CHEMICAL ENGINEERING TRANSACTIONS
VOL. 76, 2019
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Petar S. Varbanov, Timothy G. Walmsley, Jiří J. Klemeš, Panos Seferlis

ISBN 978-88-95608-73-0; **ISSN** 2283-9216
DOI: 10.3303/CET1976091

Parameters Optimization of MTBE Reactive Distillation Process with Response Surface Methodology

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Because of many variables and strong coupling effects between the reaction and distillation processes, the parameters optimization of reactive distillation (RD) process is usually a challenge work. In this study, response surface methodology (RSM) was used to design the numerical experiments and analyze process parameters of the methyl tertiary butyl ether (MTBE) reactive distillation column. Firstly, Packett-Burman design was employed to screen the significant process parameters affecting the conversion of isobutene from 10 variables. Then, a Steepest Ascent method and Box-Behnken design were applied to determine the optimum key process parameters, with maximizing the conversion of isobutene as an objective. The optimum and actual conversion of isobutene were 100 % and 97.54 % which is higher than a conversion of 91.95 % in the literature, under optimum conditions in MTBE reactive distillation process.

1. Introduction

Reactive distillation (RD) is considered as a more economical way of process realization in comparison with conventional methods, in which chemical reaction and distillation take place in the same device (Lu et al., 2017). Because of a large number of process parameters during the RD and a strong coupling between them, it is very important to optimize RD process parameters for chemical engineering and industry (Xiao et al., 2018). In this study, a RD process that produces MTBE was chosen and studied, because this RD process involves a strong coupling among process parameters and appears to be an ideal example of RD process.

In MTBE RD process, the product purity (MTBE purity) and the conversion of key reactant (isobutene) are two aspects that people pay special attention to (Huang et al., 2008). The equipment and operating parameters of MTBE RD process have a significant influence on these two aspects (Kumar and Kaistha, 2009). These parameters often interact with each other, so the analysis activity turns to be severely complicated by the difficulty of identifying feasible equipment configurations and suitable operating conditions (Almeida-Rivera et al., 2004). For example, the variation of reflux ratio can result in not only the change of liquid composition on distillation tray, but also the variation of contact conditions between liquid and catalysts (Xiao et al., 2015). Therefore, the optimization of MTBE RD process parameters is vital to industrial application, energy saving and consumption reduction (Almeida-Rivera et al., 2004).

In order to study the influence of process parameters by conventional methods, we usually change one factor while keeping the others constant. This will result in a large number of experiments. In addition, classical methods of experiments ignore the combined effects between parameters. The response surface methodology (RSM), which overcomes disadvantages of conventional methods of experiments, is an effective way for process parameters analysis which uses mathematical and statistical techniques to analyze the influence of variables on a specific response (Ahmad and Alrozi, 2004).

In this work, a study on MTBE RD process parameters optimization using RSM is reported. The MTBE RD experiments were conducted with Aspen Plus. The Plackett-Burman (PB) design was employed to determine the key process parameters affecting the conversion of isobutene. A Steepest Ascent method and Box-Behnken were used to identify the optimum process parameters for maximizing the conversion of isobutene.

Paper Received: 17/03/2019; Revised: 14/05/2019; Accepted: 14/05/2019
Please cite this article as: Xiao W., Zhang Y., Wang X., Jiang X., Ma W., He G., 2019, Parameters Optimization of MTBE Reactive Distillation Process with Response Surface Methodology, Chemical Engineering Transactions, 76, 541-546 DOI:10.3303/CET1976091

2. Experiments and methods

2.1 Validation of MTBE RD model based on Aspen Plus

The simplifying treatment is needed during simulating RD process because of its complicity. The RD simulation based on strict thermodynamic equation can be achieved by chemical process simulator Aspen Plus. Numerical experiments were conducted by Aspen Plus. To verify the modelling results with Aspen plus, under the same input parameters as the literature (Singh et al., 2005), the simulation output was compared with the corresponding results. The NRTL thermodynamic equation was used to simulate MTBE RD process.
The reaction equation of MTBE can be expressed as follows:

$$CH_3OH + (CH_3)_2C = CH_2 \longleftrightarrow CH_3O - C(CH_3)_3 \quad (1)$$

The reactant materials are isobutene (IB) and methanol (MeOH), and the catalyst is a strong H_2SO4, then the etherification reaction occurs to form MTBE product. This is a reversible exothermic reaction. Its reaction rate equation can be expressed as Arrhenius equation. The reaction rates *r* of forward and backward ($mol \cdot cm^{-3} \cdot s^{-1}$) are given as follows (Singh et al., 2005).

$$r_{forward} = 3.67 \times 10^{12} \exp(-92400 / RT) a_{IB} / a_{MeOH} \quad (2)$$

$$r_{backward} = 2.67 \times 10^{17} \exp(-134454 / RT) a_{MTBE} / a_{MeOH}^2 \quad (3)$$

The MTBE RD model was conducted with Aspen Plus, the results represented that the bottom temperature was 428.88 K and the purity of MTBE was 99.55 %. The percentage of error of MTBE purity and bottom temperature were 0.31 % and 0.54 % compared with the experiment results. For this reason, the simulation results of MTBE RD with Aspen Plus are highly reliable.

