催化学报
2012 Chinese Journal of Catalysis Vol. 33 No. 3

Article ID: 0253-9837(2012)03-0494-08 **DOI**: 10.1016/S1872-2067(11)60357-4 **Article:** 494–501

Alkylation of Benzene with 1-Decene Using Silica Supported Preyssler Heteropoly Acid: Statistical Design with Response Surface Methodology

A. HAFIZI[1], A. AHMADPOUR[1,*], M. M. HERAVI[2], F. F. BAMOHARRAM[3], M. KHOSROSHAHI[2]

[1]*Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran*

[2]*Department of Chemistry, School of Sciences, Alzahra University, Tehran 1993893973, Iran*

[3]*Department of Chemistry, Mashhad Branch-Islamic Azad University, Mashhad 9187147574, Iran*

Abstract: The response surface method (RSM) was applied to study the liquid phase alkylation of benzene with 1-decene catalyzed by means of silica supported Preyssler heteropoly acid. A three step experimental design was developed based on the central composite design (CCD). Catalyst loading, catalyst mass percent, and benzene to 1-decene molar ratio were used to optimize 1-decene conversion and linear alkylbenzene (LAB) yield. The results indicated that the quadratic model was significant for these two responses. The experimental results revealed that all variables had positive effect on 1-decene conversion. While increasing the catalyst loading tends to decrease LAB yield. Benzene to 1-decene molar ratio was found to be the most important factor that influenced LAB yield with a positive effect. Design expert software suggested several optimized solutions, among them the best choice was to use 31% catalyst loading, benzene to 1-decene molar ratio of 13, and catalyst percent of 3.6 wt% for obtaining 100% conversion and 88% LAB production yield.

Key words: linear alkylbenzene; heteropoly acid; Preyssler; silica; supported catalyst; response surface method

CLC number: O643 **Document code:** A

Received 10 August 2011. Accepted 8 December 2011.

**Corresponding Author. Tel/Fax: +98-511-8816840; E-mail: ahmadpour@um.ac.ir*

This work was supported by the office of vice chancellor of research of Sharif University of Technology.

English edition available online at Elsevier ScienceDirect (http://www.sciencedirect.com/science/journal/18722067).

Alkylation of benzene with C_{10}–C_{14} linear alkenes has been used for the synthesis of linear alkylbenzene (LAB). LAB is the primary raw material for the production of linear alkylbenzene sulfonate (LABS), which is a surfactant detergent intermediate [1]. LAB production has experienced continuous growth and is currently estimated to reach up to 3 million tons per year [2]. Traditionally, LAB production is mostly based on homogeneous catalytic reaction with HF and $AlCl_3$ as catalysts. Nonetheless, using these catalysts has their limitations such as environmental pollution, equipment corrosion, safety, and separation difficulty. Owing to the problems of conventional catalysts, solid acid catalysts have been developed to replace the existing catalysts [3]. In 1995, Universal Oil Products (UOP) and Central European Political Science association (CEPSA) notified their Detal process based on a fixed bed of solid acid catalyst [1,4]. Various catalysts like zeolites [2,5], clays [6], ionic liquids [7], and different metal oxides [8] were tested for the alkylation of benzene.

The use of heteropoly acids (HPAs) has received considerable attentions as nontoxic, eco-friendly, and environmentally benign catalysts for alkylation reactions [9]. Heteropoly acids have been actuated strong Brönsted acidity which are comparable to strong acids like H_2SO_4 and HF and even higher than zeolites and mixed oxides. Keggin type HPA has been applied for alkylation of benzene in the past decade [4,10–13].

Recently, we have applied Preyssler HPA catalyst ($H_{14}NaP_5W_{30}O_{120}$) to various reactions to develop the most effective environmental friendly catalysts [14–17]. Preyssler type HPA has considerable advantages such as 14 acidic protons, high thermal stability, high hydrolytic stability ($0 < pH < 12$), regeneration efficiency, safety, easy separation, and less corrosiveness [18]. The important problems in using heteropoly acids as heterogeneous catalyst are their low surface areas (7–10 m^2/g) and high solubility in polar solvents. Therefore, they could be supported on some acidic neutral solids that interact weakly with HPAs such as activated carbons, zeolites, silica, and acidic ion-exchange resins [19,20]. SiO_2 is one of the best choices as the support of HPAs owing to its low interaction with HPAs, high thermal resistance, and amphoteric character.

Majority of industrial reactions are optimized by observing the effect of one variable in the course of the reaction.

Moreover, this method does not consider the interaction of various treatment parameters and is only functionalized for single varied factor. To solve this problem, response surface method (RSM) was used. This method is one of the relevant multivariate techniques that can deal with experimental design, statistical modeling, and process optimization. It is used to examine the relationship between one or more response variables and a set of quantitative experimental variables or factors [21,22].

To the best of our knowledge, there is no report regarding the use of Preyssler heteropoly acid for LAB production. The other innovation of this paper is the use of experimental design for LAB production. Previous researches did not use experimental design for the optimization of the reaction parameters. In the present work, RSM was taken up to optimize the variables of liquid phase alkylation of benzene with 1-decene over silica supported Preyssler catalyst.

