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MODELLING OF m-CRESOL ISOPROPYLATION FOR OBTAINING n-THYMOLS

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ABSTRACT

A theoretical model of the reaction of m-cresol isopropylation to n-thymol has been fitted, using a sequential response surface method. The model quality was assessed by comparing the predicted values of the outcome of the reaction and the observed values from the experimental design. So the data obtained from the theoretical models were in good agreement with the experimental ones because the residues (difference between predicted values and experimental values) were less than the double of experimental standard deviation. According to the theoretical models the optimum value for the desired product (n-thymol) was 67 % with an error of 4.4%.

Key words: modelling, experimental design, thymol synthesis, response surface method.

INTRODUCTION

In a previous work (Yao et al., 2000), a non-selective isopropylation reaction of m-cresol to n-thymol has been optimized using the simplex method (Porte et al., 1984). It was shown that a best compromise between the n-thymol selectivity and the m-cresol conversion could be obtained when the reaction occurs under optimum condition (Temperature = 280 °C, catalyst; $Fe_2(SO_4)_3/\gamma\text{-}Al_2O_3$, molar ratio of propylene/m-cresol = 0.5 and 10 g of quartz powder). In prospect of industrial application of the process, it is interesting to fit a theoretical model of the reaction using a sequential response surface method (Feinberg, 1996; Plackett and Burmann, 1946; Deming, 1983). This method allows to make a quantitative study of different responses as a function of criteria, and to test the estimated quality of each model. The m-cresol isopropylation leads to n-thymol, m-thymol, 4,6-diisopropyl-3-methylphenol, p-thymol, 2-isopropyl-3-methylphenol and is shown in figure 1.

EXPERIMENTAL METHODS

Variables and design

The different variables of the reaction were molar ratio of propylene/m-cresol (X_3) and the mass of the catalyst (X_4). X_3 and X_4 were coded variables and the corresponding real variables were U_3 and U_4. The Responses studied were selectivity (S_2, S_3, S_4, S_5) respectively of n-thymol, m-thymol, 4,6-*diiso*-propyl-3-methylphenol, p-thymol and m-cresol conversion (T_1)

The experimental design used was a composite matrix that was a first order polynomial model (Feinberg, 1996; Plackett and Burmann, 1946; Deming, 1983,). This model was generally adequate to describe phenomenon in a small experimental field. The model equation was the following:

$$Y = b_0 + \Sigma b_i X_i + \Sigma b_{ij} X_i X_j + \Sigma b_{ii} X_i^2$$

Y: The response studied (a selectivity for instance)

b_0: the medium effect, b_i: the first order effect of variables

b_{ij}: interaction effect of variables, b_{ii}: the second order effect of variables

General procedure

All reactants were appropriately distilled and degassed prior to use.

The reaction was carried out under fixed flow of nitrogen (15 ml/min) and propylene in a tubular reactor, heated by a regulated electronic oven. The reaction temperature was set at 280 °C. A fixed flow of m-cresol was introduced in the

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Table 1: Composite matrix

Trials	1	2	3	4	5	6	7	8	9	10	11
X_3	-1.00	+1.00	-1.00	+1.00	-1.41	+1.41	0.00	0.00	0.00	0.00	0.00
X_4	-1.00	-1.00	+1.00	+1.00	0.00	0.00	-1.41	+1.41	0.00	0.00	0.00

X_3, molar ratio of propylene/m-cresol in coded value: -1,41; -1; 0; +1; +1,41.
X_4, catalyst mass in coded value: -1,41; -1; 0; +1; +1,41.

Table 2: Experimental design and results obtained for selectivities (S_i) and conversion (TT_1)

Trials	U_3	U_4/g	S_2/%	S_3/%	S_4/%	S_5/%	TT_1/%
1	0.50	1.50	69.5	02.7	04.6	17.5	06.0
2	1.00	1.50	62.6	06.3	09.2	14.0	20.2
3	0.50	3.00	70.0	08.3	04.3	14.1	12.5
4	1.00	3.00	58.4	08.6	12.2	12.9	**38.2**
5	0.40	2.25	60.8	09.1	07.7	15.0	23.4
6	1.10	2.25	62.7	05.5	05.6	17.9	11.1
7	0.75	1.19	59.2	14.9	07.2	12.0	32.7
8	0.75	3.31	62.9	09.4	08.9	12.7	27.8
9	0.75	2.25	63.2	10.0	06.5	14.6	20.9
10	0.75	2.25	65.1	11.5	07.0	11.9	24.1
11	0.75	2.25	65.5	11.6	05.5	13.0	13.9

U_3, molar ratio of propylene/m-cresol in real value: 0.40; 0.50; 0.75; 1.00; 1.10.
U_4, catalyst mass in real value: .1.19 g; 1.5 g; 2.25 g; 3.00 g; 3.31 g.

