# Application of Plackett-Burman Design and Linear Programming to Light-Duty Liquid Detergent Formulation

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**Plackett-Burman experimental design is applied to a seven-component light-duty liquid detergent formulation to determine which components affect five different properties of the formulation. Regression analysis and linear programming are then applied to the results of the Plackett-Burman analysis. It is shown that the formulation can be optimized by linear programming, even if some of the properties are nonlinear. The procedure saves much of the experimental effort required to find the quadratic and interaction terms for nonlinear models of the properties and the difficulties of optimization with nonlinear constraints.**

**KEY WORDS: Linear programming, liquid detergent formulation, nonlinear constraints, Plackett-Burman experimental design, quadratic.**

Light-duty liquid detergents (LDLD) are multi-component systems, and their properties depend, in a complex way, on some or all of the components of the system. Attempting to optimize such a multicomponent system by trial and error methods is unlikely to succeed. The alternative is to assume a model of each LDLD property and use mathematical methods to optimize the overall system. In such a system it is unlikely that all property models, if any, will be linear, and it will be necessary to use quadratic and transformation models for at least some properties (1). However, a large number of experiments are required to determine linear, quadratic and interaction effects for each component, and the nonlinear optimization techniques required to obtain an optimum formula are difficult. An optimum formula in this paper is considered to be the lowest-cost formula that matches or exceeds a set of property specifications. Steinle *et al.* (1) used central composite experimental design, regression analysis and the modified simplex method to optimize a six-component (two fixed) LDLD. Thirty experiments were required. As many LDLD formulations contain more than four components to be varied, the number of experiments will increase dramatically and it becomes too expensive and/or time-consuming to use these methods in low-volume production formulations. In such situations, less rigorous methods will always be sought (2). Less ambitious methods have been described by Narcy and Renaud (2), Galante and Dillon (3) and Chan and Kavanagh (4). Narcy and Renaud showed how to optimize a four-component detergent by using simplex experimental design (5) for two properties. Galante and Dillon showed how to optimize a three-component formulation by means of ternary blend diagrams. Chan and Kavanagh optimized an LDLD formulation with seven variable components in nine steps with a sequential strategy involving regression analysis and linear programming. This strategy was first described by Kavanagh (6).

In this paper, another possible method is investigated. This method uses Plackett-Burman (PB) experimental design (7), regression analysis and linear programming. Although restricted to linear models, PB designs have the potential to estimate the effects of N components in (N + 1) experiments (8). Thus, they have the obvious advantage of limiting the amount of experimental work, provided the detergent properties can be represented by linear models over a sufficiently small component space. The PB designs are most often confined to two-level main-effect designs for which the number of components, N, is a multiple of four but not a power of two. The PB designs have been applied to a number of process and product development problems; for example, a new catalyst preparation (9), ceramic powder processing (10), and an epoxide adhesive system (11) but not detergents. In all these cases, the PB designs were used as an efficient method for screening every variable in all processing steps to select the more important ones for detailed studies. In all cases, only one property of the formulation or process was investigated. If the interactions between the variables are small or negligible compared with the sizes of some or all main effects, the PB designs will allow efficient estimation of the main effects of all variables being examined. Thus, each design of N experiments is useful for studying up to N-1 variables. In practice, however, it is best to leave two or three additional experiments to estimate the standard error or variance due to experimental errors and interactions (12). The details of analyzing the PB designs can be found in references 9 and 12. Isaacson (12) cautions against drawing conclusions from the results of the PB analysis alone and suggests it is best to try to relate the experimental results to the system from basic theory. However, this procedure is unlikely to be available to detergent formulators.

Through the use of PB design, the important components that affect the properties are identified, and regression analysis can be used to determine the linear equations for each detergent property. The linear property equations are set up from the identified important components. Regression analysis is described in many texts and that by Draper and Smith (13) is a good example. Steinle *et al.* (1) reported that Ross-Miles flash foam height and dishwashing performance were linear functions of some of the components in the detergent system, whereas viscosity and clear point were not. Although the functional forms of viscosity and clear point are not linear, it will be shown that the formulation can still be optimized by linear programming, by assuming these properties are approximately linear in the component space selected.

