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A Comparative Optimization Study of Flame Retardancy of Wool Fabric with and Without Robust Parameter Design Approach

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Abstract: In this study, the optimal factor value estimates of the effect of Zirconium Oxychloride (ZrOCl2) with different concentrations of citric and formic acids on the flame-retardant properties of wool which is assessed by thermal analysis, mass loss, the limiting oxygen index and vertical flame is considered and compared by two different optimization approaches, namely, with and without Robust Parameter Design (RPD) using standard design matrix of Response Surface Methodology (RSM) in both cases to produce representative data. The results of optimization methods for the data of recent published research article which was only based on general mean function show that the estimation of optimal factor values through new methodology of RPD approach is 86 percent more efficient.

Key words: Flame retardant · Wool · Zirconium oxychloride · Central composite design · Robust parameter design

INTRODUCTION

The flammable nature of fibrous products is one of the major problems of the present time. Fibers from textiles causing many deaths and injuries and considerable financial losses. Hazards from flammable fabrics have been recognized for many centuries and repeated attempts have been made to control them [1].

One of the concern fibrous products is wool which is a cutin fibrous protein and contains many kinds of cysteine, thiocarbamic acid and cross-linking polypeptides with ahelical structure [2]. The natural flame-resistant (FR) properties of wool are connected with its relatively high nitrogen content (16%), high moisture content (10-14%) [3], high ignition temperature (570-600°C) [4], low heat of combustion 920.5kj/g), low flame temperature (680°C) and a relatively high limiting oxygen index (LOI) (25-28%) [5].

Wool, when heated alone, pyrolyses by a complex series of reactions which yield a number of products at increasing temperatures. Initially at 230-240°C, rupture of the helical structure occurs and the major ordered part of the wool protein undergoes a solid to liquid phase change [6]. At 250-295°C, an endothermic reaction occurs associated with release of sulfur compounds due to the breaking of the cystine disulfide bonds and simultaneous release of hydrogen sulfide [2]. Above 250°C, general pyrolytic decomposition occurs, including char-forming reaction and loss of other volatiles. In the presence of air, formation of sulfur dioxide occurs between 270-320°C [6]. Cleavage of the cystine disulfide bond is seen to play a very important role in the thermal degradation and combustion of keratin and it has been suggested that the oxidation of cystine may be the initial exothermic reaction in the burning of wool [6].

In recent years, there have been a number of reports of treatments which enhance the natural flame-resistant properties of wool [7-11]. Benisek when working at the International Wool Secretariat Laboratories has observed that mordanting treatments based on zirconium and titanium salts markedly improve flame-resistance of wool [7-11]. They used vertical flame test and differential scanning calorimetric (DSC) and thermogravimetry analysis (TGA) to study the flame-resistance and thermal behavior. Also, scanning election microscopy (SEM) and energy dispersive X-ray microanalysis (EDXS) were used to study the morphology of treated wools [2].

Here, zirconium oxychloride (ZrOCl2) along with two different organic acids (citric and formic acids) were used to produce a FR wool fabric [2]. In this study, the optimal factor value estimates of the effect of Zirconium Oxychloride (ZrOCl2) with different concentrations of citric and formic acids on the flame-retardant properties of wool which is assessed by thermal analysis, mass loss,

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the limiting oxygen index and vertical flame is considered and compared by two different optimization approaches, namely, with and without Robust Parameter Design (RPD). Since it is impractical and unnecessary to produce all data points of the different combinations of levels of four considered factors, a standard design matrix, namely, Central Composite Design (CCD) of Response Surface Methodology (RSM) was used in both cases to produce representative data. This design of experiment, not only produces effective data, but also provides us an opportunity of modeling the whole experimental space.

