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Optimization of saponification process in multi-response framework by using desirability function approach

Özlem Türkşen[1*], Suna Ertunç[2]

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ABSTRACT

In chemical engineering field, there are many processes which need to optimize more than one responses, called multi-response, simultaneously. In this study, it is aimed to analyse the effects of operating parameters (modeling) and to obtain the compromise process factor values (optimization) for a continuous saponification process. The novelty of this study is considering the saponification process as a multi-response problem. It is important both engineering and statistical aspects. For the continuous saponification process, sodium hydroxide (X1), ethyl acetate concentrations (X2), and their volumetric flow rates (X3, X4) were regarded as the process factors in order to maximize the conversion of sodium hydroxide (Y1) and to minimize the space time (Y2) which is calculated analytically by using X3 and X4. Response Surface Methodology (RSM) and Desirability Function Approach (DFA) were used for modeling and optimization of the process, respectively. Therefore, it is clear that compromise factor conditions which are obtained by the optimization of conversion and space time simultaneously will satisfy the product quality and process economy.

Keywords: saponification process, response surface methodology (rsm), desirability function, optimization

İstenebilirlik fonksiyonu yaklaşımı kullanılarak çok yanıtlı çerçevede sabunlaşma sürecinin optimizasyonu

ÖZ

Kimya mühendisliği alanında, çok yanıtlı problem olarak adlandırılan, birden fazla yanıtın eşanlı optimizasyonunu gerektiren pek çok süreç mevcuttur. Bu çalışmada, bir sürekli sabunlaşma süreci için süreç parametrelerinin etkilerinin analizi (modelleme) ve uzlaşık süreç parametre değerlerinin elde edilmesi (optimizasyon) amaçlanmıştır. Bu çalışmanın özgünlüğü, sabunlaşma sürecinin çok yanıtlı bir problem olarak ele alınmasıdır. Bu, mühendislik ve istatistiksel yönden önemlidir. Sürekli sabunlaşma süreci için, sodyum hidroksit (X1), etil asetat derişimleri (X2) ve onların hacimsel akış hızları (X3, X4), sodyum hidroksit dönüşümünü (Y1) maksimum ve işletme süresini (Y2) minimum yapmak amacıyla süreç faktörleri olarak ele alınmıştır. Burada, Y2 değişkeni, X3 ve X4 değişkenlerini kullanarak analitik olarak hesaplanmıştır. Yanıt Yüzey Yöntemi (YYY) ve İstenebilirlik Fonksiyonu Yaklaşımı (İFY), sırasıyla sürecin modellenmesi ve optimizasyonu için kullanılmıştır. Böylece, dönüşüm ve işletme süresi yanıtlarının eşanlı optimizasyonu ile elde edilen uzlaşık faktör koşullarının, üretim kalitesini ve süreç ekonomisini sağlayacağı açıktır.

Anahtar Kelimeler: sabunlaşma süreci, Yanıt Yüzey Yöntemi (YYY), istenebilirlik fonksiyonu, optimizasyon

*Sorumlu Yazar / Corresponding Author
1 Ankara Üniversitesi, Fen Fakültesi, İstatistik, Ankara – turksen@ankara.edu.tr
2 Ankara Üniversitesi, Mühendislik Fakültesi, Kimya Mühendisliği, Ankara – suna.ertunc@eng.ankara.edu.tr

1. INTRODUCTION

A reaction of an ester with sodium hydroxide to give a carboxylic acid salt and an alcohol is called saponification reaction, though not the final product is soap. This reaction is also known as hydrolysis of esters with base catalyst. Although water, alcohol or similar solvents can not solve esters, product of the saponification reaction is definitely soluble in all these solvents. This property is important in view of the usage area of carboxylic acid salt obtained at the end of the saponification reaction. Sodium acetate is a commercially important carboxylic acid salt which is used in a large area in industry such as petroleum, cosmetic, textile, paint, food etc. In addition to the commercial importance, the saponification reaction is often preferred in both education and research purposes as a model reaction. In the study of Simandi et al. (1996), a mixing model with non-ideal mixing using saponification reaction is presented. A dynamic model based on the pseudo bond graph technique is developed by Heny et al. (2000) to represent the behavior of a continuous stirred tank reactor (CSTR) for the saponification of ethyl acetate with sodium hydroxide. A new method for the determination of rate constant is presented by Krupska et al. (2002). In chemical engineering education, this second order reaction is used to understand the kinetic analysis and reactor performance [4].

