Multi-Response Optimization via Desirability Functionfor the Black Liquor DATA

Anwar Fitrianto[1,2,3,*], Habshah Midi[1,2]

[1]Department of Mathematics,
[2]Institute for Mathematical Research, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor Darul Ehsan, Malaysia.
[3]Department of Statistics, Bogor Agricultural University of Indonesia

[*]*Corresponding email: anwar@math.upm.edu.my*

Abstract

The experiment that was conducted to examine the advanced oxidation of the black liquor effluent obtained from the pulp and paper industry using the dark Fenton reaction in a lab-scale experiment based on Central Composite Design. The three factors along with their range values in that experiment were temperature (298; 333, K), H_2O_2 concentration (29.4; 58.8, mM), and Fe(II) concentration (0.36; 8.95, mM). The range of the factors were examine at fixed phase pH=3. Three response variables studied in the experiment, namely, COD removal after 90 min(%), UV254 removal after 90 min(aromatic content,%), and UV280 removal after 90 min (lignin content, %). The most widespread application of the RSM is in the situation where input variables potentially influence some quality characteristics of a process. Due to the fact that the experiment has several response variables, we employed a desirability function approach to optimize the responses simultaneously at one best setting of available factors. The resulted simultaneous optimization of an experiment is, in fact, the real situation where the experimenter should deal with since in an experiment, there is certainly a single input setting. After analyzing the data, both separated for each response variable and simultaneous for all response variables provided the same terms (factors) which are significantly contribute to the quadratic model (H_2O_2 and Fe(II) concentration). Nevertheles, they produced different factor settings. Through desirability function approach, we found that the best settings are 46.84 *m*M and 6.771 *m*M of H_2O_2 and Fe(II) concentration, respectively. Those setting can be obtained at desirability function's value of 0.782.

Keywords: response surface methodology; central composite design; desirability function

1. INTRODUCTION

Response Surface Methodology (RSM) is a collection of statistical and mathematicaltechniques useful for developing, improving, and optimizing processes ([1].The most widespread application of the RSM is in situation where input variables potentially influence some quality characteristics of a process.

Its origin was the work of Box and Wilson, [2]. It is used in many practical applications in which the goal is to identify the level of p design variables or factors $x = (x_1, x_2, \ldots, x_p)$, that optimize a response, $f(x)$, over an experimental region. Additionally, RSM is used to analyze and control the processes to obtain optimal condition and parameters [3]. The main objective of response surface method is to optimize the response in a process.

Most industrial processes and products have more than one response or quality characteristic which are called multiple-response surface (MRS). This factoften leads to involvedisproportionate and conflicting qualitycharacteristics (responses).Those responses must, in some sense, be optimized simultaneously to obtain the best levels of factors during process design. Optimal factor setting for one response may be far from optimal for another response. Multiple response optimizations allows for compromise among the various responses.

In an effort of obtaining simultaneous optimization steps, we will employ a black liquor dataset, which appeared in [4]. It is an investigation of the advanced oxidation of the black liquor effluent from the pulp and paper industry using the dark Fenton reaction in a lab-scale experiment. They used central composite (CCD) in the process.But, in this article, we focus the analysis on the procedures of doing simultaneous optimization since in [4], their focused is on individual response optimization.

2. REVIEWS OF MULTI-RESPONSE DEVELOPMENT IN RSM

Before 1959, optimization of multiple response variables by using RSM was not well thought-out. A work by Hoerl[5] initiated a new era of developing multi-responses optimization. He offered two approaches to optimize multiple response optimization, those are by combining the different response functions into a single function using a weightedaverage of the response functions, and by considering one of the response variables as primary and then to optimize it subject to the limits placed on the remaining response variables. In the second approach, each response functionis optimized individually and the contour plots are superimposed on each otherto find the region where the solution lies. Then the optimal location is identifiedvisually. Unfortunately, this approach can be used for small number of responses and design variables.

