \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right) \]
– When the coefficients $\delta_{ij}$ are insignificant the simpler special cubic model can be used

\[ y = \sum_{i=1}^{p} \beta_i x_i + \sum_{i<j}^{p} \beta_{ij} x_i x_j + \sum_{i<j<k} \beta_{ijk} x_i x_j x_k \]

– *Simplex-centroid design* (SCD) is an alternate design that allows estimation of all coefficients in the special cubic model

• SCD in the three-mixture components
  – Pure component blends
    
    \( (1,0,0), (0,1,0), (0,0,1) \)
  – Binary mixtures
    
    \( \left( \frac{1}{2}, \frac{1}{2}, 0 \right), \left( \frac{1}{2}, 0, \frac{1}{2} \right), \left( 0, \frac{1}{2}, \frac{1}{2} \right) \)
  – Ternary mixture
    
    \( \left( \frac{1}{3}, \frac{1}{3}, \frac{1}{3} \right) \)
**Simplex-Lattice Design\{3,2\}:** 6 runs

\[
(1,0,0), (0,1,0), (0,0,1), \\
\left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(0, \frac{1}{2}, \frac{1}{2}\right)
\]

**Simplex-Centroid Design\{3,2\}:** 7 runs

\[
(1,0,0), (0,1,0), (0,0,1), \\
\left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(0, \frac{1}{2}, \frac{1}{2}\right), \\
\left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right)
\]
Creating mixture designs in R

- **mixexp package**
  - Creating designs: SLD and SCD functions
  - Graphical representation: DesignPoints function

```r
library(mixexp)
sld_3.2 <- SLD(3, 2)
DesignPoints(sld_3.2)

scd_3.2 <- SCD(3)
DesignPoints(scd_3.2)
```
Analysis of Mixture Experiments

• Three components were blend to form a fiber to be spun into yarn for draperies
  - Polyethylene ($x_1$)
  - Polystyrene ($x_2$)
  - Polypropylene ($x_3$)

<table>
<thead>
<tr>
<th>Design Point</th>
<th>Component Proportions</th>
<th>Observed Elongation Values</th>
<th>Average Elongation Value ($\bar{y}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 0 0</td>
<td>11.0, 12.4</td>
<td>11.7</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{2}$ $\frac{1}{2}$ 0</td>
<td>15.0, 14.8, 16.1</td>
<td>15.3</td>
</tr>
<tr>
<td>3</td>
<td>0 1 0</td>
<td>8.8, 10.0</td>
<td>9.4</td>
</tr>
<tr>
<td>4</td>
<td>0 $\frac{1}{2}$ $\frac{1}{2}$</td>
<td>10.0, 9.7, 11.8</td>
<td>10.5</td>
</tr>
<tr>
<td>5</td>
<td>0 0 1</td>
<td>16.8, 16.0</td>
<td>16.4</td>
</tr>
<tr>
<td>6</td>
<td>$\frac{1}{2}$ 0 $\frac{1}{2}$</td>
<td>17.7, 16.4, 16.6</td>
<td>16.9</td>
</tr>
</tbody>
</table>
```r
> sld_3.2<-SLD(3,2)
> y<-c(11.7,15.3,9.4,16.9,10.5,16.4)  #average values
> sld_3.2$y<-y
> MixModel(sld_3.2,"y",c("x1","x2","x3"),2)
```

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>x1</td>
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<tr>
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<tr>
<td>x3</td>
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</tr>
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<td>x2:x1</td>
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<td>NaN</td>
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</tr>
<tr>
<td>x3:x1</td>
<td>11.4</td>
<td>NaN</td>
<td>NaN</td>
<td>NaN</td>
</tr>
<tr>
<td>x2:x3</td>
<td>-9.6</td>
<td>NaN</td>
<td>NaN</td>
<td>NaN</td>
</tr>
</tbody>
</table>

Residual standard error: NaN on 0 degrees of freedom
Corrected Multiple R-squared: 1

Call:
```
  lm(formula = mixmodnI, data = frame)
```

Coefficients:
```
   x1  x2  x3  x1:x2  x1:x3  x2:x3
  11.7 9.4 16.4  19.0  11.4  -9.6
```

\[
y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3
\]
\[
y = 11.7x_1 + 9.4x_2 + 16.4x_3 + 19.0x_1x_2 + 11.4x_1x_3 - 9.6x_2x_3
\]

