Mathematical Planning for Revealing Optimal Synthetic Conditions of Naphthalene Chloromethylation

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Abstract −Chloromethylnaphthalene is a valuable compound for obtaining of the plant growing stimulator−−napthylacetic acid. Chloromethylation of naphthalene by paraformaldehyde in the presence of glacial acetic acid, phosphoric and hydrochloric acids at temperature 80−85C and duration − 6 hours the −chloromethylnaphthalene yield was 55−57%. Using Box−Wilson method for mathematical planning of experiment carried out optimization of its synthesis for purpose increasing −chloromethylnaphthalene yield. Preliminary, one − factor experiments were carried out for selecting independence main parameters influencing on the synthesis. A full factor experiment of 23 with extended matrix of planning was used for optimization. Aiming to increase the −chloromethylnaphthalene yield, the obtained mathematical model was used for program of sharp raising on the reply surface. The received optimal conditions for the −chloromethylnaphthalene synthesis were selected as following: molar ratio of naphthalene − parapfsormaldehyde of 1 : 2 temperature − 105C duration of the reaction − 3 hours. The yield of −chloromethylnaphthalene under these optimal conditions was 75 %.

It is known that -chloromethylnaphthalene is a valuable compound for obtaining of the plant growing stimulator − -napthylacetic acid [1, 2]. So, development of technological scheme of its obtaining has a practical interest. From literature it is also known [3] that at chloromethylation of naphthalene by paraformaldehyde in the presence of glacial acetic acid, phosphoric and hydrochloric acids at temperature 80−85C and duration − 6 hours the -chloromethylnaphthalene yield was 55−57%. We investigated the synthesis of this compound too [4].

Aiming to increase the -chloromethylnaphthalene yield we have carried out the process optimization of its synthesis by Box-Wilson [5] method for mathematical planning of experiment. Preliminary, one −factor experiments were carried out for determination of the product yield in dependence on molar ratio of naphthalene − paraformaldehyde, temperature and duration of the reaction.

The reaction performed at 85C, during 6 hours with changing of the molar ratio of

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Table 2. Planning matrix and experiment results

N	x0	x1	x2	x3	x1x2	x1x3	x2x3	x1x2x3	y1	y2	$\bar{y}$	S2	y	$(\bar{y}-y)2$
1	+	−	−	−	+	+	+	−	46.0	47.4	46.7	0.98	46.6	0.01
2	+	+	−	−	−	−	+	+	50.0	51.6	50.8	1.28	52.2	1.96
3	+	−	+	−	−	+	−	+	63.3	63.1	63.2	0.02	64.6	1.96
4	+	+	+	−	+	−	−	−	73.0	77.0	75.0	8.00	74.8	0.01
5	+	−	−	+	+	−	−	+	60.8	62.2	61.5	0.98	61.6	0.005
6	+	+	−	+	−	+	−	−	67.8	70.1	68.7	3.92	67.2	2.25
7	+	−	+	+	−	−	+	−	50.1	52.3	51.2	2.42	49.7	2.102
8	+	+	+	+	+	+	+	+	58.9	61.1	60.0	2.42	60.0	0.001

naphthalene − paraformaldehyde from 1:1,4 up to 1:2 shows the -chloromethylnaphthalene yield's increase. At molar ratio of naphthalene − paraformaldehyde equal 1:2 the product yield reaches 68,7%.

At temperature increasing up to 105C and duration 3 hours, at the same molar ratio the -chloromethylnaphthalene yield was equal to 75%. Prolongation of the reaction period up to 6 hours led to decrease of the product yield. The -chloromethylnaphthalene yield's decrease was observed at temperature 85, 90, 95, 100 and 105C, at fixed duration of the process.

For study of the influence of the reaction period on the -chloromethylnaphthalene yield we have chloromethylated naphthalene at molar ration naphthalene − paraformaldehyde of 1:2, temperature 85C and the final product was obtained after 4, 6, 8, 12, 16, 20, 24 hours. We found that the maximal yield of the -chloromethylnaphthalene was observed at 6 hours of duration.

On the base of the preliminary experiment results it was found out that the

main factors influencing on the process of the naphthalene chloromethylation are: x1 – molar ratio naphthalene – paraformaldehyde, x2 –reaction temperature (C), x3 – duration (hours) (Table 1).

Table 1. Factors and interval of variation

Factors	Variation level			Variation interval
	−1	0	+1	
x1	1.4	1.7	2.0	0.3
x2	85	95	105	10
x3	3	4.5	6	1.5

A full factor experiment of 23 with extended matrix of planning was used for optimization. The order of experiments was carried out according to the planning matrix and obtained results are shown in Table 2.

Calculation of statistical analysis (G0,95(1,8)=0.6798, Gexp.=0.3996; S2rep.=2.5; S2adq.=5.53; t0.05(8)=2.31; F0.95(5,8)=3.7; Fexp=2.21) showed that recieved model adequation, because of Fexp<Ftable. A regression equation of the first order was obtained from the results (Table 2) by the known method.

$$y=59.64+3.98x1+2.71x2+0.71x3+1.16x12 +0.0125x13-7.46x23-0.76x123 \quad (1)$$

Estimating of significance of the equation coefficients (1) by the Student's criteria the mathematical model (2) of the process has been deduced.

$$y=59.64+3.98x1+2.71x2-1.16x12-7.46x23 \quad (2)$$

Aiming to increase the -chloromethylnaphthalene yield, we have used the obtained equation for program of sharp raising on the reply surface. In the process of working of the sharp raising program we have changed the molar ratio of naphthalene – paraformaldehyde (x1) and reaction temperature (x2). The values in 5 time lower than multiplication of bjxj, were taken as step, and at this condition we have obtained:

b1x1=3,980,3=1.194 step=0.238≅0.25

b2x2=2,7110=27.1 step=5.42≅5.0C

The program of sharp raising didn't give the increase of the reaction product and the best result was obtained in the experiment N4.

Thus, the optimal conditions for the -chloromethylnaphthalene synthesis are the following:

– molar ratio of naphthalene – paraformaldehyde of 1:2

– temperature – 105C

– duration of the reaction – 3 hours.

References.

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