# Burning Rate of a Trimodal Composite Rocket Propellant

Lazic Zivorad*
*Military Technical Institute, Belgrade, Yugoslavia*

**Some new perceptions in the field of composite propellants are considered. The effects of trimodal oxidizer distribution on the burning rate of composite propellants are considered. It is note that reducing the oxidizer particles in the presence of depressors reduces the burning rate of these propellants. In the formulation of the experimental approach, modern and effective methods of experimental design with the application of extreme-vertices design were used.**

## I. Introduction

A SOLID composite propellant is a heterogenous mixture of crystalline oxidizer, polymer as a binder and fuel, metallic powder, burning-rate modifiers, and other additives regulating physico-chemical properties required to meet specific design objectives. For high-energy composite propellants, ammonium perchlorate (AP) is the preferred oxidizer. The polymeric binder, which acts as a fuel in the combustion process, accounts for the mechanical properties of a solid propellant charge. Metal powder improves the energetic characteristics of a propellant by increasing the combustion temperature.

Burning-rate modifiers serve to increase (catalysts) and reduce (depressors) burning rates. The most frequently used catalysts are metal oxides and solid and liquid metaboric organic compounds. For the burning-rate depressors, fluorides, oxides, and carbonates of lithium, calcium, strontium, and barium are used. The specific composition is a function of the physical and chemical properties required for each particular missile.

This complexity of composite rocket propellant compositions poses a difficult problem to research people in creating and defining compositions having specified properties. Renie et al.,[1] Cohen and Strand,[2] and Beckstead et al.[3] have analyzed the effect of particle size of ammonium perchlorate on the burning rate. Results were obtained for both unimodal and bimodal propellants with oxidizer particle size ranging from ultrafine 0.7 $\mu$m to coarse 400 $\mu$m. For unimodal propellants, it was determined that the burning rate was higher for the smaller oxidizer sizes as would be expected. For the bimodal distributions, the results were consistent with those that could be inferred from the unimodal results. Specifically, the burning rates were strong functions of the coarse-to-fine ratio and the mean diameter of the fine fraction.

Miller[4] investigated the effects of ammonium perchlorate size distribution in a series of nonaluminized propellants. Burning rates were measured using cured strands and correlated to a characteristic particle size of the ammonium perchlorate. Horton and Rice[5] analyzed the effects of different compositions (ammonium perchlorate particle size, copper chromite, and lithium fluoride) on the oscillatory combustion of a polybutyl-acrylic acid propellant.

The objective of the current research is to extend these results by investigating the effect of trimodal oxidizer distributions on the burning rate, and the effect of lithium fluoride as a burning-rate depressor. Specifically, statistically designed experiments were conducted and the results were evaluated using statistical and regression analyses to enable computational determination of optimum compositions with specified properties. Of the three AP fractions, the 400- and 200-$\mu$m diameter fractions were as-received lots of Kerr-McGee materials and the 7-$\mu$m material were prepared by conventional grinding techniques.

## II. Experimental Design

Determining the propellant composition having desired properties is classified as the "composition property" problem. Experimentally, this problem is solved using either classical experimental methods or more recently developed active experimental design methods.[6] With the active designed experiment, it is possible to vary all factors simultaneously and obtain quantitative estimates of the main effects and factor interactions. This approach ensures reduced errors in determining the effects of interest compared to the classical methods. By arranging the points in experimental, or factor space, in an optimal way and using a linear transformation of the coordinates, the experimenter can avoid some disadvantages of the classical regression analysis. Thus, the experimenter can achieve the desired results more economically than by using the experimental methods, which vary the factors one at a time.

The mathematical theory of experiments for solving the composition property problems allows extreme-vertices designs to be used to plan the experiments.[7] In such a plan, space factor usually represents a regular simplex from the $q$ vertices in $q-1$ dimensional space. In this particular study, the objective was to define the minimum possible number of experimental points required to define polynomial coefficients defining the relationship between mass fraction and burning rate. When the mass fraction is the independent variable, the constraint that their sum must be equal unity must be considered. Also, it is often necessary to constrain the independent variables to avoid compositions, which are undesirable for other reasons.