- $\beta_3 > \beta_1 > \beta_2$: component 3 (polypropylene) produces yarn with the highest elongation.
- $\beta_{12}$ and $\beta_{13} > 0$: blending components 1 and 2 or 1 and 3 produces higher elongations than would be expected just by averaging the elongations the pure blends (synergistic blending effects).
- $\beta_{23} < 0$: components 2 and 3 have antagonistic blending effects.
If the maximum elongation is desired, a blend of components 1 and 3 should be chosen consisting of about 80% component 3 and 20% component 1.
> MixturePlot(des=sld_3.2,x1lab="Polyethylene (x1)",
  x2lab="Polystyrene (x2)",x3lab="Polypropylene (x3)",
  corner.labs=c("x3","x2","x1"),
  constrts=FALSE,contrs=TRUE,cols=TRUE,
  mod=2,n.breaks=9)
• In mixture experiments with several components, it is important to determine which components are most influential (focus on optimization).
  – The coefficients in the models for mixture experiments do not represent effects in the same way as they do for independent factors;
  – Tests of the significance of the coefficients in the model are not a good way to determine the important components.

• **Effect plot**
  – This is a very useful tool that allows the user to see the response trace along the direction through the simplex introduced by Cox in 1971.
EffPlot(des=sld_3.2, mod = 2, dir=1)

Effect Plot (Cox direction)

Predicted Response

Deviation from centroid
Constrained mixture experiments

- In some mixture experiments, it is impossible to test pure components.
- For example: fuel for solid rocket boosters is a mixture of binder, oxidizer, and fuel, and it must contain a percentage of each.

Conventional Composite

- Fuel
  - 5-22% Powdered Aluminum
- Oxidizer
  - 65-70% Ammonium Perchlorate (NH₄ClO₄ or AP)
- Binder
  - 8-14% Hydroxyl-Terminated Polybutadiene (HTPB)
• Proportions can be varied but must remain within certain constraints in order for the propellant to work.
  - Kurotori (1966) described an example of this situation where experiments with rocket propellant were performed.
    \( x_1 \): the binder, had to be at least 20% of the mixture;
    \( x_2 \): the oxidizer, could be no less than 40% of the mixture;
    and \( x_3 \): the fuel, had to comprise at least 20% of the mixture.
  - three new constraints: \( x_1 \geq 0.20 \), \( x_2 \geq 0.40 \), and \( x_3 \geq 0.20 \)
  - the experimental region is *restricted*
• When only lower bound constraints are present, the *feasible design region* is still a simplex
• The component space within this smaller simplex can be conveniently transformed into a *pseudo component* space where the same simplex-lattice and simplex-centroid designs can be used for an experimental design.
  – Lower bound constraint: \( l_i \leq x_i \leq 1 \)
• *Pseudo components*

\[
x'_i = \frac{x_i - l_i}{1 - \sum_{i=1}^{p} l_i}
\]

with

\[
\sum_{i=1}^{p} l_i < 1
\]

and \( x'_1 + x'_2 + \cdots + x'_p = 1 \).

Solving for \( x_i \):

\[
x_i = l_i + \left( 1 - \sum_{j=1}^{p} l_i \right) x'_i
\]

and a simplex-lattice design can be constructed in the pseudo components and the actual mixtures to be tested can then be obtained.
<table>
<thead>
<tr>
<th>Run</th>
<th>$x_1'$</th>
<th>$x_2'$</th>
<th>$x_3'$</th>
<th>$x_1$=Fuel</th>
<th>$x_2$=Oxidizer</th>
<th>$x_3$=Binder</th>
<th>Response Elasticity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.400</td>
<td>0.400</td>
<td>0.200</td>
<td>2350</td>
</tr>
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<td>0</td>
<td>1</td>
<td>0</td>
<td>0.200</td>
<td>0.600</td>
<td>0.200</td>
<td>2450</td>
</tr>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>0.200</td>
<td>0.400</td>
<td>0.400</td>
<td>2650</td>
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<td>$\frac{1}{2}$</td>
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<td>0.300</td>
<td>0.500</td>
<td>0.200</td>
<td>2400</td>
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<td>5</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.300</td>
<td>0.400</td>
<td>0.300</td>
<td>2750</td>
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<tr>
<td>6</td>
<td>0</td>
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<td>$\frac{1}{2}$</td>
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<td>0.500</td>
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<td>2950</td>
</tr>
<tr>
<td>7</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>0.266</td>
<td>0.466</td>
<td>0.266</td>
<td>3000</td>
</tr>
</tbody>
</table>