1 Experimental

1.1 Catalyst preparation

The chemicals were obtained from Merck Company and used as received. The Preyssler's anion $[NaP_5W_{30}O_{120}]^{14-}$ was prepared according to the literatures [23,24]. $H_{14}[NaP_5W_{30}O_{110}]$ was prepared by passage a solution of the potassium salt in water through a column (50 cm × 1 cm) of Dowex 50W × 8 resin in the H^+ form and evaporation of the elute to dryness.

SiO_2 with particle size of about 100 μm was impregnated in an aqueous solution of $H_{14}[NaP_5W_{30}O_{110}]$ for different loadings of catalysts. Catalyst loading was calculated from the following equation:

$$\text{Loading}(\%) = \frac{\text{Preyssler mass}}{\text{Preyssler mass} + \text{support mass}} \quad (1)$$

The mixture was stirred at room temperature for 12 h followed by evaporation at 50 °C and drying at 100 °C overnight. Then, catalysts were calcined at 240 ºC for 3 h in an oven prior to each test.

1.2 Catalyst testing

Liquid phase alkylation of benzene with 1-decene was carried out under atmospheric pressure in a 25 ml glass batch reactor equipped with a magnetic stirrer and a reflux condenser. The reactor was heated using a glass jacket and hot water. The reaction temperature was 80 °C with typical reaction time of 2 h. Silica supported $H_{14}[NaP_5W_{30}O_{110}]$ catalyst was calcined in air for 3 h at 240 °C and then introduced into the reactor. The known amounts of benzene and 1-decene were introduced to the reactor according to the experimental design tests. Filtration of reaction mixture was done after each run to remove catalyst particles. The filtrate was analyzed using a Agilent 6890 GC system equipped with an HP-5 capillary 30 m × 530 μm × 1.5 μm nominal GC/mass.

1.3 Experimental design

The most popular RSM is the central composite design (CCD) procedure. In this study, the central composite design was picked out for the RSM in the experimental design, which was well suited for fitting the complicated surfaces. The CCD usually works well for the process optimization and is an effective design that is perfect for chronological experimentation. This method also allows a reasonable amount of information for lack of fit testing, while not involving an unusually large number of test points [25].

Each numeric factor is varied out in 5 levels consisting two-level factorial or fractional factorial design points, two axial points (sometimes called "star" points) and the center point.

Our CCD design includes studying the effects of 3 factors in 2 levels (high, +1 and low, −1 levels), with 3 central points (coded level 0), and the axial points are based on α = 2 in a single block and 17 sets of test conditions. The process parameters involved in the present study are shown in Table 1.

Table 1 Experimental levels of independent variables

Variable	Symbol	Variable level				
		−α	−1	0	+1	+α
Catalyst loading (%)	A	10	20	30	40	50
Catalyst percent (wt%)	B	0.6	1.6	2.6	3.6	4.6
Bz/C_{10} molar ratio	C	1	5	9	13	17

All those independent variables used in the experimental design are coded according to Eq. 2:

$$x_i = (X_i - X_o) / \Delta X_i \quad (2)$$

where x_i is the coded value of the i^{th} independent variable, X_i independent variable, X_0 the real value of independent variable on the centre point and ΔX_i step change value. The experimental result obtained from the CCD model can be explained by the following equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j} \beta_{ij} x_i x_j + \varepsilon \quad (3)$$

where β_0 is offset or constant term, β_i is the linear coefficient, β_{ii} is the quadratic effect, β_{ij} is the cross product coefficient and ε is the statistical error.

In this study, the design of experiment and the response surface analysis were carried out using Design Expert version 8.0.0 software. The experimental plan is shown in Table 2. The responses of this design are 1-decene conversion and LAB production yield.

Table 2 Design arrangement and experimental results

Run	Input variable			Response variable	
	A	B	C	1-decene conversion	LAB yield
1	0	0	–α	61.981	49.576
2	–1	–1	1	59.185	82.434
3	–1	1	–1	63.422	70.094
4	1	–1	–1	64.549	64.764
5	0	0	0	85.716	83.654
6	0	0	A	100.000	87.740
7	0	0	0	71.697	73.299
8	–1	–1	–1	41.121	72.310
9	0	–α	0	44.437	73.919
10	α	0	0	79.735	70.451
11	–α	0	0	15.107	85.825
12	1	–1	1	87.318	77.328
13	1	1	–1	80.843	58.496
14	0	0	0	81.371	67.788
15	1	1	1	98.149	85.450
16	–1	1	1	66.300	94.633
17	0	α	0	98.392	78.561

2 Results and discussion

CCD was applied to develop correlation between the alkylation of benzene variables, 1-decene conversion, and LAB production yield. 1-Decene conversion was found in the range of 15% to 100%, while LAB production yield was found from 49.6% to 94.6%.

According to the sequential model, sum of squares were selected based on the highest order polynomials, where the additional terms were significant [26].