These relationships are expressed mathematically below:

$$\sum_{i=1}^{q} X_i = 1, \qquad 0 \le a_i \le X_i < b_i \le 1 \tag{1}$$

where $i = 1,\ldots,q$, $a_i$, and $b_i$ are constraints on $X_i$, and there are $q$ components in the system being investigated. From Eq. (1), the actual number of independent variables in a $q$-component system is $q-1$.

The experimental design for such a system has been covered extensively in the literature. Scheffe[6] introduced the topic of mixture experiments for cases where $a_i = 0$ and $b_i = 1$ [Eq. (1)]. Lazic and Orescanin,[8] Lazic et al.,[9] and McLean and Anderson[10] introduced a design for the constrained situation. Specif-

Received Dec. 7, 1987; revision received Aug. 11, 1989. 

*Chief, Department for Composite Rocket Propellant.

ically, they give an example of a three-component system with upper and lower constraints on each of the independent variables. These conditions apply to the experiments where the extreme vertices have no physical sense, or where interest is limited to a local area of factor space. Designs that take these facts into consideration are called extreme-vertices designs. These conditions obviously apply to the present investigation.

For this investigation, it is essential that the complexity of the response surface (burning rate) of the multicomponent mixture be considered. Thus, a mathematical expression of this system higher order is required, as for example:

$$Y = \sum_{1\le i\le a}\beta_i X_i + \sum_{1\le i\le j\le a}\beta_{ij} X_i X_j + \sum_{1\le i\le j\le a}\tau_{ij} X_i X_j (X_i - X_j) + \sum_{1\le i\le j\le k\le a}\beta_{ijk} X_i X_j X_k \tag{2}$$

where $\beta_i$, $\beta_{ij}$, and $\beta_{ijk}$ are regression coefficients and $X_i$, $X_j$, and $X_k$ are coded mass fractions of components $i, j$, and $k$. The term $Y$ represents the measured property of the composition. Regression coefficients for the third-order model can be calculated following these equations:

$$\beta_i = Y_i, \qquad \beta_{ij} = 9/4(Y_{iij} + Y_{ijj} - Y_i - Y_j) \tag{3}$$

$$\tau_{ij} = 9/4(3Y_{iij} - 3Y_{ijj} - Y_i + Y_j) \tag{4}$$

$$\beta_{ijk} = 27Y_{ijk} - 27/4(Y_{iij} + Y_{ijj} + Y_{ijk} + Y_{ikk} + Y_{jjk} + Y_{jkk}) + 9/2(Y_i + Y_j + Y_k) \tag{5}$$

where $Y_{ijk}$ and respective combination of subscripts represent the properties measured for a particular composition. The methodology for checking the adequacy of the regression model is given in Refs. 8 and 9.

## III. Experimental Studies

Polyurethane composite rocket propellants were formulated using polyether diols and triols, toluene di-isocianate TDI-80 as curative, and a solids content of 86%. Dioctyladiapate was used as the plasticizer, the binder stabilizer was phenyl $\beta$-naphtylamine, and ferric-acetylacetonate was the curing catalyst. The aluminum in powder form was supplied by "Benda Lutz" ($d = 30$ μm). The mass fractions of these ingredients were held constant at 12%. The only exception was the lithium fluoride: initially it was 2.0% by mass, but in the second part of the program, it was removed from the composition.

Particle size distributions of AP are shown in Fig. 1. The mass fraction of each AP fraction was varied in the following ranges:

7-μm fraction: 30–70%
400-μm fraction: 0–40%
200-μm fraction: 30–70%

The real fractions of oxidizer and coded factors are related as follows:

$$x_1 = 0.70\ X_1 + 0.30\ X_2 + 0.30\ X_3 \tag{6}$$

$$x_2 = 0.40\ X_2 \tag{7}$$

$$x_3 = 0.30\ X_1 + 0.30\ X_2 + 0.70\ X_3 \tag{8}$$

where $x_i$ ($i = 1, 2, 3$) are the real mass fractions of the $i$th fraction, and $X_i$ are coded fractions of the $i$th fraction. Relations (6–8) also transform the design matrix into a real matrix (Table 1). According to the theory of local-extreme-vertices designs,[6] the limiting values of intervals of varied mass fractions represent the vertices, that is, the coordinates of the vertex of a local factor space.

