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Production of Ethylene Glycol Diacetate Ester Using a Heterogeneous Titanium (IV) Isopropoxide Catalyst: Response Surface Methodology

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Abstract

In this study, the reactive batch distillation of ethylene glycol monoacetate (EGMA) and ethylene glycol diacetate (EGDA) was investigated experimentally and numerically via the esterification reaction of acetic acid (AA) and monoethylene glycol (MEG) in the presence of heterogeneous titanium (IV) isopropoxide catalyst. Four operating parameters, including time (4-12 hr), temperature (60-100°C), the molar ratio of acetic acid to ethylene glycol (0.4-2.2 M), and catalyst weight (1-5wt%), were selected to design experiments, model and optimize the process through the response surface methodology (RSM). By applying the central composite design (CCD) method in RSM, two linear and second-order models were proposed for the responses of MEG conversion and EGD selectivity. The response surface plots showed that the reaction temperature and time had a more significant effect on increasing the reaction yield, while the molar ratio of reactants and catalyst weight were two critical parameters in increasing selectivity. The results of process optimization to maximize the responses indicated that the optimum process point in the operating range was at 9.5 hr, the temperature of 90°C, the molar ratio of 2.92:1, and catalyst weight of 2wt% where the predicted MEG conversion and selectivity were 100% and 94.72%, respectively. The MEG conversion reduced from 91.1% to 56.7% after using the catalyst four times.

Keywords: Ethylene glycol diacetate, Acetic acid, Ethylene glycol, Batch reactive distillation, Response surface methodology.

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Introduction

Solvents used in dye industries are volatile liquids whose importance is obvious. Completely pure non-volatile resins can not be utilized in such industries; thus, with the help of solvents, they can be converted to 30 to 80% non-volatile to reduce their viscosity and consequently increase their commercial value. One of these solvents is ethylene glycol diacetate (EGDA), which has two esterification factors used as a coating vapor rate regulator [1, 2]. This substance has negligible solubility in water, which causes two phases in it. Due to its high boiling point, it has many applications in the dye and thinner industry. This ester can be produced from Fisher's esterification reaction by combining acetic acid and monoethylene glycol (MEG) in the presence of a strong acid catalyst [3].

In the esterification reaction, products can be synthesized by heating a mixture of acetic acid and MEG. Since this reaction is prolonged, by increasing the temperature or adding some acid to produce more H^+ ions, the rate of esterification reaction increases [4]. This reaction as the molecular structure of the reactants in two steps is shown in Figure 1 schematically. In the first stage, the reaction between acetic acid and MEG occurs in the presence of an acid catalyst, forming ethylene glycol monoacetate (EGMA) and water. In the second step, EGMA reacts with acetic acid with the help of a catalyst in the medium to generate water and EGDA[5].

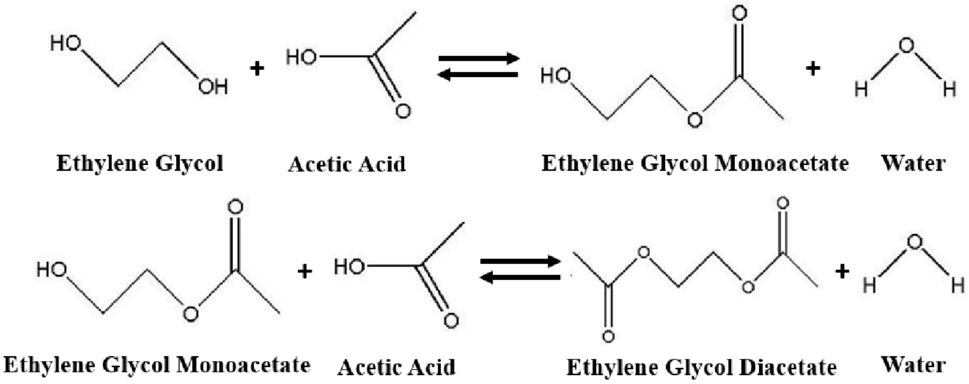


Figure 1. Esterification reaction of acetic acid with MEG with a molecular structure perspective.

For the first time, Schmid et al. [6] used the Amberlyst 63 catalyst to study the kinetics and chemical equilibrium of the reaction between acetic acid and MEG. They examined the effect of temperature and AA: MEG molar ratio on reaction performance in the range of 60-90°C and two different values of 0.5:1 and 1:1, respectively, resulting in the maximum conversion rate of 83%. Suman et al. [7]presented two laboratory systems of batch and continuous distillation to investigate this reaction in the presence of Amberlyst 63 catalyst and azeotropic solvent 1,2-ethane chloride. By increasing the reaction temperature at the AA: MEG molar ratio of 2:1 and catalyst amount of 2wt% in one step, they achieved 100% MEG conversion and approximately 100% selectivity of EGDA.