When the linear equations for each detergent property have been found, linear programming (14) can be used to find the lowest cost formulation that matches or exceeds each required property specification. Linear programming is a technique for optimizing a linear function when the variables in the function are constrained. When used to optimize a formulation, the linear cost equation is minimized and the constraints are the property equations. The

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technique is described by Ignizio (15) and has been used to optimize formulations of paint (6), detergents (4), insecticides (16), ceramics (17,18) and refinery blends (19).

## EXPERIMENTAL PROCEDURES

The LDLD components were sodium chloride (NaCl), alcohol ethoxylate (AEO), alcohol ethoxysulphate (AEOS), linear alkyl benzene sulphonic acid neutralized with sodium hydroxide (NaLAS), diethanolamine (DEALAS), triethanolamine (TEALAS), and coconut diethanolamine (CDEA). The CDEA contained some free diethanolamine, which was neutralized with linear alkyl benzene sulfonate (LAS). Formalin, a preservative, was added at a constant amount of 0.2% by weight to all formulations. Water was the only diluent. All components were commercial-grade materials and used as received. All neutralization was carried out in the detergent preparation.

A published method (20) was followed to prepare the LDLDs. All the LDLDs were tested one day after they were prepared. The Ross-Miles foam test was determined with 0.1% detergent in 60-ppm water hardness at 50°C according to ASTM D1173-53. The Ross-Miles flash foam height (RMFH) is the height of the foam after all the detergent solution has been delivered from the top pipette to the bottom of the receiver. The Ross-Miles foam stability (RMFS) is the drop in RMFH after five-minutes standing. The dishwashing performance in this study was run according to Shell Chemical Test Method CLS 1/84 and called the Geelong Soil Titration Test (GSTT). GSTT was tested with 1% detergent solution in 60-ppm water hardness. Due to day-to-day variation of the absolute values, the values of dishwashing performance are reported here as a percentage of the control test. Viscosity (VISC) was determined at 25°C according to ASTM D445-74. Clear point (CLPT) was measured according to Shell Chemical Test Method CLM 8/77. All tests were replicated three times and the averages are reported.

The calculations were carried out on an IBM-compatible AT personal computer. The statistical package, MINITAB (Minitab Inc., State College, PA), was used to obtain the regression equations. A modification of a published program (21) was used to solve the linear program models on the personal computer (PC). A copy of this program is available from the authors on request.

The PB design selected was a twelve-experiment design, which is capable of analyzing the main effects of eleven components. The layout of this design is shown in Table 1. The levels chosen for the seven varied components were based on the experience of the authors and were thought to be near the optimum region. These twelve formulas were then prepared and tested in random order. A commercially available LDLD, of unknown formula, was used as a guide to the properties required of an LDLD. This detergent was used as a control in all tests, and its RMFH, RMFS and GSTT properties became the specifications that the optimum formula must match or exceed at lowest cost. Also, a viscosity in the range of 150 to 500 centistokes (cSt) and a clear point of less than 5°C were the remaining property requirements. The properties of this control detergent are listed in Table 2.

## RESULTS AND DISCUSSION

The experimental results of the PB design at the levels specified in Table 3 are shown in Table 4. The results for the analysis for this PB design are shown in Table 5. The results for RMFS are not reported because NaCl was the only component with a significant effect. Based on a 90% confidence level, the most important components affecting the properties, for the levels specified, are listed in the order of importance in Table 6. The components in brackets are the ones with confidence levels between 60 and 90%. The property equations were obtained with MINITAB by using stepwise variable selection (22) and are listed in Table 7. It is clear that the properties RMFH and GSTT show good linearity, while VISC and CLPT do not, for this region of component space. No variables were selected for the RMFS property with MINITAB. Because all experiments were within experimental error of the required property value of RMFS, this property was not included in the linear programming (LP). However, it was measured.