Harrington, [6], presented an optimization schemeutilizing what he termed the desirability function. Meanwhile, [7] and [8] describedoptimization schemes based upon the linearprogramming model. However, a major disadvantageof these schemes is the philosophy upon whichthey are based. These methods involve optimizationof one response variable subject to constraints on the remaining response variables. [9] then gave a slight modificationof Harrington's function.The dual response approach for two responses was given by Myers and Carter, [10].The responses were categorized as primary and secondary responses. In this approach, we need to identify the levels of the design variables that optimize a primary response which is depended on a secondary response that has been set to a particular value. The tworesponse functions are then combined into a single response function which is then optimized.

Thus far, the most commonly used approaches are desirability functions, [11], the generalized distance measure method by Khuri and Conlon, [12], and the weighted squared error loss methodby Vining, [13]. The desirability function method is one of the most popular for multiple response problems. In desirability function method, the response variable is transformed to give a desirability value which is proportional to the priority given to the response variable. In other words, this approach incorporates the priorities on the response function as a part of optimization by Osborne and Armocost, [14]. In this approach, multiple response functions are estimated as polynomial functionsof the factors or design variables.

2.1 Optimization in RSM

Let say we have a set of data containing observations on a response variable y and k controllable factors. The true value of the response variable can be expressed as:

$$y = f(x_1, x_2, \ldots, x_k) + \varepsilon,$$

where ε is noise or error which is usually assumed to be distributed with mean zero and constant variance σ_ε^2. The function f is a response surface model, usually unknown. One goal in experimental design is to fit a mathematical model as the function f. Knowledge of the form of the function, f, often found by fitting models to data obtained from designed experiments in order to provide a summary representation of the behavior of the response, as the predictor variables are changed. This might be done in order to optimize the response or to find what regions of the x-space lead to a desirable product, [15].

In a multiple responses experiment, suppose that each response variable can be expressed as:

$$y_i(\mathbf{x}) : \Re^n \to \Re \quad (i = 1,2,\ldots,m),$$

where $\mathbf{x} \in \Re$, real sets.

2.2 Desirability Function for Multi-Response Optimization

One useful approach to optimization of multiple responses is to utilize the simultaneousoptimization technique popularized by [11]. It is one of the most widely used methods in industry which is based on the idea that the "quality" of a product or process that has multiple quality characteristics, with one of them outside of some "desired" limits, is completely unacceptable. Their proceduremakes use of desirability functions. The common approach is to first transform each response y_i into an individual desirability function $d_i(y_i)$ that varies over the range $0 \le d_i(y_i) \le 1$, where it takes a range of between 0 and 1, and increases as the correspondingresponse value becomes more desirable [16].

Depending on whether a particular response y_i is to be maximized, minimized, or assigned to a target value, different desirability functions $d_i(y_i)$ can be used. The individual desirability $d_i(y_i)$ will be as follows:

Target is the best (TB), the objective is $\min_x \left(\hat{y}_i(\hat{\theta};\mathbf{x}) - T_i\right)^2$,

$$d_i(\hat{y}_i) = \begin{cases} 0 & \text{if } \hat{y}_i(\mathbf{x}) \le L_i \\ \left(\dfrac{\hat{y}_i(\mathbf{x}) - L_i}{T_i - L_i}\right)^r & \text{if } L_i \le \hat{y}_i(\mathbf{x}) \le T_i \\ \left(\dfrac{\hat{y}_i(\mathbf{x}) - U_i}{T_i - U_i}\right)^r & \text{if } T_i \le \hat{y}_i(\mathbf{x}) \le U_i \\ 0 & \text{if } \hat{y}_i(\mathbf{x}) > U_i \end{cases} \tag{1}$$

Smaller better (SB), the objective is $\min_{\mathbf{x}} \hat{y}_i(\hat{\theta};\mathbf{x})$, or

$$d_i(\hat{y}_i) = \begin{cases} 1 & \text{if } \hat{y}_i(\mathbf{x}) < T_i \\ \left(\dfrac{\hat{y}_i(\mathbf{x}) - U_i}{T_i - U_i}\right)^r & \text{if } T_i \le \hat{y}_i(\mathbf{x}) \le U_i \\ 0 & \text{if } \hat{y}_i(\mathbf{x}) > U_i \end{cases} \tag{2}$$