$x_1$ = Fuel

Constrained Region

$x_2$ = Oxidizer

$x_3$ = Binder
• Upper and Lower Constraints
  – In some special cases when there are only upper constraints or both upper and lower constraints, the constrained experimental region will result in a smaller inverted simplex within the simplex component space.
  – However, in the more common situation, the constrained region will be an irregular *hyper polyhedron*.
  – *Xvert* function
    • Generate the vertices and centroids of a multi-constrained experimental region (*mixexp* package).
– Example:

- Barbuta and Lepadatu (2008) investigated mechanical properties such as compressive strength, flexural strength, and adhesion stress of polymer concrete.
- Polymer concrete (PC) has many uses: precast components for buildings, bridge panels, repair of structural members, waterproofing, and decorative overlay of pavements.
- Polymer concrete is formed by binding aggregates together with a resin that reacts with a hardener.
- The relatively high cost of PC led Barbuta and Lepadatu (2008) to study ways of reducing the dosage of polymer in the mix without diminishing the mechanical properties.
- The mixture components they studied were
  \[ x_1: \text{Epoxy resin} \]
  \[ x_2: \text{Silica Fume (SUF)} \]
  \[ x_3: \text{Aggregate Sort I;} \]
  and \[ x_4: \text{Aggregate Sort II.} \]
- Constraints on the mixture components:
  \[ 0.124 \leq x_1 \leq 0.188 \]
  \[ 0.064 \leq x_2 \leq 0.128 \]
  \[ 0.374 \leq x_3 \leq 0.438 \]
  \[ 0.374 \leq x_4 \leq 0.438 \]
**Extreme vertex design:**

- Point 0 in the center of the feasible region is the *overall centroid*.
- The other red points are the *axial points*. They are at the middle of the lines connecting the center point with the vertices.
• The last line in the data frame is the overall centroid;
• The two vectors uc and lc contain the upper and lower constraints for each component.

An optional argument ndm can be included in the Xvert function call that specifies the maximum order of centroids to be generated.

- The overall centroid is always included but, by including ndm = 1 edge centroids will be added, and by including ndm = 2 face centroids will be added, and so forth.
- For example, the code below finds the four extreme vertices shown in the listing above, plus the six edge centroids and the overall centroid:

```r
> library(mixexp)
> Xvert(4,uc=c(.188,.128,.438,.438),lc=c(.124,.064,.374,.374))
   x1  x2  x3   x4 dimen
 1 0.124 0.064 0.374 0.4379999  0
 2 0.188 0.064 0.374 0.3740000  0
 3 0.124 0.128 0.374 0.3740000  0
 4 0.124 0.064 0.438 0.3740000  0
 5 0.140 0.080 0.390 0.3900000  3
```
For many constrained mixture problems, the number of extreme vertices and edge centroids will be much greater than the number of coefficients in the Scheffé quadratic model.

To reduce the number of mixtures and still allow fitting a quadratic model to the resulting data, a $D$-optimal subset can be selected using the `optFederov` function in the `AlgDesign` package.

