STUDIES IN DEALKYLATION— A STATISTICAL ANALYSIS OF PROCESS VARIABLES

G. S. SARMA* AND M. RAVINDRAM

(*Department of Chemical Engineering, Indian Institute of Science, Bangalore*-560012)

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ABSTRACT

A central composite rotatable experimental design was constructed for a statistical study of the vapour phase dealkylation of xylene isomers over a nickel on silica gel catalyst. A second order response surface was generated and the effect of each variable on the system was studied with the help of ridge analysis within the range of experimentation. For all the three systems investigated the effects are compared.

Key words: Dealkylation; Process Variables.

INTRODUCTION

In the study of chemical processes, the behaviour of the system in response to changes in the process variables such as reaction temperature, time factor and feed mole ratio (if the feed consists of more than one reactant) can be established either by one-variable-at-a-time method or by the design of experiments using statistical methods. Experimental designs have obvious advantages in that they furnish with minimum experimentation the effect of each variable and their interaction. Box and Wilson [3], Box and Hunter [2], Davies [6], Hunter [9], Carr [4] amongst others have contributed to the application of statistical techniques in this field. A preliminary study of the system is necessary to plan the experimental designs. This is made use of in the following studies on the dealkylation of isomers of xylene.

Many investigators have studied the kinetics of dealkylation of toluene, xylene isomers and higher homologues of benzene. Maslyanskii and Robinovich [10], Maslyanskii *et al.* [11], [12], [13], Silsby and Sawyer [17], Betts *et al.* [1], Zimmerman and York [22], Weiss and Doelp [18], Weiss [19], Weiss *et al.* [20], Weiss and Friedman [21], Doumani [7], Ravindram [14] have studied the steam and hydro-dealkylation of various hydrocarbons

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* Present Address: Toshniwal Bros. (P.) Ltd., Bombay.

But till now, no attempt was made to establish the range of process variables to be employed with the different reactants.

REACTIONS

The main reactions in the dealkylation of xylene isomers, can be written as :

$$C_6H_4(CH_3)_2 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \quad (1)$$

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \quad (2)$$

Xylene dealkylation is a series reaction. Xylene is dealkylated to benzene, toluene being the traceable intermediate.

EXPERIMENTAL

Apparatus and procedure.—The layout of the experimental set up used for the present work is shown in Fig. 1. It mainly consists of feeding devices for hydrocarbon and hydrogen, preheaters for the reactants, reactor proper and product collection unit.

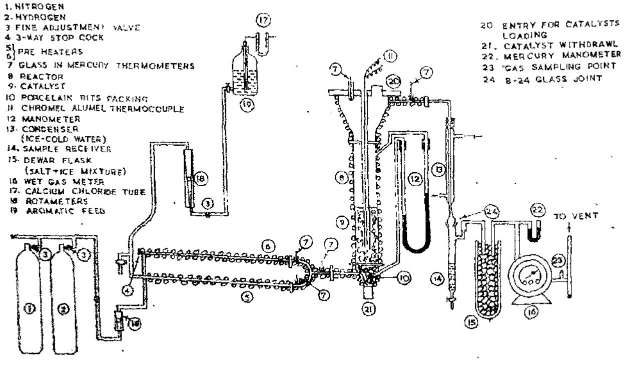

FIG. 1. Layout of apparatus used for dealkylation studies.

Catalyst preparation and properties.—It was pointed out by Maxted *et al.* [14], Schait and Reijm [16] that the method of preparation of a catalyst has considerable influence on its activity and surface area. Thus the method outlined below was followed in preparing Nickel on Silica gel (13% Ni) catalyst in the course of this work. A known amount of the support, *i.e.*, silica gel was soaked in nickel nitrate solution for about 24 hours to ensure a uniform distribution. The supernatant water was evaporated on a steam bath. The wet cake was roasted to nickel oxide, and to ensure total decomposition of nickel nitrate, the catalyst was kept in a muffle furnace for about 6 hours at 450° C. The nickel oxide was reduced *in situ.*

Reduction of the catalyst.—A known amount of catalyst was loaded into the reactor. The reactor and the preheater were maintained at the desired temperature in a flowing nitrogen atmosphere. When the desired temperature was reached (450° C), the nitrogen supply was cut off and hydrogen was passed. The reduction was continued for 5 hours to ensure complete reduction. The properties of the catalyst were:

Catalyst : Nickel supported on Silica gel

Partical size: $-48+65$ Tyler Mesh (0·251 mm).