Yadaw [8] employed two different catalysts, Molecular Sieve-13 and Seralite SRC-120, to examine the desired reaction in a batch laboratory system. They assessed the MEG conversion and the selectivity of the two products, EGMA and EGDA, at various temperatures and molar ratios of the reactants. The maximum values include 99.66% conversion, 35.42% selectivity of EGMA, and 64.57% selectivity of EGDA under the optimal conditions of 90°C, 2wt% catalyst, and AA: MEG molar ratio of 3. Using two kinetic models, Yadav et al. [9] studied the kinetics of the desired reaction in a batch distillation system in the presence of a Seralite SRC-120 catalyst and investigated the influence of various parameters affecting the reaction. Their study demonstrated that increasing all three factors of temperature, catalyst content, and AA: MEG molar ratio enhanced the selectivity of EGDA and MEG conversion.

Manohar et al. [10]examined the conversion of acetic acid in the esterification reaction of AA and MEG in the presence of two catalysts, ZrO_2 and Mo/ZeO_2. According to the reported results, the obtained AA conversion were21% and 19.9%for ZrO_2 and Mo/ZrO_2 catalysts, respectively. Zhou and Huang [11] simulated the sequential esterification of MEG and AA at stoichiometric molar ratios in a two-step distillation system using the Amberlyst 63 catalyst. Their simulation data indicated that a distillation system with one additional reaction step performed better than the single reaction step, reducing the final product's total annual cost (TAC) by 58.23% and improving the separation performance. Huang et al. [12] investigated the process of synthesis of EGDA from the reaction of MEG and AA in a single reaction distillation column in the presence of water. Their results proved that the hydration of ethylene oxide consumes water and improves the equilibrium of the esterification reaction to the right side and produces MEG in situ.

In this study, a heterogeneous titanium (IV) isopropoxide catalyst was utilized to maximize the production of EGDA through the esterification reaction of AA and MEG in a batch reactive distillation laboratory system. The design of the experiment is according to the response surface methodology (RSM) by considering the reaction pressure constant, the effect of four variable operating parameters, such as reaction temperature, catalyst weight, AA: MEG molar ratio, and reaction temperature on MEG conversion. The RSM approach investigates the optimum points of all operational conditions.

Experimental

Materials

Acetic acid, monoethylene glycol, and ethylene dichloride have been used to produce EGDA, whose properties, along with the percentage of purity and manufacturing company, are listed in Table 1.

Table 1. Chemical and physical properties of the materials used in the present study.

Material	Acetic Acid	Monoethylene glycol	Ethylene dichloride
Molecular formula	$C_2H_4O_2$	$C_2H_6O_2$	$C_2H_2Cl_2$
Purity	98%	98%	99%
Manufacturer	Shazand Petrochemical Company, Arak, Iran	Shazand Petrochemical Company, Arak, Iran	Merck Company, Germany
Molecular weight ($g.mol^{-1}$)	60.05	62.07	98.96
Density ($g.mL^{-1}$)	1.05	1.2	1.25
Boiling point (°C)	16	-13	-35
Melting point (°C)	118	197	83

A heterogeneous titanium (IV) isopropoxide catalyst with molecular formula $Ti[OCH(CH_3)_2]_4$ and molecular weight of 284.222 $g.mol^{-1}$ and a purity of 97% was purchased from Merck Company.

Experimental measurements

The progress of the esterification reaction is evaluated by calculating the MEG conversion, which is equal to the ratio of moles of MEG consumed in the reaction to its initial moles in the reaction medium calculated by the following equation[13]:

$$C\% = \frac{n_i - n_f}{n_i} \times 100 \qquad (1)$$

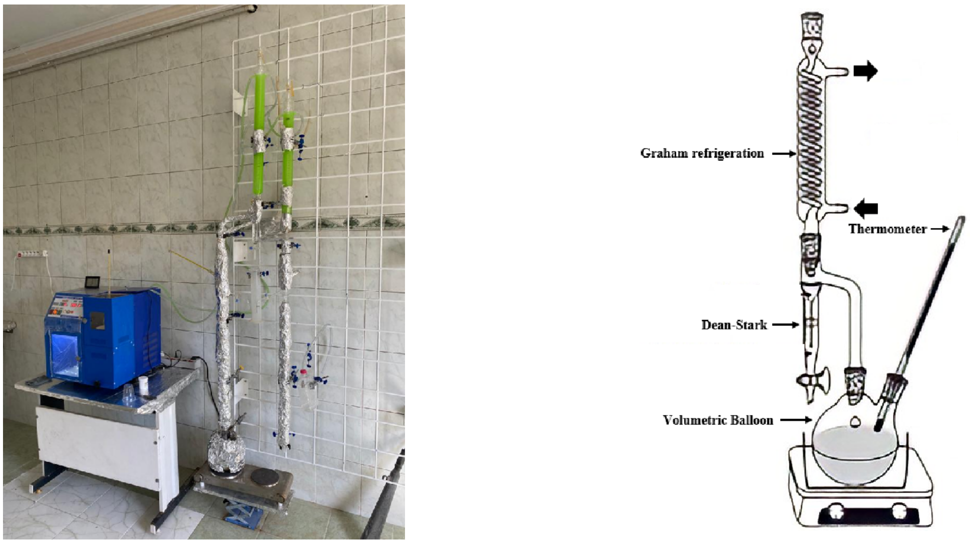
where n_i is the initial moles of MEG, n_f is the number of moles remaining of ethylene glycol after the experimental test, and C is the MEG conversion throughout the reaction. Also, the selectivity is used to evaluate the degree of selectivity between the esters produced, calculated as follows [14]:

$$R\% = \frac{n_p}{n_t} \times 100 \qquad (2)$$

in which,n_p is the number of moles of each ester produced, n_t is the total number of moles of all esters produced, and R is the selectivity of each ester.