- A 12-run $D$-optimal subset of 15 mixtures in the data frame `exvert` will be output to the data frame `desMix$design`.

```r
> library(mixexp)
> exvert<-xvert(4,uc=c(.188,.128,.438,.438),
+ l1c=c(.124,.064,.374,.374),ndm=2)
> xvert
   x1         x2        x3        x4 dimen
 1 0.1240000 0.06400000 0.3740000 0.4379999     0
 2 0.1880000 0.06400000 0.3740000 0.3740000     0
 3 0.1240000 0.12799999 0.3740000 0.3740000     0
 4 0.1240000 0.06400000 0.4380000 0.3740000     0
 5 0.1240000 0.06400000 0.4060000 0.4060000     1
 6 0.1240000 0.09600000 0.3740000 0.4060000     1
 7 0.1240000 0.09600000 0.4060000 0.3740000     1
 8 0.1560000 0.06400000 0.3740000 0.4060000     1
 9 0.1560000 0.06400000 0.4060000 0.3740000     1
10 0.1560000 0.09600000 0.3740000 0.3740000     1
11 0.1240000 0.08533334 0.3953333 0.3953333     2
12 0.1453333 0.06400000 0.3953333 0.3953333     2
13 0.1453333 0.08533332 0.3740000 0.3953333     2
14 0.1453333 0.08533334 0.3953333 0.3740000     2
15 0.1400000 0.08000000 0.3900000 0.3900000     3

> library(AlgDesign)
> desMix<-optFederov(~-1+x1+x2+x3+x4+x1:x2+x1:x3+x1:x4+
+                      x2:x3+x2:x4+x3:x4, data=exvert,
+                      nTrials=12 )
> desMix$design
   x1         x2        x3        x4 dimen
 1 0.1240000 0.06400000 0.3740000 0.4379999     0
 2 0.1880000 0.06400000 0.3740000 0.3740000     0
 3 0.1240000 0.12799999 0.3740000 0.3740000     0
 4 0.1240000 0.06400000 0.4380000 0.3740000     0
 5 0.1240000 0.06400000 0.4060000 0.4060000     1
 6 0.1240000 0.09600000 0.3740000 0.4060000     1
 7 0.1240000 0.09600000 0.4060000 0.3740000     1
 8 0.1560000 0.06400000 0.3740000 0.4060000     1
 9 0.1560000 0.06400000 0.4060000 0.3740000     1
10 0.1560000 0.09600000 0.3740000 0.3740000     1
11 0.1240000 0.08533334 0.3953333 0.3953333     2
12 0.1453333 0.06400000 0.3953333 0.3953333     2
13 0.1453333 0.08533332 0.3740000 0.3953333     2
14 0.1453333 0.08533334 0.3953333 0.3740000     2
15 0.1400000 0.08000000 0.3900000 0.3900000     3
```
DesignPoints(exvert)

DesignPoints(desMix$design)

15 mixtures

12-run D-optimal subset
The models used to analyze constrained mixture experiments are the same as those used for unconstrained problems. For example, consider the three-component mixture studied by Juan et al. (2006).

- They studied consumer acceptance of polvoron composed of a mixture of sugar ($x_1$), peanut fines ($x_2$), and butter ($x_3$).
- Polvoron is a Philippine ethnic dessert or candy usually composed of milk powder, toasted flour, sugar, and butter.
  - Ground nuts can be added to vary its flavor and texture properties.
  - If acceptable to consumers, utilizing peanut fines (which are usually a discarded byproduct of the roasted peanut process) in polvoron could reduce waste and create an additional product line.
  - The constraints on the mixture space are
    
    $0 \leq x_1 \leq 0.8$
    $0.1 \leq x_2 \leq 0.95$
    $0.05 \leq x_3 \leq 0.5$
> data("polvdat")
> polvdat

<table>
<thead>
<tr>
<th></th>
<th>x1</th>
<th>x2</th>
<th>x3</th>
<th>y</th>
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<tr>
<td>1</td>
<td>0.8</td>
<td>0.15</td>
<td>0.05</td>
<td>5.33</td>
</tr>
<tr>
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> DesignPoints(polvdat)
```r
> model<-lm(y ~ x1 + x2 + x3 + x1:x2 + x1:x3 + x2:x3 + x1:x2:x3 -1, data=polvdat)
> summary(model)

Call:
  lm(formula = y ~ x1 + x2 + x3 + x1:x2 + x1:x3 + x2:x3 + x1:x2:x3 - 1, data = polvdat)

Residuals:
   1       2       3       4       5       6       7       8
-0.1796 -0.0214  0.0336 -0.1201  0.1442 -0.2017  0.0963 -0.1431
   9      10      11      12
  0.2080  0.0112  0.2912 -0.1188

Coefficients:  
                        Estimate  Std. Error t value  Pr(>|t|)
intercept                4.426     0.448    9.87  0.00018 ***
x2                        3.518     0.308   11.43   9e-05 ***
x3                        1.237     1.615    0.77  0.47840
x1:x2                    6.900     2.018    3.42  0.01885 *
x1:x3                    8.953     4.143    2.16  0.08307 .
x2:x3                    5.313     3.499    1.52  0.18931
x1:x2:x3                 25.546    11.202    2.28  0.07150 .
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 0.237 on 5 degrees of freedom
Multiple R-squared:  0.999,        Adjusted R-squared:  0.998
F-statistic:  921 on 7 and 5 DF,  p-value: 1.81e-07
```
- Model using *only* \( P < 0.1 \) terms

```r
> reduced.model<-lm(y~x1+x2+x1:x2+x1:x3 +x1:x2:x3-1,data=polvdat)
> anova(reduced.model,model)  #lack-of-fit test
```