Surface area: 240 m^2/g.

Apparent density: 1·563 g/cm^3.

Bulk density: 0·92 g/cm^3.

Before starting a run, the preheaters and the reactor were heated to the desired temperature in a flowing stream of nitrogen. After the required temperature was reached, the supply of nitrogen was cut off and predetermined amounts of hydrocarbon and hydrogen were passed. After attaining the steady state a run was conducted for a fixed period of time. After the run, the reactants supply was cut off and the reactor was cooled in a nitrogen atmosphere and was maintained thus till a subsequent run.

Bulk diffusion.—In investigations of this type one should make sure that the data that are collected are in the kinetic region. Bulk diffusion is the main physical factor that is to be eliminated. The investigator can examine this aspect by performing a series of experiments varying the flow rate, keeping the time factor constant. This was done for all the systems that were studied. A known quantity of the catalyst was taken and data were obtained at different time factors (W/F). In the second series the weight of the catalyst was increased by two fold and the experiments were conducted for the same time factors. It was found that the conversion remained the same in both the cases, thereby showing that bulk diffusion is not rate controlling.

EXPERIMENTAL DESIGNS

Dealkylation of xylene isomers was undertaken for a comparitive study of each of the isomers. Three variables, time factor (W/F), feed mole ratio and reaction temperature, were taken to be the three major factors influencing the dealkylation reaction. A second order design like the central composite rotatable design was constructed to develop a response surface to obtain the response of the system. Tables I and II, give the three factors under

TABLE I

Factorial design for m-*xylene and* o-*xylene*

Variable	Coded name	Unit	Coded levels —1·682 (—α)	 —1	 0	 +1	 1·682 (+α)
Time factor (W/F)	X_1 or A	7·5	9·9	15	22·5	30	35·1
Feed mole ratio (hydrogen : hydrocarbon	X_2 or B	1 : 1	2·72 :1	3 : 1	4 : 1	5 : 1	5·7 : 1
Temperature °C	X_3 or C	50	416	450	500	550	584

TABLE II

Factorial design for p-*xylene*

Variable	Coded name	Unit	Coded levels —2 (—α)	 —1	 0	 +1	 +2 (+α)
Reaction temperature	X_1 or A	50	400	450	500	550	600
Time factor	X_2 or B	7·5	7·5	15	22·5	30	37·5
Feed mole ratio	X_3 or C	0·5 : 1	1·5 : 1	2 : 1	2·5 : 1	3 :1	3·5 : 1

study, their actual and coded levels and the defined units. The design consistc of eight experiments forming a complete 2^3 factorial design, supplemented with six experiments at levels ± 1·682 (values of α) of each variable and six deentre points—twenty experiments in all. The complete design is presents in Table III with the experimental observations of each xylene isomer.

TABLE III

Experimental results of complete composite design

Design No.	Treatment	Response Y (% conversion)		
		m-xylene % Total conversion	*o*-xylene % Total conversion	*p*-xylene % Total conversion
1.	(1)	6·5	9·8	21·3
2.	*a*	12·6	14·6	34·5
3.	*b*	7·4	3·1	25·5
4.	*ab*	14·8	9·2	43·3
5.	*c*	20·7	12·0	37·3
6.	*ac*	20·4	16·5	34·5
7.	*bc*	18·0	8·0	46·3
8.	*abc*	11·7	11·7	34·1
9.	α A, 1	16·2	11·7	9·3
10.	α 1, A	26·5	19·3	30·3
11.	α B, 1	8·0	15·8	11·3
12.	α 1, B	13·9	13·0	22·0
13.	α C, 1	15·4	10·7	9·6
14.	α 1, C	34·0	14·0	26·7
15.	Centre	14·3	10·3	18·1
16.	Centre	15·6	12·1	20·1
17.	Centre	13·7	9·4	21·4
18.	Centre	16·0	10·9	16·4
19.	Centre	14·7	11·7	17·1
20.	Centre	13·2	10·5	17·0

RESULTS AND DISCUSSION

From the above data a second order equation of the type :

$$Y = b_0 + \sum_{i=1}^{k} (b_i x_i + b_{ii} x_i^2) + \sum_{1 \leqslant i \leqslant k} b_{ij} x_i x_j \tag{3}$$

can be estimated, where k is the number of factors.