Larger better LB), the objective is $\max_{\mathbf{x}} \hat{y}_i(\hat{\theta};\mathbf{x})$,

$$d_i(\hat{y}_i) = \begin{cases} 0 & \text{if } \hat{y}_i(\mathbf{x}) < L_i \\ \left(\dfrac{\hat{y}_i(\mathbf{x}) - L_i}{T_i - L_i}\right)^r & \text{if } L_i \le \hat{y}_i(\mathbf{x}) \le T_i \\ 1 & \text{if } \hat{y}_i(\mathbf{x}) > T_i \end{cases}, \tag{3}$$

where $\mathbf{x}$ is the factors, $\hat{\theta}$ is parameter estimates of polynomial regression coefficients obtained by least square method. The L_i and U_i are lower and upper acceptable values of y_i, while T_i *is* target values desired for ith response, where $L_i \le T_i \le U_i$, [17]. At this point, r is the parameters that determine the shape of $d_i(\hat{y}_i)$. A value of $r = 1$ means that the desirability function is linear, $r > 1$ means that the desirability function is convex, more importance should be attached to close with the target value, and when the shape of the $d_i(\hat{y}_i)$ is concave when the value is $0 < r < 1$ which means less importance tobe attached. The individual desirabilities are then combined using the geometric mean, which gives the *overall desirability D*:

$$D = \left(d_1(\hat{y}_1) \times d_2(\hat{y}_2) \times \ldots \times d_m(\hat{y}_m)\right)^{1/m},$$

Where m denotes the number of responses.

In fact, RSM normally starts with a series of steepest ascent/descent method based on a first-order model until a practicable higher-order model is suitable. For its simplicity, let assume here that y has been determined to be of second-order after steepest ascent method.

3. THE BLACK LIQUOR DATA

In this case-study, the main focus will be the real-life experiment that was conducted by [4]. They examine the advanced oxidation of the black liquor effluent obtained from the pulp and paper industry using the dark Fenton reaction in a lab-scale experiment based on CCD. The three factors along with their range values in that experiment were temperature (298; 333, K), H_2O_2 concentration (29.4; 58.8, *m*M), and Fe(II) concentration (0.36; 8.95, *m*M). The range of the factors were examine at fixed phase pH=3. According to CCD design of experiment, those factors would result in 17 experimental runs; consist of 8 factorial points, 3 centre points and 6 axial. Three response variables studied in the experiment, namely, COD removal after 90 min (%), UV254 removal after 90 min(aromatic content,%), and UV280 removal after 90 min (lignin content, %). Table 1 shows the levels of each factors and response variables in the experimental design.

Table 1: Central composite design for Black Liquor data with the actual and coded values

Temp, *K* (A)	H_2O_2, *mM* (B)	Fe(II), *mM* (C)	% Removal		
			COD	UV_{254}	UV_{280}
298.0 (-1)	29.4 (-1)	0.36 (-1)	16.5	10.6	15.6
333.0 (+1)	29.4 (-1)	0.36 (-1)	17.2	11.2	16.2
298.0 (-1)	58.8 (+1)	0.36 (-1)	24.1	14.1	19.1
333.0 (+1)	58.8 (+1)	0.36 (-1)	24.3	14.7	19.4
298.0 (-1)	29.4 (-1)	8.95 (+1)	73.4	53.4	59.6
333.0 (+1)	29.4 (+1)	8.95 (+1)	73.5	54.1	60.1
298.0 (-1)	58.8 (+1)	8.95 (+1)	80.2	61.9	65.4
333.0 (+1)	58.8 (+1)	8.95 (+1)	80.1	61.3	66.7
286.0 (-1.68)	44.1 (0)	4.65 (0)	91.2	74.3	80.1
345.0 (+1.68)	44.1 (0)	4.65 (0)	80.2	60.6	66.1
315.5 (0)	19.4 (-1.68)	4.65 (0)	40.2	30.3	34.6
315.5 (0)	68.8 (+1.68)	4.65 (0)	70.4	55.6	60.3
315.5 (0)	44.1 (0)	-2.57 (-1.68)	4.3	5.2	6.1
315.5 (0)	44.1 (0)	11.88 (+1.68)	60.4	46.1	49.3
315.5 (0)	44.1 (0)	4.65 (0)	94.2	78.4	83.1
315.5 (0)	44.1 (0)	4.65 (0)	93.1	77.6	82.3
315.5 (0)	44.1 (0)	4.65 (0)	93.8	76.9	84.6