It should be mentioned that in the response $Y_{ijk}$, subscripts $i, j$, and $k$ represent the portions of components in the formulation. For example, $Y_1$ denotes the response for the formulation with coded mass fraction of the component $X_1 = 1$, and of component $X_2 = 0$ and $X_3 = 0$. By analogy, $Y_{233}$ denotes the response with coded mass fraction of the following components: $X_1 = 0$, $X_2 = 1/3$ and $X_3 = 2/3$, etc.

The matrices for these experimental tests are given in Table 1. As indicated, 30 tests were made with 30 batches of propellant. Fifteen batches of propellant contained a burning-rate depressor and 15 batches contained no depressor. Also, five identical batches were made to evaluate the reproducibility of the experiment. These five batches are not explicitly shown in Table 1. For each batch of oxidizer, the average particle size and specific surface were measured on a Fischer subsieve sizer. The results of these measurements are given in Table 2.

Seven Standard Test Motors (STM's) were cast from each batch, following a standard procedure. After curing, STM's were trimmed. Static tests were conducted at pressures between 20–200 bar to measure burning rates. The pressure and thrust were recorded as a function of time. Burning rates were corrected to 70 bar using the usual burning-rate law. Test results of all of the measurements are summarized in Table 1.

Equation (9) was derived from the experimental results obtained from depressor-containing batches, in accordance with the theory of the local-extreme-vertices design:

$$Y = 3.92X_1 + 4.75X_2 + 4.95X_3 - 1.31X_1X_2 - 0.43X_1X_3 - 0.4X_2X_3 - 0.9X_1X_2(X_1 - X_2) + 0.97X_1X_3(X_1 - X_3) + 2.07X_2X_3(X_2 - X_3) - 3.31X_1X_2X_3 \tag{9}$$

The adequacy of Eq. (9) was verified using control points 11–15 of Table 1 (ten tests for regression analysis, five control points, and five repetitions). The regression model for the composition without depressor was not made because it was not the aim of the work.

From Table 1, it is obvious that the burning rate with depressor from test 12 is an "outlier." This is not too important since this is a control point and, as such, is not taken into consideration in determination of the regression coefficients.

With the burning rates from batches without depressors, outliers in tests 3 and 9 were found. This result had little consequence since the regression analysis for the burning rate without depressor was not made. Note that outliers were identified by statistical testing.

The burning-rate behavior was also correlated as a function of specific surface. These correlations were developed using the graphical capability of the Tektronix 4052A computer.

