Journal of the Taiwan Institute of Chemical Engineers 000 (2016) 1–16

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Optimization studies on a continuous catalytic reactive distillation column for methyl acetate production with response surface methodology

Mekala Mallaiah, Goli Venkat Reddy*

Department of Chemical Engineering, National Institute of Technology, Warangal 506004, India

ARTICLE INFO

Article history:
Received 19 December 2015
Revised 26 July 2016
Accepted 7 October 2016
Available online xxx

Keywords:
Esterification
Solid catalyst
Response surface methodology
Optimization
Reactive distillation

ABSTRACT

Esterification of acetic acid with methanol to produce methyl acetate has been studied in a continuous packed bed catalytic reactive distillation column. A novel solid catalyst Indion 180 ion exchange resin was used. The response surface methodology (RSM) technique based on central composite design (CCD) optimization method was used to design the experiments. Experiments were performed under different operating conditions of reboiler temperature, reflux ratio, total feed flow rate, methanol to acetic acid mole ratio, feed locations of acetic acid and methanol with respect to reactive zone and their effect on the conversion of acetic acid as well as on compositions of distillate and bottom products. Based on experimental data and central composite design, a regression model has been developed. The model correlates the purity of methyl acetate in the distillate and six most significant independent variables. From the statistical tests it has been established that the model truly represents the experimental data. There is a good agreement between optimum conditions for methyl acetate concentration in the distillate, predicted by model and experimental data. The comparison of the experimental results with the simulation results from equilibrium stage-wise model compared and found that there is good agreement between them.

1. Introduction

Distillation of liquid mixture into its components is highly energy intensive unit operation. The mixture is usually formed from a reaction, which also requires thermal energy. There is scope for minimizing the total energy requirement for the reaction and distillation processes if they are integrated. Such process intensification could be achieved by combining reactor and distillation functions in the distillation apparatus itself and it is known as reactive distillation, (RD). In catalytic reactive distillation (CRD) unit, the reaction and separation takes place simultaneously in a packed column containing a solid catalyst in the reactive section. In addition, the columns of this type contain a rectifying section above and stripping section below the reaction section, for separation of the product components.

When reactions are equilibrium limited, reactive distillation continuously removes products from the reaction zone, which drastically increases the overall conversion. This technique may also increase selectivity in certain competing reaction systems by continuously separating products from the reaction mixture. Therefore the lower capital investment, lower energy consumption, higher product yields and purity make reactive distillation an attractive alternative to conventional process [1–4].

The production of high purity methyl acetate in a tray reactive distillation column using sulphuric acid catalyst was investigated by Agreda et al. [5]. Methyl acetate synthesis in a heterogeneous catalytic reactive distillation process was investigated by Bessling et al. [6].

Kruel et al. [7] have carried out the experiments in a batch reactive distillation column using Montz structured packing in which catalyst particles was immobilized. The removal of dilute acetic acid from water was studied using the catalytic distillation apparatus by Xu et al. [8]. Amberlyst 15, a heterogeneous catalyst was used for the esterification reaction of acetic acid with methanol to remove acetic acid from the water using a tray column. Popken et al. [9] have performed experiments for the synthesis as well as hydrolysis of methyl acetate using a structured catalytic packing Katapak-S in a packed bed reactive distillation column with Amberlyst-15 ion exchange resin acid catalyst. Gorak and Hoffmann [10] have studied the catalytic distillation using a structured packing's for the synthesis of methyl acetate. The simulated results were compared with the experimental data and observed that

* Corresponding author. Fax: +91 8702459547.
E-mail addresses: v.reddy@nitw.ac.in, goli_venkat_reddy@outlook.com (G.V. Reddy).

http://dx.doi.org/10.1016/j.jtice.2016.10.007
1876-1070/

Nomenclature

B	bottoms flow rate (mol/l)
D	distillate flow rate (mol/l)
F_A	acetic acid feed flow rate (mol/l)
F_M	methanol feed flow rate (mol/l)
RR	reflux ratio
T_{RB}	reboiler temperature (°C)
W_{CR}	catalyst loading (g/cc)
x_{Ab}	mole fraction of acetic acid in bottoms
x_{Af}	mole fraction of acetic acid in distillate
X_A	acetic acid conversion

some deviations between the experimental and simulation results. Sandesh et al. [11] have investigated the synthesis of methyl acetate by esterification of acetic acid and methanol using an ion-exchange resin catalyst in packed bed reactive distillation column.

Different kinds of the catalyst envelopes are available in the literature [12–15]. The most applicable type of packing for reactive distillation now a day is structured wire mesh packing in which the catalyst particles are immobilized between the two corrugated sheets [16].

The main focus of the present study is to find the relationship between operating conditions and methyl acetate purity and to find the optimal operating conditions for the process. Response surface methodology (RSM), with central composite design (CCD) has been used for the design of experiments, the same experiments are performed and data generated. The data is used to develop a statistical mathematical model relating the six significant parameters as cited above and concentration of methyl acetate in distillate. Optimum model parameters were obtained from the ANOVA analysis. The six significant variables considered for the model and optimization are reflux ratio, reboiler temperature, total feed flow rate, mole ratio of methanol to acetic acid in the feed, acetic acid feed position and methanol feed position with respect to reactive zone. Further the experimental results are compared with the simulation results of equilibrium stage-wise model using Aspen Plus.