Response Surface Methodology (RSM) is used in many chemical engineering applications. RSM is used as a useful tool for optimization in analytical chemistry by Bezerra et al. (2008). In the studies of Chi et al. (2012) and Istadi (2005), multi-response optimization (MRO) is interested in RSM framework about catalytic epoxidation process and carbon dioxide oxidative capling of methane, respectively. Desirability function approach (DFA) is used for MRO of nickel electroplanting process by Seritan et al. (2011). Salimon et al. (2012) and Bursali et al. (2006) used D-optimal design and RSM for saponification reaction, respectively.

In this study, it is aimed to model a continuous saponification process and to obtain the optimal values of operating parameters. The RSM and the DFA are used for modeling and optimization stages of saponification process, respectively. It is seen from the statistical analysis that the obtained compromise operating parameter values satisfy the product quality and process economy simultaneously.

2. RESPONSE SURFACE METHODOLOGY AND LINEAR MULTI-RESPONSE MODEL

Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques applied to obtain a proper functional relationship between a response of interest and a number of associated factors (input or independent variables) [11]. A complete and detailed explanation about RSM is referred to [12-14]. In the field of RSM, there are three main stages: (i) designing a set of experiments, (ii) determining a mathematical model, and (iii) determining the optimal settings of factors. An experiment can involve several response (dependent) variables, which is called multi-response experiment, as well as single response variable. If a multi-response experiment is designed, which means that the factors are selected and their values during the actual experimentation are designated, the task then is to find a proper approximation for the true functional relationship between the factors and unknown response surfaces. Regression analysis helps to form the relationship between response variables and factors denoted by $(Y_1, Y_2, ..., Y_r)$ and $(X_1, X_2, ..., X_k)$, respectively. In general, such a relationship is unknown. In order to model an unknown response (Y), first and second degree polinomial regression models, given in Eq.(1) and Eq.(2), are used.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \varepsilon \tag{1}$$

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j + \varepsilon. \tag{2}$$

Here, β_0 is constant, ε is error term, $(X_1, X_2, ..., X_k)$ is linear terms vector, $(X_1^2, X_2^2, ..., X_k^2)$ is squared terms vector, $(X_1X_2, X_1X_3, ..., X_{k-1}X_k)$ is first interaction terms vector of each paired combination, and $\beta_i, \beta_{ii}, \beta_{ij}$, $i = j = 1, 2, ..., k$ are unknown model coefficients.

The data analysis of multi-response experiments need a careful consideration. In the design of multi-response experiment, design criterian should be based on perceiving the responses as a group rather than as individual entities [12]. The correlation structure of the response variables should be considered during the modeling stage. In this case, simultaneous modeling of unknown responses as a function of the input variables is necessary within some region of interest. The model associated with such a function is called multi-response model.

A multi-response model is composed of r number of polinomial regression models which are considered as an approximation function of each unknown responses. In this case, the i th response model can be written in a vector form as

$$\mathbf{Y}_i = \mathbf{X}_i\boldsymbol{\beta}_i + \boldsymbol{\varepsilon}_i \ , \ i = 1,2,...,r \tag{3}$$

where $\mathbf{Y}_i$ is a $n \times 1$ vector of observations (experimental runs for each setting of a group of k coded variables), $\mathbf{X}_i$ is a $n \times p_i$ matrix of rank p_i of known functions of the settings of the coded variables, $\boldsymbol{\beta}_i$ is a $p_i \times 1$ vector of unknown constant parameters, and $\boldsymbol{\varepsilon}_i$ is a random error vector associated with the i th response $(i = 1,2,...,r)$. Here, it is assumed that

$$\begin{aligned} &E(\boldsymbol{\varepsilon}_i) = 0 \ , \ i = 1,2,...,r \\ &Var(\boldsymbol{\varepsilon}_i) = \sigma_{ii}\mathbf{I}_N \ , \ i = 1,2,...,r \\ &Cov(\boldsymbol{\varepsilon}_i, \boldsymbol{\varepsilon}_j) = \sigma_{ij}\mathbf{I}_N \ , \ i,j = 1,2,...,r \ ; \ i \neq j \end{aligned} \tag{4}$$

