Optimization of synthesis of dioctyl phthalate using response surface methodology

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Abstract

Esterification reaction of phthalic anhydride with 2-ethyl hexanol was investigated using sulfated titanium dioxide nano catalyst. The influence of reaction time, catalyst amount and alcohol/anhydride molar ratio was studied using a rotatable central composite design (CCD). The optimum values of factors were: 83 min for the time, 9 %wt catalyst, 9:1 alcohol:anhydride molar ratio. The maximum yield of 93% at optimum conditions was obtained.

1. Introduction

Plasticizers are important non-volatile and low molecular substances which are used in the polymer industry [1-3]. Plasticizers are usually synthesized via esterification reaction of corresponding anhydride/acid with alcohol in the presence of acid catalysts.

The optimization of the factors affecting the esterification reactions is usually based on one variable-at-a-time approaches, which facilitate the interpretation of the results obtained, but interactions between variables are not taken into consideration [4, 5]. Consequently, a false value for the factors may be attained, leading to certain conditions in which the combination of the variables is not that which provides the best analytical response. Experimental design methods have been recently applied extensively to optimize the esterification reactions [6-8].

In this study, esterification reaction of phthalic anhydride with 2-ethyl hexanol was studied. Optimization of the variables affecting the reaction such as time of reaction, catalyst amount, and alcohol/anhydride molar ratio was performed by a central composite design (CCD). Products of reactions were analyzed using gas chromatography.

2. Results and discussion

2.1. Data analysis

Development of a model using central composite design was presented by box and Wilson. In general a CCD for k factors consists of three parts: a factorial design, containing a total of $n_{fact}=2^k$ points, an axial (or star) part, formed by $n_{ax}=2k$ points and finally a total of n_c runs at the center point of the experimental region, where of course, $x_1=x_2=\ldots=x_k=0$.

Response surface methodology (RSM) was used to evaluate the influence of three variables on the yield of dioctyl phthalate. The investigated variables were reaction time (A), catalyst/phthalic anhydride mass ratio (B) and 2-ethyl hexanol/phthalic anhydride molar ratio (C). The levels of the factors were chosen by reviewing previous repots on similar reactions and performing a few trivial experiments. Reaction time, catalyst amount and alcohol:anhydride molar ratio were varied over the following ranges 30-70 min, 4-8 %wt and 4-8, respectively.

Tables 1 and 2 show the levels of factors for the central composite design and the design matrix, respectively.

Table 1
Factors and their levels for central composite design.

Factor	Notation	Level				
		-α	-1	0	1	+α
Time (min)	A	16.36	30	50	70	83.64
Catalyst amount (%wt)	B	2.64	4	6	8	9.36
Molar ratio	C	2.64	4	6	8	9.36

Table 2
Design matrix for central composite design.

Run order	Point type	A	B	C
1	Fact	30	4	8
2	Center	50	6	6
3	Fact	70	4	4
4	Center	50	6	6
5	Fact	70	8	8
6	Center	50	6	6
7	Fact	70	4	8
8	Center	50	6	6
9	Axial	50	6	2.64
10	Fact	30	4	4
11	Center	50	6	6
12	Fact	70	8	4
13	Fact	30	8	4
14	Axial	50	6	9.36
15	Axial	50	9.36	6
16	Center	50	6	6
17	Axial	50	2.64	6
18	Fact	30	8	8
19	Axial	83.64	6	6
20	Axial	16.36	6	6