Estimation of the coefficients.—For the three variable central composite design, Cochran and Cox [5] gave simplified equations to estimate the regression coefficients. The coefficients are presented in Table IV.

Regression analysis.—The regression analysis was conducted on the responses. The sum of squares for the first and second order terms are obtained from the general formulae given by Cochran and Cox [5].

TABLE IV

Regression Coefficients

Coefficient	*m*-xylene Total conversion	*o*-xylene Total conversion	*p*-xylene Total conversion	Conversion to Toluene
b0	13·82	10·99	32·92	28·64
b1	1·78	2·34	3·62	2·87
b2	0·12	—1·88	2·67	2·72
b3	4·44	1·70	3·87	3·54
b11	1·28	0·86	—1·47	—1·21
b22	—2·39	0·47	—2·25	—1·85
b33	2·47	—0·25	—1·88	—1·54
b12	—0·61	0·06	—1·51	—0·58
b13	—2·51	0·34	—5·73	—4·42
b23	—1·81	0·41	—0·55	—0·13

The total sum of squares and error sum of squares (from six central points) are computed and the sum of squares for "lack of fit" is obtained by subtraction. The results are presented in Table V. It can be seen from the results that the second order equation adequately fits two systems, namely, *o*-xylene and *p*-xylene, of the three that were studied. Even in the third system, *i.e.*, *m*-xylene, because the error mean sum of squares is having a low value and hence the high variance ratio, the quadratic equation is not adequate. However, the response surface equation can be visualised in a different manner by means of Hoerl's ridge analysis [8].

TABLE V

Analysis of Variance

Source of estimate	*m*-xylene	*o*-xylene	*p*-xylene
First order terms :			
Sums of squares	312·61	161·7	560·7
Degrees of freedom	3	3	3
Mean sums of squares	104·20	53·5	186·9
Second order terms :			
Sums of squares	369·47	16·99	1,936·24
Degrees of freedom	6	6	6
Mean sums of squares	61·57	2·66	3 22·54
Lack of fit :			
Sums of squares	71·09	36·06	31·7
Degrees of freedom	5	5	5
Mean sums of squares	14·21	7·21	6·30
Error :			
Sums of squares	5·77	5·65	18·3
Degrees of freedom	5	5	5
Mean sums of squares	1·15	1·13	3·6
Variance ratio	12·3	6·37	1·7
5% line F-statistic	8·81	8·81	8·81

In ridge analysis, a K-dimensional response surface is visualised as a two-dimensional response. The interpretation of ridge analysis consists mainly in the explanation of several ridges (peaks and valleys) running from the centre of the experimental design to its bounds. This analysis has no bearing on the number of variables. The ridge encountered in the domain of interest is readily generated by Lagrange multipliers. By definition, this utilizes a spherical search method which lends itself readily to experimental designs that are restricted to spherical bounded regions like the Box-Wilson type that was used in the present work. The response equation (3) can be written as

$$Y = bo + (\tfrac{1}{2})\, X^T b + (\tfrac{1}{2})\, \lambda R^2 \tag{4}$$

where λ is the Lagrange multiplier

$$R = \pm \sqrt{X_1^2 + X_2^2 + X_3^2 \ldots X_n^2} \tag{5}$$

and superscript T denotes the transpose of a particular matrix.

Computation of the ridges.—To compute the ridges, one has to:

(*a*) construct the coefficient matrix A

(*b*) augment the diagonal elements with Lagrange multiplier to form the parametric equation of the type:

$$X = -(A - \lambda I)^{-1} b \tag{6}$$

where I is a unit matrix,

(*c*) determine the eigen values (λI) of the coefficient matrix A and arrange them in the decreasing magnitude,

(*d*) assume various λ values as dictated by the eigen values to trace the corresponding maximum, minimum or intermediate ridge, each time computing $(A - \lambda I)^{-1}$ and then X vector from equation (6),

(*e*) compute corresponding R from equation (5).