and also the $r \times r$ matrix whose (i,j) th element is $\sigma_{ij}, (i,j = 1,2,...,r)$ will be denoted by Σ. The r equations given in Eq. (3) may be represented as

$$\mathbf{Y} = \mathbf{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon} \tag{5}$$

where $\mathbf{X}$ is the block-diagonal matrix, $\mathbf{X} = diag(\mathbf{X}_1, \mathbf{X}_2, ..., \mathbf{X}_r)$; $\mathbf{Y} = [\mathbf{Y}_1' : \mathbf{Y}_2' : ... : \mathbf{Y}_r']'$, $\boldsymbol{\beta} = [\boldsymbol{\beta}_1' : \boldsymbol{\beta}_2' : ... : \boldsymbol{\beta}_r']'$, and $\boldsymbol{\varepsilon} = [\boldsymbol{\varepsilon}_1' : \boldsymbol{\varepsilon}_2' : ... : \boldsymbol{\varepsilon}_r']'$ are vectors with dimensions $nr \times 1$, $p \times 1$, and $nr \times 1$, respectively. The best linear unbiased estimator (BLUE) of $\boldsymbol{\beta}$ is given by

$$\hat{\boldsymbol{\beta}} = \left(\mathbf{X}'\Delta^{-1}\mathbf{X}\right)^{-1}\mathbf{X}'\Delta^{-1}\mathbf{Y} \tag{6}$$

where $\Delta = \Sigma \otimes \mathbf{I}_n$ and $\otimes$ is a symbol for the Kronecker product of matrices, hence $\Delta^{-1} = \Sigma^{-1} \otimes \mathbf{I}_n$. The estimator given in Eq. (6) is called Generalized Least Square Estimator (GLME). The GLME of $\boldsymbol{\beta}$ requires knowledge of Σ. If Σ is unknown, then an estimate of $\boldsymbol{\beta}$ can be obtained by replacing Σ by an estimate $\hat{\Sigma}$ provided that the estimate is nonsingular. Zellner [15] proposed an estimate such as $\hat{\Sigma} = (\hat{\sigma}_{ij})$, $i,j = 1,2,...,r$ where

$$\hat{\sigma}_{ij} = \frac{\mathbf{Y}_i'\left(\mathbf{I}_n - \mathbf{X}_i\left(\mathbf{X}_i'\mathbf{X}_i\right)\mathbf{X}_i'\right)\left(\mathbf{I}_n - \mathbf{X}_j\left(\mathbf{X}_j'\mathbf{X}_j\right)\mathbf{X}_j'\right)\mathbf{Y}'}{n}.$$

As a special case, if in Eq. (3), $\mathbf{X}_i = \mathbf{X}_0$ for $i = 1,2,...,r$, then $\mathbf{X} = diag(\mathbf{X}_1, \mathbf{X}_2, ..., \mathbf{X}_r)$ reduces $\mathbf{X} = \mathbf{I}_r \otimes \mathbf{X}_0$. In this case, it is easy to show that

$$\hat{\boldsymbol{\beta}} = \left(\mathbf{I}_r \otimes \left(\mathbf{X}_0'\mathbf{X}_0\right)^{-1}\mathbf{X}_0'\right)\mathbf{Y} \tag{7}$$

Thus the BLUE of $\boldsymbol{\beta}$ does not depend on Σ. Hence, the BLUE of $\boldsymbol{\beta}_i$ is the same as the OLS estimator obtained from fitting the i th model $(i = 1,2,...,r)$ individually [12]. In addition, if the responses are uncorrelated the covariance matrix, Σ, will approximate the unit matrix, I. Then, the multi-response estimation reduces to individual estimation of responses.