Table 3: Computed coefficients of the theoretical models

Coefficients	S_2	S_3	S_4	S_5	TT_1
b_0	64.60	11.00	6.30	13.20	19.60
b_3	-2.00	-0.15	1.19	-0.80	2.69
b_4	0.19	0.02	0.64	-0.44	2.23
b_{33}	-0.49	-2.68	0.22	1.70	-2.14
b_{44}	-0.84	-0.25	0.92	-0.35	4.14
b_{34}	-1.18	-0.83	0.83	0.58	2.95

Table 4: Experimental standard deviation of different models

σ_{S2}/%	σ_{S3}/%	σ_{S4}/%	σ_{S5}/%	σ_{TT1}/%
4.4	3.6	2.5	1.9	11.2

reactor with a syringe pump. The mixture propylene and m-cresol passed through a fixed bed of catalyst (figure 7). The crude reaction products were cooled in ice batch, diluted in diethylether and analysed by gas chromatography with a GIRDEL capillary column OV 1701, 25 m x 0.32 mm, immobilized phase. A flame ionisation detector was used in the following conditions:

Temperature programming 70 °C – 180 °C with 2 °C/min
Nitrogen pressure = 0.8 atm, Hydrogen pressure = 1.0 atm, Air pressure = 0.8 atm.

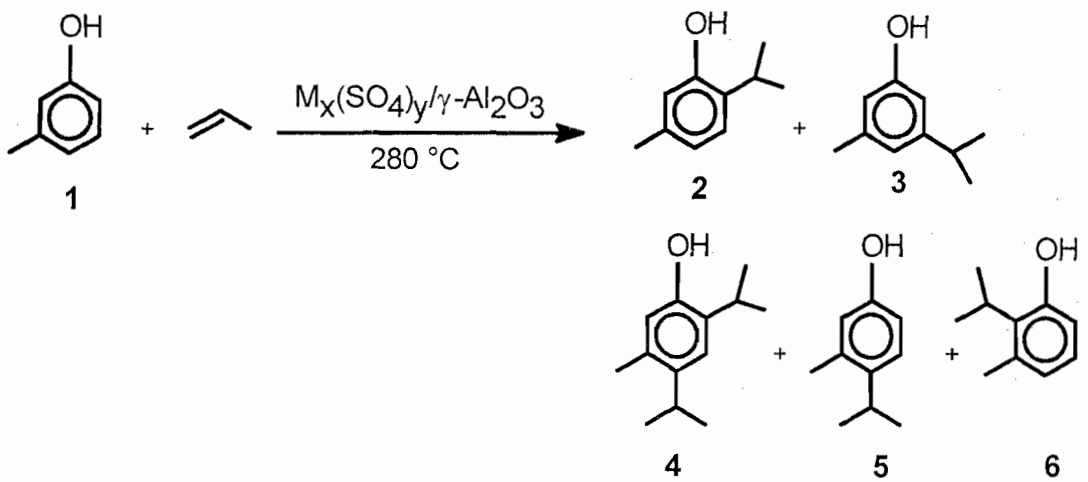
The internal standard used was *p-tert*-butylphenol and the catalyst was synthesized according to the procedure developed in the literature (Thor and Fumio, 1977).

Calculations

All the coefficients (b_o, b_i, b_{ij}, b_{ii}) were computed by the least square method (Phan and Mathieu, 1990). The coded variables X_3 and X_4 and the corresponding real variables U_3 and U_4 were determined from the following equation:

$$U_{ij} = U_{0j} + X_{ij}\Delta U_j$$

X_{ij}: coded variable j for experiment i, U_{ij}: value of real variable j for the i^{th} experiment



1: m-cresol; 2: n-thymol; 3: m-thymol; 4: 4,6-diisopropyl-3-methylphenol; 5: p-thymol; 6: 2-isopropyl-3-methylphenol
Figure 1 – Isopropylation reaction of m-cresol