2.2 Experimental designs

2.2.1 Plackett-Burman design

PB design was employed to screen the significant parameters from 10 parameters. The conversion of isobutene (Y) was considered as the response in the design. According to the general discipline about MTBE RD process, along with the previous study (Singh et al., 2005), ten parameters were selected as variables that affects the conversion of isobutene. There is no specific rule for the selection of high and low levels of each parameter. The selection of levels of each parameter of PB design was based on previous literature (Singh et al., 2005). The level and code of variables are shown in Table 1, and the parameters matrix of PB design and response values are given in Table 2, where X11 is dummy variable that was used to calculate the standard error. Then the conversion of isobutene can be calculated by Aspen Plus simulation of MTBE RD. The results show the conversion of isobutene varies from 0.5441 to 0.9700.

Table 1: Parameters and levels of Plackett-Burman design

Parameters	Symbol	Coded levels	
		Low (-1)	High (+1)
Feed position of methanol	X1	5	9
Feed position of isobutene	X2	7	11
Number of trays	X3	15	19
Feed temperature of methanol (K)	X4	320	380
Feed temperature of isobutene (K)	X5	320	350
Liquid holdup on every tray (m^3)	X6	3	4
Reflux ratio	X7	4	9
Flow rate of methanol (kmol/h)	X8	600	700
Column pressure (kPa)	X9	911.9	1, 418.6
Number of reactive trays	X10	4	9
Dummy factor	X11	-	-

2.2.2 Steepest Ascent Method

Steepest Ascent method is a procedure for moving in a direction that quickly improves the response. Experiments were conducted along with the steepest ascent path until the response showed no further increase. This point would be near the optimal point and will be selected as the center point of Box-Behnken design (BBD).

Table 2: Plackett-Burman design for 11 parameters and response values

Run Order	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11	Y
1	1	1	1	-1	-1	-1	1	-1	1	1	-1	0.8367
2	1	-1	1	1	-1	1	1	1	-1	-1	-1	0.8275
3	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	0.5420
4	1	-1	1	1	1	-1	-1	-1	1	-1	1	0.6860
5	-1	1	1	-1	1	1	1	-1	-1	-1	1	0.5441
6	1	1	-1	1	1	1	-1	-1	-1	1	-1	0.8459
7	-1	-1	1	-1	1	1	-1	1	1	1	-1	0.8985
8	-1	1	-1	1	1	-1	1	1	1	-1	-1	0.5933
9	1	1	-1	-1	-1	1	-1	1	1	-1	1	0.6807
10	1	-1	-1	-1	1	-1	1	1	-1	1	1	0.9700
11	-1	1	1	1	-1	-1	-1	1	-1	1	1	0.9398
12	-1	-1	-1	1	-1	1	1	-1	1	1	1	0.8222

2.2.3 Box-Behnken design

BBD is a rotatable second order design and requires three levels of each factor. The number of experiments of BBD is defined as $N = k^2+k+c_p$, where k is the number of factors and c_p is the replicate number of the central point, which has been applied to optimization of several chemical and energy processes (Aslan and Cebeci, 2007). BBD was used to optimize the MTBE RD process parameters. The complete design consisted of three levels (low, center point and high coded as −1, 0, and +1). By the RSM, a quadratic polynomial equation was developed to predict the response as a function of independent variables involving their interactions:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_i \sum_j \beta_{ij} x_i x_j \quad (4)$$

Where, y is predicted value; β_0 is constant value; β_i, β_{ii}, β_{ij} are regression coefficients to be determined. In this study, the experiment design and RSM were employed using Design Expert Software Trial Version 8.0.

3. Results and discussion

3.1 Selection of the key process parameters using PB design

The results of analysis of variance (ANOVA) for evaluations of model are shown in Table 3.

