Synthesis of dipropylene glycol: Optimization of operating condition through a statistical technique

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Introduction

The dipropylene glycol (DPG) is one kind of fine chemicals that was used to synthesize the plasticizers dipropylene glycol dibenzoate (DPGDB) [1] and widely used as solvent due to its ether bond and hydroxyl group, respectively [2]. Moreover, it is a component of many widely used commercial products such as antifreeze, air fresheners, cosmetic products, chemical intermediates and plastics [3].

The mostly convenient and industrial feasible method for synthesis DPG is through the reaction called O-alkylation [4] of propylene oxide (PO) with 1, 2-propanediol (1, 2-PDO) over catalysts [5, 6]. Unfortunately, the main source of DPG is as the by-product in the process of producing 1, 2-PDO, and few studies have reported about the synthesis of DPG.

In this paper, a secondary amine [3] was selected as the catalyst for the synthesis of DPG and the effects of five operating parameters (reaction time, pressure, temperature, mol ratio of material and the amount of catalysts) were studied using orthogonal design experiment to find the optimal condition.

Experimental

Materials and Apparatus

1,2-propanediol, propylene oxide and organic amine, analytical grade pure, purchased from Shanghai chemical regents company, were dried by magnesium sulfate before use.

High pressure kettle and temperature controller were used in the process. The qualitative analysis and quantitative analysis were carried out by Agilent 6820 gas chromatograph.

Orthogonal experiment

Based on our previous work, an orthogonal array experiment with variation of five experimental parameters is constructed without considering their mutual interactions. Each parameter has four selected levels and the level covered a broad range (Table 1). In Table 1, A, B, C , D, E indicate the Reaction Temperature (K), the Reaction Pressure (gauge pressure/ atm), the Reaction Time (min), the Mol ratio of material ($n_{mol} = N_{PDO} / N_{PO}$), and the Amount of Catalysts ($n'_{mol}=N_{Cat} /N_{PO}$), respectively.

Table 1 Experimental variables: factors and levels

Level	Factors				
	A:T(K)	B: Pressure (atm)	C: Time (min)	D: Material ratio (n_{mol})	E: Catalysts dose (n'_{mol})
1	330	1.0	50	2.0	0.01
2	350	2.0	70	1.5	0.04
3	370	3.0	90	1.0	0.07
4	370	4.0	110	0.5	0.10

Table 2 Design matrix and measured response of each designed experiment

Run no.	A	B	C	D	E	Yield (%)	Selectivity (%)
1	1	1	1	1	1	1.58	70.16
2	1	2	2	2	2	2.57	80.11
3	1	3	3	3	3	2.51	82.40
4	1	4	4	4	4	9.63	86.03
5	2	1	2	3	4	23.16	85.93
6	2	2	1	4	3	16.66	86.32
7	2	3	4	1	2	19.84	85.53
8	2	4	3	2	1	7.13	84.05
9	3	1	3	4	2	33.85	86.59
10	3	2	4	3	1	4.85	84.92
11	3	3	1	2	4	32.26	85.75
12	3	4	2	1	3	37.66	85.82
13	4	1	4	2	3	33.17	85.64
14	4	2	3	1	4	35.97	85.42
15	4	3	2	4	1	15.13	84.34
16	4	4	1	3	2	21.20	84.89

Results and Discussion

Analysis of experimental data

Each variable (each factor) was tested at four levels and the level covered a broad range (Table 1). The factorial design led to a total of 16 experimental runs listed in Table 2, which comprised of five columns and sixteen rows constructed. From the Analysis of Range (Table 3), we can get the information as followings: 1) the order of the factor's effect on DPG yield and selectivity were A> E> D> B> C and A >E >D > C> B, respectively. 2) the optimal levels of design parameters about DPG yield and selectivity were A3, B4, C3, D1, E4 and A3, B4, C4, D4, E4, respectively.