2.2. Effects of the parameters

The effects of time and molar ratio towards diester's yield can be seen in Fig.1.
These two effects show a positive influence on the yield of diester. The yield of reaction gradually increases from 45% to 80% by increasing the time. It can be seen that time plays a significant role in the yield of the reaction. Since the esterification is a reversible reaction, molar ratio of 2-ethyl hexanol must be in excess to force the reaction towards the diester. In this study, molar ratio of 2-ethyl hexanol was increased from 4 to 8. The highest yield of reaction was obtained at alcohol:anhydride molar ratio of 8:1.
The interaction effects of the two parameters on the synthesis of dioctyl phthalate were examined by three dimensional response surface plots (Fig. 2). It is shown that the effect of catalyst amount interacts with the time during the reaction. The initial catalyst's amount has a positive effect on the yield of the reaction.
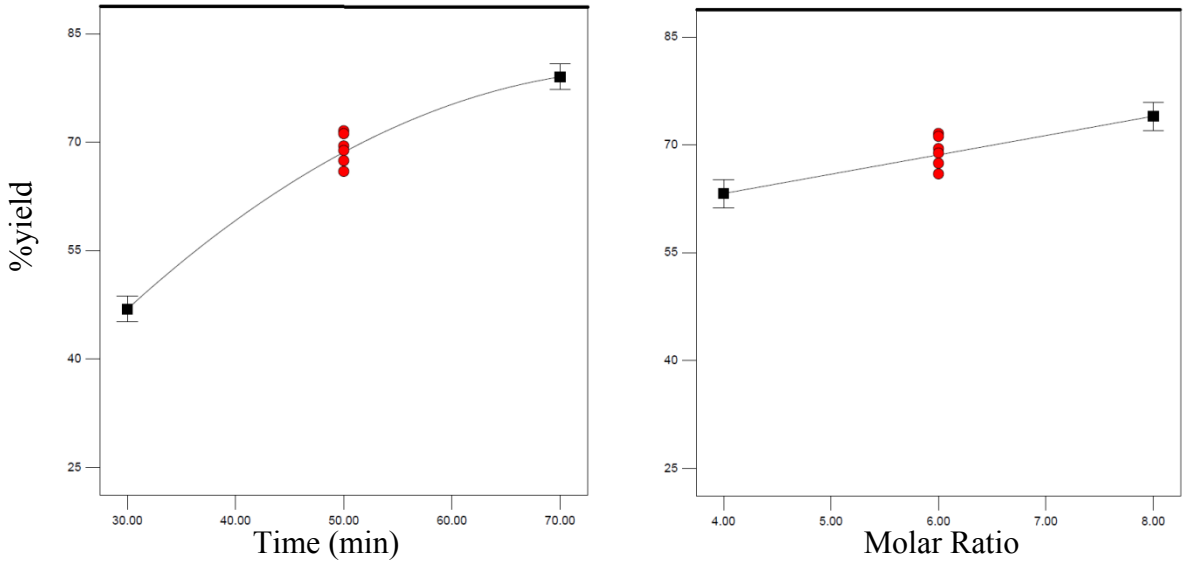
Fig.1. Effect of individual parameters on the synthesis of dioctyl phthalate