3. MULTI-RESPONSE OPTIMIZATION USING DESIRABILITY FUNCTION APPROACH

The process optimization of a collection of response functions simultaneously is called multi-response optimization (MRO). The MRO is concerned with the minimization or maximization of a vector of objectives that may be subject to a series of equality and nonequality constraints or bounds as

$$\begin{aligned} \min/\max \ & \hat{\mathbf{Y}} = \left[\hat{Y}_1(\mathbf{X}), \hat{Y}_2(\mathbf{X}), ..., \hat{Y}_r(\mathbf{X})\right] \\ s.t. \ & g_j(\mathbf{X}) \leq 0 \ , \ j = 1,2,...,m \\ & h_i(\mathbf{X}) = 0 \ , \ i = 1,2,...,q \\ & \mathbf{X} \in S \end{aligned} \tag{8}$$

where S denotes the feasible set. The MRO problem given in Eq. (8) is a typical multi-objective optimization (MOO) problem. There is no solution which optimizes all of the objectives simultaneously. In this case, the results of MOO problem composed of nondominated solution set called Pareto solution set. However, in engineering science, a single compromise solution for all responses is the most requested in terms of process operation.

A simple and straightforward approach for MRO is to construct the response contour plots [16]. The contour plots are achieved from regression models developed to estimate the location of responses. However, this approach can only be useful when the dimensions of the inputs and response variables are low. A general solution approach is to change the problem given in Eq. (8) into a single objective optimization problem as

$$\min/\max_{s.t.} \ \rho(\mathbf{X}) \quad \mathbf{X} \in S \tag{9}$$

where ρ is an aggregation function. The single measure $\rho(\mathbf{X})$ has conventionally been defined as the following: (i) the desirability function approach [17- 21], (ii) distance function approach [22], and (iii) loss function approach [23-26]. In this study, DFA is used for the optimization of multi-response problem.

The DFA, originally developed by Harrington (1965), is one of the most frequently used MRO method in practice. The DFA transforms an predicted response (e.g. the ith response $\hat{Y}_i$) into a scale free value, called a desirability (denoted as d_i for $\hat{Y}_i$). Desirability varies from 0 to 1 and approaches to 1 as the corresponding response becomes more desirable. Individual desirabilities for different responses are then combined to form the overall desirability function D. Then the optimal setting is determined by maximizing

$$D = \left(d_1 \times d_2 \times \ldots \times d_r\right)^{1/r} \tag{10}$$

The objective function given in Eq. (10) has values inside the interval $[0,1]$ and approaches unity as the desirability of the responses increases. The geometric mean is chosen as an objective function because it vanishes whenever any d_i , $i = 1,2,\ldots,r$ is equal to zero, that is, if at least one of the response variables is unacceptable [12]. Harrington's approach is extended by Derringer and Suich (1980) by offering systematic transformations to desirability function. In addition, a new form of overall desirability by using a weighted geometric mean suggested by Derringer (1994) as

$$D = \left(d_1^{w_1} \times d_2^{w_2} \times \ldots \times d_r^{w_r}\right)^{1/\Sigma w_i} \tag{11}$$

where the w_i , $i = 1,2,\ldots,r$ are the weights among the response. If all the w_i's are set to 1, Eq. (11) reduces to Eq. (10).

The individual desirability function for the case of minimization and maximization of a response is defined, respectively, as

$$d_i\left(\hat{Y}_i(\mathbf{X})\right) = \begin{cases} 1 & , \quad \hat{Y}_i(\mathbf{X}) \le Y_i^{\min} \\ \left(\dfrac{Y_i^{\max} - \hat{Y}_i(\mathbf{X})}{Y_i^{\max} - Y_i^{\min}}\right)^s & , \quad Y_i^{\min} < \hat{Y}_i(\mathbf{X}) < Y_i^{\max}, i = 1,\ldots,r \\ 0 & , \quad \hat{Y}_i(\mathbf{X}) > Y_i^{\max} \end{cases} \tag{12}$$

$$d_i\left(\hat{Y}_i(\mathbf{X})\right) = \begin{cases} 1 & , \quad \hat{Y}_i(\mathbf{X}) \ge Y_i^{\max} \\ \left(\dfrac{\hat{Y}_i(\mathbf{X}) - Y_i^{\min}}{Y_i^{\max} - Y_i^{\min}}\right)^s & , \quad Y_i^{\min} < \hat{Y}_i(\mathbf{X}) < Y_i^{\max}, i = 1,\ldots,r \\ 0 & , \quad \hat{Y}_i(\mathbf{X}) \le Y_i^{\min} \end{cases} \tag{13}$$