Table 3: ANOVA for the model of Plackett-Burman design

Source	Degree of freedom	Sum of Squares(10^{-3})	Mean square (10^{-3})	F-value	Probility > F P-value
X_1	1	21.000	21.000	26.24	0.1227
X_2	1	7.784	7.784	9.53	0.1994
X_3	1	6.456	6.456	7.91	0.2175
X_4	1	4.909	4.909	6.01	0.2465
X_5	1	1.028	1.028	1.26	0.4634
X_6	1	2.170	2.170	0.27	0.6969
X_7	1	7.584	7.584	0.00	0.9939
X_8	1	33.000	33.000	40.90	0.0987
X_9	1	1.922	1.922	2.35	0.3677
X_{10}	1	170.000	170.000	211.50	0.0437
Model	10	250.000	25.000	30.60	0.1399
Residual	1	0.816	0.816		
Cor Total	11	250.000			

The model *F*-value of 30.60 implies that the model is not significant compared with the noise. There is a 13.99 % chance that a “model F-value” could occur due to noise. Therefore, the insignificant model terms X_5, X_6, X_7, X_9, which own larger P-value (less significant) compared with other model terms, should be eliminated from the model. The ANOVA results of PB model after eliminating these insignificant model terms are shown in Table 4. ANOVA analysis shows that the model with F-value of 51.59, P-value of 0.0002, R2 of 0.9841 and C.V.% of 3.69 indicate that the model is statistically significant and highly reliable. There is only a 0.02 % chance that a "Model F-Value" could occur due to noise.

Table 4: ANOVA for the model after eliminating insignificant model terms

Source	Degree of freedom	Sum of Squares(10^{-3})	Mean square (10^{-3})	F-value	Probility > F P-value
Model	6	250.000	41.000	51.59	0.0002
Residual	5	3.983	0.799		
Cor Total	11	250.000			

R^2=0.9841 and C.V.=3.69 %

The significance of each parameter is determined by P-value which is listed in Table 5. Table 5 indicates that X_1, X_8 and X_{10} are (the P-value are 0.0035, 0.0013 and <0.0001) more significant than other variables at 95 % confidence level. The coefficient of each term in Table 5 shows that X_1, X_3, X_4, X_8 and X_{10} had a positive effect on the conversion of isobutene, whereas X_2 had a negative effect on the conversion of isobutene. Therefore, PB design suggests that feed position of methanol(X_1), flow rate of methanol(X_8) and number of reactive trays(X_{10}) are key parameters for future optimization of conversion of isobutene.

Table 5: *Parameters estimates from the regression analysis*

Source	Degree of freedom	Sum of Squares(10^{-3})	Mean square (10^{-3})	F-value	Probility > F P-value
Intercept	1	0.770	8.148		
X_1	1	0.042	8.148	26.89	0.0035
X_2	1	-0.025	8.148	9.77	0.0261
X_3	1	0.023	8.148	8.10	0.0360
X_4	1	0.020	8.148	6.16	0.0557
X_8	1	0.053	8.148	41.91	0.0013
X_{10}	1	0.120	8.148	216.72	<.0001

3.2 Determining the direction of experiment using Steepest Ascent method

In this work, steepest ascent experiment was used to determine the direction of the experiment. This experiment starts at the point that the conversion of isobutene is 0.9700 in the PB design and moves along the direction in which X_1, X_8 and X_{10} increase because of their positive effects on the conversion of isobutene. Since statistical analysis shows that X_1, X_8 and X_{10} are more significant than other factors at 95% confidence level, these three factors are selected for the steepest ascent experiment and the other factors are fixed at a point that the conversion of isobutene is 0.9700. The results of steepest ascent method are shown in Table 6.

Table 6: Experimental design of steepest ascent and experimental data

Experiment	X_1	X_8	X_{10}	Y
1	4	620	5	0.6206
2	5	640	6	0.7771
3	6	660	7	0.8783
4	7	680	8	0.9344
5	8	700	9	0.9432
6	9	720	10	0.9748
7	10	740	11	0.9595
8	11	760	12	0.8788
9	12	780	13	0.7883
10	13	800	14	0.7127

The results indicate that the conversion of isobutene increases when X_1, X_8 and X_{10} increase during the first to sixth experiment, but after the sixth experiment, the conversion of isobutene decreases. This suggests that the highest conversion of isobutene is achieved during the sixth step of the experiment. The value of each parameter in sixth experiment should be selected as medium level of the future BBD.

3.3 Optimization of MTBE RD process parameters

3.3.1 RSM regression equation and model analysis

The range and levels used in the experiments were listed in Table 7. The experimental design matrix obtained by the BBD consists of 17 runs in coded terms were shown in Table 8. According to Table 8, a series of

experiments were conducted for obtaining the response, that is, conversion of isobutene carried out at the corresponding independent variables addressed in the experimental design matrix.