The LP model consisted of an objective cost equation to be minimized and a number of constraint equations. The property constraints were obtained by replacing the

**TABLE 1**

**Plackett-Burman Experimental Design**

| Plan | Variables | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| number | NaCl | $D^a$ | AEO | AEOS | $D^a$ | NaLAS | DEALAS | TEALAS | CDEA | $D^a$ | $D^a$ |
| 1 | + | − | + | − | − | − | + | + | + | − | + |
| 2 | + | + | − | + | − | − | − | + | + | + | − |
| 3 | − | + | + | − | + | − | − | − | + | + | + |
| 4 | + | − | + | + | − | + | − | − | − | + | + |
| 5 | + | + | − | + | + | − | + | − | − | − | + |
| 6 | + | + | + | − | + | + | − | + | − | − | − |
| 7 | − | + | + | + | − | + | + | − | + | − | − |
| 8 | − | − | + | + | + | − | + | + | − | + | − |
| 9 | − | − | − | + | + | + | − | + | + | − | + |
| 10 | + | − | − | − | + | + | + | − | + | + | − |
| 11 | − | + | − | − | − | + | + | + | − | + | + |
| 12 | − | − | − | − | − | − | − | − | − | − | − |

[a] Dummy variable.

**TABLE 2**

**Properties of the Commercial LDLD**

| Property | | Value |
|---|---|---|
| Ross-Miles flash foam height | (RMFH) | 10.3 cm |
| Ross-Miles foam stability | (RMFS) | 1.0 cm |
| Geelong Soil Titration Test | (GSTT) | 10.2 gm |
| Viscosity | (VISC) | 214.3 cSt |
| Clear point | (CLPT) | 0°C |
| pH | | 6.6 |
| Active matter | | 12.3% |

**TABLE 3**

**Levels and Costs of Components of Plackett-Burman Design**

| | Level | | | |
|---|---|---|---|---|
| Variable | Low − | High + | Cost A$/kg | Active matter (%) |
| NaCl | 0 | 0.5 | 0.12 | |
| Dummy | — | — | — | |
| AEO | 0 | 1.0 | 1.71 | 100 |
| AEOS | 1.0 | 4.0 | 0.68 | 25 |
| Dummy | — | — | — | |
| NaLAS | 2.39 | 4.78 | 1.24 | 100 |
| DEALAS | 1.89 | 5.69 | 1.24 | 100 |
| TEALAS | 0.61 | 2.42 | 1.43 | 100 |
| CDEA | 0.59 | 2.35 | 1.22 | 86 |
| Dummy | — | — | — | |
| Dummy | — | — | — | |

dependent variables of the property equations in Table 7 with their corresponding specification and by replacing the equality sign with an appropriate inequality sign, depending on whether the property is required to be above or below this specification.

Because most of the property equations obtained by regression analysis do not show good fit to linear models, the application of LP, while using these property constraints, is unlikely to be successful. A strategy is needed to compensate for the poor linear fit. Some possible strategies are: (i) Use bounds constraints so that the LP does not extrapolate outside the component space investigated by the PB design; (ii) Put in extra constraints in the LP based on the formulator's knowledge. For example, the overall quality of a LDLD would be expected to be influenced by the amount of active matter. Therefore,

**TABLE 4**

**Experimental Results of the Plackett-Burman Design**

| Experiment | RMFH (cm) | RMFS (cm) | GSTT (%) | VISC (cSt) | CLPT (°C) | Active matter (%) | Cost ($/100 kg) |
|---|---|---|---|---|---|---|---|
| 1 | 12.0 | 1.2 | 102.2 | 458.4 | 2.5 | 14.4 | 18.79 |
| 2 | 11.7 | 1.2 | 98.0 | 293.3 | 0.4 | 10.5 | 14.43 |
| 3 | 8.7 | 0.8 | 93.0 | 5.3 | 1.1 | 8.3 | 11.44 |
| 4 | 11.2 | 1.2 | 92.0 | 103.2 | 10.9 | 10.2 | 14.35 |
| 5 | 12.8 | 1.0 | 90.0 | 80.5 | 0.5 | 10.7 | 14.37 |
| 6 | 10.9 | 1.1 | 89.0 | 231.8 | 11.1 | 11.2 | 14.91 |
| 7 | 13.4 | 1.0 | 121.0 | 302.1 | 0.7 | 15.1 | 21.13 |
| 8 | 12.3 | 0.9 | 101.0 | 19.0 | 0.9 | 13.1 | 18.62 |
| 9 | 13.0 | 0.7 | 113.0 | 30.2 | 0.5 | 12.2 | 17.34 |
| 10 | 13.0 | 0.9 | 104.0 | 562.5 | 15.9 | 13.9 | 17.44 |
| 11 | 12.7 | 0.8 | 72.0 | 57.3 | 1.1 | 13.6 | 17.83 |
| 12 | 9.6 | 1.0 | 55.0 | 1.9 | 1.2 | 5.6 | 7.58 |