where $d_i\left(\hat{Y}_i(\mathbf{X})\right)$, $i = 1,2,\ldots,r$ is the desirability function of $\hat{Y}_i(\mathbf{X})$. s is the parameter that define the shape of desirability functions. In this study, $s = 1$ is chosen which denotes linear transformation. $Y_i^{\min}$ and $Y_i^{\max}$ can be set at the extreme values of the individual predicted responses as $Y_i^{\min} = \min_{\mathbf{X} \in S}\left\{\hat{Y}_i(\mathbf{X})\right\}$ and $Y_i^{\max} = \max_{\mathbf{X} \in S}\left\{\hat{Y}_i(\mathbf{X})\right\}$ which represent the minimum and maximum possible values of the predicted response within the experimental region S, respectively. The proposed desirability functions given in (12) and (13) transform the each response to a corresponding desirability value between 0 and 1. The optimization process is relatively simple since the overall desirability is a well-behaved continuous function of the factors.

4. APPLICATION

4.1. Problem Definition

In this study, a continuous saponification process was carried out as a multi-response problem. The saponification reaction between ethyl acetate (EtOAc, $CH_3COOC_2H_5$) and sodium hydroxide (NaOH) can be represented by the following stochiometric equation:

$$NaOH + CH_3COOC_2H_5 \rightarrow CH_3COONa + C_2H_5OH \tag{14}$$

As the reaction proceeds consumption of hydroxide ions results in the formation of acetate ions. Since the hydroxide ions have much larger specific conductance than the acetate ions, sodium hydroxide concentration can be monitored by measuring the conductivity of the reaction mixture. The continuous operation concentrations of the reactants in the feed flow can be calculated as given in Eqs. (15)-(16) where C_{Ao} and C_{Bo} are the concentrations of sodium hydroxide and ethyl acetate, respectively. The Q_A and Q_B represent the volumetric feed flow rates of sodium hydroxide and ethyl acetate. Reservoir concentrations of sodium hydroxide and ethyl acetate were represented as $C_{\tan k1}$ and $C_{\tan k2}$, respectively

$$C_{Ao} = \frac{Q_A}{Q_A + Q_B} C_{\tan k1} \tag{15}$$

and

$$C_{Bo} = \frac{Q_B}{Q_A + Q_B} C_{\tan k2}. \tag{16}$$

Concentration of sodium hydroxide during the course of the reaction is calculated by using Eq. (17) from the conductivity measurements of the reaction mixture [28]. Conversion of sodium hydroxide (x_A) is calculated for each continuous operation by using the Eq. (18) for the steady state value of C_A

$$C_A = (C_{A\infty} - C_{Ao}) \left[\frac{\kappa_o - \kappa}{\kappa_o - \kappa_\infty} \right] + C_{Ao} \tag{17}$$

and

$$x_A = \frac{C_{Ao} - C_A}{C_{Ao}} \tag{18}$$

In order order to model the process, C_{Ao} , C_{Bo} , Q_A , and Q_B were considered as factors denoted with X_1, X_2, X_3 , and X_4 , respectively. The first response variable (Y_1) was chosen x_A and the space time was considered as second response (Y_2) given in Eq. (19)

$$\tau = \frac{V}{Q_A + Q_B} \tag{19}$$

Figure 1. Experimental system for continuous saponification process

The experimental system used in the study is given in Fig. 1. A 2 L bench-top reactor (Armfield CEM-Liquid Phase Chemical Reactor, England) with temperature and agitation rate control units was used. Reactants (sodium hydroxide and ethyl acetate) were fed at constant rates by using computer controlled pumps into the reactor. The conductivity measurements of the reaction mixture were done by using WTW LF39 (Welheim, Germany) type conductivity meter. Temperature and agitation rate were kept at the values of 25°C and 250 rpm in all experiments, respectively, since these were found as insignificant operating parameters at their selected ranges from previous study [10].