Table 7: Factors and levels of Box–Behnken design

Factors	Symbol	Level		
		-1	0	1
Feed position of methanol	X_1	4	9	14
Flow rate of methanol (kmol/h)	X_8	680	720	760
Number of reactive trays	X_{10}	7	10	13

Table 8: Design for the optimization experiment and experimental data

Experiment	X_1	X_8	X_{10}	Y
1	-1	0	-1	0.8638
2	0	-1	-1	0.9039
3	0	0	0	0.9749
4	0	0	0	0.9749
5	0	1	1	0.9146
6	1	1	0	0.9569
7	-1	-1	0	0.9539
8	-1	0	1	0.9407
9	0	0	0	0.9749
10	0	0	0	0.9749
11	1	0	1	0.6751
12	1	0	-1	0.8943
13	0	1	-1	0.9185
14	1	-1	0	0.9146
15	-1	1	0	0.9846
16	0	-1	1	0.8449
17	0	0	0	0.9749

Table 9: ANOVA for the regressive model

Error source	Degree of freedom	Sum of squares(10^{-3})	Mean squares (10^{-3})	F-value	P-value	Significance
X_1	1	11.000	11.000	18.48	0.0036	Significant
X_8	1	3.092	3.092	5.00	0.0604	
X_{10}	1	5.274	5.274	8.53	0.0223	
X_1X_1	1	5.823	5.823	9.42	0.0181	
X_1X_8	1	0.034	3.410	0.05	0.8210	
X_1X_{10}	1	0.022	22.000	35.48	0.0006	Significant
X_8X_8	1	0.925	9.252	1.50	0.2607	
X_8X_{10}	1	0.759	7.589	1.23	0.3044	
$X_{10}X_{10}$	1	0.037	37.000	60.49	0.0001	Significant
Model	9	0.088	9.737	15.75	0.0007	Significant
Residual	7	4.326	6.181			
Lack of Fit	3	4.326	1.442			
Cor Total	16	92.000				

R^2=0.9530 and C.V.=2.7%

can be seen from Table 8, there is a considerable difference in the conversion of isobutene at different values of selected parameters. The coefficients of the model for the response were estimated using multiple regression analysis method based on Eq(5). The empirical relationship between conversion of isobutene and three test variables in coded units is given by:

$$Y = 0.97 - 0.038x_1 + 0.020x_8 - 0.026x_{10} + 0.00292x_1x_8 - 0.074x_1x_{10} + 0.014x_8x_{10} - 0.037x_1^2 + 0.015x_8^2 - 0.094x_{10}^2 \quad (5)$$

Where *Y* is the conversion of isobutene, X_1, X_8 and X_{10} are the coded values of the test variables.

The results in terms of ANOVA for Eq. (5) are summarized in Table 9. The results show that the regression model for the conversion of isobutene is statistically significant and highly reliable with F-value of 15.75, P-value of 0.0007, R^2 of 0.9530 and coefficient of variation C.V.of 2.7%. By analyzing the P-value, it is observed that X_1 $X_{10}X_{10}$ and X_1X_{10} are key model terms.

3.3.2 Optimization of process parameters

The obtained parameters for maximum conversion of isobutene (100 %) are: feed position of methanol 5th tray, feed position of isobutene 7th tray, the number of trays 15, feed temperature of methanol 320 K, feed temperature of isobutene 350 K, liquid holdup on every tray 3 m^3, reflux ratio 9, flow rate of methanol 720 kmol/h, column pressure 9 kPa, the number of reactive trays 10. For the validation, the experiment was conducted using the obtained optimized MTBE process parameters and percentage of error of the response (conversion of isobutene) was 2.46 %. Under the optimized process parameters, a higher isobutene conversion of 97.54 % was achieved compared with the reported isobutene conversion of 91.95 % (Singh et al., 2005).

4. Conclusions

The following conclusions are drawn from this investigation: RSM is an effective way to optimize the MTBE reactive process parameters. By fitting the empirical models, the maximum conversion of isobutene can achieve 97.54 % under optimized conditions. PB design suggests that feed position of methanol, flow rate of methanol and the number of reactive trays are key parameters among ten process parameters for MTBE RD. The desired conversion of isobutene can be achieved by choosing the conditions predicted using the developed models. The high value of R2 > 95.3 % for the present mathematical model indicates the high correlation between the observed and predicted values.

Acknowledgments

The authors thank National Natural Science Foundation of China (21676043, U1663223); Fundamental Research Funds for the Central Universities (DUT17JC33, DUT17ZD203); MOST innovation team in key area (No. 2016RA4053), Education Department of the Liaoning Province of China (LT2015007) for financial support. The simulation by Aspen Plus was done in affiliation a, and other research work was done in affiliation b.

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