Source :[4]

4. RESULTS AND DISCUSSION

4.1 Model Fitting for Individual Response Variable

Finding a correct model for each response variable is displayed in Table 2. We tried to fit with four possible models from the first order model (linear) to the third order model (cubic). Data analysis with first oder model indicates that except for COD Removal, all variables do not fit with linear model. For the COD Removal response variable, even linear model is significant at 5% level of significant, but it produces reasonably small value of adjusted R^2 (38.65%).

Table 2: Sequential model sum of squares and coefficient of determination of COD Removal, UV254 Removal, and UV280 Removal after 90 minutes (%)

Response Variable	Source	DF	Sum of Squares	Mean Square	F	p	R^2Adj
COD Removal	Linear	3	7950.64	2650.21	4.36	0.0248	0.3865
	2FI	3	0.37	0.12	1.58E-04	1	0.2025
	Quadratic	3	7175.48	2391.83	23.05	0.0005	0.8953
	Cubic	4	572.05	143.01	2.78	0.2135	0.9481
	Residual	3	154.23	51.41			
	Total	17	76705.27				
UV254 Removal	Linear	3	4882.093	1627.364	3.408879	0.0501	0.311136
	2FI	3	9.82375	3.274583	0.005285	0.9994	0.105894
	Quadratic	3	5491.727	1830.576	18.18835	0.0011	0.85477
	Cubic	4	487.5367	121.8842	1.685175	0.3483	0.895633
	Residual	3	216.9819	72.32731			
	Total	17	47456.85				
UV280 Removal	Linear	3	5046.004	1682.001	3.296517	0.0547	0.300991
	2FI	3	4.19375	1.397917	0.002109	0.9999	0.091863
	Quadratic	3	5985.804	1995.268	21.71911	0.0006	0.874145
	Cubic	4	479.8064	119.9516	2.204154	0.2711	0.925445
	Residual	3	163.2621	54.4207			
	Total	17	56059.42				

Then we tried to fit the data with higher order model since, in general, first order model is not suitable, and we found that quadratic polynomial fits to all response variables with quite high value of adjusted R^2.

Next step is then to find out terms in the suitable model for each response variable.A full quadratic response surface model with design variable inputs, x_1, x_2 and x_3 with corresponding jth response variable y_j is formulated as follows:

$$y_j = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1 x_2 + \beta_5 x_1 x_3 + \beta_5 x_2 x_3 + \beta_6 x_1 x_2 x_3 + \varepsilon, \qquad (4)$$

where β_i's are polynomial regression coefficients of the input variables that were estimated by least squares fitting of the model to the experimental results obtained at the design points, and ε is random errors. But since we found that the temperature (A, x_1) in all terms were not significant in the quadratic model, then we remove all x_1 related term from the Eq. (4).Curvature contribution was determined through central composite design to obtain final reduced second-order model in the terms of x_1 = temperature evel , x_2 = concentration of H_2O_2 and x_3 = concentration of Fe(II), fitted model for COD, UV_{254} and UV_{280} response variable as follows:

$$\hat{y}_{COD} = -104.57 + 6.05x_2 + 16.52x_3 - 0.06x_2^2 - 1.19x_3^2 \qquad (R^2 = 0.9188)$$
$$\hat{y}_{UV254} = -97.31 + 5.43x_2 + 13.63x_3 - 0.06x_2^2 - 1.01x_3^2 \qquad (R^2 = 0.87)$$
$$\hat{y}_{UV280} = -94.63 + 5.52x_2 + 14.28x_3 - 0.06x_2^2 - 1.07x_3^2 \qquad (R^2 = 0.8777)$$