4.2. Data Set

A series of experiments were carried out in order to examine the saponification process. The purpose of the experiments was to determine the effects of X_1, X_2, X_3, X_4 on Y_1 and Y_2 , which wanted to be maximized and minimized, respectively. The experiments were conducted in 2^4 Full Factorial Design. In the design, each input variable was measured at two levels which can be coded to take the value -1 when the input is at its low level and $+1$ when at its high level. The coded values and actual values of input variables were given in Table 1. In Table 2, experimental data set with four added center points were given.

Table 1. Coded and real settings of the input variables

Coded levels	Input variables			
	X_1	X_2	X_3	X_4
-1	0.01	0.01	0.02	0.02
+1	0.1	0.1	0.1	0.1
0	0.055	0.055	0.06	0.06

Table 2. Experimental data set obtained for 2^4 full factorial design with four center points in real and coded values

	Input variables								Responses	
	X_1		X_2		X_3		X_4		Y_1	Y_2
No	C_{A0} (mol/L)	levels	C_{B0} (mol/L)	levels	Q_A (L/min)	levels	Q_B (L/min)	levels	x_A	τ (min)
1	0.01	-1	0.01	-1	0.02	-1	0.02	-1	0.53	50
2	0.1	+1	0.01	-1	0.02	-1	0.02	-1	0.28	50
3	0.01	-1	0.1	+1	0.02	-1	0.02	-1	0.82	50
4	0.1	+1	0.1	+1	0.02	-1	0.02	-1	0.8	50
5	0.01	-1	0.01	-1	0.1	+1	0.02	-1	0.46	16.6
6	0.1	+1	0.01	-1	0.1	+1	0.02	-1	0.2	16.6
7	0.01	-1	0.1	+1	0.1	+1	0.02	-1	0.78	16.6
8	0.1	+1	0.1	+1	0.1	+1	0.02	-1	0.88	16.6
9	0.01	-1	0.01	-1	0.02	-1	0.1	+1	0.2	16.6
10	0.1	+1	0.01	-1	0.02	-1	0.1	+1	0.22	16.6
11	0.01	-1	0.1	+1	0.02	-1	0.1	+1	0.8	16.6
12	0.1	+1	0.1	+1	0.02	-1	0.1	+1	0.28	16.6
13	0.01	-1	0.01	-1	0.1	+1	0.1	+1	0.42	10
14	0.1	+1	0.01	-1	0.1	+1	0.1	+1	0.26	10
15	0.01	-1	0.1	+1	0.1	+1	0.1	+1	0.79	10
16	0.1	+1	0.1	+1	0.1	+1	0.1	+1	0.99	10
17	0.055	0	0.055	0	0.06	0	0.06	0	0.84	16.6
18	0.055	0	0.055	0	0.06	0	0.06	0	0.8	16.6
19	0.055	0	0.055	0	0.06	0	0.06	0	0.72	16.6
20	0.055	0	0.055	0	0.06	0	0.06	0	0.79	16.6

4.3. Modeling and Optimization of Multi-Responses

The observed responses were checked that if there were correlations between the responses before modeling. It was seen that the responses were uncorrelated according to the correlation analysis ($p = 0.99 > \alpha = 0.05$). Then, the experimental data set was statistically analyzed using Minitab 14 [29]. The goodness of fit of the models were evaluated by the analysis of variance (ANOVA) given in Table 3.

Table 3. Analysis of Variance (ANOVA) results of the responses Y_1 and Y_2

ANOVA for response Y_1

Source	DF	SS	MS	F	P
Regression	5	1.11938	0.22388	10.56	0.000
Residual Error	14	0.29684	0.02120		
Total	19	1.41622			

ANOVA for response Y_2

Source	DF	SS	MS	F	P
Regression	4	4061.9	1015.5	*	*
Residual Error	15	0	0		
Total	19	4061.9			

The obtained models for both responses were fitted as

$$\hat{Y}_2(\mathbf{X}) = 0.788 - 0.0556X_1 + 0.223X_2 + 0.0531X_3 - 0.0494X_4 - 0.243X_1^2, \quad R^2 = 79\% \qquad (20)$$

$$\hat{Y}_2(\mathbf{X}) = 16.6 - 10X_3 - 10X_4 + 6.70X_3^2 + 6.70X_3X_4, \quad R^2 = 100\% \qquad (21)$$

