Optimization of Spray Pulse Reactor Conditions Used for Dehydrogenation of Liquid Organic Hydrides by Using Response Surface Methodology

Patil, Shubhangi Prakash*+; Bhatu, Minakshi N.●

Department of Chemistry, The Institute of Science, Fort, Mumbai, Maharashtra, INDIA

Patil, Aniruddha B.

Department of Chemistry, Maharshi Dayanand College, Parel, Mumbai, Maharashtra, INDIA

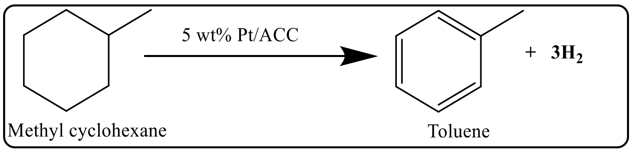
ABSTRACT: *Dehydrogenation of liquid organic hydrides is the key reaction for the process where these hydrides are viewed as a potential candidate for hydrogen storage and delivery application. Methylcyclohexane is used as a liquid organic hydride for dehydrogenation reaction. Using a spray pulse reactor, we determine the possible reaction conditions for the greatest percentage conversion of methylcyclohexane during dehydrogenation and hence maximal hydrogen evolution with the help of response surface methodology. The suggested regression model with independent variables based on the Box-Behnken design is explained using an Analysis of Variance. R^2 and R^2adj correlation coefficients of 0.90 and 0.74 are used in this model. The estimated optimum conditions for percentage conversion of methylcyclohexane in this study are 389 °C temperature, 14 sec pulse frequency interval, and 1 ms pulse width where 44.51 % conversion of methylcyclohexane is expected. This was confirmed by the actual experimental value of 46.36 % conversion of methylcyclohexane during dehydrogenation using a 5 wt% Pt/ Activated carbon cloth catalyst. The entire study demonstrates that the Box-Behnken design combined with response surface methodology may be utilized to efficiently optimize the reaction conditions of a spray pulse reactor during methylcyclohexane dehydrogenation with 5 wt% Pt/Activated carbon cloth catalyst.*

KEYWORDS: *Dehydrogenation, Methylcyclohexane, ANOVA analysis, Spray pulse reactor, 5 wt% Pt/ACC.*

INTRODUCTION

Aside from the reactant and catalyst, one of the most important aspects is the reactor in the dehydrogenation reaction of Liquid Organic Hydrides (LOH) [1,2]. A spray pulse reactor is used for the dehydrogenation of LOH, which is controlled by three critical parameters: temperature, pulse width, and pulse frequency interval. It is desirable to understand these factors and their impact on the percentage conversion of LOH to maximize the rate of H_2 evolution during the LOH dehydrogenation reaction. The traditional technique for optimizing reactor conditions

* *To whom correspondence should be addressed.*
+*E-mail: patil.shubh7@gmail.com*
1021-9986/2022/11/3788-3798 11/$/6.01
● *Another Address:* *Department of Chemistry, Vartak College, Dist. Palghar, Maharashtra, INDIA*



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entails doing a large number of trials by modifying various temperatures, pulse frequency interval, and pulse width, which would be highly expensive, time-demanding, and yet unreliable [3,4]. It is also challenging to determine how these parameters interact with each other for the best results.

Response Surface Methodology (RSM) is a powerful approach for optimizing and evaluating all response circumstances and their interactions [4]. The reaction of numerous factors with their interacting impact is explored in RSM investigations. RSM has recently been used in a variety of investigations, including culture process studies in microbiology, fermentation studies in biochemistry, drug formulation studies in the pharmaceutical sector, and so on. In RSM research, a specific series of trials with defined parameters is necessary [5,6]. These experiments may be used to optimize all of the reaction parameters and their interactions with the reaction circumstances. As a result, RSM is a collection of experimental, mathematical, and statistical data that may be used to optimize, develop, and improve a given process. RSM approaches provide the following benefits [3,4];

- ♦ Reduces the number and cost of experiments
- ♦ Shows the interactive effect of various parameters
- ♦ Possible to find out better reaction parameters for a particular experiment
- ♦ Possible to predict the results of unplanned experiments

As shown in Fig. 1, RSM was employed in this work to optimize a spray pulse reactor, which has three essential parameters: temperature, pulse frequency interval, and pulse width. The purpose of this optimization was to look into the percentage conversion of LOH with varied reactor settings for efficient H_2 evolution in a spray pulse reactor [7,8]. Despite its low coverage of the corner of nonlinear design space, the Box-Behnken design is nonetheless seen to be more effective and powerful than other designs like the three-level complete factorial design, Central Composite Design (CCD), and Doehlert design. The Box-Behnken design was utilized for dehydrogenation experiment optimization utilizing RSM to analyze the influence of temperature, pulse frequency interval, and pulse width on the percentage conversion of methylcyclohexane during the dehydrogenation reaction.