MATERIALS AND METHODS

Materials: Base upon recent published research article of Forouharshad Et Al [2], the wool fabric with plain woven structure from 48/2 Nm yarns was supplied by Iran Merino. The fabric was scoured with 0.5% nonionic detergent at 50 for 30 min (L :R¼40 : 1) and then washed with tap water and dried at room temperature. The zirconium oxychloride (35%ZrO2) used in that study was supplied by Shanghai Yancui Co, China. Formic acid and citric acid were obtained from Merck, Germany. Then formic acid (HCOOH) and citric acid (C6H8O7) were mixed with ZrOCl2 according to the CCD in Table 2, after which water was added until the solution achieved a 20 : 1 ratio of liquor to wool. Formic acid was added to each of the above flame retardants in order to maintain a pH of 3 during the exhaustion procedure. Mordanting of samples was started at 408C for 20 min and the temperature was raised for 30 min to the specified temperature in the CCD matrix (Table 2) and heated for 45 min. After being exhausted, the treated samples were rinsed with tap water and dried at room temperature. The criterion for flame retardation in that work was that the fabric must pass the vertical strip-test prescribed by the United States Federal Aviation Administration (F.A.A test) [10]. The ranges of these variables are shown in Table 1 and details of CCD for mordanting of wool with ZrOCl2 are demonstrated in Table 2. According to preparation and test procedure explained in [2], the values of Char Length (CL) which its minimization is desired are obtained (Table 2).

Methods: Given the data from a crossed array, there are a number of potential approaches to directly modeling the mean and variance as a function of the control factors. A general approach is to assume that the underlying functional forms for the mean and variance models can be expressed parametrically. Assuming a d point design with n_i replicates at each location (i = 1, 2, …, d), the point estimators of the process mean and variance, $\bar{y}_i$ and s_i^2, respectively, form the data for the dual response system. Since the purpose of this article is to demonstrate the utility of a hybrid approach (combining a parametric and nonparametric approach to modeling) for robust design, we will consider an “off the shelf” model for the mean. An “off the shelf” model for the process mean is linear in the model parameters and can be written as:

Means Model:

$$\bar{y}_i = x_i'\beta + g^{1/2}(x_i^{*\prime};\gamma)\varepsilon_i \tag{1}$$

where X_i' and $X_i^{*\prime}$ are $1\times k$ and $1\times l$ vectors of means model and variance model regressors, respectively, expanded to model form, β and γ are $k\times 1$ and $m\times 1$ vectors of mean and variance model parameters, respectively, g is the underlying variance function and ε_i denotes the random error for the mean function. The ε_i are assumed to be uncorrelated with mean zero and variance of one. Note that the model terms for the i^{th} observation in the means model are denoted by X_i' while the model terms for the variance model are denoted by $X_i^{*\prime}$. This allows for the fact that the process mean and variance may not depend on the same set of regressors.

Similar to the modeling of the mean, various modeling strategies have been utilized for estimating the underlying variance function. Bartlett and Kendall [12] demonstrated that if the errors are normal about the mean model and if the design points are replicated, the variance can be modeled via a log-linear model with the d sample variances utilized for the responses. A great deal of work has also been done using generalized linear models for estimating the variance function. Although not an

Table 1: Input Variables and their Ranges

Variable	Lower limit	Upper limit
Temperature (°C)	77	95
Zirconiun oxychloride ($ZrOCl_2$)	5.60	10.30
Cotric acid ($C_8H_8O_7$) (%)	6.30	12.80
Formic acid (HCOOH) (%)	5.65	10.35

Table 2: Design Matrix and Data Points

Run number	A: Zirconiunm oxychloride (%)	B: Temperature (°C)	C: Citric acid (%)	D: Formic acid (%)	Char length (cm)
1	10.30	95	12.8	5.6	1.2
2	10.30	77	12.8	10.3	1.65
3	4.00	86	9.5	8.3	1.7
4	5.60	95	12.8	10.3	2.5
5	10.30	95	6.3	5.6	1
6	7.95	101	9.5	8.0	1
7	5.60	95	6.3	10.3	1.65
8	11.90	86	9.5	8.0	1.35
9	7.95	86	15.0	8.0	1.3
10	5.60	77	12.8	5.6	1.7
11	7.95	86	9.5	8.0	1.75
12	7.95	86	9.5	8.0	0.95
13	7.95	86	9.5	8.0	0.95
14	7.95	86	4.1	8.0	2.1
15	5.60	77	6.3	5.6	1.95
16	7.95	86	9.5	8.0	0.9
17	7.95	71	9.5	8.0	1.3
18	7.95	86	9.5	11.9	1.2
19	10.30	77	6.3	10.3	1.25
20	7.95	86	9.5	4.0	1.6
4.021	7.95	86	9.5	8.0	0.86

exhaustive list, the reader is referred to Box and Meyer [13], Aitkin [14], Grego [15] and Myers *et al.* [16-17]. As mentioned previously, since the purpose of this manuscript is to demonstrate the utility of a hybrid approach to modeling, we choose an "off the shelf" approach to variance modeling. The log-linear model proposed by Bartlett and Kendall [12] is a popular one [see Vining and Myers [18] and Myers and Montgomery [19]] and is written explicitly as:

Variance model:

$$\ln(s_i^2) = g^*(X_i^*) + \eta_i = X_i^{*}\gamma + \eta_i \qquad (2)$$

Where η_i denotes the model error term whose expectation is assumed to be zero and whose variance is assumed constant across the d design points.