**TABLE 5**

**Effects of Components on Properties of PB Design**

| | Property | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | RMFH | | GSTT | | VISC | | CLPT | |
| Variable | Effect | *t*-test | Effect | *t*-test | Effect | *t*-test | Effect | *t*-test |
| NaCl | 0.317 | 1.6 | 3.333 | 0.77 | 218.983 | 3.43 | 5.983 | 2.47 |
| Dummy | −0.150 | | −0.067 | | −34.150 | | −2.850 | |
| AEO | −0.717 | −3.68 | 11.000 | 2.56 | 15.683 | 0.24 | 1.283 | 0.53 |
| AEOS | 1.250 | 6.41 | 16.667 | 3.88 | −81.483 | −1.27 | −3.150 | −1.30 |
| Dummy | 0.017 | | 8.333 | | −47.817 | | 2.217 | |
| NaLAS | 1.183 | 6.06 | 8.667 | 2.02 | 71.450 | 1.12 | 5.583 | 2.30 |
| DEALAS | 1.850 | 9.48 | 8.333 | 1.94 | 135.683 | 2.12 | −0.617 | −0.25 |
| TEALAS | 0.650 | 3.33 | 3.333 | 0.77 | 5.750 | 0.09 | −2.317 | −0.95 |
| CDEA | 0.383 | 1.96 | 22.000 | 5.12 | 193.017 | 3.02 | −0.750 | −0.31 |
| Dummy | −0.350 | | −1.667 | | −10.717 | | 2.283 | |
| Dummy | −0.083 | | −1.000 | | −112.617 | | −2.283 | |

**TABLE 6**

**Components Affecting the Properties**

| Property | Components (in the order of importance) |
|---|---|
| RMFH | DEALAS, AEOS, NaLAS, AEO, TEALAS (CDEA) |
| RMFS | NaCl |
| GSTT | CDEA, AEOS, AEO, (NaLAS, DEALAS) |
| VISC | NaCl, CDEA, DEALAS, (AEOS, NaLAS) |
| CLPT | NaCl, NaLAS, (AEOS, TEALAS) |

constrain the active matter to be greater than or equal to a certain value in the LP; (iii) Tighten the property constraints by an amount equivalent to the standard error expected in the predicted value of the property. For example, the standard error in the predicted value of RMFH is 0.3 cm at 10.3 cm. Therefore, constrain RMFH to be 10.6 cm or better in the LP, so that the error will be allowed for. The standard errors of the other property equations are larger, corresponding to the poorer linear fit. The standard errors at the required property value can be found with MINITAB and are listed in Table 7.

Each of the above strategies was tried. Four LP solutions were obtained. The four solutions correspond, in turn, to strategies (i), (ii) with 10% active matter, (ii) with 9% active matter, and (iii). The properties of these formulations are listed in Table 8 under formula 1 to 4. None of these formulations meet all the property requirements. Formulation 4 is closest in being satisfactory for all properties. However, the viscosity is only 140 cSt when required to be 150 cSt. Two further strategies were tried to improve the formulations. These were: (i) Careful addition of NaCl to adjust viscosity as recommended by Shell Chemical (Australia) (20); (ii) further tightening of the viscosity constraint by setting the required viscosity in the LP solution to be 10 cSt higher than in formulation 4.