Fit summary output of Design Expert software revealed that the quadratic model was statistically significant for the 1-decene conversion. Linear and quadratic models were both statistically significant for LAB production yield. Based on the accuracy and flexibility of quadratic model and its higher adjusted R square compared with the linear model, it was chosen for statistical study of LAB yield response. Therefore, quadratic model was used to represent each response for further analysis.

The results obtained from the analysis of variance (ANOVA) demonstrate the validity of the models. Table 3 represents the ANOVA for the reduced quadratic model of 1-decene conversion. Values of Prob > F less than 0.05 indicate that the model terms are significant, whereas values greater than 0.1 are not significant. Among several variables, catalyst loading, catalyst mass percent, Bz/C_{10} molar ratio, and second order effect of catalyst loading (A^2) are significant terms of the model. Other terms are not significant according to their *P*-value at 99% confidence level. These insignificant terms were removed to obtain the improved model.

Table 3 ANOVA for response surface reduced quadratic model for 1-decene conversion

Source	Sum of square	df	Mean square	F-value	*P* value Prob > F	
Model	7597.95	4	1899.49	41.03	< 0.0001	significant
A	3308.75	1	3308.75	71.48	< 0.0001	
B	1690.26	1	1690.26	36.51	< 0.0001	
C	1174.00	1	1174.00	25.36	0.0003	
A^2	1424.94	1	1424.94	30.78	0.0001	
Residual	555.48	12	46.29	—	—	
Lack of fit	452.48	10	45.25	0.88	0.6414	not significant
Pure error	103.00	2	51.50	—	—	
Cor total	8153.43	16	—	—	—	

R^2 = 0.9319, R^2 (adjusted) = 0.9092, R^2 (predicted) = 0.8489, adequate precision = 22.945.

Catalyst loading has the greatest effect on 1-decene conversion in accordance with the highest F-value of 71.48, while Bz/C_{10} molar ratio is found to be the least important.

The model F-value of 41.03 implies model significance. The predicted R^2 value of 0.8489 is in reasonable agreement with the adjusted R^2 of 0.9092 and they show the suitability of the model. Adequate precision measure of the signal to noise ratio is another important parameter for model evaluation and a ratio greater than 4 is desirable. Hence, in the quadratic model of 1-decene conversion, the ratio of 22.945 indicates adequate signal for the model to be applied to navigate the design space.

To investigate the LAB production yield as the second response, ANOVA is listed in Table 4 for the reduced quadratic model. The Model *F*-value of 25.61 implies that the model is significant.

For the LAB production yield, Bz/C_{10} molar ratio (C) is the most important variable according to its F-value (95.86), while catalyst mass percent has the least effect on the response.

Considering their importance, the effective parameters

Table 4 ANOVA table for response surface reduced quadratic model for LAB production yield.

Source	Sum of square	df	Mean square	F-value	*P* value Prob > F	
Model	1891.44	5	378.29	25.61	< 0.0001	significant
A	257.45	1	257.45	17.43	0.0015	
B	27.88	1	27.88	1.89	0.1968	
C	1415.81	1	1415.81	95.86	< 0.0001	
BC	103.72	1	103.72	7.02	0.0226	
C^2	86.59	1	86.59	5.86	0.0339	
Residual	162.47	11	14.77	—	—	
Lack of fit	32.69	9	3.63	0.056	0.9993	not significant
Pure error	129.78	2	64.89	—	—	
Cor total	2053.91	16	—	—	—	

R^2 = 0.9209, R^2 (adjusted) = 0.8849, R^2 (predicted) = 0.8859, adequate precision = 18.721.

can be ranked as C > A > BC > C^2 > B. The other parameters were removed from the model due to their high P value. Hierarchical Term (B) was added after backward eliminating regression in consequence of BC variable which has the P value of 0.0226 at 95% confidence level.

The R^2 of LAB production yield is 0.9209 that is close to 1. The predicted R^2 (0.8859) is in a very good agreement with the adjusted R^2 (0.8849). The adequate precision value of 18.721 is well above 4 and can be used to navigate the design space. The lack of fit insignificance in both ANOVA tables demonstrates the unimportancy of the eliminated terms which is prefered for the model.

The regression coefficient values were evaluated and the subsequent refined equations, including only the significant terms, were derived using the coefficients of the coded variables for 1-decene conversion and LAB production yield:

$$Y_1 = 77.66 + 14.38A + 10.28B + 8.57C - 7.56A^2 \quad (4)$$

$$Y_2 = 76.83 - 4.01A + 1.32B + 9.4C + 3.60BC - 1.86C^2 \quad (5)$$

The experimental and predicted 1-decene conversion and LAB production yield are shown in Figs. 1 and 2. The two figures demonstrate a close proximity of the model prediction with the experimental data signifying the validity of the regression models. R^2 of these two figures are 0.9319 and 0.9209, respectively, those are close to 1.