The response surface models were developed with values of R^2, 79% and 100% for Y_1 and Y_2, respectively. It is obvious from Eq. (20) that the feed concentration of ethyl acetate (X_2) affects the conversion of sodium hydroxide (Y_1) directly proportional whereas the feed concentration of sodium hydroxide (X_1) affects the conversion of sodium hydroxide (Y_1) inversely proportional. In other words, increasing sodium hydroxide concentration in the feed from 0.01 mol/L to 0.1 mol/L decreased the conversion and increasing ethyl acetate concentration in the feed from 0.01 mol/L to 0.1 mol/L increased the conversion. These results are compatible with the previous study performed in batch process [10]. If the coefficients of the first model, given in Eq. (20), are evaluated according to their absolute values it is clear that the most effective parameter is the feed concentration of ethyl acetate. It can be said that from the Eq. (21), the increment in the feed flow rates of sodium hyroxide and ethyl acetate cause to decrease in the space time. This result reflects the hydrolic behavior of the continuous stirred tank reactor. The obtained individual optimization results of the predicted response functions are $\hat{Y}_1^* = 1$, $\mathbf{X}^* = [-0.1365 \; 0.8664 \; 0.1587 \; -0.1476]$ and $\hat{Y}_2^* = 6.1937$, $\mathbf{X}^* = [0.2463 \;\; 1]$. The contour plots of predicted response functions, given in Eq. (20) and Eq. (21), are shown in Fig. 2 and Fig. 3 by using Matlab 7.9 [30], respectively.

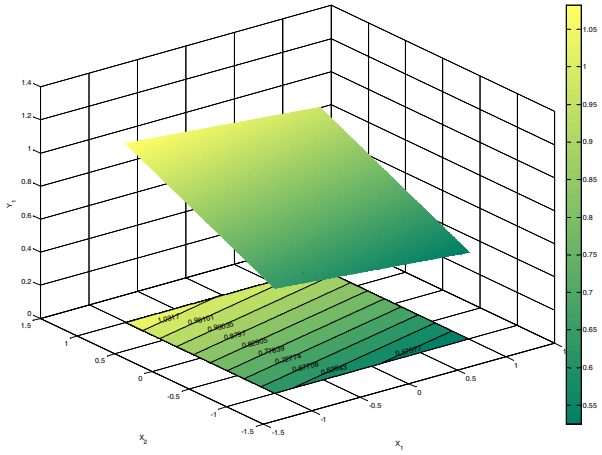

Figure 2. Predicted response surface plot of Y_1 as a function of X_1 and X_2 in which the $X_3 = 0.1587$ and $X_4 = -0.1476$ are kept their optimal values obtained by the individual maximization of Y_1

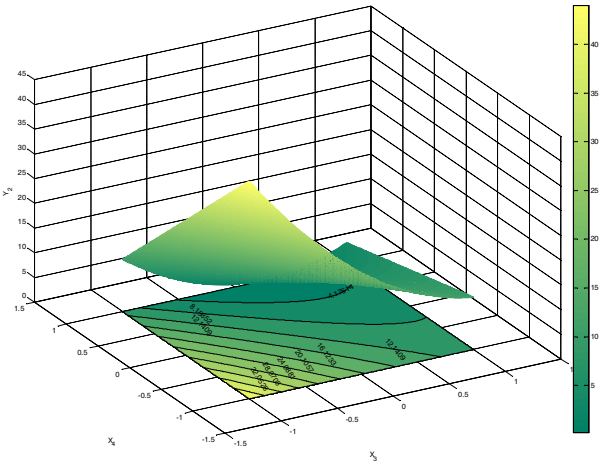

Figure 3. Predicted response surface plot of Y_2 as a function of X_3 and X_4

The aim of the study is to get maximum value of the $\hat{Y}_1(\mathbf{X})$ and minimum value of the $\hat{Y}_2(\mathbf{X})$. Therefore, the MRO problem can be written as

$$\begin{aligned} &\max\ \hat{Y}_1(\mathbf{X}) \\ &\min\ \hat{Y}_2(\mathbf{X}) \\ &0.1639 \le \hat{Y}_1(\mathbf{X}) \le 1 \\ &6.1937 \le \hat{Y}_2(\mathbf{X}) \le 50 \\ &\mathbf{X} \in S \end{aligned} \tag{22}$$