Experimental setup

The synthesis of EGDA was performed in an atmospheric reactor using the batch distillation laboratory system shown in Figure 2 (a). The water resulting from the reaction is removed from the reaction medium. To continuously eliminate the produced water at reflux temperature caused by the chemical reaction, a combination of Dean-Stark with Graham refrigeration and volumetric balloons was harnessed. Since the esterification reaction of MEG is an equilibrium, reversible reaction, water with acetic acid forms an azeotrope due to its proximity to the boiling point, which can reduce the rate of reaction. Therefore, by removing water as one of the products from the reaction medium, the reaction will move towards the formation of products. Therefore, ethylene dichloride was utilized in this system to form an azeotrope with water and finally separate it, which removes water from the environment at a temperature lower than the boiling point of ethylene dichloride (84°C). Both liquids condense after entering the refrigeration and then enter the sidearm of the Dean-Stark apparatus. At this stage, at a low temperature, the water is separated from ethylene dichloride and collected at the bottom of the sidearm, which can be separated and weighed by opening the valve at the end of the sidearm of Dean-Stark. A schematic view of the current experimental system is depicted in Figure 2(b).



(a) **(b)**

Figure 2. (a) Laboratory system and (b) schematic view of batch reactive distillation using an atmospheric reactor.

Response Surface Methodology (RSM)

One of the efficient methods for optimizing chemical processes is RSM, which has recently attracted the attention of many researchers. RSM is a practical statistical approach used to design and analyze experimental data. In RSM, different methods such as central composite design (CCD) can evaluate the interaction between influential parameters on a response. In other words, RSM-CCD is a practical tool for empirically understanding the relationship between the studied parameters and the system response. Considering this, RSM helps to find the optimum conditions efficiently by reducing experimental time and cost. In this procedure, a set of experiments is first designed for a reliable measurement to achieve the desired response. A highly consistent polynomial mathematical model is then developed. Finally, the most desirable experimental parameters are predicted to minimize or maximize the corresponding response [15].

The present study employed the RSM-CCD method to design the experiment and evaluate the MEG conversion in Design-Expert software. The operational factors affecting the reaction conversion, including reaction temperature, reaction time, reaction pressure, catalyst weight, and AA: MEG molar ratio, were contemplated in the experiment design. According to an experiment in an atmospheric reactor under constant pressure, the reaction was performed. Here, the other four parameters are defined as variables, the range of which is reported in Table 2. The CCD method requires three types of tests, $2k$ factorial tests, $2k$ axial tests, and n_c central point, where k is the number of factors studied in the test. To be comparable, the design is presented in 5 levels $-\alpha$, -1, 0, +1, $+\alpha$. After entering the numerical values of response or responses, the process performance is evaluated by analyzing response (y). The relationship between process input parameters and responses is as follows [16]:

$$y = f\,(x_1, x_2, \ldots, x_k) + \varepsilon \tag{3}$$

According to Eq. (3), y is the response depending on the input parameters x_1, x_2,…x_k, andε is the remaining error calculated experimentally. In RSM, quadratic polynomial equations are the most common model to fit empirical data. Accordingly, the experimental data are utilized to develop the quadratic polynomial model according to the equation below[16].

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j \sum_{j=1}^{k} \beta_{ii} X_i^2 + \varepsilon \tag{4}$$

This method is an effective evaluation method that improves the quality of experimental data. In Eq. (4), β_0 is a constant term, β_i and β_j are the coefficients of the linear parameters, β_{ij} are the coefficients of the interaction parameters, β_{ii} and β_{jj} are the coefficients of the second-order parameters. The values of the center points can help to detect the curvature of the response, the axial points (located at an alpha distance from the center point) estimate the coefficients of second-order terms, factorial points (located in the center of the cube with side length equal to estimate the coefficients of linear term.

Table 2. Operating range and level of parameters studied in RSM modeling.

Parameter	**Unit**	**Name**	**Lower limit**	**Upper limit**	**Level**				
					-α	**-1**	**0**	**+1**	**+α**
Reaction time	hr	*A*	4	12	4	6	8	10	12
Reaction Temperature	°C	*B*	60	100	60	70	80	90	100
AA:MEG ratio	molar	*C*	0.2	4.2:1	0.2:1	1.2:1	2.2:1	3.2:1	4.2:1
Catalyst weight	wt%	*D*	1	5	1	2	3	4	5

According to the laboratory and operational range selected in Table 2, the experimental design of the present study is presented in Table 3 by reporting the laboratory results of both responses, MEG conversion, and selectivity of EGDA.