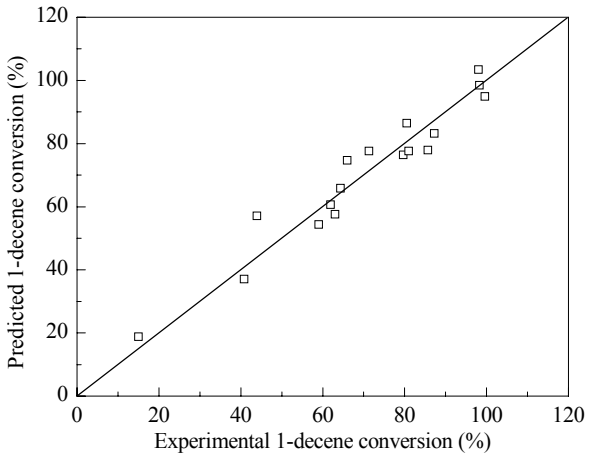

Fig. 1. Predicted versus experimental conversion of 1-decene.

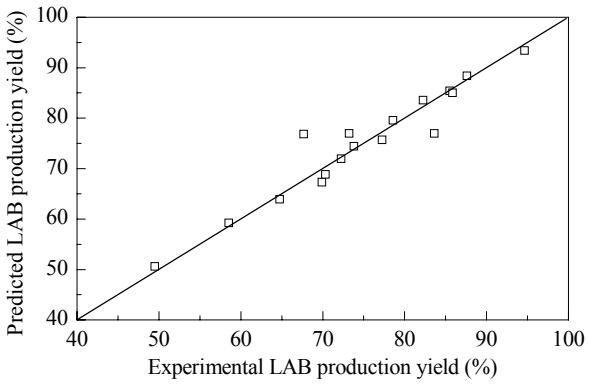

Fig. 2. Predicted versus experimental yield of LAB production.

The other adequacy check for the acquired models is the normal probablity plot of the studentized residuals. Figure 3 and 4 represent normal probablity versus studentized residuals. The residual points in both figures are appropriately located near the straight line, confirming the normal distribution of errors and normality of the data.

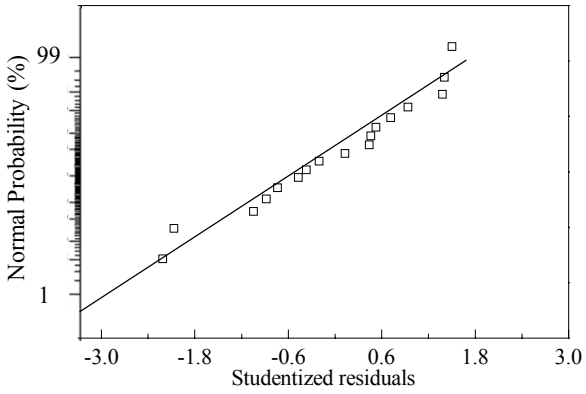

Fig. 3. Normal probability plot of studentized residuals for 1-decene conversion.

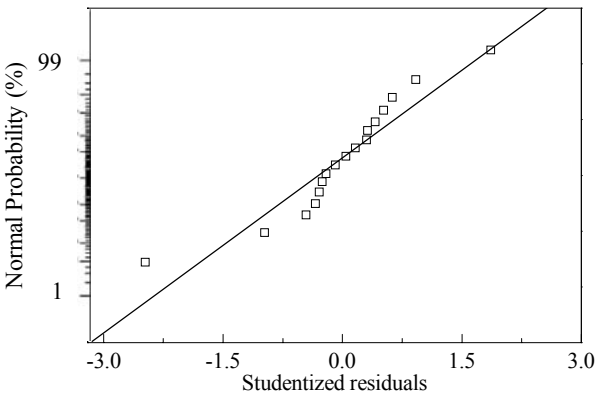

Fig. 4. Normal probability plot of studentized residuals for LAB production yield.

Studentized residuals versus predicted for 1-decene conversion and LAB yield are shown in Figs. 5 and 6, respectively. These figures show that there is no need to suppose any violation of the independence. The plot should be a random scatter. Figures 5 and 6 illustrate that they don't have any obvious pattern and unusual structure. Equal scatters above and below the *x*-axis in these figures imply that the models proposed are sufficient and there is no reason to suspect any infringement of the independence or constant variance assumption.

To evaluate the effects of different process variables on

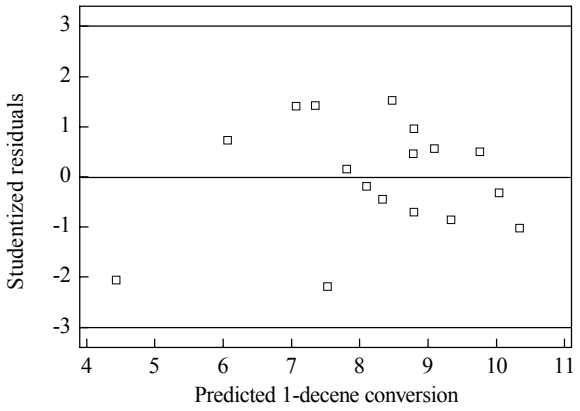

Fig. 5. Residual versus predicted plot of 1-decene conversion.