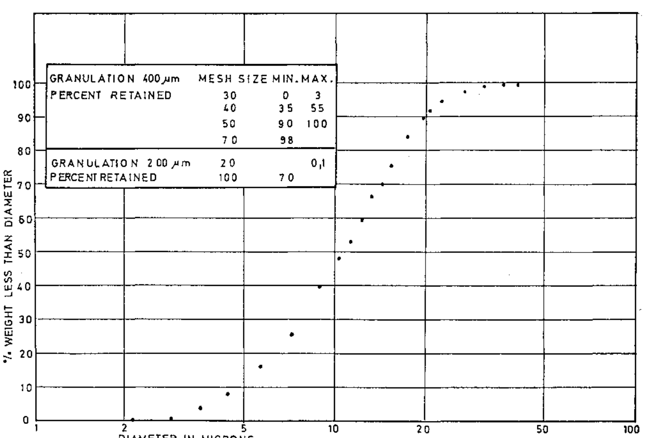


**Fig. 1 Particle size distribution analysis of ammonium perchlorate ($d = 7$ μm).**

**Table 1 Matrix of extreme-vertices experimental design**

| No. of tests | Designed matrix | | | Code for response | Real matrix | | | Burning-rate units[e] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $X_1$, %[b] | $X_2$, %[c] | $X_3$, %[d] | | $x_1$, % | $x_2$, % | $x_3$, % | $A$ | $\bar{R}_1$ | $\bar{R}_2$ |
| 1 | 1 | 0 | 0 | $Y_1$ | 70.00 | 0.00 | 30.00 | 29.00 | 3.29 | 5.99 |
| 2 | 0 | 1 | 0 | $Y_2$ | 30.00 | 40.00 | 30.00 | 13.40 | 4.75 | 5.75 |
| 3 | 0 | 0 | 1 | $Y_3$ | 30.00 | 0.00 | 70.00 | 14.00 | 4.95 | 4.59 |
| 4 | 1/3 | 2/3 | 0 | $Y_{122}$ | 43.33 | 26.66 | 30.00 | 27.00 | 4.25 | 5.65 |
| 5 | 1/3 | 0 | 2/3 | $Y_{133}$ | 43.33 | 0.00 | 56.66 | 20.00 | 4.44 | 6.21 |
| 6 | 0 | 1/3 | 2/3 | $Y_{233}$ | 30.00 | 13.13 | 56.66 | 16.00 | 4.82 | 6.03 |
| 7 | 2/3 | 1/3 | 0 | $Y_{112}$ | 56.66 | 13.13 | 30.00 | 31.00 | 3.84 | 5.87 |
| 8 | 2/3 | 0 | 1/3 | $Y_{113}$ | 56.66 | 0.00 | 43.33 | 32.00 | 4.24 | 5.91 |
| 9 | 0 | 2/3 | 1/3 | $Y_{223}$ | 30.00 | 26.66 | 43.33 | 14.00 | 5.06 | 5.18 |
| 10 | 1/3 | 1/3 | 1/3 | $Y_{123}$ | 43.33 | 13.33 | 43.33 | 22.40 | 4.27 | 5.75 |
| 11[a] | 1/2 | 1/4 | 1/4 | $Y_{1123}$ | 50.00 | 10.00 | 40.00 | 26.00 | 4.09 | 6.10 |
| 12[a] | 1/4 | 1/4 | 1/2 | $Y_{1223}$ | 40.00 | 10.00 | 50.00 | 21.00 | 3.75 | 6.00 |
| 13[a] | 3/4 | 1/4 | 0 | $Y_{1112}$ | 60.00 | 10.00 | 30.00 | 30.00 | 3.83 | 5.97 |
| 14[a] | 3/4 | 0 | 1/4 | $Y_{1113}$ | 60.00 | 0.00 | 40.00 | 31.00 | 4.04 | 6.12 |
| 15[a] | 1/4 | 3/4 | 0 | $Y_{1222}$ | 40.00 | 30.00 | 30.00 | 22.00 | 4.56 | 5.90 |

[a]Control points. [b]Fine fraction. [c]Coarse fraction. [d]Average fraction. [e]Experimental values: $A$ = specific surface of oxidizer; $\bar{R}_1$ = burning rate for the formulation with depressor; and $\bar{R}_2$ = burning rate for the formulation without depressor.

**Table 2 Oxidizer mixture properties**

| Oxidizer mixture | Humidity, % | Average diameter, μm | Specific surface, $cm^2/g \times 10^{-4}$ |
|---|---|---|---|
| 1 | 0.124 | 10.60 | 29.00 |
| 2 | 0.120 | 23.07 | 13.40 |
| 3 | 0.125 | 22.40 | 14.00 |
| 4 | 0.125 | 11.49 | 27.00 |
| 5 | 0.123 | 15.10 | 20.00 |
| 6 | 0.124 | 19.30 | 16.00 |
| 7 | 0.123 | 9.90 | 31.00 |
| 8 | 0.120 | 9.70 | 32.00 |
| 9 | 0.125 | 21.65 | 14.00 |
| 10 | 0.124 | 13.75 | 22.40 |
| 11 | 0.123 | 11.85 | 26.00 |
| 12 | 0.123 | 14.50 | 21.00 |
| 13 | 0.124 | 10.28 | 30.00 |
| 14 | 0.120 | 9.80 | 31.00 |
| 15 | 0.120 | 14.00 | 22.00 |