Results and discussion

Experimental analyses

Fourier-transform infrared spectroscopy (FTIR) analysis has been used to examine and confirm the structural information of the products produced. Figure 3 depicts the spectrum of the synthesized EGMA and EGDA. For EGMA, the infrared spectrum has two adsorption regions at 1735 and 3461 cm^{-1}, which belong to the two functional groups C=O and OH. Also, the narrowing of the adsorption peak at 1151 cm^{-1} indicates the reaction of acetic acid with one of the groups of alcohol and ester production. Based on the spectrum of EGDA, in the region of 1735 cm^{-1}, a sharp peak associated with the C=O functional group is identified, and the removal of the adsorption region of3460 cm^{-1}[17] demonstrates the reaction of the OH functional group with acetic acid and EGDA production.

Table 3. Experiment design of the esterification reaction using RSM-CCD method to model the MEG conversion and EGDA selectivity.

Run No.	**Factor 1** *A*: **Time** **hr**	**Factor 2** *B*: **Temperature** **°C**	**Factor 3** *C*: **Molar ratio** **M**	**Factor 4** *D*: **Catalyst weight** **wt%**	**Response 1** ***C%***	**Response 2** ***R%***
1	6	70	1.2	2.5	75.1	13.2
2	6	90	1.2	1.5	78.3	17.3
3	8	80	2.2	2	87.2	75.6
4	8	80	2.2	2	88	72.5
5	8	100	2.2	2	99.7	79.4
6	8	80	2.2	1	83.1	70.6
7	10	70	1.2	2.5	91.3	17.8
8	10	70	3.2	2.5	95.6	81.3
9	8	80	2.2	2	88.4	74.9
10	4	80	2.2	2	62.8	45.1
11	6	90	1.2	2	79.9	17.5
12	6	70	3.2	2.5	84.9	69.1

13	10	90	1.2	2.5	95.1	19.6
14	8	60	2.2	2	78.2	60.4
15	8	80	2.2	2	88.5	75.9
16	10	90	3.2	2.5	99.8	94.5
17	6	90	3.2	2.5	91.1	79.2
18	12	80	2.2	2	100	85.7
19	8	80	0.2	2	16.9	0.7
20	10	70	1.2	1.5	85.3	18.5
21	8	80	2.2	2	89.1	79.1
22	8	80	2.2	2	87.7	75.2
23	10	90	3.2	1.5	97.4	90.2
24	6	90	3.2	1.5	85.1	66.9
25	8	80	4.2	2	94.1	79.3
26	10	70	3.2	1.5	89.6	82.2
27	10	90	1.2	1.5	88.2	18.9
28	6	70	1.2	1.5	69.5	17.1
29	8	80	2.2	3	90.3	76.6
30	6	70	3.2	1.5	76.5	65.5

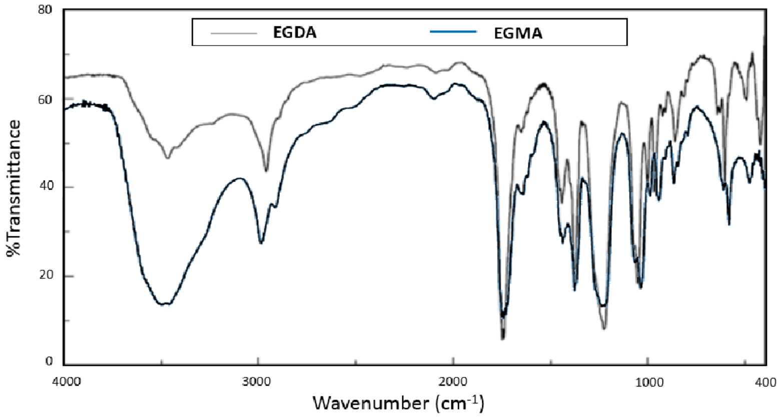


Figure 3. FTIR results of the synthesized EGMA and EGDA.

The chromatograms of the total ions produced relative to the retention time in the GC-MS device for a sample are reported in Figure 4. The mass spectra of EGMA and EGDA are shown in Fig. 5 (a) and (b), presenting a good match with their library ranges.

