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Process improvement approach to the saponification reaction by using statistical experimental design

Nihal Bursali [a], Suna Ertunc [b], Bulent Akay [b,*]

[a] *Yenimahalle Municipality Precidency, 06170 Yenimahalle, Ankara, Turkey*
[b] *Ankara University, Faculty of Engineering, Department of Chemical Engineering, 06100 Tandoğan, Ankara, Turkey*

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Abstract

The purpose of this study was to determine the effective operating parameters and the optimum operating conditions of a batch saponification process in the frame of the process improvement. Full two-level factorial and face-centered central composite (FCCC) statistical experimental design methods were used successively. Examined parameters were the main and interaction effects of temperature, agitation rate, initial sodium hydroxide (NaOH) and ethyl acetate (EtOAc, $CH_3COOC_2H_5$) concentrations. Selected process response was the fractional conversion rate of NaOH (X_A). Temperature and agitation rate were found to have no effect on the response at the 10% selected significance level ($\alpha = 0.1$). The dependence of response on the NaOH and EtOAc concentrations was illustrated by a linear second-order polynomial model. Examination of the residuals served as a diagnostic check of the model and it was found that the model was good enough to fit the experimental data. Optimum operating conditions at which maximum X_A was obtained about 100% were found to be 0.01 mol L^{-1} NaOH and 0.1 mol L^{-1} EtOAc by applying response surface method (RSM). With the use of residual analysis and statistical techniques, more reliable and proper results were obtained at the process improvement stage of the saponification process.

Keywords: Process improvement; Statistical experimental design; Response surface methodology; Saponification reaction; Residual analysis

1. Introduction

Experimentation is made to determine the effect of the independent variable (factor) on the dependent variable (response) of a process and a relation between them illustrated by a regression model by using experimental data. Statistical design of experiment (DOE) is a well known efficient experimentation technique and has been applied in a wide range of fields such as drug and food industry, chemical and biological processes, etc., to produce high quality products, to operate more economical process, to ensure more stable and reliable process [1,2]. The studies including application of DOE methods have been made for more than 40 years and the advance of DOE applications has been assisted by the developments in the field of computer science. Carr et al., applied statistical program planning for process improvement to reduce the process development time by applying fractional factorial design [3]. Lind et al. applied response surface methodology (RSM) and full two-level factorial design to a chemical process in which antibiotic was produced [4]. Xu et al. used statistically based experimental designs for the medium optimization of an important medical microorganism [5]. Andersons, applied design of experiments technique to the problem of preparing microwave popcorn [6]. More studies are available in e-journals [7,8].

There are a lot of DOE methods and the selection of them is made according to objectives and the number of examined factors [2]. The objectives of the experiment can be classified as screening, comparing and applying RSM. Screening experiment is applied to determine the most effective factors on the process response. RSM is generally used to find the optimal condition by using quadratic polynomial model and it is applied in consequence of a screening experiment.

In this study, the hydrolysis process of an ester called ethyl acetate (EtOAc, $CH_3COOC_2H_5$) in an alkaline condition was examined in terms of process improvement. As it is well known,

Abbreviations: ANOVA, analysis of variance; DOE, statistical design of experiments; CCC, central composite circumscribed design; CCI, central composite inscribed design; EtOAc, ethyl acetate; FCCC, face-centered central composite design; RSM, response surface method

* Corresponding author. Tel.: +90 312 2126720; fax: +90 312 2121546.
E-mail address: bakay@eng.ankara.edu.tr (B. Akay).

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the hydrolysis of a fat or an oil in alkaline condition produces soap for cleaning purpose and the reaction is called saponification. The reaction which occurs in the alkaline condition is also called saponification. Thus, the hydrolysis of EtOAc to produce sodium acetate (CH_3COONa) and ethyl alcohol (C_2H_5OH) by using NaOH is called saponification reaction, although the end product is not soap. When the related literature on the alkaline hydrolysis of EtOAc is searched, it is observed that there are not so many studies on the process improvement stage of this process. Previously published studies are generally related to kinetics of this reaction [9].