For the above computations CDC3600 computer was used.

Results.—The canonical forms along with the corresponding eigen values and eigen vectors are presented in Table VI. Based on these eigen values the ridges were calculated following the procedure outlined earlier. These results are presented in Tables VII–X and Figs. 2 to 5. The figures represent the maximum and minimum ridges and the effect of variables at maximum ridge for all the systems. It can be seen that for all the systems the maximum and minimum ridges rise and fall respectively. The effect of tempe-

TABLE VI

Canonical form of the quadratic models

$$Y - Y_m = \lambda_1 Z_1^2 + \lambda_2 Z_2^2 + \lambda_3 Z_3^2$$

where λ s' are the eigenvalues and Zs' are the associated eigen vectors.

m-*xylene* :

$YT = +1{\cdot}8620 = 3{\cdot}2626\ Z_1^2 + 0{\cdot}5134\ Z_2^2 - 2{\cdot}4184\ Z_3^2$
$Z1 = -0{\cdot}6368\ M1 + 0{\cdot}0283\ M2 + M3$
$Z2 = M1 - 0{\cdot}1116\ M2 + 0{\cdot}6399\ M3$
$Z3 = 0{\cdot}0922\ M1 + M2 + 0{\cdot}0304\ M3$
$M1 = X1 + 5{\cdot}8328$
$M2 = X2 - 0{\cdot}8558$
$M3 = X3 + 4{\cdot}7531$

o-*xylene* :

$YT - 9{\cdot}57 = 0{\cdot}8972\ Z_1^2 + 0{\cdot}5136\ Z_2^2 - 0{\cdot}3255\ Z_3^2$
$Z1 = M1 + 0{\cdot}1592\ M2 + 0{\cdot}1756\ M3$
$Z2 = -0{\cdot}1989\ M1 + M2 + 0{\cdot}2260\ M3$
$Z3 = -0{\cdot}1354\ M1 - 0{\cdot}2529\ M2 + M3$
$M1 = X1 + 3{\cdot}8701$
$M2 = X2 - 1{\cdot}7699$
$M3 = X3 - 5{\cdot}6170$

p-*xylene* :

$YT - 37{\cdot}1336 = 1{\cdot}2009\ Z_1^2 - 2{\cdot}1902\ Z_2^2 - 4{\cdot}6027\ Z_3^2$
$Z1 = 0{\cdot}7320\ M1 + 0{\cdot}0002\ M2 - 0{\cdot}6812\ M3$
$Z2 = -0{\cdot}1074\ M1 + 0{\cdot}9875\ M2 - 0{\cdot}1151\ M3$
$Z3 = 0{\cdot}6728\ M1 + 0{\cdot}1574\ M2 + 0{\cdot}7229\ M3$
$M1 = X1 - 0{\cdot}7295$
$M2 = X2 - 1{\cdot}0061$
$M3 = X3 - 0{\cdot}8011$

$Y\ \text{Toluene} - 32{\cdot}9981 = 0{\cdot}8689\ Z_2^2 - 1{\cdot}8061\ Z_2^2 - 3{\cdot}6109\ Z_3^2$
$Z1 = 0{\cdot}7321\ M1 - 0{\cdot}0939\ M2 - 0{\cdot}6748\ M3$
$T_2 = 0{\cdot}0096\ M1 - 0{\cdot}0939\ M2 - 0{\cdot}1272\ M3$
$Z3 = 0{\cdot}6812\ M1 + 0{\cdot}0864\ M2 + 0{\cdot}7270\ M3$
$M1 = X1 - 1{\cdot}3677$
$M2 = X2 - 1{\cdot}2668$
$M3 = X3 - 0{\cdot}3826$

TABLE VII

Results of Ridge Analysis

o-xylene : [Response : % Total Conversion]