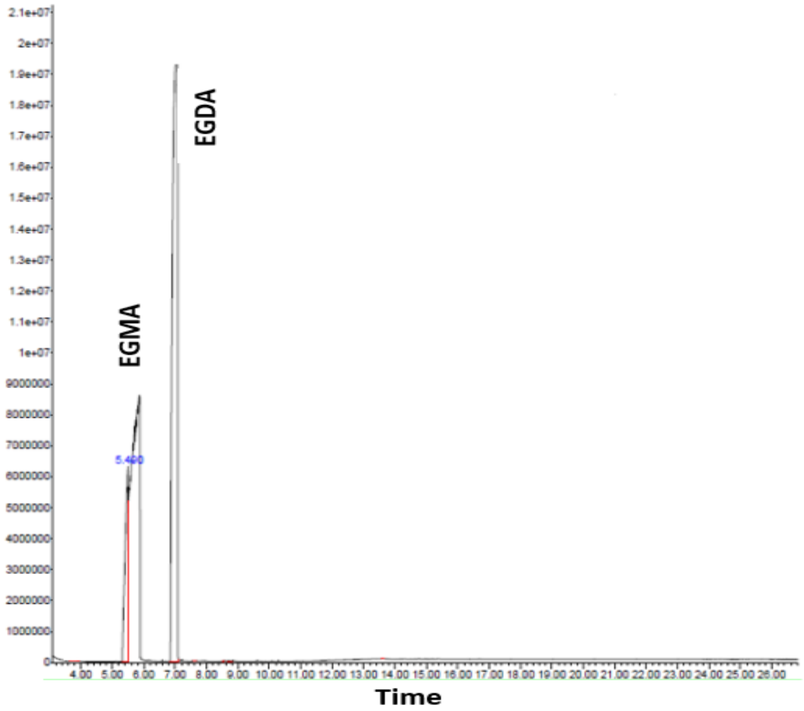


Figure 4.GC-MS results of the produced sample from the reaction between AA and MEG in the presence of a heterogeneous titanium (IV) isopropoxide catalyst.

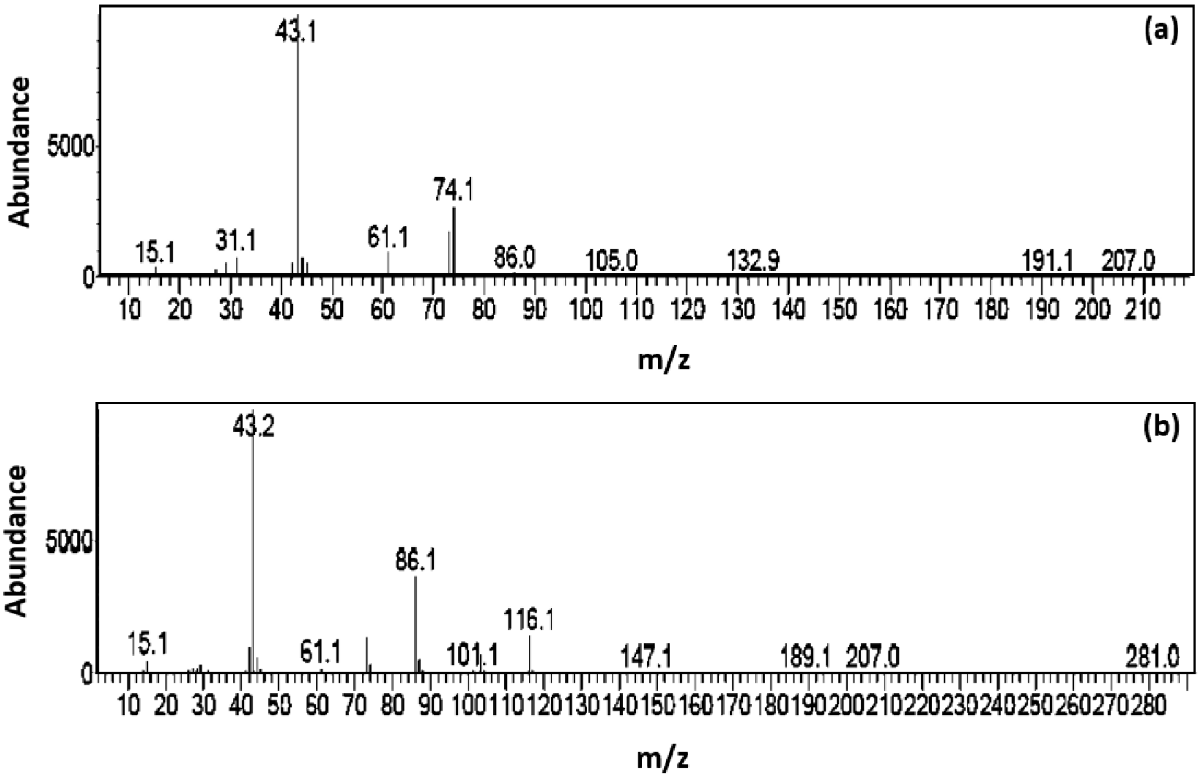


Figure 5. Mass spectra obtained correspond to the peak of (a) EGMA and (b) EGDA.

RSM results

Analysis of Variance (ANOVA)

As mentioned, the RSM method was employed to analyze the experimental data. The coefficients of independent variables and their interaction based on ANOVA are presented in Tables 4 and 5 for

MEG conversion and EDGA selectivity, respectively. The *p*-values were chosen as a criterion for determining the importance of parameters. A parameter with a p-value less than 0.001 indicates that this model parameter is very significant, while the model parameters with a *p*-value greater than 0.1 are not significant[18]. Here, *A* (time), *B* (temperature), *C* (molar ratio of reactants), and *D* (catalyst weight) were considered as independent parameters for modeling both responses. Based on the results reported in Table 4, in the linear model of MEG conversion, three parameters of reaction temperature, time, and molar ratio were significant, while in the second-order model of selectivity, time, molar ratio as well as the interaction parameter of C^2were significant factors of the model.

Table 4. ANOVA results of the linear model for MEG conversion.