2. Materials and methods

2.1. Materials

Methanol (purity = 99% w/w) and acetic acid (purity = 99.95%w/w), supplied by SD Fine Chemicals Ltd. (Mumbai, India), were used in the study. The solid acid catalyst, Indion 180 used for the esterification reaction [17,18] was supplied by Ion-Exchange India Limited, Mumbai.

2.2. Statistical methods

2.2.1. Response surface methodology (RSM)

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for the modeling and analysis of chemical and other processes, in which the output is influenced by several independent variables and the objective is to optimize the output [19].

The response surface method (RSM) has been used for the optimization of the process parameters for the production of methyl acetate in a reactive distillation column. A central composite design (CCD) with six most significant independent process variables was used to determine the effect of these variables on the methyl acetate composition. The CCD is a suitable design for sequential experiments to obtain approximate information for testing the lack of fit without a large number of design points [20,21]. The independent variables are coded at three levels between −1, 0 and +1, where −1 corresponds to minimum value and +1 corresponds to maximum value of each variable and 0 corresponds to the central value of maximum and minimum values as shown in Table 1. For example reboiler temperature is varied from 75 to 85 °C. Here −1 corresponds to 75 °C, 0 corresponds to 80 °C and +1 corresponds to 85 °C. The ranges of the minim and maximum values are selected based on the practical consideration relating to our laboratory RD column. The six factors investigated are reboiler temperature (X_1), total feed flow rate (X_2), reflux ratio (X_3), mole ratio of methanol to acetic acid (X_4), acetic acid feed position with respect to reactive zone (X_5) and methanol feed position with respect to reactive zone (X_6). Prior to experimental design, the feasible experiments were performed to determine the ranges of the reboiler temperature, total feed flow rate, reflux ratio, mole ratio of methanol to acetic acid, acetic acid and methanol feed positions with respect to reactive zone [22]. The ranges of the parameters were chosen based on feasibility of experiments as given in Table 1.

The total number of experiments with full CCD was eighty six (2^k+2k+6), where k is the number of factors, *i.e.* six for the present study. The number experiments were reduced to minimum using the small CCD. The total number of experiments with small CCD was thirty three. Twenty eight experiments and five replication experiments at design center were carried out randomly to estimate the error. The test factors are coded based on Eq. (1) in the regression equation.

$$X_i = \frac{W_i - W_{i0}}{\Delta W_i} \tag{1}$$

Where W_i is the independent variable real value, X_i is the independent variable coded value, W_{i0} is the independent variable real value at the center point and ΔW_i is the step change in the W_i. Thus the coded values are in the range of −1 and +1.

The response is related to the selected variables by linear and quadratic terms to formulate a simple model as given in Eq. (2)

$$\beta = \alpha_0 + \sum_{j=1}^{k} \alpha_j x_j + \sum_{j=1}^{k} \alpha_{jj} x_j^2 + \sum_{i} \sum_{<j=2}^{k} \alpha_{ij} x_i x_j + e_i \tag{2}$$

β is the response, x_i and x_j are the independent factors, α_0 is the constant coefficient, α_j, α_{jj}, α_{ij} are linear, quadratic and interaction effect coefficients and e_i is the error.

$$R^2 = 1 - \frac{SS_{resid}}{(SS_{\mathrm{mod}\,el} + SS_{resid})} \tag{3}$$

$$R^2_{adj} = 1 - \frac{SS_{resd}/DF_{resid}}{(SS_{\mathrm{mod}\,el} + SS_{resid})/(DF_{\mathrm{mod}\,el} + DF_{resid})} \tag{4}$$

$$\text{Adequate precision} = \frac{Max(\hat{Y}) - Min(\hat{Y})}{\sqrt{\bar{V}\,\hat{Y}}} \tag{5}$$

$$\bar{V}\,(\hat{Y}) = \frac{1}{n}\sum_{1}^{n} V(\,(\hat{Y}) = \frac{P\sigma^2}{n} \tag{6}$$

The coefficients of determination, *i.e.* R^2 and $R^2{}_{adj}$ in Eqs. (3) and (4) indicate the quality of the fit of the polynomial. The statistical significance is checked with Eqs. (5) and (6) and also by using *F*-value and *P*-value [19]. In this model *DF* is the degrees of freedom, *P* is the number of model parameters, *SS* is the sum of the squares, σ^2 is the mean square of the residuals from the ANOVA result and n is number of experiments. The response of the methyl acetate purity was measured at the end of the experiments. The trial version of design expert 9.0.3.1 software was used in the present study to plot response surface and analyzed experimental data.

Please cite this article as: M. Mallaiah, G.V. Reddy, Optimization studies on a continuous catalytic reactive distillation column for methyl acetate production with response surface methodology, Journal of the Taiwan Institute of Chemical Engineers (2016), http://dx.doi.org/10.1016/j.jtice.2016.10.007