λ	R	Yield	X1	X2	X3
Stationary point :					
0·0000	7·0471	9·7507	—3·8701	1·7699	5·6170
Maximum Ridge :					
1·2612	6·8177	50·7339	6·4031	—1·7062	1·6033
1·9902	2·5535	21·7102	2·1636	—1·0801	0·8200
4·1772	0·9474	14·4806	0·7197	—0·4786	0·3080
10·7332	0·3358	12·1707	0·2385	—0·1788	0·1546
Minimum Ridge :					
— 0·6895	5·3316	—6·2552	—1·0526	2·4571	—4·6120
— 1·4185	2·1351	4·2809	—0·9270	1·1728	—1·5144
— 3·6055	0·8697	8·1419	—0·5068	0·4804	—0·5098
—10·1665	0·3251	9·8921	—0·2096	0·1802	—0·1711

TABLE VIII

m-xylene : [Response : % Total Conversion]

λ	R	Yield	X1	X2	X3
Stationary point :					
0·0000	7·5727	—1·8620	—5·8328	0·8558	—4·7531
Maximum Ridge :					
4·3556	2·7460	35·7632	—0·5233	0·0279	2·6955
6·5426	1·0664	19·9762	0·0843	0·0065	1·0630
13·1026	0·4187	15·9638	0·1073	0·0047	0·4047
Minimum Ridge :					
— 2·7824	1·7005	6·6538	—0·8395	—1·0384	—1·0529
— 3·5114	1·1114	9·1453	—0·6182	—0·2987	—0·8740
— 5·5984	0·7089	10·7360	—0·3657	—0·0754	—0·6002
—12·2594	0·3543	13·2081	—0·1008	—0·0180	—0·3152

TABLE IX

p-xylene : [Response : % Total Conversion)

λ	R	Yield	X1	X2	X3
Stationary point :					
0·0000	1·4795	37·1336	0·7295	1·0061	0·8011
Maximum Ridge :					
1·2049	3·6347	44·1331	3·1317	0·6782	—1·7156
1·2139	1·5361	37·5841	1·3767	0·6761	—0·0840
1·2409	1·1540	36·9568	0·8478	0·6711	0·4031
1·3219	1·0895	36·8652	0·6706	0·6571	0·5528
1 5649	1·0354	36·7827	0·5930	0·6183	0·5815
2·2939	0·9131	36·5557	0·5176	0·5260	0·5377
4·4809	0·6785	35·9543	0·3928	0·3648	0·4159
11·0419	0·3862	34·8877	0·2295	0·1914	0·2446
Minimum Ridge :					
— 5·6957	5·1979	9·1074	—3·4261	—1·3221	—3·6786
— 7·8827	1·7524	15·6583	—1·1267	—0·5840	—1·2085
—14·4437	0·5930	28·6339	—0·3713	—0·2357	—0·3978

TABLE X

p-xylene : [Response : % Conversion to toluene)

λ	R	Yield	X1	X2	X3
Stationary point :					
0·0000	1·9024	32·9981	1·3677	1·2658	0·3826
Maximum Ridge :					
0·9269	9·4428	75·9245	6·1208	1·7761	6·9677
1·0079	4·1127	41·5772	2·1460	1·2405	3·2818
1·2509	1·8731	31·3816	0·3648	0·9418	1·5775
1·9799	1·1462	32·7736	0·2288	0·0759	0·8736
4·1669	0·7376	31·7045	0·3005	0·4420	0·5083
10·7279	0·3820	30·4336	0·1878	0·2128	0·2557
Minimum Ridge :					
— 4·7039	4·4315	8·8576	—2·9051	—1·1779	—3·1322
— 6·8909	1·5223	16·6646	—0·9425	—0·5798	—1·0455
—13·4519	0·5235	25·4110	—0·3039	—0·2397	—0·3525