Factor	**Sum of Squares**	***df***	**Mean Square**	***F* Value**	***p*-value Prob >*F***
Model	2029.10	4	507.28	60.64	<0.0001
A-Time	1295.07	1	1295.07	154.82	<0.0001
B-Temperature	338.25	1	338.25	40.44	<0.0001
C-Molar ratio	258.98	1	258.98	30.96	<0.0001
D-Catalyst weight	136.80	1	136.80	16.35	0.0005
Residual	200.76	24	8.37		
Lack of Fit	198.55	19	10.45		
Pure Error	2.21	5	0.44		
Cor Total	2229.87	28			

Table 5. ANOVA results of the second-order model for EGDA selectivity.

Factor	**Sum of Squares**	***df***	**Mean Square**	***F* Value**	***p*-value Prob >*F***
Model	19749.88	14	1413.92	39.79	<0.0001
A-Time	1143.85	1	1143.85	32.19	<0.0001
B-Temperature	326.29	1	326.29	9.18	0.0097
C-Molar Ratio	16400.65	1	16400.65	461.52	<0.0001
D-Catalyst Weight	70.15	1	70.15	1.97	0.1835
AB	28.35	1	28.35	0.80	0.3880
AC	291.26	1	291.26	8.20	0.0133
AD	2.40	1	2.40	0.068	0.7989
BC	93.27	1	93.27	2.62	0.1292
BD	65.94	1	65.94	1.86	0.1963
CD	80.26	1	80.26	2.26	0.1568
A^2	324.66	1	324.66	9.14	0.0098
B^2	149.77	1	149.77	4.21	0.0608
C^2	4761.00	1	4761.00	133.98	<0.0001
D^2	56.03	1	56.03	1.58	0.2313
Residual	461.97	13	35.54		
Lack of Fit	438.68	8	54.83		
Pure Error	23.29	5	4.66		
Cor Total	20256.85	27			

Validation and prediction models

The experimental values predicted by the RSM-CCD approach for MEG conversion and selectivity are shown in Figures 6 (a) and (b), respectively. The data distribution on a straight line for both models indicates the high accuracy of the proposed models, proved by the values of the coefficient of correlation (R^2) reported in Table 6.

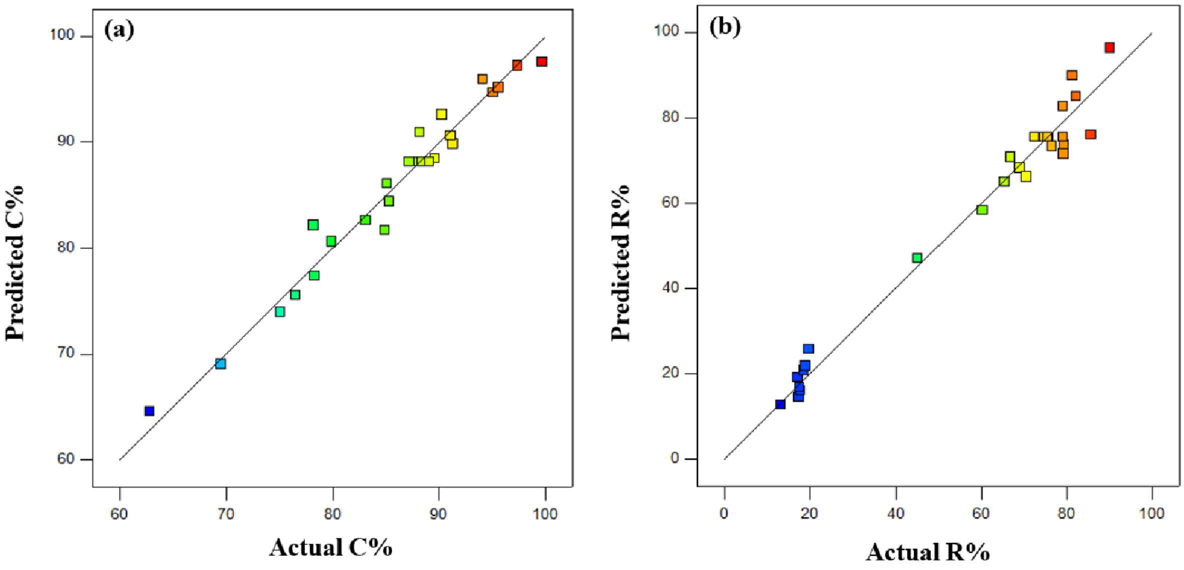


Figure 6. Experimental and predicted data by RSM modeling for (a) MEG conversion and (b) EGDA selectivity.

According to the RSM method, two linear and second-order models are proposed for the responses of MEG conversion and EGDAselectivity as a function of the considered parameters, which are as follows:

$$C\,\% = 7.32A + 3.73B + 3.58C + 2.36D + 86.62 \qquad (5)$$

$$\begin{aligned} R\% = {} & 6.60A + 3.23B + 31.73C + 1.15D + 0.46AB + 3.61AC - 0.55AD \\ & + 1.63BC + 1.21BD + 1.44CD - 3.70A^2 - 2.57B^2 - 17.25C^2 - 1.65D^2 + 75.55 \end{aligned} \qquad (6)$$