Table 5: Test of different models Quality

Trials	$S_{2\ exp.}$ (%)	$S_{2\ calc.}$ (%)	$S_{3\ exp.}$ (%)	$S_{3\ calc.}$ (%)	$S_{4\ exp.}$ (%)	$S_{4\ calc.}$ (%)	$S_{5\ exp.}$ (%)	$S_{5\ calc.}$ (%)	$TT_{1\ exp.}$ (%)	$TT_{1\ cal.}$ (%)
1	69.5	63.9	02.7	07.4	04.6	06.5	17.5	15.6	06.0	19.6
2	62.6	62.3	06.3	08.8	09.2	07.2	14.0	14.3	20.0	19.1
3	70.0	66.6	08.3	09.1	04.3	06.1	14.1	13.6	12.5	18.2
4	58.4	60.3	08.6	07.1	12.2	10.1	12.9	14.6	38.2	29.5
5	60.8	66.4	09.1	05.9	07.7	05.1	15.0	16.7	23.4	11.6
6	62.7	60.8	05.5	05.5	05.6	08.4	17.9	16.5	11.1	19.1
7	59.2	62.6	14.9	10.5	07.2	07.3	12.0	13.1	32.7	24.7
8	62.9	63.2	09.4	10.5	08.9	09.1	12.7	11.8	27.8	31.0
9	63.2	64.6	10.0	11.0	06.5	06.3	14.6	13.2	20.9	19.6
10	65.1	64.6	11.5	11.0	07.0	06.3	11.9	13.2	21.4	19.6
11	65.5	64.6	11.6	11.0	05.5	06.3	13.0	13.2	13.9	19.6

Exp., experimental value; Calc., calculated value

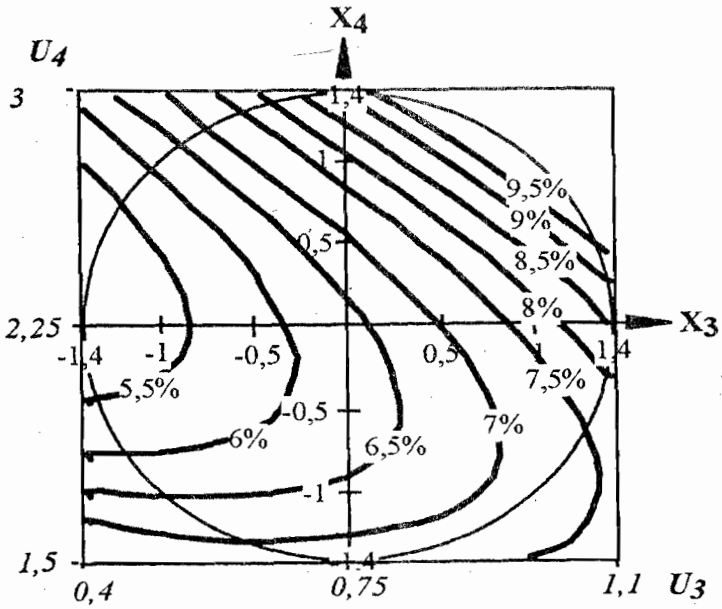


Figure 2 – Variation of n-thymol selectivity (S_2) as a function of molar ratio of propylene/m-cresol and catalyst mass

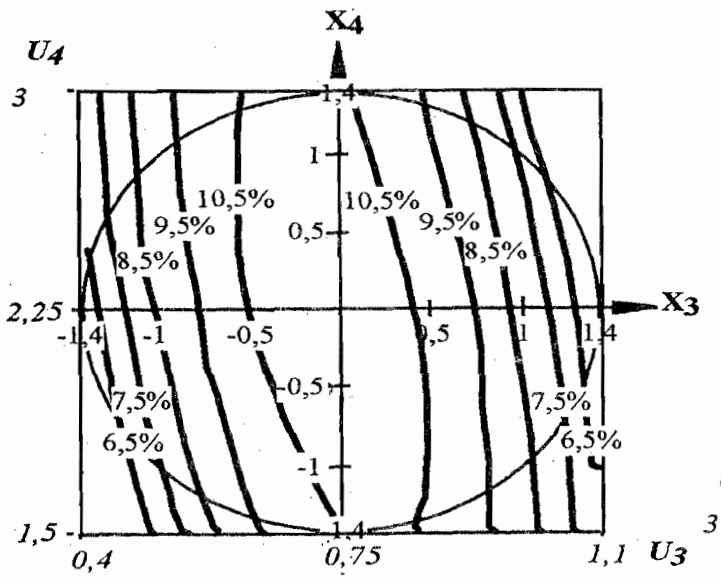


Figure 3 – Variation of m-thymol selectivity (S_3) as a function of molar ratio of propylene/m-cresol and catalyst mass

U_{0j}: value of the variable j in the experimental field centre, ΔU_j: half of the variation between maximum and the minimum value of the real variable.