Table 3: Analysis of variance for response variables with full quadratic polynomial model

Source	DF	COD Removal		UV254 Removal		UV280 Removal	
		Sum of Squares	*p*	Sum of Squares	*p*	Sum of Squares	*p*
Model	9	15126.5	0.0007	10383.64	0.002	11036	0.0013
A	1	22.68	0.6543	34.60914	0.576	31.81686	0.5747
B	1	455.72	0.0743	311.7467	0.1218	284.4023	0.1219
C	1	7472.25	< 0.0001	4535.737	0.0003	4729.784	0.0002
A^2	1	215.25	0.193	332.0617	0.1122	304.0773	0.1117
B^2	1	2576.46	0.0016	2237.877	0.0022	2293.127	0.0016
C^2	1	6084.39	0.0001	4602.648	0.0003	5088.195	0.0001
AB	1	0.061	0.9813	0.21125	0.9647	0.03125	0.9858
AC	1	0.1	0.976	0.15125	0.9702	0.10125	0.9744
BC	1	0.21	0.9653	9.46125	0.7681	4.06125	0.8395
Residual	7	726.28		704.5186		643.0685	
Cor Total	16	15852.78		11088.16		11679.07	

4.2 Individual and Composite Desirability

Optimal factor setting can be obtained for each response variable. But, when we have more than one response variable, we need to obtain factor setting which suitable to optimize all response variables according to a criteria. Because, certain factor settings may yield a high desirability for one response, but desirability for other responses. The criteria to find the best overall factor setting are a desirability function. The overall desirability, *D, is* a measure of how well a researcher has satisfied the combined goals for all responses. The ‘optimal’ factor settings are a setting that maximizes overall desirability.

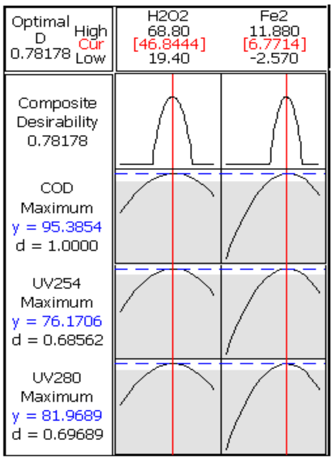

Figure 1: Individual and Comppsitedesirabilities for COD removal, UV254 removal, and UV280 removal.

In this study, there are three response variables on which the responses are competing with one another to determine the H_2O_2 and Fe(II) factor settings. The predicted maximum values of the responses are COD removal = 95.3854%, UV254 removal = 76.1706%, and UV280 removal = 81.9689% along with individual desirabilities of 1.0, 0.6856, and 0.6968, respectively (Figure 1). At the individual desirabilities, it has its own factor setting for each response variable which most probably have different factor setting. In fact, in a single experiment, it will have a single factor setting which is required to optimize all response variables.

The problem is solved through composite desirability. We obtained a value of composite desirability of $D = 0.78178$ to get a factors setting which optimize all response variables. The factors setting are 46.84 *m*Mconcentration of $H_2O_2$and 6.771 *m*Mconcentration of Fe(II).

5. CONCLUSIONS

The statistical analysis (ANOVA) indicated that the effect of the $H_2O_2$and Fe(II) concentration are the significantfactor on the process responses.The reduced second-polynomial regression fit to the experimental data. The fitted model is then used to obtain optimum response variables. The optimum range of input variables that produced desired process output was estimated through the use of composite desirability function. Using the function, we are able to obtain a one factor setting which maximize all response variables of COD, UV254, and UV280 removal.

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