According to the important parameters reported in Table 5, the selectivity correlation can be reduced to the following formula with a good approximation:

$$R\% = -17.25C^2 + 631.73C + 75.55 \qquad (7)$$

The statistical data for both proposed models are reported in Table 6. As can be observed, the mean data for MEG conversion and EDGA selectivity were 86.89% and 58.80%, respectively, and the R^2 value for both models was more than 90%, indicating acceptable accuracy of suggested linear and second-order models. A difference of less than 0.2 between the predicted correlation coefficient (Predicted-R^2) and the adjusted correlation coefficient (Adjusted-R^2) proves the reliability of the models. The ratio of the standard error to the mean value of the response observed as a percentage determines the coefficient of variance (*CV*), which means the reproducibility of the model. A model can be considered reproducible if its *CV* is less than ten based on a general rule of thumb [19]. The *CV* values for MEG conversion and EGDA selectivity were 3.33 and 8.02, confirming the logical reproducibility of the generated models.

Table 6. Statistical parameters of both developed models by RSM modeling for both responses.

Parameter	**Response**	
	Conversion (C%)	**Selectivity (R%)**
Mean	86.89	58.80
CV%	3.33	8.02
Standard Deviation	2.89	4.71
R^2	0.9100	0.9850
Predicted-R^2	0.8615	0.9700
Adjusted-R^2	0.8950	0.8905

Response surface plots

The response surface plots obtained from the interaction effects of the parameters affecting both responses, MEG conversion, and EGDA selectivity, are reported in Figures 7 and 8, respectively. In these plots, two independent parameters are considered variables, while the others are assumed to be constant at one point (usually the center point). As can be seen in both figures, four parameters of reaction time, temperature, AA: MEG molar ratio, and catalyst weight positively affected the rate of both responses. According to Figure 8, the conversion changes dramatically by increasing temperature and reaction time; while increasing the other two parameters, namely the molar ratio of reactants and catalyst content, the conversion variation is relatively small. Also, based on Figure 8, the EGDA selectivity, in contrast to the previous case, increased dramatically by enhancing the catalyst weight and molar ratio of reactants, while changing the temperature and reaction time did not have a significant effect on selectivity; however, they have had a positive impact on its increase.

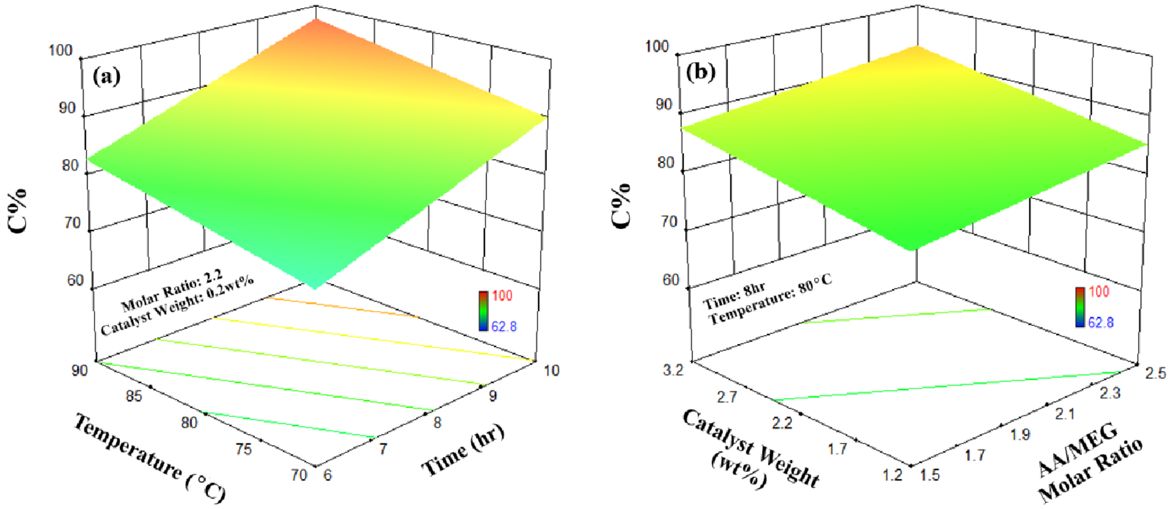


Figure 7. Response surface 3D plots of MEG conversion;(a) the interaction of reaction time and temperature, and (b) the interaction of catalyst weight and molar ratio of reactants.