Analysis of Variance Table

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<tr>
<th>Model 1: y ~ x1 + x2 + x1:x2 + x1:x3 + x1:x2:x3 - 1</th>
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---

Signif. codes: 0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

The low \( p \)-value indicates that we must conclude that there is a **lack of fit**

So, back to the full model...
> MixturePlot(des=polvdat, lims=c(0,.8,.1,.95,.05,.5),
+ constrts=TRUE, cols=TRUE, pseudo=TRUE, mod=4)

- Contour plot over the constrained region produced by the MixturePlot call.
- constrts=TRUE adds the constraint lines to the plot;
- pseudo=TRUE restricts the region to the pseudo component space bounded by the lower constraints on all components.
- lims=c(0,.8,.1,.95,.05,.50) option supplies the constraint lines to the function.
> EffPlot(des=polvdat,nfac=3,mod=2,dir=1)
Blocking Mixture Experiments

• Whenever experimental units for a mixture experiment (which may simply be the conditions that exist at the time a mixture is made and tested) are not homogeneous, a blocked design should be used.

• Levels of a blocking factor could include things such as the batches of mixture components or the times or different pieces of equipment used to test and measure a response.

• If runs can be blocked into groups that are large enough to include a complete replicate of the mixture experiment, a complete block design can be utilized.

• On the other hand, if the block size is smaller than a complete replicate of the mixture design, some kind of incomplete block design must be used.
Orthogonally Blocked Constrained Mixtures Using Latin Squares Design

D-Optimal Blocked Mixture Experiment
In some mixture experiments, the qualities or characteristics of the product are influenced by process variables in addition to the proportions of the mixing components.

For example, the strength of carbide ceramics used in advanced heat engines depends not only on the proportions of the mixture components but also on the sintering time and sintering temperature.

In mixture experiments involving process variables (MPV experiments) let $z_1$ represent the coded level of the $l$th process variable.

- When there are three mixture components and one process variable $z_1$, the experimental region changes from a simplex like to a prism.

\[ x_1 = 1 \]
\[ z_1 = +1 \]
\[ x_1 = 1 \]
\[ z_1 = -1 \]

\[ x_1 = 1 \]
\[ z_1 = +1 \]
\[ x_1 = 1 \]
\[ z_1 = -1 \]
As an example of a mixture experiment with a process variable, or MPV, consider the situation studied by Chau and Kelly (1993).

They studied the opacity of a printable coating material used for identification labels and tags.

The coating material was a mixture of two pigments, $x_1$ and $x_2$, and a polymeric binder ($x_3$).

The opacity of the coating was not only influenced by the mixture of the three components, but also by the thickness of the coating ($z$).

Constraints on the component proportions were

- $0.13 \leq x_1 \leq 0.45$
- $0.21 \leq x_2 \leq 0.67$
- $0.20 \leq x_3 \leq 0.34$

If two levels (-1 and +1) of the coded process variable $z$ are used, an appropriate experimental design would consist of the extreme vertices and edge centroids of the mixture space crossed with each level of the process variable.
The `xvert` function creates the data frame `ev` that contains a list of the extreme vertices of the mixture region including the edge centroids and the overall centroid.

The next three statements delete the overall centroid, and repeats each line of `ev` at the low and high levels of the process variable `z`.