As methylcyclohexane (MCH) exhibits a better dehydrogenation reaction than cyclohexane, which we had previously examined, we chose MCH as a LOH and 5 wt% Pt/ACC (activated carbon cloth) as a catalyst in this investigation [9,10]. Box-Behnken designs include spherical and revolving designs as well as the center point and middle point of the cube on the spherical design [3,11].

EXPERIMENTAL SECTION

Materials

A 5 wt% Pt/ACC catalyst was used for the dehydrogenation of various LOH. An activated carbon cloth having a BET surface area of 800 m²/g was used as a catalytic support [7]. $PtCl_4$ (Platinum chloride) Merck, India was used for the synthesis of the catalyst. The Pt metal loading on ACC was achieved by the catalytic adsorption method as reported in our previous work [8-10]. In this case, the stoichiometric amount of Platinum(IV) chloride salt dissolved in the same acetone solvent and ACC was stirred in this solution for 24 h. After adsorption, the catalysts were dried at 100 ºC for 2 h. The weight of plane carbon cloth was found to be 248 mg before loading of catalyst and after adsorption, the weight found was 260 mg . Before the reaction, the catalyst was activated at 300 ºC in the presence of an inert atmosphere of nitrogen gas for well dispersion and activation of catalyst [7,10]. These 5 wt% Pt/ACC catalysts were used for the dehydrogenation of various LOHs. Here, Analytical reagent grade Methylcyclohexane, (Merck, India) was used as LOH which undergoes dehydrogenation reaction.

Catalyst Characterization

X-ray diffraction patterns were taken for the activated 5 wt% Pt/ACC catalyst by using a RigakuMiniflex II Desktop X-ray diffractometer with CuKα radiations (λ=1.5405). The XRD patterns of the 5 wt% Pt/ACC are shown in Fig. 2 The characteristic peak at 2θ on 40.52° matched with JCPDS Card No: 87-0641 which indicates the presence of crystalline phase of platinum metal. Atomic Absorption Spectroscopy (AAS) analysis was carried out by following the conventional acid digestion process. The platinum metal content in the catalyst was found to be in the expected range with a deviation of ± 0.3 wt%.

The morphology of 5 wt% Pt/ACC catalyst was studied before activation and after activation by using Scanning