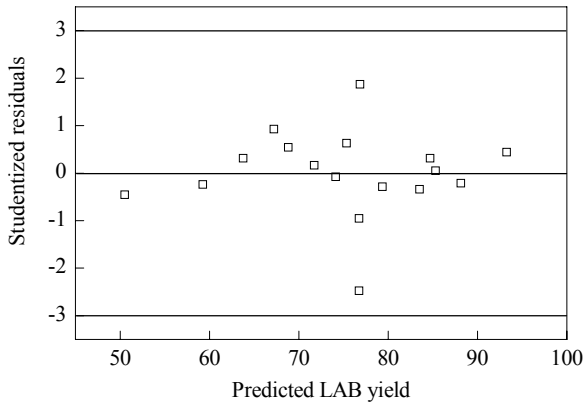

Fig. 6. Residual versus predicted plot of LAB yield.

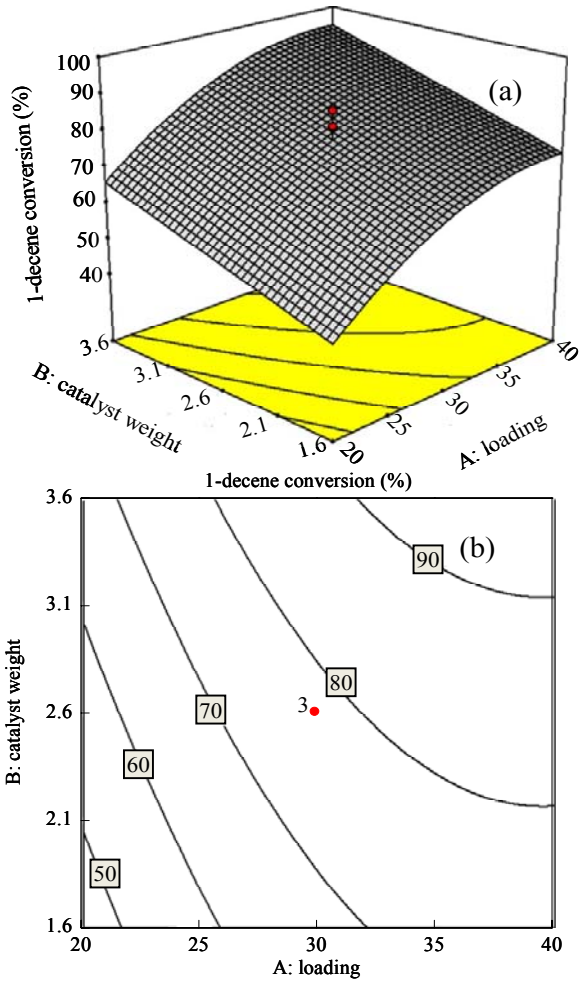

Fig. 7. Catalyst loading vs catalyst mass percent on 1-decene conversion at constant $Bz/C_{10} = 9$. (a) 3D surface; (b) Contour plot.

1-decene conversion and LAB yield, graphical representations have been made in Figs. 7–12 which demonstrate three dimensional model surfaces and contour plots.

The effects of catalyst loading and catalyst mass percent on 1-decene conversion are shown in Figs. 7(a) and (b), when Bz/C_{10} molar ratio is at the middle point. Both of these parameters have positive effect on 1-decene conversion. For example, by increasing catalyst loading from 20% to 40%, the conversion enhances from 66% to 95% at catalyst mass percent of 3.6%. Catalyst mass percent has the same effect on this response and increases the conversion from 74% to 95% at 40% catalyst loading. The effect of catalyst loading on 1-decene conversion is higher than other parameters according to Eq. (4) and the values reported in Table 3. The curvature of 3D surface in Fig. 7(a) is due to the more effectiveness of catalyst loading on 1-decene conversion than the catalyst mass percent.

Figures 8(a) and (b) illustrate the 3D surface and contour plot generated by B_Z/C_{10} molar ratio versus catalyst loading on 1-decene conversion. As indicated in these figures, B_Z/C_{10} molar ratio has positive effect on 1-decene conversion similar to those of catalyst loading and catalyst percent. The enhancement of 1-decene conversion by catalyst percent is due to the enhancement in acidic proton. Activity of catalyst improves by increasing the catalyst loading in consequence of enhancement of the acidic active sites on catalyst support.

Simultaneous effect of B_Z/C_{10} molar ratio and catalyst mass percent on 1-decene conversion is shown in Figs. 9(a) and (b). Consequently, when catalyst mass percent and B_Z/C_{10} molar ratio are at their maximum points, 1-decene conversion would obtain the highest value.