Assuming the model forms for the mean and variance given in (1) and (2), the model parameters are estimated using the following estimated weighted least squares (EWLS) algorithm:

Step 1: Fit the variance model, $\ln(s_i^2) = X_i^{*}\gamma + \eta_i$, via ordinary least squares (OLS), obtaining $\hat{\gamma}^{(OLS)} = (X^{*\prime}X^*)^{-1}X^{*}y^*$ where y^* is the $d \times 1$ vector of log transformed sample variances.

Step 2: Use $\hat{\sigma}_i^2 = \exp(X_i^{*\prime}\hat{\gamma}^{(OLS)})$ as the estimated variances to compute the d×d estimated variance–covariance matrix for the means model, $\hat{V} = diag(\hat{\sigma}_1^2, \hat{\sigma}_2^2, ..., \hat{\sigma}_d^2)$.

Step 3: Use $\hat{V}^{-1}$ as the estimated weight matrix to ?t the means model, yielding $\hat{\beta}^{(EWLS)} = (X'\hat{V}^{-1}X)^{-1}X'\hat{V}^{-1}\bar{y}$ where $\bar{y}$ denotes the d × 1 vector of sample averages.

The algorithm above yields the following estimates of the process mean and variance functions:

Estimated Process Mean:

$$\hat{E}[y_i]^{(EWLS)} = x_i' \hat{\beta}^{(EWLS)}, \qquad (3)$$

Estimated Process Variance:

$$\hat{Var}[y_i]^{(OLS)} = \exp(x_i^{*\prime}\hat{\gamma}^{(OLS)}). \qquad (4)$$

Once estimates of the mean and variance have been calculated, the goal becomes ?nding the operating conditions for the control factors such that the mean is as close as possible to the target while maintaining minimum process variance.

Table 3: Analysis of Variance

Source	Sum of Squares	df	Mean Square	F. Value	P-value prob>F	
Model	2.80	14	0.20	1.12	0.4727	Not signi
A-ZROCL2	0.061	1	0.061	0.34	0.5787	
B-Temp	0.045	1	0.045	0.25	0.6329	
C-CH3COOH	1.549 E-003	1	1.549 E-003	8.707 E-003	0.9287	
D-HCOOH	0.080	1	0.080	0.45	0.5274	
AB	0.24	1	0.24	1.35	0.2898	
AC	0.000	1	0.000	0.000	1.0000	
AD	0.014	1	0.014	0.077	0.7910	
BC	0.10	1	0.10	0.57	0.4791	
BD	0.18	1	0.18	1.02	0.3525	
CD	0.21	1	0.21	1.19	0.3176	
A^2	0.39	1	0.39	2.19	0.1896	
B^2	0.012	1	0.012	0.070	0.8006	
C^2	0.14	1	0.74	4.19	0.0867	
D^2	0.21	1	0.21	1.15	0.3240	
Residual	1.07	6	0.18			
lack of Fit	0.50	2	0.25	1.76	0.2832	Not sign.
Pure Error	0.75	4	0.14			
Cor Total	3.86	20				

Any control factor which influences the expression in (4) is known as a dispersion factor. Any control factor that does not influence the expression in (4) but does in?uence the expression in (3) is known as an adjustment factor. When both dispersion and adjustment factors are present, the robust design problem can be approached in a two-step fashion. Speciflcally, levels of the dispersion factors are chosen so as to minimize the estimated process variance in (4) and then the levels of the adjustment factors are chosen so as to bring the estimated process mean in (3) to a desired level. If only dispersion factors are present and these factors also influence the process mean, the researcher is left with flnding the levels of the control factors that yield a desirable trade-off between low variance and a deviation from the targeted mean. This is often accomplished via minimization of an objective function such as the squared error loss (SEL):

$$SEL = E[y(x) - T]^2 = \{E[y(x)] - T\}^2 + Var[y(x)], \quad (5)$$

where T denotes the target value for the process mean. Minimization can be accomplished via non-linear programming using a method such as the generalized reduce gradient or the Nelder–Mead simplex algorithm. The SEL approach is also useful when adjustment factors are present but are not strong enough to bring the mean to the targeted value. Note that the determined set of optimal operating conditions is highly dependent on quality estimation of both the mean and variance functions. Misspeci?cation of the forms of either the mean or variance models can have serious implications in process optimization [20, 21].