Although esters are not soluble in alcohol, water and in similar solvents, the salt obtained at the end of the saponification reaction is soluble in such kind of 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, obtained as an end product in this study, is a commercially important carboxylic acid salt, is used in a large area in industry such as petrol, cosmetic, textile, paint etc. It is used to remove the insoluble calcium salts in textile, to intensify the color of paint in paint industry and is used in food industry being as a tampon and protector. It is also used as a tampon in haemodialysis and leather industry and used in the neutralisation of mineral acids. By considering commercial and industrial importance of this process, optimum operating condition and operating factors effects were examined for this process to obtain high purity end product, to operate more economical and reliable process.

In this work, statistical design of experimental method was applied on the hydrolysis process of ethyl acetate in an alkaline condition. This study focused specifically on the improvement of this hydrolysis process. The optimal condition was determined and the factor effects were investigated.

This study based on experimentation consists of two stages: screening experimentation and applying RSM. Screening experimentation aimed to find the most important factors and it was planned according to full two-level factorial experimental design method. Fractional conversion rate of NaOH (X_A) was selected as response. All possible factors thought to have an effect on the response and their levels were considered at the brainstorming stage of the study and it was decided to examine the main and interaction effects of the temperature (°C), agitation rate (rpm), initial NaOH and EtOAc concentrations (mol L^{-1}) on the response. Experimental results were analyzed statistically by analysis of variance (ANOVA) using Fisher's F-ratio [1,2].

Optimal values of significant factors were determined as 0.01 mol L^{-1} NaOH and 0.1 mol L^{-1} $CH_3COOC_2H_5$ for 100% of X_A by obtaining response surface contours at different levels of factors by using second-order polynomial model.

2. Material and method

2.1. Reaction kinetic

The stochiometric representation of saponification reaction between EtOAc and NaOH is given by Eq. (1):

$$NaOH + CH_3COOC_2H_5 \rightarrow CH_3COONa + C_2H_5OH \quad (1)$$

This irreversible reaction is a second-order overall but first order with respect to each reactant and rate expression is given by Eq. (2):

$$-r_{NaOH} = -r_{EtOAc} = kC_{NaOH}C_{EtOAc} \quad (2)$$

In this reaction, hydroxyl ions are consumed and acetate ions are produced. Since hydroxyl ions are more conductive than the acetate ions, a decrease in the conductivity is observed as the reaction progresses. The change in conductivity is used to monitor the alkaline hydrolysis of EtOAc. Based on this principle, a relation between the conductivity of the reaction mixture and NaOH concentration is obtained as given below [11]:

$$\frac{C - C_\infty}{C_0 - C_\infty} = \frac{C_{NaOH} - C_{NaOH\infty}}{C_{NaOH_0} - C_{NaOH\infty}} \quad (3)$$

since,

$$C_{NaOH\infty} \rightarrow 0 \quad \text{as} \quad t \rightarrow \infty \quad (4)$$

Eq. (3) is rearranged and given in Eq. (5):

$$\frac{C_{NaOH}}{C_{NaOH_0}} = 1 - X_A = \frac{C - C_\infty}{C_0 - C_\infty} \quad (5)$$

The relation between reaction rate and X_A is given by Eq. (6):

$$-r_{NaOH} = kC_{NaOH}C_{EtOAc} = kC^2_{NaOH_0}(1 - X_A)\left(\frac{C_{EtOAc_0}}{C_{NaOH_0}} X_A\right). \quad (6)$$

2.2. Experimental apparatus

In this study a bench-top batch reactor (Armfield CEM-liquid phase chemical reactor, Hempshire, England) with temperature, flow rate and agitation rate control units was used as given schematically in Fig. 1. Two-liter mixed batch reactor was used with 1.5 L working volume. Temperature was controlled by circulating hot water through a coil immersed in reactor.

2.3. Analytical methods

The conductivity of the NaOH was measured by using WTW LF39 (Welheim, Germany) type conductivity meter. The sampling time was determined on the basis of the experimental design treatments and 10 mL of reaction mixture sample was taken from the reactor to measure the conductivity.

2.4. Plan of experiments

2.4.1. Screening experiment—full two-level factorial experimental design

At this stage, factors were studied at their maximum and minimum levels determined according to our experience about the process and from the literature research. The number of experiments for four factors was determined as $2^4 = 16$ according to full two-level factorial experimental design method [2,10]. To simplify the calculations, factors were studied with