Table 3 Results of the DPG Range Analysis

	Yield (%)				
	A	B	C	D	E
K 1	4.072	12.940	17.925	23.762	7.173
K 2	16.697	15.012	19.630	18.782	19.365
K 3	27.155	17.435	19.865	12.930	22.500
K 4	26.367	18.905	16.873	12.817	25.255
R	23.083	7.928	2.992	10.832	18.082
	Selectivity (%)				
	A	B	C	D	E
K 1	79.675	82.080	81.780	81.733	80.868
K 2	85.457	84.193	84.050	83.888	84.280
K 3	85.770	84.505	84.615	84.535	85.045
K 4	85.073	85.197	85.530	85.820	85.783
R	6.095	3.117	3.750	4.087	4.915

Analysis of variance

The test result difference caused by the changes of factor levels or by the mutual interactions and the erroneous fluctuation can't be separated out by range analysis, through the analysis of variance, from it the information about which process parameter is statistically significant can be got, was introduced.

Table 4 The results of Variance Analysis about DPG yield

Sym-bol	Para-mete r	SS	d. f.	$F_{0.05}$ (3, 3)	F_I	Signi f-icant
A	T (K)	1392.748	3	57.099	9.280	*
B	P (atm)	132.612	3	5.437	9.280	
C	Time (min)	24.392	3	1.000	9.280	
D	Mate -rial ratio	235.512	3	9.655	9.280	*
E	Catal -ysts dose	762.676	3	31.267	9.280	*
Error		24.39	3			

Table 5 The results of Variance Analysis about DPG selectivity

Sym-bol	Para-mete r	SS	d. f.	$F_{0.05}$ (3,3)	F_I	Signi f-icant
A	T (℃)	100. 452	3	4.640	9.28 0	
B	P (atm)	21.6 49	3	1.000	9.28 0	
C	Time (min)	30.5 99	3	1.413	9.28 0	
D	Mate -rial ratio	35.0 11	3	1.617	9.28 0	
E	Catal -ysts dose	56.6 41	3	2.616	9.28 0	
Error		21.6 5	3			

Conclusion

From the laboratory scale production, the factors on the synthesis of the DPG were studied using the orthogonal experiment design and some conclusions can be drawn as following:

1. The optimal condition for the synthesis of dipropylene glycol is: 370K, 1atm, 90min, 1:1 mol ratio of PDO to PO, addition 0.06 mol catalyst to PO.
2. The order of importance for the several factors studied on dipropylene glycol yield and selectivity are T (K)> n'_{cat} > n_{mol} > P (atm)> T (min) and T (K) > n'_{cat} > n_{mol} > T (min)> P(atm), respectively.
3. The parameters that reaction temperature, mol ratio of material and the amount of catalysts gave more significant on dipropylene glycol yield, and all parameters had in significant effect on dipropylene glycol selectivity.

Reference

(1) Zhang, W. Y. Wang, H. Wei, W. Sun, Y.H. (2005). Solid base and their performance in synthesis of propylene glycol methyl ether, J. Mol. Catal. A. Chem. 231, 83-88.

(2) Opdyke, D.L. (1978). Fragrance rawmaterials monographs: Dipropylene Glycol, Food Cosmet Toxicol, 16, 729–730.

(3) Staples, C. A. Davis, J. W. (2002). An examination of the physical properties, fate, ecotoxicity and potential environmental risks for a series of propylene glycol ethers, Chemosphere, 49, 61-73.

(4) Zhou, Q. F. Ma, H. Z. Wang, B. Fan, F. (2007). Degradation of methylene blue: Optimization of operating condition through a statistical technique and environmental estimate of the treated wastewater. J. Hazard. Mater, 153,44-51.

(5) Zhang, X. H. Zhang, W. Y. Li, J. P. Zhao, N. Wei, W. Sun, Y. H. (2007). Synthesis of propylene glycol methyl ether over amine modified porous silica by ultrasonic technique, Catal. Commun., 8, 437-441.

(6) SEXTON, A.R. BRITTON, E.C. (1953). Synthesis and Identification of Dipropylene Glycol Isomers, Org. Syntheses, 4357-4358.