The results are output to the data frame `mp`.

```r
> library(mixexp)
> mvp <- xvert(3, uc=c(.45, .67, .34),
                 lc=c(.13, .21, .20), ndm=1)
> DesignPoints(mvp)
> mp <- subset(mvp, dimen <= 1)
> DesignPoints(mp)
> mp <- rbind(mp, mp)
> z <- c(rep(-1, 8), rep(1, 8))
> mp <- cbind(z, mp)
> mp

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```
Models for Mixture Experiments with Process Variables

- Model for the mixture components: $\eta_x = f(x)$
- Model for the process variables: $\eta_z = g(z)$
- Combined model: $\eta_{xz} = f(x) \times g(z)$

For example: quadratic mixture model for the three mixture components and one two-level process variable

$$f(x) = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3$$
$$g(z) = \alpha_0 + \alpha_1 z$$

$$\eta_{xz} = \beta_1(z) x_1 + \beta_2(z) x_2 + \beta_3(z) x_3 + \beta_{12}(z) x_1 x_2 + \beta_{13}(z) x_1 x_3 + \beta_{23}(z) x_2 x_3$$

where $\beta_i(z) = \beta_i \times (\alpha_0 + \alpha_1 z)$

$$\eta_{xz} = \gamma_1^0 x_1 + \gamma_2^0 x_2 + \gamma_3^0 x_3 + \gamma_{12}^0 x_1 x_2 + \gamma_{13}^0 x_1 x_3 + \gamma_{23}^0 x_2 x_3 +$$
$$\gamma_1^1 x_1 + \gamma_2^1 x_2 + \gamma_3^1 x_3 + \gamma_{12}^1 x_1 x_2 + \gamma_{13}^1 x_1 x_3 + \gamma_{23}^1 x_2 x_3$$

where $\gamma_i^0 = \beta_i \times \alpha_0$ and $\gamma_i^1 = \beta_i \times \alpha_1$

- In this model, the first six terms represent the linear and quadratic blending of the mixture components since these terms involve only the mixture components.
- The last six terms in the model represent the changes in the linear and quadratic blending effects caused by changes in the process variable.
design for an MPV with three mixture components and two process variables:

- The 6-run SLD{3,2} for the mixture components is crossed with a 4-run $2^2$ design in the process variables, resulting in a product array of $6 \times 4 = 24$ experiments.
- The runs in the design can be represented graphically:
  - as a $2^2$ design with a simplex-lattice repeated at each corner (left side of the figure), or
  - as a simplex-lattice with a $2^2$ design repeated at each lattice point as shown on the right side of the figure
This design can be easily created in R by repeating the six runs of the simplex-lattice (created by the `SLD` function) at each run of a $2^2$ factorial (created by `expand.grid` function):