Fig. 2 also shows that the parameters of time and catalyst amount interact with each other and the highest value for the yield is due to the largest values for both parameters. In addition, Fig. 2 shows that there is a logical relation between the molar ratio and the time influencing the reaction yield. The reaction yield will increase by increasing the parameters of molar ratio and time.
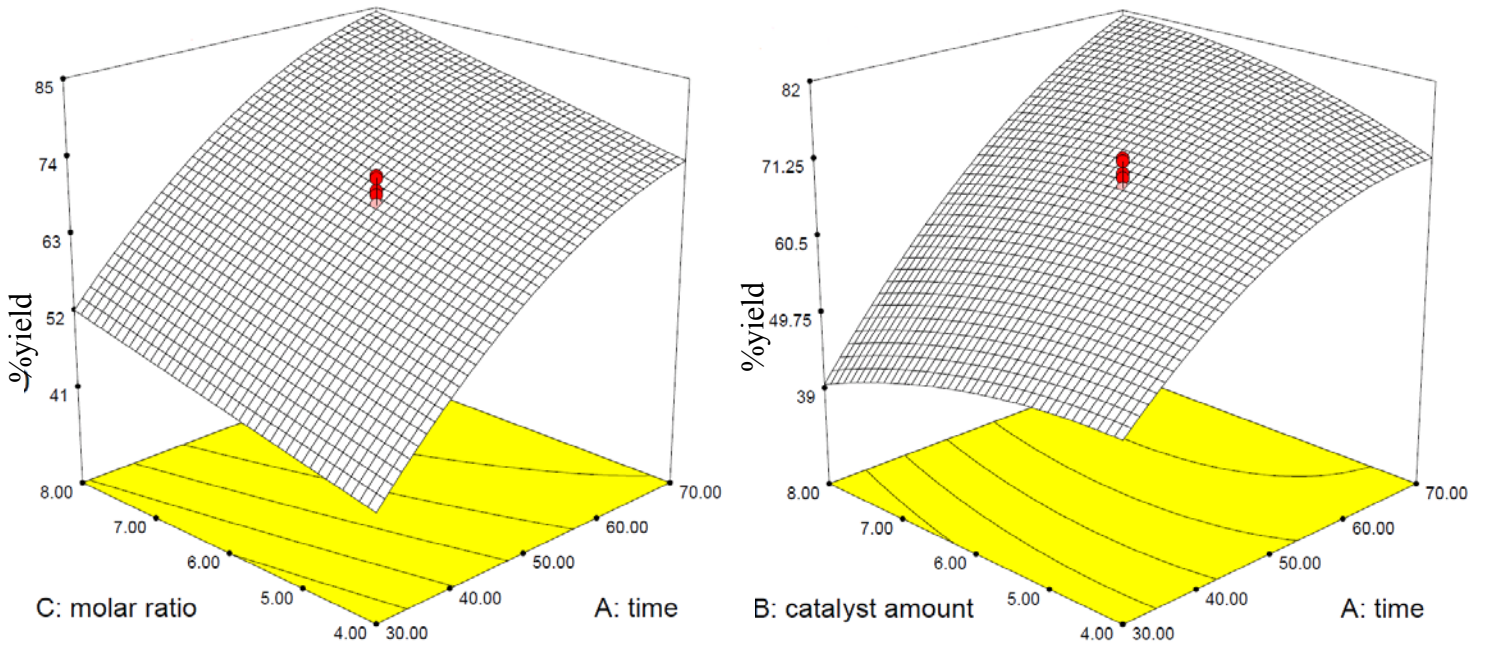

Fig. 2. Response surface plot showing the interaction between the variables

2.3.   Optimization of reaction condition

The optimized values for the parameters affecting the yield of the esterification reaction were determined by using the Design-Expert 7.0.0, trial version, software. The optimized values obtained for the factors were as following: 83 min for time, 9 (%wt) for catalyst amount and 9 for 2-ethyl hexanol/phthalic anhydride molar ratio. The esterification reaction was performed using the optimum values of the factors and the yield of 93.7% was obtained. This value is in agreement with that predicted with the CCD model.

3. Conclusion

In this study, catalytic synthesis of dioctyl phthalate was optimized by using the factorial based method of the CCD. The influences of three factors of catalyst amount, molar ratio of 2-ethyl hexanol to phthalic anhydride and the time on the synthesis of dioctyl phthalate were studied. It is shown that the time and substrate molar ratio play a significant role on the improvement of the yield of the synthesis of dioctyl phthalate. Time and molar ratio show a positive effect on the yield of the reaction. It is also shown that the parameters of catalyst amount and time interact with each other.

4. Experimental

Esterification reaction

The estrification reactions were carried out under solvent free condition in a 10 mL round bottom flask equipped with a reflux condenser, dean stark trap, and magnetic stirrer. Certain amounts of phthalic anhydride and 2-ethyl hexanol, in presence of different amounts of catalyst were placed in the flask. The mixture was stirred and heated at 170 $^{\circ}$C in an oil bath for an appropriate time. After filtration to remove the catalyst, the products were analyzed by using FID-Gas chromatography. GC chromatograms were recorded on a Shimadzu 2010 instrument and n-dodecane was used as an internal standard.

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