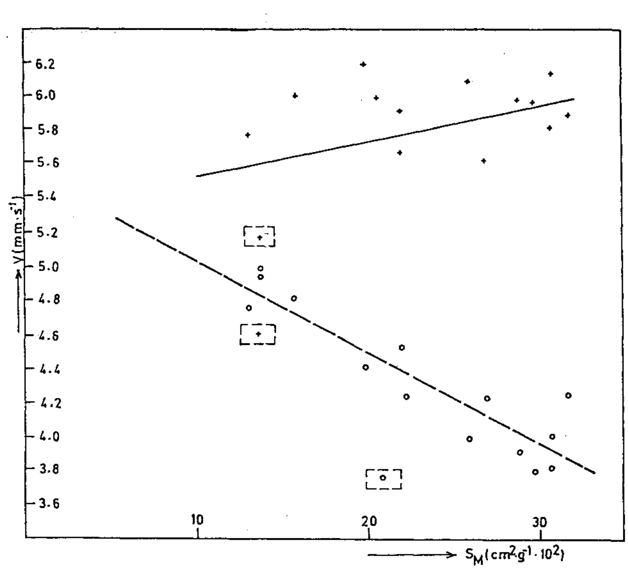


**Fig. 2 Burning rate vs ammonium perchlorate specific surface. —— : composite rocket propellant without depressor; ---- : composite rocket propellant with depressor; and [ ] : indication of "outliers."**

The resulting relations between burning rate and specific surface of oxidizer are shown in Fig. 2. Two curves are shown, one for the propellants without the depressor and the other with the lithium fluoride depressor. The formulations without depressor were repeated to check the trend. There was no doubt that results obtained with lithium fluoride show significant changes in the combustion mechanism. Note that the burning rate decreases with increasing specific surface of oxidizer, whereas the expected opposite effect is observed when no lithium fluoride was included in the propellant.

These results also contrast with the data reported by Horton and Rice,[5] who observed that lithium fluoride did not alter the trend of burning rate with particle size. It should be noted that Horton and Rice used unimodal compositions, no aluminum, and a polybutadiene-acrylic acid binder.

## IV. Hypothesis

A possible explanation for these results is the following:

1) The lithium fluoride shifts the balance of the ammonium perchlorate decomposition so as to reduce the rate of decomposition.

2) The average diameter of the lithium fluoride particles is about 3 μm, which would statistically increase the probability of contact with small oxidizer particles. This contact would therefore have a greater effect on the contribution of the small particles compared to the larger particles.

3) The burning-rate depressor would, therefore, have an increased effect in compositions having higher concentrations of smaller particles. This hypothesis is consistent with the data in Table 1 that show a 53.57% burning rate reduction with smaller particles and only a 5.0% reduction with larger particles.[3]

## References

[1]Renie, J. P., Condon, J. A., and Osborn, J. R., "Oxidizer Size Distribution Effects on Propellant Combustion," *AIAA Journal*, Vol. 1, Jan. 1978, pp. 1-10.

[2]Cohen, N. S., and Strand, L. D., "An Improved Model for the Combustion of AP Composite Propellants," *AIAA Journal*, Vol. 20, No. 12, 1982, pp. 240-248.

[3]Beckstead, M. W., Derr, R. L., and Price, C. F., "A Model of Composite Solid Propellant Combustion Based on Multiple Flames," *AIAA Journal*, Vol. 8, No. 12, 1970, pp. 2200-2207.

[4]Miller, R. R., "Effects of Particle Size on Reduced Smoke Propellant Ballistics," AIAA 18th Joint Propulsion Conf., AIAA, New

York, June 1982.

[5]Horton, M. D., and Rice, D. W., "The Effect of Compositional Variables upon Oscillatory Combustion of Solid Propellants," *Combustion and Flame,* Vol. 8, 1964, pp. 21–28.

[6]Scheffe, H., "Experiments with Mixtures," *Journal of the Royal Statistical Society, Series B,* No. 2, 1958, p. 344.

[7]Lazic, R. Z., "Development Procedures for Transfer of Production Conditions to the Rocket Propellant Production," Ph.D. Thesis, Beograd, Faculty of Technology and Metallurgy, Belgrade, Yugoslavia, 1982.

[8]Lazic, R. Z., and Orescanin, R., "Application of Vertices Design for Obtaining Regression Models and Diagrams Composition-Property ," *Naucno-tehnicki pregled,* No. 8, 1980.

[9]Lazic, R. Z., Vuga, S., and Jaukovic, D., "Optimization of Composite Rocket Formation in Ballistic Parameters by the Application of Extreme Vertices Design," *Naucno-tehnicki pregled,* Vol. XXXII, No. 3, 1982, p. 45.

[10]McLean, R. A., and Anderson, V. L., "Extreme Vertices Design of Mixture Experiments," *Technometrix,* Vol. 8, No. 3, 1966, pp. 447–454.