where $S \in [\mathbf{-1},\mathbf{1}]$. In (22), the lower and the upper bounds of the predicted responses, $\hat{Y}_1(\mathbf{X})$ and $\hat{Y}_2(\mathbf{X})$, are calculated as the individual minimum and maximum values of each responses. Afterwards, the individual desirability functions for the responses can be defined as

$$d_1\left(\hat{Y}_1(\mathbf{X})\right) = \begin{cases} 1 & , \quad \hat{Y}_1(\mathbf{X}) \ge 1 \\ \left(\dfrac{\hat{Y}_1(\mathbf{X}) - 0.1639}{1 - 0.1639}\right) & , \quad 0.1639 \le \hat{Y}_1(\mathbf{X}) < 1 \\ 0 & , \quad \hat{Y}_i(\mathbf{X}) < 0.1639 \end{cases} \tag{23}$$

and

$$d_2\left(\hat{Y}_2(\mathbf{X})\right) = \begin{cases} 1 & , \quad \hat{Y}_2(\mathbf{X}) \le 6.1937 \\ \left(\dfrac{50 - \hat{Y}_2(\mathbf{X})}{50 - 6.1937}\right)^s & , \quad 6.1937 < \hat{Y}_2(\mathbf{X}) \le 50 \\ 0 & , \quad \hat{Y}_2(\mathbf{X}) > 50. \end{cases} \tag{24}$$

The formulation of overall desirability function which wanted to be maximized can be written as

$$\max\ D(\mathbf{X}) = \left(d_1(\mathbf{X}) \times d_2(\mathbf{X})\right)^{1/2} \quad \mathbf{X} \in [\mathbf{-1},\mathbf{1}] \tag{25}$$

The optimal input vector values of the $D(\mathbf{X})$, defined by Eq.(25), is $\mathbf{X}^* = [-0.1137\ 1\ 0.4564\ 1]$ with the overall desirability value $D^* = 1 = 99\%$. The individual predicted response values are calculated as $\hat{Y}_1^* = 0.989$ and $\hat{Y}_2^* = 6.4895\ \text{min}^{-1}$ by using the DFA factor conditions.

5. CONCLUSION

The objective of this study was to optimize the operating conditions of the continuous saponification process with respect to both conversion and space time. The maximization of conversion (x_A) and the minimization of space time (τ) are important from the point of process economy and yield. Therefore, the saponification process can be considered as a multi-response problem in which the responses are uncorrelated. Investigation of the multi-response problem were performed in three steps: (i) data gathering, (ii) modeling, and (iii) optimization. At the first step, the process factors were selected as C_{Ao} (concentration of sodium hydroxide), C_{Bo} (concentration of ethyl acetate), Q_A (feed flow rate of sodium hydroxide), and Q_A (feed flow rate of ethyl acetate). Temperature and agitation rate were not considered as factors in this study since the experiments were performed at their optimal values which were given in [10]. 2^4 Full Factorial Design was used for the experiments with four center points. At the second step, second order polynomial response surface models were identified by using least square analysis. The analytical functions were calculated in Minitab 14. The validation of predicted models was confirmed by using ANOVA. It was seen that the first predicted response function was related to main effects of all factors and quadratic effect of C_{Ao}. On the other hand, it was concluded that the second predicted response function was only related with Q_A and Q_B At the final step, DFA was used for MRO since the interested responses are uncorrelated. In order to apply DFA, individual optimal values of predicted responses were needed to determine the constraints. By considering the physical meaning of the responses, individual operating conditions were obtained. The MRO problem denoted by Eq. (22) was converted to the single objective optimization problem given in Eq. (25) by using DFA. It is seen from the optimization results that the obtained process factor levels, $\mathbf{X}^* = [-0.1137\ 1\ 0.4564\ 1]$, make the conversion maximum and the space time minimum as 0.989 and $6.4895\ \text{min}^{-1}$, respectively. These response values are satisfactory in the view of process economy and yield. It can be said that simultaneous optimization is more realistic for multi-response saponification process in the case of feasibility.

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