Figures 10 (a) and (b) illustrate the effect of catalyst loading versus Bz/C_{10} molar ratio on LAB yield. As indicated in these figures, by increasing B_Z/C_{10} molar ratio at constant catalyst loading, the LAB production yield is remarkably enhanced. For instance, at 20% loading and 2.6% catalyst mass percent, the LAB yield improves from 69% to 89% by increasing the ratio of benzene to 1-decene from 5 to 13. On the other hand, according to these figures and Eq.5, catalyst loading has negative effect on this response and decreases

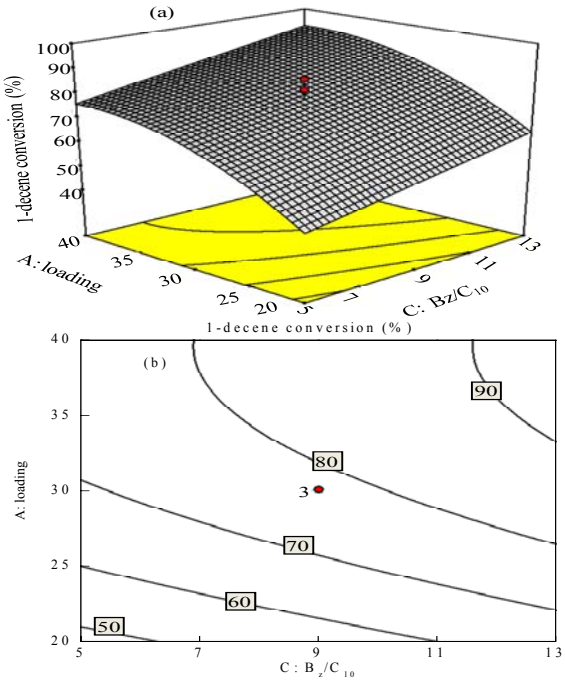

Fig. 8. Catalyst loading versus B_2/C_{10} molar ratio on 1-decene conversion at constant catalyst mass percent of 2.6%. (a) 3D surface; (b) Contour plot.

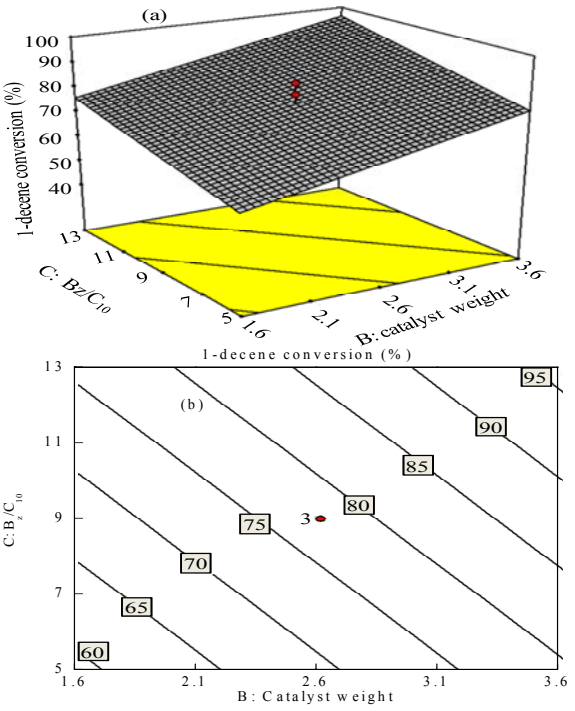

Fig. 9. Catalyst mass percent versus B_Z/C_{10} molar ratio on 1-decene conversion at constant catalyst loading of 30%. (a) 3D surface; (b) Contour plot.

the LAB production yield. The curvature of Fig. 12(a) is mainly due to the B_Z/C_{10} molar ratio. Catalyst mass percent

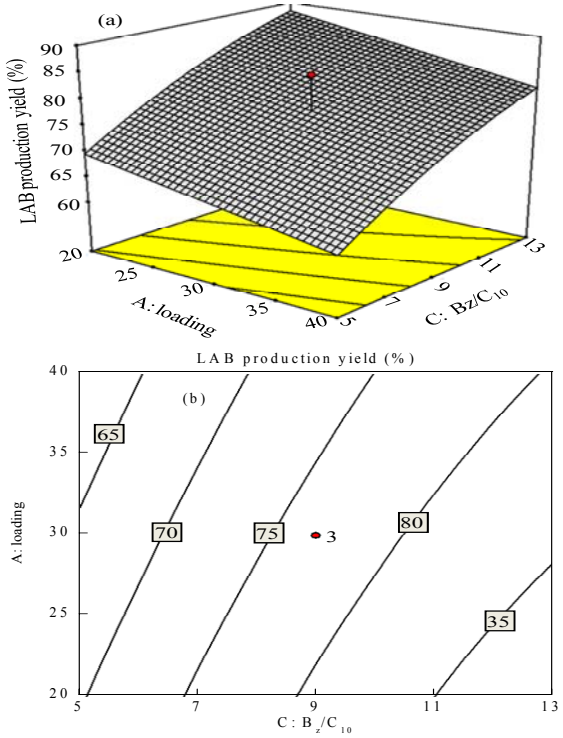

Fig. 10. Catalyst loading versus B_2/C_{10} molar ratio on LAB yield at constant catalyst mass percent of 2.6%. (a) 3D surface; (b) Contour plot.

has negligible positive effect on LAB production yield which is demonstrated in Figs. 11 (a) and (b). Because of slight effect of these parameters, the 3D graph is a flat surface with small slope. Catalyst mass percent has the low F-value of 1.89 and high *P*-value of 0.1968 as indicated in Table 4. This factor should be removed from the significant variables on LAB yield response at confidence level of 95%. Because of large effect of BC on this response, catalyst mass percent parameter was not removed from the variables and it was called hierarchical term.