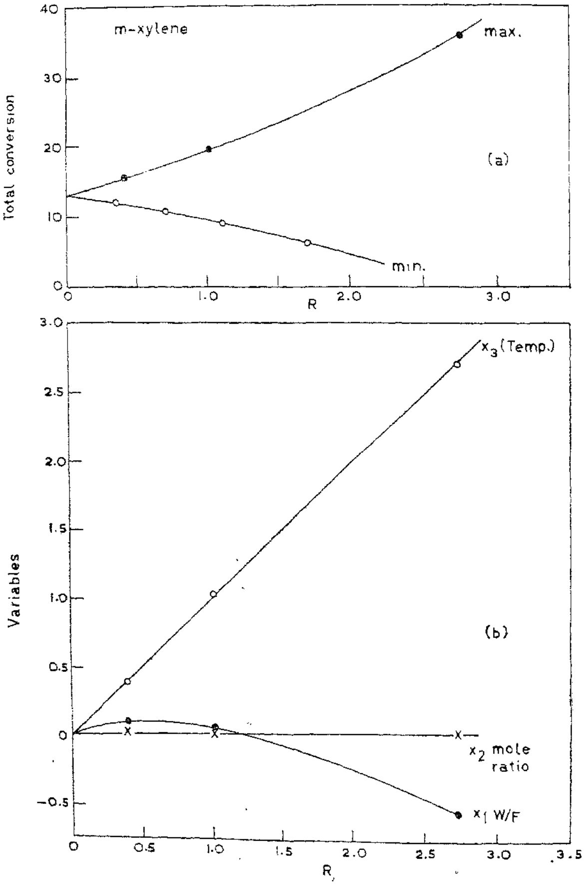

FIG. 2. (*a*) Maximum and Minimum ridge. (*b*) Effect of variables at maximum ridge RESPONSE : TOTAL CONVERSION (*M*-XYLENE).

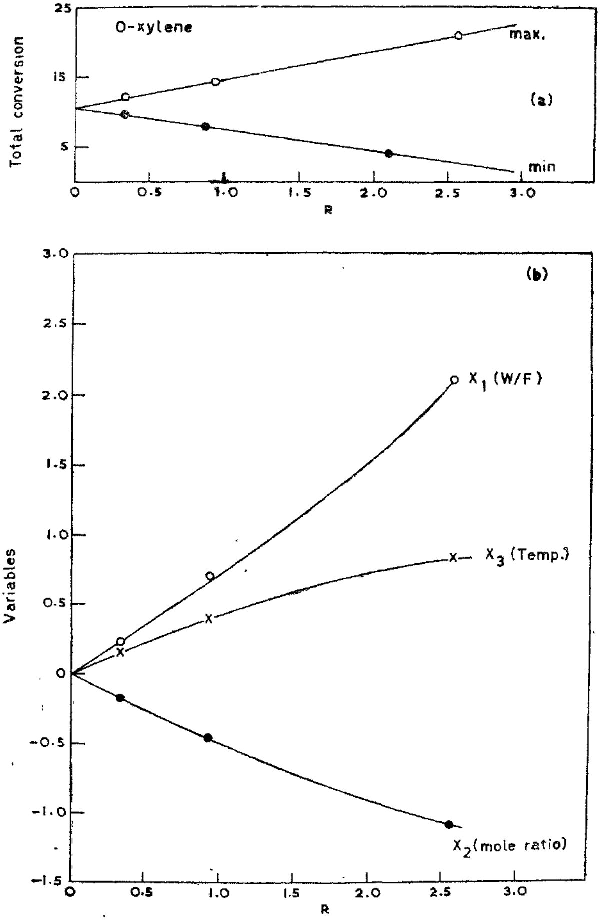

FIG. 3. (*a*) Maximum and minimum ridges. (*b*) Effect of variables at maximum ridges. P ONSE : TOTAL CONVERSION (*O*-XYLENE).