The values of the studied responses were computed according to the following equations:

$$S_i = 100n_i/\Sigma n_i$$

$$TT_1 = 100\Sigma n_i/(n_1 + \Sigma n_i)$$

$$n_i = t_i/M_i$$

n_1 and n_i were respectively converted m-cresol mole number and compound i mole number in relation to 100 g of crude reaction mixture isolated, t_i was the chromatographic mass percentage and M_i the molar mass of compound i.

The experimental standard deviation σ was computed with the following formula:

$$\sigma_{Si}^2 = \Sigma (Y_{iexp} - Y_{icalc})^2/(n - p)$$

n: experiments number, p: coefficients number, n-p: degrees of freedom

RESULTS AND DISCUSSION

The composite matrix and the results are given in tables 1, 2, and 3. Table 4 and 5 illustrate respectively the experimental standard deviation and the comparison of the experimental and the theoretical value of the different models.

In this kind of problem, the discussion does not concern the meaning of coefficients but the quality of the model. So for each measured response, the experimental values (Y_{iexp}) and the calculated values (Y_{icalc}) are compared. The difference between these values is called residues. If the residues obtained are less or equal to the double of the experimental standard deviation ($2\sigma_{exp}$), the fitted model can be considered suitable.

It is noticed that the residues are generally less than 2σ. So the different models are suitable and can be used to anticipate the experimental responses when the reaction occurs. Therefore, it is important to be careful in the use of the conversion model. In fact the determination of the m-cresol conversion is less accurate than selectivities that are directly obtained from GC, while conversion is obtained without taking into consideration cooking and hold-up phenomena.

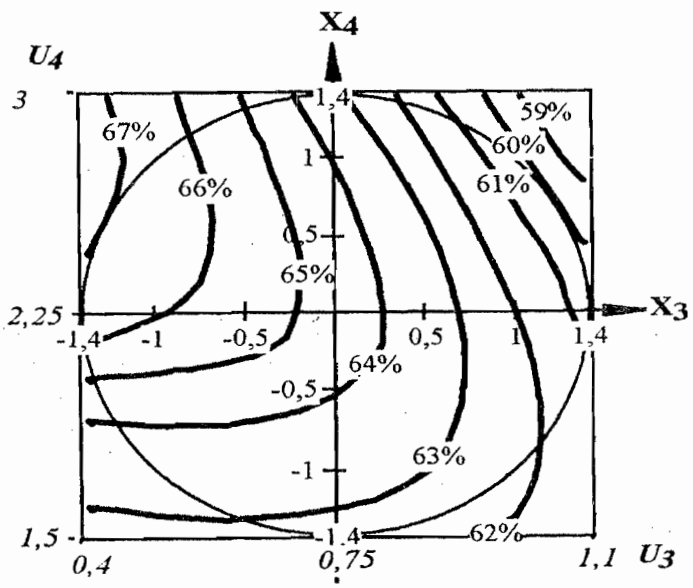


Figure 4 – Variation of 4,6-diiso-propyl-3-methylphenol selectivity (S_4) as a function of molar ratio of propylene/ m-cresol and catalyst mass

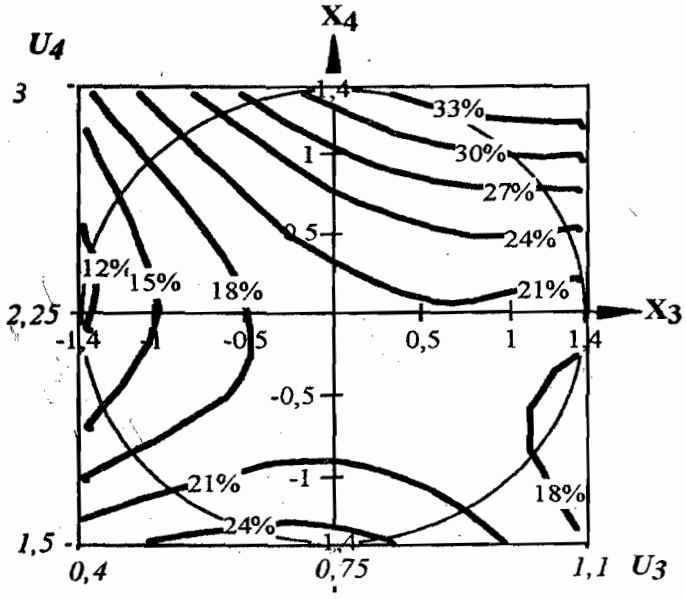


Figure 5 – Variation of p-thymol selectivity (S_5) as a function of molar ratio of propylene/m-cresol and catalyst mass