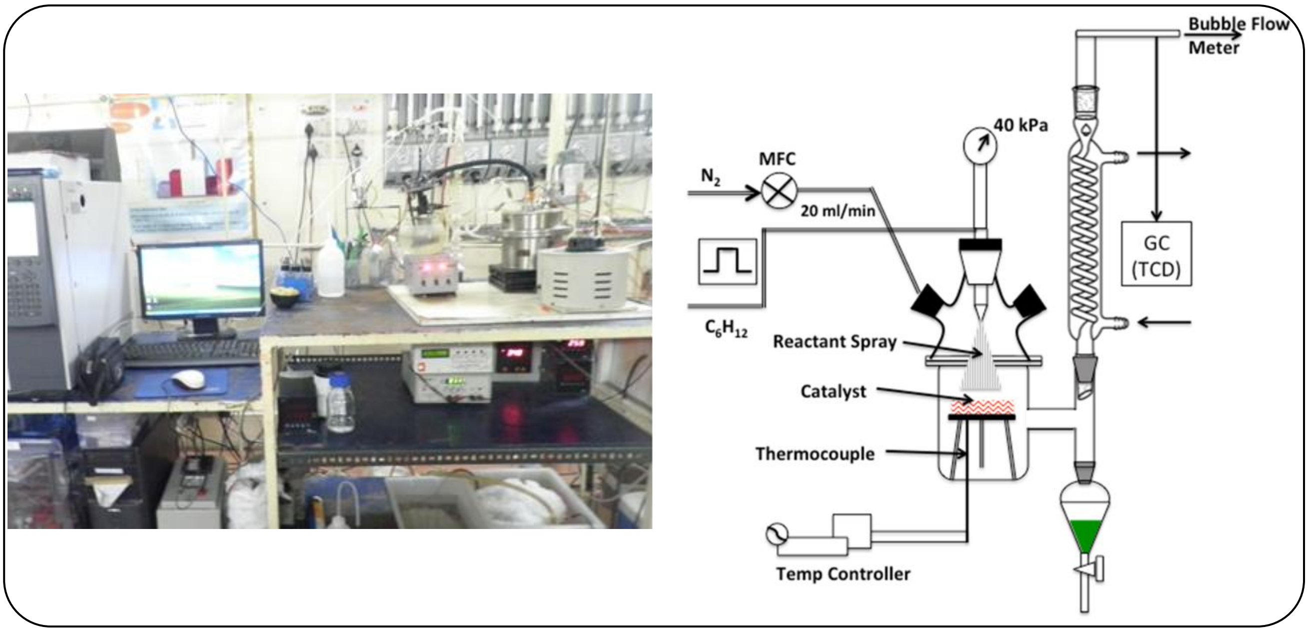

Fig. 1: Spray Pulse Reactor and its schematic diagram

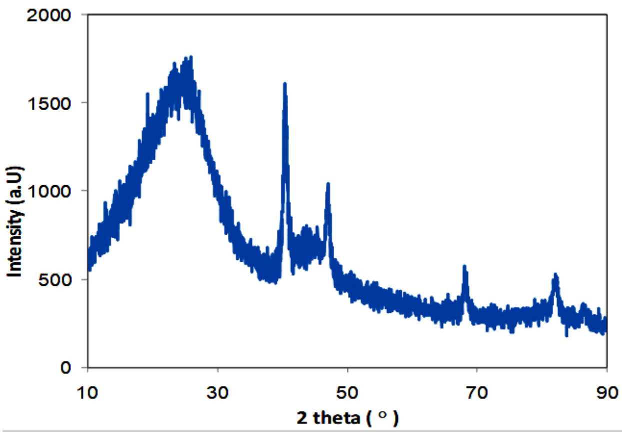

Fig. 2: XRD Spectra of Activated 5 wt% Pt/ACC

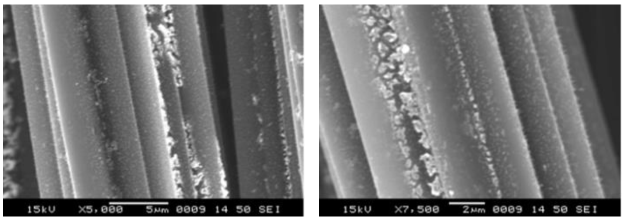

Fig. 3: SEM Images of 5 wt% Pt/ACC Before Activation

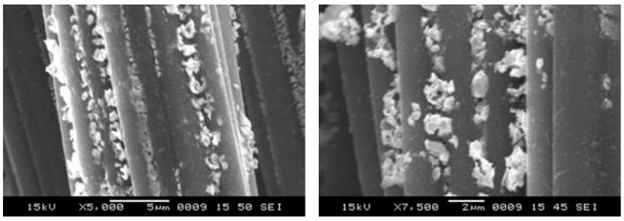

Fig. 4: SEM images of 5 wt% Pt/ACC after activation

Electron Micrographs (SEM) in Fig. 3 and Fig. 4 respectively. These images showed the catalyst's morphology and made it abundantly evident that the catalyst had not been evenly distributed over the carbon cloth before activation. On carbon cloth, the same catalyst exhibits good dispersion after activation.

Experimental

Fig. 1 shows a schematic diagram of a spray pulse stainless steel reactor that was used for the dehydrogenation of LOH. 50 ml/min flow of nitrogen was required for the pretreatment of 5 wt% Pt/ACC at 300 °C to maintain an inert environment and then the catalyst was subjected to activation in the presence of 50 ml/min nitrogen and 50 ml/min hydrogen followed by the heating cycle up to 450°C. The reactant was fed into the catalyst in pulse injection mode. The unreacted reactant and product were collected by the simple condensation method. The hydrogen evolved during the reaction was continuously monitored using GC-TCD (Shimadzu GC-2014 with packed column Por-apack-Q). The amount of reactant fed on the catalyst was calculated by using values of pulse frequency and pulse width of the reactor and evolved hydrogen was calculated by continuously monitoring using GC-TCD per minute. These values give the percentage conversion of MCH to toluene [7,10,12]. According to Box-Behnken

Table 1: Experimental Range and Levels of Variables

Variables	Code	Unit	Range and Levels			Step Change (ΔX_i)
			Low Level (-1)	Centre Level (0)	High Level (+1)	
Temperature	X_1	°C	300	350	400	50
Pulse frequency interval	X_2	sec	1	10	20	9.5
Pulse width	X_3	ms	1	5	10	4.5

experimental design matrix, 15 experiments were carried out by following the given values of temperature, pulse frequency interval, and pulse width.