The amounts of NaCl required to adjust the viscosity of each formulation are also shown in Table 8, along with the viscosity and clear points measured after adjustment. However, formulations 1 to 3 are still slightly deficient in the Geelong Soil Titration Test. Also, formulation 1 fails

**TABLE 7**

**Property Equations**

| Property equations | | $R^2$ | S.E.[a] |
|---|---|---|---|
| RMFH = 6.61 | −0.72 AEO + 0.42 AEOS + 0.50 NaLAS + 0.49 DEALAS + 0.36 TEALAS + 0.22 CDEA | 97 | 0.3 |
| GSTT = 35.11 | + 11.00 AEO + 5.56 AEOS + 3.63 NaLAS + 2.20 DEALAS + 12.51 CDEA | 92 | 5.0 |
| VISC = −227 | + 438 NaCl + 36 DEALAS + 110 CDEA | 79 | 70 |
| CLPT = −7.48 | + 11.97 NaCl + 2.34 NaLAS | 62 | 1.1 |

[a]Standard error of predicted value at property requirement.

**TABLE 8**

**Formulas and Properties of Some LP Solutions**

| Formula | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| NaCl | 0.115 | 0.115 | 0.115 | 0.275 | 0.298 |
| NaCl ([a]adj.) | 0.300 | 0.18 | 0.15 | 0.02 | |
| AEO | 0.042 | 0.853 | 0.692 | 0.500 | 0.500 |
| AEOS | 4.000 | 1.153 | 2.175 | 4.000 | 4.000 |
| NaLAS | 2.390 | 4.336 | 3.243 | 2.390 | 2.390 |
| DEALAS | 1.890 | 1.890 | 1.890 | 1.890 | 1.890 |
| TEALAS | 0.610 | 0.610 | 0.061 | 0.610 | 0.610 |
| CDEA | 2.350 | 2.350 | 2.350 | 2.350 | 2.350 |
| RMFH/cm | 10.6 | 11.4 | 10.3 | 10.9 | |
| RMFS/cm | 0.6 | 0.6 | 0.7 | 0.7 | |
| GSTT/% | 93 | 97 | 99 | 105 | |
| VISC/cSt | 6 | 49 | 23 | 140 | |
| VISC[b] (adj) | 190 | 173 | 165 | 152 | |
| CLPT/°C | 0.0 | 0.0 | 0.0 | 0.0 | |
| CLPT[b] (adj) | 20.0 | 0.0 | 0.0 | 0.0 | |
| Cost/$100 kg | 11.85 | 13.72 | 12.78 | 12.65 | 12.65 |
| Active matter/% | 8.0 | 10.0 | 9.0 | 8.4 | 8.4 |

[a]Additional NaCl required to adjust viscosity (see text).

[b]Property after adjustment with NaCl.

the CLPT test. Formulation 4 now meets all property requirements. Formulation 5 in Table 8 is the LP solution obtained by tightening the viscosity constraint a further 10 cSt. As can be seen, this formulation is the same, within experimental error, as the adjusted formulation 4. The strategy used to obtain formulation 5 is not formulation-specific as is the viscosity adjustment with NaCl. Hence, the application of Plackett-Burman experimental design, regression analysis and linear programming with constraints tightened by an amount determined by the standard error of the predicted value of the property, followed by further tightening as required, appears to be a reasonable procedure for optimizing formulations when the property equations are not all linear.

The results of Table 8 also show that the strategy of selecting a minimum active matter will not automatically result in a good LDLD at low cost. The costs of formulations 2 and 3 are higher than formulation 5 and the properties are not as good. It seems that the best way to include a margin of safety in a formulation is to tighten the constraints. As in all optimization procedures, the last question is "Is this the best price/performance ratio that can be obtained with these components?". A perusal of Tables 4 and 8 indicates that formula 5 in Table 8 should be close to the best for the component space investigated, and further savings would be in the low cents/100 kg range. To realize these savings, a more elaborate experimental design would be required. Of more significance is the fact that all components except AEO and NaCl have been selected by the LP at the boundaries of the component space. This indicates that an optimum formulation may be outside the investigated range and in particular at higher AEOS and lower CDEA and LAS salts. This possibility was not investigated.

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