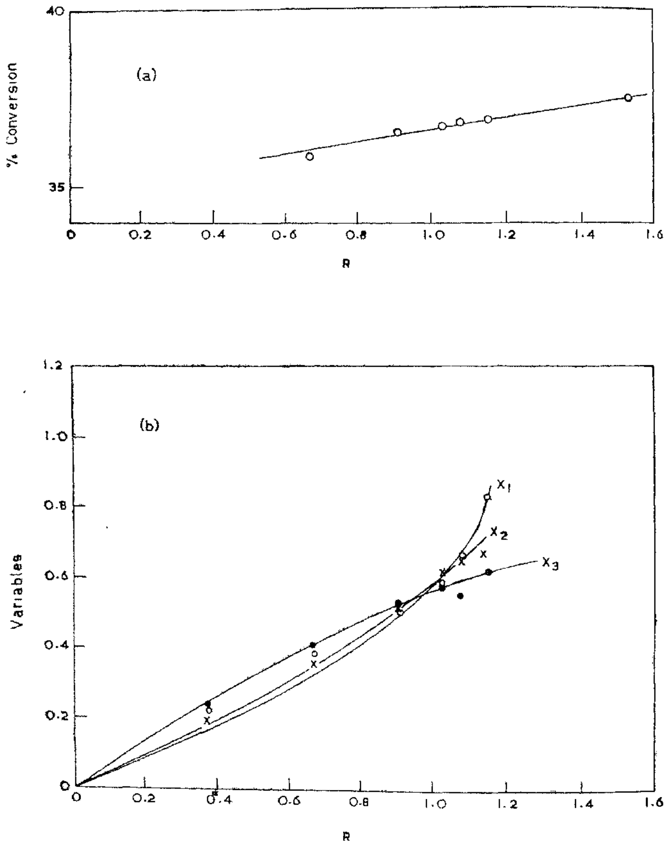

FIG. 4. (*a*) Maximum ridge. (*b*) Effect of variables at maximum ridge. RESPONSE : TOTAL CONVERSION (*P*-XYLENE).

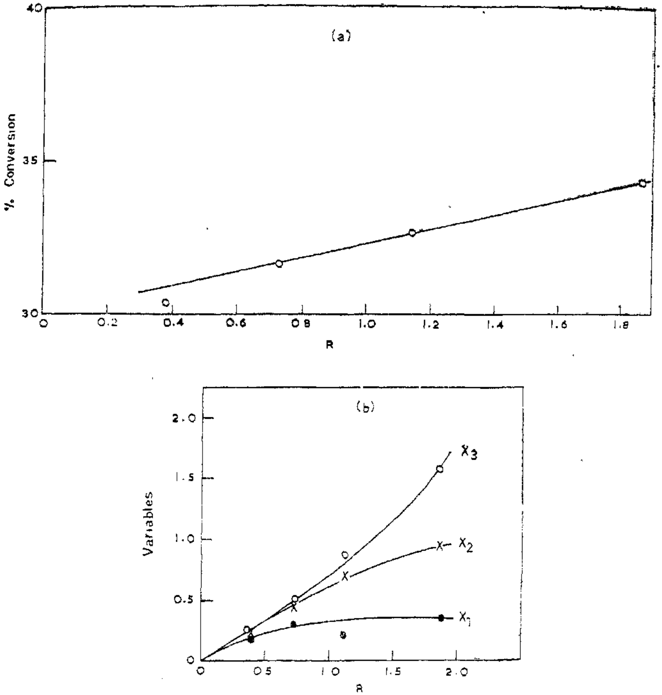

FIGURE 5 (a) MAXIMUM RIDGE
(b) EFFECT OF VARIABLES AT MAXIMUM RIDGE
RESPONSE : CONVERSION TO TOLUENE (p-xylene)

rature is maximum for *m*-xylene. Though the time factor has an effect, it is not to the same extent as that of temperature. The feed mole ratio has little effect at this maximum ridge.

In the case of *o*-xylene the effect of time factor is maximum, the temperature effect is much less and that of mole ratio is minimum. Figs. 4 and 5 represent the maximum ridge and the effect of the three variables at maximum ridge for *p*-xylene. In this system two responses are worked out, one being the total conversion and the other being conversion to toluene. Temperature has the maximum effect when total conversion is taken as the response, time factor has less effect and the effect of feed mole ratio is minimum.

CONCLUSIONS

From the above investigation one can conclude that for the dealkylation of xylene isomers, when processed individually, the effect of each variable can be pinpointed. In the case of *m*-xylene the process can be operated at a higher temperature and an optimum can be reached by adjusting the time factor. The system behaviour is well established in the experimental region. As discussed earlier, *o*-xylene, when compared with *m*-xylene is easily dealkylated even when the reaction temperature is low and again the true optimum can be obtained by adjusting the time factor. In these operations the feed mole ratio can be kept at the stoichiometric ratio.

NOMENCLATURE

a : treatment in the factorial design.

ba : regression coefficients.

F : Flow rate of the feed; g. moles/hr.

F : F-distribution value.

M : Eigen Vector.

R : Radius of the experimentation region.

X : Factors.

Y : Response function.

Z : Eigen Vectors.

λ : Eigen values.

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