```r
> sld<-SLD(3,2); sld
   x1  x2  x3
1 1.0 0.0 0.0
2 0.5 0.5 0.0
3 0.0 1.0 0.0
4 0.5 0.0 0.5
5 0.0 0.5 0.5
6 0.0 0.0 1.0
> id<-c(rep(1,6),rep(2,6),rep(3,6),rep(4,6)); id
 [1] 1 1 1 1 1 1 2 2 2 2 2 2 3 3 3 3 3 3 3 4 4 4 4 4 4
> sld1<-rbind(sld,sld,sld,sld); sld1
   x1  x2  x3
1 1.0 0.0 0.0
2 0.5 0.5 0.0
3 0.0 1.0 0.0
4 0.5 0.0 0.5
5 0.0 0.5 0.5
6 0.0 0.0 1.0
11 1.0 0.0 0.0
21 0.5 0.5 0.0
31 0.0 1.0 0.0
41 0.5 0.0 0.5
51 0.0 0.5 0.5
61 0.0 0.0 1.0
12 1.0 0.0 0.0
22 0.5 0.5 0.0
32 0.0 1.0 0.0
42 0.5 0.0 0.5
52 0.0 0.5 0.5
62 0.0 0.0 1.0
13 1.0 0.0 0.0
23 0.5 0.5 0.0
33 0.0 1.0 0.0
43 0.5 0.0 0.5
53 0.0 0.5 0.5
63 0.0 0.0 1.0
```
```r
facdes <- expand.grid(z1 = c(-1, 1), z2 = c(-1, 1)); facdes
z1  z2
1  -1 -1
2   1 -1
3  -1  1
4   1  1
id <- c(1, 2, 3, 4)
facades <- cbind(facades, id); facades
z1  z2  id
1  -1 -1  1
2   1 -1  2
3  -1  1  3
4   1  1  4
comdes <- merge(sld1, facades, by = "id", all = TRUE); comdes
id  x1  x2  x3  z1  z2
 1  1.0 0.0 0.0 -1 -1
 2  1.0 0.5 0.0 -1 -1
 3  1.0 0.0 1.0 -1 -1
 4  1.0 0.5 0.0 -1 -1
 5  1.0 0.0 0.5 -1 -1
 6  1.0 0.0 0.0 -1 -1
 7  1.0 0.0 0.0  1 -1
 8  0.5 0.5 0.0  1 -1
 9  0.0 1.0 0.0  1 -1
10 2.0 0.5 0.0  1 -1
11 2.0 0.0 0.5  1 -1
12 2.0 0.0 0.0  1 -1
13 2.0 0.0 0.0  1 -1
14 3.0 1.0 0.0  0 -1 1
15 3.0 0.5 0.5  0 -1 1
16 3.0 0.5 0.0  0 -1 1
17 3.0 0.0 0.5  0 -1 1
18 3.0 0.0 0.0  1 -1 1
19 4.0 0.0 0.0  1  1
20 4.0 0.5 0.0  1  1
21 4.0 0.0 1.0  0  1 1
22 4.0 0.5 0.0  0  1 1
23 4.0 0.0 0.5  1  1
24 4.0 0.0 0.0  1  1
```
• An MVP example:
  – Sahni et al. (2009) studied a process to produce low-fat mayonnaise.
  – The product was a mixture of three components
    • $x_1$: stabilizer, $x_2$: starch 1, and $x_2$: starch 2.
  – The response they were interested in was the viscosity of the final product that was influenced not only by the ingredients but also by two process variables:
    • $z_1$: heat exchanger temperature and $z_2$: the flow rate through the system.
  – The goal was to achieve a viscosity of 3657 at the lowest cost.
  – The constraints on the mixture components are
    \[
    0 \leq x_1 \leq 0.0549 \\
    0 \leq x_2 \leq 0.9725 \\
    0 \leq x_3 \leq 0.9725
    \]

- $7 \times 5 = 35$ experiments
- A Scheffé quadratic model was used for the mixture components
  \[
  \eta_x = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3
  \]
- The model $n_z = \alpha_0 + \alpha_1 z_1 + \alpha_2 z_2 + \alpha_{12} z_1 z_2$ for the process variables;
- By crossing the two models, the resulting combined model is
  \[
  \eta_{xz} = \gamma_1^0 x_1 + \gamma_2^0 x_2 + \gamma_3^0 x_3 + \gamma_{12}^0 x_1 x_2 + \gamma_{13}^0 x_1 x_3 + \gamma_{23}^0 x_2 x_3 \\
  + \gamma_1^1 x_1 z_1 + \gamma_2^1 x_2 z_1 + \gamma_3^1 x_3 z_1 + \gamma_{12}^1 x_1 x_2 z_1 + \gamma_{13}^1 x_1 x_3 z_1 + \gamma_{23}^1 x_2 x_3 z_1 \\
  + \gamma_1^2 x_1 z_2 + \gamma_2^2 x_2 z_2 + \gamma_3^2 x_3 z_2 + \gamma_{12}^2 x_1 x_2 z_2 + \gamma_{13}^2 x_1 x_3 z_2 + \gamma_{23}^2 x_2 x_3 z_2 \\
  + \gamma_1^{12} x_1 z_1 z_2 + \gamma_2^{12} x_2 z_1 z_2 + \gamma_3^{12} x_3 z_1 z_2 + \gamma_{12}^{12} x_1 x_2 z_1 z_2 + \gamma_{13}^{12} x_1 x_3 z_1 z_2 + \gamma_{23}^{12} x_2 x_3 z_1 z_2
  \]

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```r
> library(daewr)
> data("MPV")
> MPV

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> modmp<-lm(y~x1+x2+x3+x1:x2+x1:x3+x2:x3+
+     x1:z1+x2:z1+x3:z1+x1:x2:z1+x1:x3:z1+x2:x3:z1+
+     x1:z2+x2:z2+x3:z2+x1:x2:z2+x1:x3:z2+x2:x3:z2+
+     x1:z1:z2+x2:z1:z2+x3:z1:z2+x1:x2:z1:z2+x1:x3:z1:z2+
+     x2:x3:z1:z2 -1, data=MPV)
> summary(modmp)

Call:
lm(formula = y ~ x1 + x2 + x3 + x1:x2 + x1:x3 + x2:x3 + x1:z1 +
    x2:z1 + x3:z1 + x1:x2:z1 + x1:x3:z1 + x2:x3:z1 + x1:z2 +
    x2:z2 + x3:z2 + x1:x2:z2 + x1:x3:z2 + x2:x3:z2 + x1:z1:z2 +
    x2:z1:z2 + x3:z1:z2 + x1:x2:z1:z2 + x1:x3:z1:z2 + x2:x3:z1:z2 -
    1, data = MPV)

Residuals:
     Min      1Q  Median      3Q     Max