Experimental Design and Analysis: One of the most efficient design, namely, central composite design (CCD) with four input variables is used to produce representative two data points for each test of the design matrix in experimental space (Table 2). The ranges of these four input variables, namely, ZrOCl2, foemic acid, citric acid and temperature are given in Table 1.

The results of ANOVA analysis (Table 3) which uses functional mean only with fixed variances show that none of the main and interaction effects including model itself are significant. However, using non-hierarchical stepwise method in this approach, the analysis of variance (Table 4) not only shows the fitted model is appropriate but BD and C^2 effects are significant. In this way, the Ajd. R^2 was improved from 0.08 to 0.33 and model became significant.

Using the following second-order polynomial model,

$$C.L. = b_0 + \sum b_{ixi} + \sum b_{ij} x_i x_j + \sum C_i x_i^2$$
$$i \geq j$$
$$i = 1,2,3,4$$

The estimated coefficients (Table 5) and the final equation in term of coded factors are as follow:

Below is one of the response surfaces as an example:

The optimal factor values for minimization of Char Length and statistical properties of predicted value are given in Tables 6 and 7, respectively.

Table 4: Analysis of Variance with Hierarchical Stepwise Method

Source	Sum of Squares	df	Mean Square	F. Value	P-value prob>F	
Model	1.55	2	0.77	6.02	0.0099	Significant
BD	0.91	1	0.91	7.09	0.0159	
C^2	0.64	1	0.64	4.96	0.0390	
Residual	2.31	18	0.13			
lack of Fit	1.75	14	0.12	0.88	0.6215	Not singificant
Pure Error	0.57	4	0.14			
Cor Total	3.86	20				

Table 5: Estimated Coefficients of the Model

Factor	Coefficient Estimate	df	Standared Error	95% CI Low	95% CI High	VIF
Intercept	1.29	1	0.099	1.08	1.50	
BD	0.34	1	0.13	0.071	0.60	1.00
C^2	0.21	1	0.092	0.012	0.40	1.00

Table 6: Optimal Factor Values

ZrOCl2	Temprature	CH3COOH	HCOOH	Char Length
6.63	95.00	9.55	5.65	0.950393

Table 7: Statistical Properties of Predicted Char Length

Response	Prediction	SE Mean	95% CL low	95% CL high	SE Pred	95% PL low	95% PL high
Char Length	0.950393	0.16	0.61	1.29	0.39	0.12	1.78

Table 8: Optimal Factor Values with PRD Approach

ZrOCl2	Temprature	CH3COOH	HCOOH	Char Length
10.03	95.00	8.45	8.05	0.650393

Table 9: Statistical Properties of Predicted Char Length

Response	Prediction	SE Mean	95% CL low	95% CL high
Char Length	0.650393	0.07	0.51	0.79

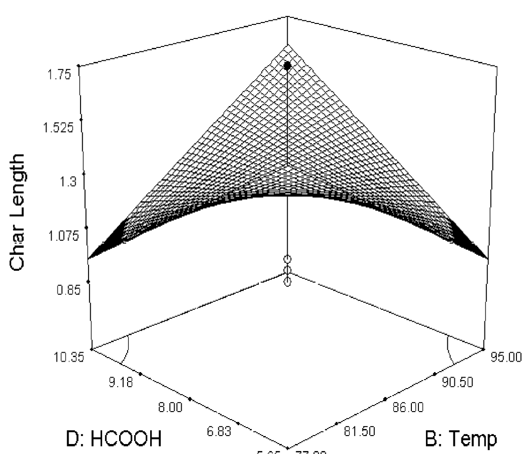

Fig. 1: Response Surfaces of Char Length

However, the analysis results of using parametric model with PRD approach in which it uses the mentioned functional mean along with variance model gives optimal factor values and statistical properties of predicted value as in Tables 8 and 9, respectively.

CONCLUTION

The analysis results of using parametric model with RPD approach in which it uses functional mean along with a variance model show that the calculated mean square error (MSE) in this model (MSE = 0.07) is almost as half of the MSE of parametric model without RPD approach (MSE = 0.13). Also, the obtained Char Length which its minimization is desired is reduced, tremendously.

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