Figs. 12(a) and (b) show the dependency of LAB production yield on catalyst mass percent and Bz/C_{10} molar ratio at constant catalyst loading of 30%. Similar results as above can be obtained from these figures.

Consequently, the investigation of Figs. 7–12 reveals that for maximizing 1-decene conversion and LAB production yield, we can utilize the B_Z/C_{10} molar ratio and catalyst mass percent at their highest possible values because of their positive influence on both responses. Catalyst loading reveals positive effect on 1-decene conversion and negative outcome on LAB production yield, so it should be chosen according to the magnitude of its effect on each response. Design expert software suggests several optimized solutions, among them the best choice is to use 31% catalyst loading, B_Z/C_{10} molar ratio of 13, and the catalyst mass percent of 3.6%.

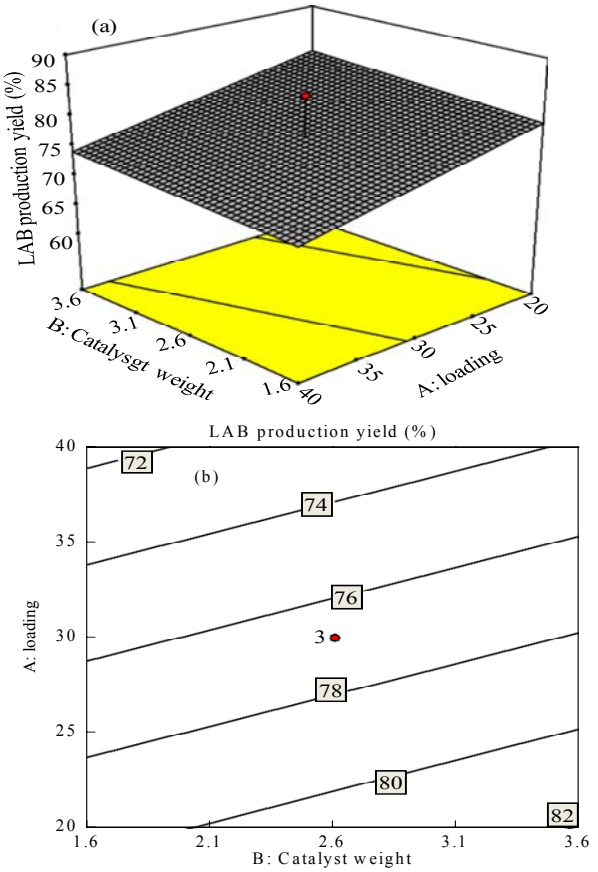

Fig. 11. Catalyst loading versus catalyst percent on LAB yield at constant Bz/C_{10} = 9. (a) 3D surface; (b) Contour plot.

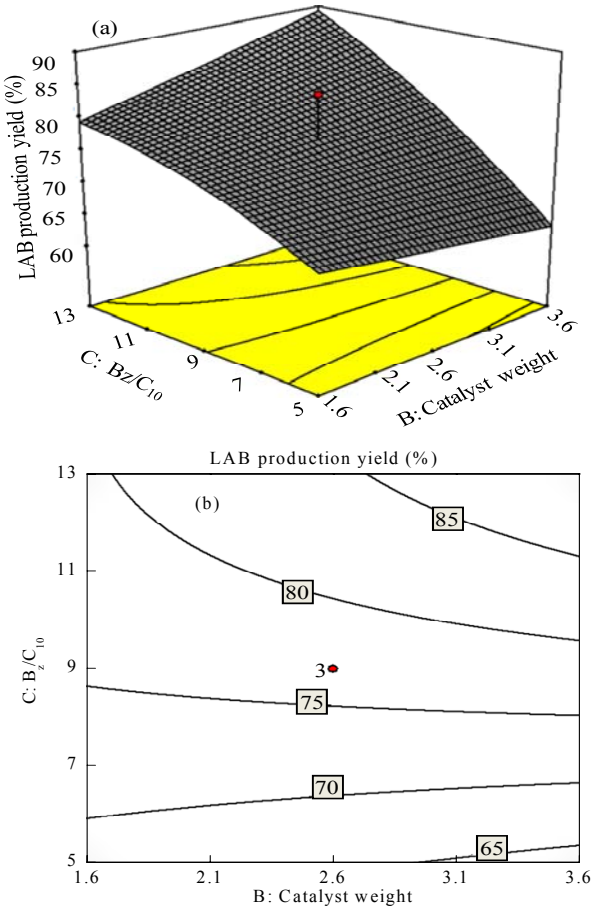

Fig. 12. Catalyst mass percent versus B_2/C_{10} molar ratio on LAB yield at constant catalyst loading of 30%. (a) 3D surface; (b) Contour plot.