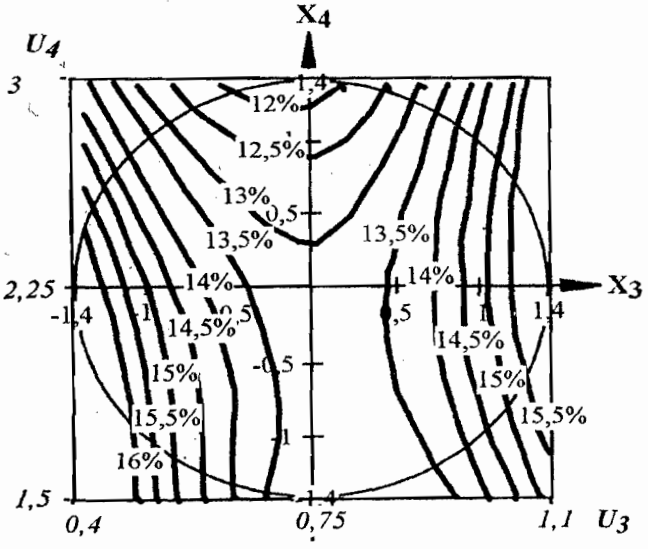


Figure 6 – Variation of m-cresol conversion (TT_1) as a function of molar ratio of propylene/m-cresol and catalyst mass

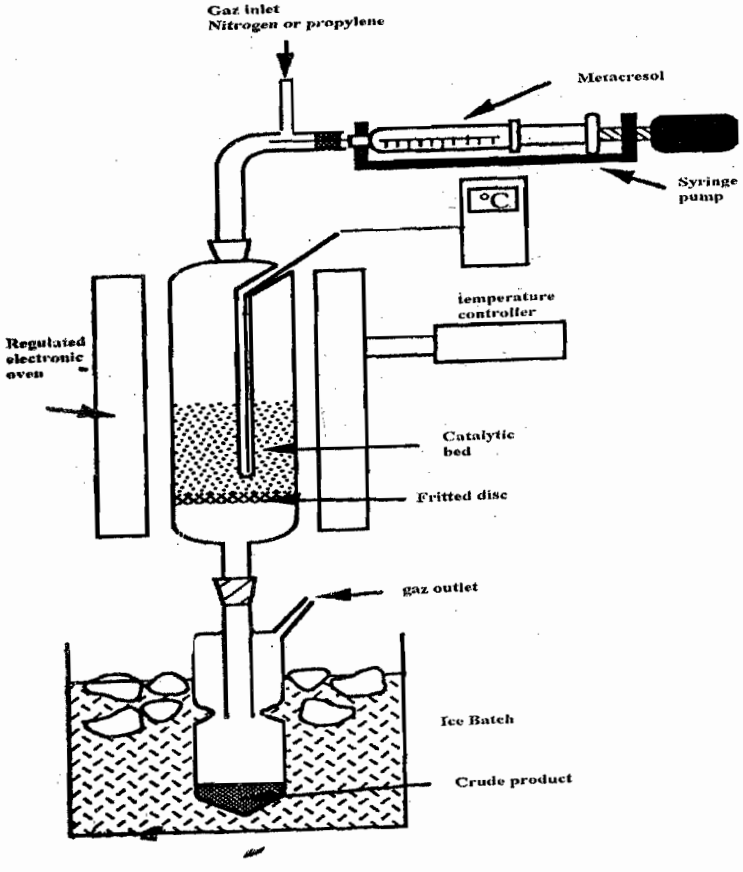


Figure 7 – Experimental arrangement scheme

At the end it is possible to give the cartography of each response as a function of catalyst mass and molar ratio of propylene/cresol (figures 2, 3 4, 5 and 6).

According to theses figures, the following remarks can be made:

-The selectivity S_2 of n-thymol depends essentially on molar ratio of propylene/ m-cresol when catalyst mass U_4 is less than 2.25 g. The optimum value of S_2 is 67 %.

-The selectivity of m-cresol S_3 depends only on the molar ratio U_3. The optimum is 10 %. While the selectivity of 4,6-*diiso*-propyl-3-methylphenol S_4 is simultaneously controlled by the two factors.

-The optimum of m-cresol conversion (33%) is obtained when the molar ratio U_3 and the catalyst mass U_4 are at their optimum values. It can be noticed that when the conversion of m-cresol increases, the selectivity of the desired product (n-thymol) decreases on behalf of the other products.

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