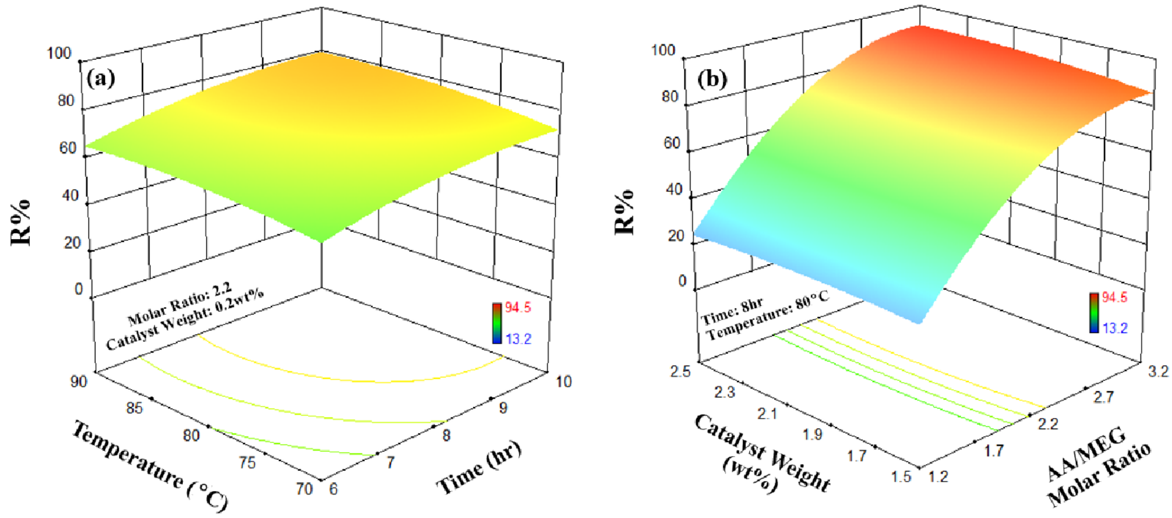


Figure 8. Response surface 3D plots of EGDA selectivity;(a) the interaction of reaction time and temperature, and (b) the interaction of catalyst weight and molar ratio of reactants.

Optimization

As mentioned, the RSM method was employed to optimize the reaction process. The aim was to find the optimal operating conditions by simultaneously maximizing MEG conversion responses and EGDA selectivity. The optimization results of the corresponding reaction are reported in Table 7. Based on the data obtained in the studied operational range, two maximum values of 100% and 94.72% for conversion and selectivity were achieved at 9.5 hr, the temperature of 90°C, AA: MEG molar ratio of 2.92, and catalyst weight of 2 wt%.

Table 7. Optimization results of RSM modeling to maximize both responses under the studied range of operation.

Parameter	Limit	Unit	Objective	Optimum value
Reaction time	4-12	hr	in range	9.5
Reaction Temperature	60-100	°C	in range	90
AA: MEG ratio	0.2-4.2	molar	in range	2.92
Catalyst weight	1-5	wt%	in range	2
Conversion	62.8-100	%	Maximize	100
EGDA selectivity	13.2-64.5	%	Maximize	94.72

Catalyst reusability

The catalyst reusability was examined by checking the variation of MEG conversion after employing the catalyst in the reaction for four cycles. Figure 9 depicts the results of catalyst reusability in terms of MEG conversion. All experiments were repeated three times, and the reported data is the average value. An approximately 10% reduction in the MEG conversion was observed after three times of use, while the highest reduction (of about 20%) is related to the fourth cycle. The decrease in MEG conversion is because of the deactivation of active sites of the catalyst.

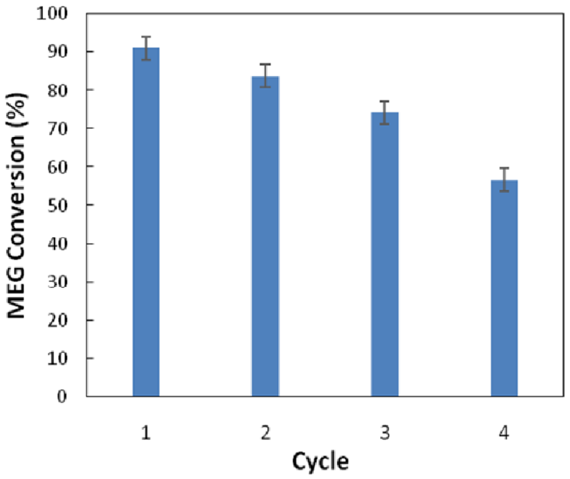


Figure 9. Catalyst reusability after four cycles at the temperature of 90°C, reaction time of 6 hr, and AA:MEG molar ratio of 3.2:1, and catalyst weight of 2.5wt%.

Conclusion

In this study, the esterification reaction of monoethylene glycol (MEG) with acetic acid (AA) with simultaneous water removal from the system was investigated. For the first time, a commercial heterogeneous inhomogeneous titanium (IV) isopropoxide catalyst was used to produce ethylene glycol monoacetate (EGMA) and ethylene glycol diacetate (EGDA) for faster reaction development in a reactive batch system. Four influential operating parameters, such as reaction time, temperature, molar ratio reactants, and catalyst weight, were considered to design the experiment by response surface methodology (RSM). MEG conversion and EGDA selectivity were selected for modeling and optimization. The results showed that increasing all four parameters increases both responses in the considered operating range. However, changes in the reaction time and temperature had a more significant impact on increasing the conversion, while the other two parameters were two important parameters in enhancing the selectivity of the desired product. Two linear and second-order models were presented for conversion and selectivity, respectively, using the RSM-CCD approach. Also, intending to maximize both responses, the optimal process point was at 9.5 hr, 90°C, 2.92, and 2wt% as reaction time, temperature, AA: MEG molar ratio, and catalyst weight, respectively, in which the MEG conversion and EGDA selectivity were 100% and 94.72%. After using the catalyst four times, the MEG conversion decreased from 91.1% to 56.7%.

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