-564.8  -138.7   -31.9   189.9  615.3

Coefficients:
                 Estimate Std. Error t value Pr(>|t|)
                 x1          346947.7   294196.9    1.18  0.26316
                 x2           8222.6      489.8   16.79  3.5e-09 ***
                 x3           1655.6      458.6    3.61  0.00409 **
                 x1:x2         -414463.2   312262.4  -1.33  0.21130
                 x1:x3         -334746.7   311425.6  -1.07  0.30544
                 x2:x3          -6476.3     1198.6   -5.40  0.00022 ***
                 x1:z1         103044.0   328922.1   0.31  0.75993
                 x2:z1          -2241.1     547.6   -4.09  0.00178 **
                 x3:z1           823.2      512.7    1.61  0.13667
                 x1:z2         244320.3   328922.1   0.74  0.47317
                 x2:z2           886.4      547.6    1.62  0.13381
                 x3:z2            85.6      512.7   -0.17  0.87043
                 x1:x2:z1       -64013.3   349120.0  -0.18  0.85785
                 x1:x3:z1       -123730.4   348184.4  -0.36  0.72904
                 x2:x3:z1         4658.7     1340.1    3.48  0.00158 **
                 x1:x2:z2       -266051.6   349120.0  -0.76  0.46205
                 x1:x3:z2       -253151.0   348184.4  -0.73  0.48238
                 x2:x3:z2        -1821.6     1340.1  -1.36  0.20127
                 x1:z1:z2        259037.7   328922.1   0.79  0.44761
                 x2:z1:z2         -136.9     547.6  -0.25  0.80719
                 x3:z1:z2            100.2     512.7   0.19  0.84860
                 x1:x2:z1:z2     -269526.8   349120.0  -0.77  0.45637
                 x1:x3:z1:z2     -269248.7   348184.4  -0.77  0.45565
                 x2:x3:z1:z2       -328.1    1340.1  -0.24  0.81111

---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1

Residual standard error: 481 on 11 degrees of freedom
Multiple R-squared:  0.995,  Adjusted R-squared:  0.985
F-statistic: 96.7 on 24 and 11 DF,  p-value: 1.14e-09

\[
\eta_{xz} = 8222.6x_2 + 1655.6x_3 - 6476.3x_2x_3 - 2241.1x_2z_1 + 4658.7x_2x_3z_1
\]

\[z_1 = -1 \text{ (lowest heat exchanger temperature)}:\]

\[
\eta_{xz} = 10,463.7x_2 + 1655.6x_3 - 11,135x_2x_3
\]
Mixture Experiments in Split-Plot Arrangements

• When running mixture experiments with process variables, experiments are often large, and due to the combination of mixture proportions and process variables, it may be inconvenient to run all combinations in a random order.

  • For example, the mayonnaise experiments were actually run by making large batches of each of the seven mixtures on separate days;
    – While running each batch through the processing equipment, the combinations of the heat exchanger temperature and flow rate were varied.
    – The specific mixtures were randomized to 7 days, and the order of the processing conditions were randomized within a day, but the entire sequence was not randomized.
    – Due to this restricted randomization, the resulting experiment was actually a split-plot experiment.
    – We call the designs for this type of an experiment a split-plot mixture process variable, or SPMPV, experiment.
    – The whole-plot experimental units were days, and the sub-plot experimental units were times within a day.
    – The terms in the quadratic Scheffé mixture model were the whole-plot effects, since they were held constant within the whole plots, and the interactions between the mixture model terms and the process variables were the sub-plot factors.
Synthesis of Nanocomposites

Emília C. de O. Lima (IQ)

Simplex centroid design

feasible design region
Carotenoid Content of Pequi

- Ana C Lima (Eng. Al.)
- Extraction procedure
  - Acetone
  - Petroleum ether
  - Etanol

(Augmented) Simplex Centroid Design
- Simplex points: 7
- Augmented design: 3
- Replicates: 3
- Total runs: 30
Reference Books