3 Conclusions

The advantages of this study are both dependent on the choice of catalyst used and the application of improved experimental design. Silica supported Preyssler type heteropoly acid was investigated for the alkylation of benzene using the central composite design. Liquid phase alkylation of benzene with 1-decene was performed in an attempt to investigate the processing parameters namely, catalyst loading, benzene to 1-decene molar ratio and catalyst weight percent on the conversion of 1-decene and LAB production yield. By applying central composite design, the quadratic model was selected for both responses. Catalyst loading is the most important factor that influences 1-decene conversion, followed by catalyst weight percent and benzene to 1-decene molar ratio. They all have positive effect on 1-decene conversion. LAB production yield was investigated and benzene to 1-decene molar ratio showed the most significant influence on the increase in yield. Catalyst loading showed minor effect on LAB production yield.

In conclusion, to maximize 1-decene conversion and LAB production yield, benzene to 1-decene molar ratio and catalyst mass percent as well as catalyst loading ranges should be optimized. The design expert software provides several independent variable values for maximizing the former two responses. The best optimized condition was achieved by loading 31% catalyst, using benzene to 1-decene molar ratio of 13, and catalyst mass percent of 3.6% to obtain 100% conversion and 88% LAB production yield.

References

1 Kocal J A, Vora B V, Imai T. *Appl Catal A*, 2001, **221**: 295
2 Borutskii P N, Kozlova E G, Podkletnova N M, Gil'chenok N D, Sokolov B G, Zuev V A, Shatovkin A A. *Petrol Chem*, 2007, **47**: 250
3 Tian L, Li J, Li Y, Chen B. *Chin J Catal*, 2008, **29**: 889
4 de Angelis A, Amarilli S, Berti D, Montanari L, Perego C. *J Mol Catal A*, 1999, **146**: 37
5 Cao Y, Kessas R, Naccache C, Ben Taarit Y. *Appl Catal A*, 1999, **184**: 231
6 Guerra S R, Merat L M O C, San Gil R A S, Dieguez L C. *Catal Today*, 2008, **133**: 223

7 Cai X, Cui S, Qu L, Yuan D, Lu B, Cai Q. *Catal Commun*, 2008, **9**: 1173
8 Devassy B M, Lefebvre F, Bohringer W, Fletcher J, Halligudi S B. *J Mol Catal A*, 2005, **236**: 162
9 Nociar A, Hudec P, Jakubik T, Smieskova A, Zidek Z. *Petrol Coal*, 2003, **45**: 184
10 Hernández-Cortez J G, Martinez L, Soto L, López A, Navarrete J, Manríquez M, Lara V H, López-Salinas E. *Catal Today*, 2010, **150**: 346
11 Zhu H-O, Wang J, Zeng C-Y, Zhao D-Y. *Stud Surf Sci Catal*, 2003, **146**: 661
12 Zhang J, Zhu Z, Li C, Wen L, Min E. *J Mol Catal A*, 2003, **198**: 359
13 Sawant D P, Halligudi S B. *J Mol Catal A*, 2005, **237**: 137
14 Heravi M M, Motamedi R, Seifi N, Bamoharram F F. *J Mol Catal A*, 2006, **249**: 1
15 Hekmatshoar R, Heravi M M, Sadjadi S, Oskooie H A, Bamoharram F F. *Catal Commun*, 2008, **9**: 837
16 Heravi M M, Bakhtiari K, Bamoharram F F. *Catal Commun*, 2006, **7**: 499
17 Bamoharram F F, Heravi M M, Roshani M, Jahangir M, Gharib A. *Appl Catal A*, 2006, **302**: 42
18 Heravi M M, Bamoharram F F, Rajabzadeh G, Seifi N, Khatami M. *J Mol Catal A*, 2006, **259**: 213
19 Wu Y, Ye X, Yang X, Wang X, Chu W, Hu Y. *Ind Eng Chem, Res*, 1996, **35**: 2546
20 Revathi S, Preethi M E L, Manikandan D, Divakar D, Rupa A V, Sivakumar T. *Chin J Catal*, 2008, **29**: 1202
21 Parajo J C, Alonso J L, Lage M A, Vazquez D. *Bioprocess Eng*, 1992, **8**: 129
22 Bezerra M A, Santelli R E, Oliveira E P, Villar L S, Escaleira L A. *Talanta*, 2008, **76**: 965
23 Alizadeh M H, Razavi H, Bamoharram F F, Daneshvar K. *J Mol Catal A*, 2003, **206**: 89
24 Alizadeh M H, Razavi H, Bamoharram F F, Hassanzadeh M K, Khoshnavazi R, Mohammadi Zonoz F. *Kinet Catal*, 2003, **44**: 524
25 Tiwari B K, Muthukumarappan K, ÓDonnell C P, Cullen P J. *J Food Eng*, 2008, **88**: 553
26 Tan I A W, Ahmad A L, Hameed B H. *Chem Eng J*, 2008, **137**: 462