RESULTS AND DISCUSSION

Response Surface Methodology

For the optimization of the dehydrogenation reaction of LOH, three independent and important reaction parameters were selected based on the spray pulse reactor system. Table 1 shows the operating parameter ranges for temperature (X_1), pulse frequency interval (X_2), and pulse width (X_3) [9,13,14]. In the first section of RSM, some experiments are carried out to fix the ranges of parameters and then according to RSM, Box-Behnken design produced one set of experiments, these experiments were carried out using ranges of parameters from 300 to 400°C, 1 to 20 sec and 1 to 10 ms for X_1, X_2 and X_3 respectively [3,15]. Plotting RSM graphs, including maximum and lowest ranges, helped determine the final range of these variable components [16].

The interactive effect between these three parameters and their responses were analyzed using Box-Behnken design under the RSM study [17]. According to Box-Behnken design, 15 trial experiments were carried out to study the independent variables at three different stages; low (-1), medium (0), and high (+1). Here we selected Box-Behnken design over the full factorial design because Box Behnken design required only 15 trial experiments while the full factorial design required 27 trial experiments [18,19]. The box behenken design is time-saving and has good performance with fewer errors. After the 15 trial experiments, this design presents an approximately rotatable design with three levels per parameter and also involves fractional factorials with incomplete block design and avoids extreme vertices. For statistical calculations, the three independent variables were designed as X_1, X_2 and X_3 coded according to the following equation [20,21].

$$Xi = \frac{Xi - Xo}{\Delta Xi} \tag{1}$$

Where, Xi = coded value of an independent variable, Xo = real value of the independent variable at the centre point and ΔXi= step change value.

The percentage conversion of LOH i.e., Methylcyclohexane is taken as a response Y of the experimental design. These Y responses are related to our selected parameters by linear or quadratic models. A quadratic model also includes a linear model by following equation [22,23];

$$Y = \beta 0 + \sum \beta i\ xi\ _{i=1}^{k} + \sum \beta ii\ xi2_{i=1}^{k} + \sum\sum \beta ij\ xi\ xj_{j=1}^{k}{}_{i=1}^{k} + \varepsilon \tag{2}$$

Where Y is the responses X_1, X_2… X_k is coded variables while βi, βii, *and* βij are linear, quadratic, and interaction coefficients, respectively. $\beta 0$ is a constant error and ε is a random error.

Statistical Evaluation

Three independent variables of the spray pulse reactor for dehydrogenation of methylcyclohexane were studied by conducting the experiments with different reaction conditions by using the Box-Behnken design model [19]. The temperature range studied was 300 to 400°C. The pulse frequency interval of the reactant was varied between 1 to 20 sec and the pulse width of the reactant was kept between 1 to 10 ms. Table 2 contains all these experiments of various combinations of three independent variable factors and their results [7,8]. This design matrix of experiments and their responses were studied by multiple regression analysis which gave approximate function for percentage conversion of LOH during dehydrogenation of LOH with the studied independent variables by using spray pulse reactor is given in Eq. (3) [24,25].

$$Y = -623.65 - 3.201 * X_1 + 5.051 * X_2 + 16.76 * X_3 - 0.0004 * X_1^2 - 0.170 * X_2^2 - 0.362 * X_3^2 - 0.038 * X_1 X_3 - 0.161 X_2 X_3 \tag{2}$$

In the above equation, Y is the % Conversion of methylcyclohexane (predicted response variable) while X_1, X_2 and X_3 are the independent variables i.e., temperature, pulse frequency interval and pulse width respectively.

Table 2: Box-Behnken Experimental Design Matrix with Variables and % Conversion of LOH

Standard Run Order	Run Order	Coded Variables			Uncoded Variables			Response % Conversion of MCH
		X_1	X_2	X_3	Temp. (°C)	P.Freq.Int. (sec)	P. Width (ms)	
14	1	0	0	0	350	10	5	23.5
1	2	-1	-1	0	300	1	5	24.65
6	3	1	0	-1	400	10	1	45.09
3	4	-1	1	0	300	20	5	4.46
8	5	1	0	1	400	10	10	5.77
10	6	0	1	-1	350	20	1	32.90
12	7	0	1	1	350	20	10	3.95
4	8	1	1	0	400	20	5	11.56
7	9	-1	0	1	300	10	10	17.33
13	10	0	0	0	350	10	5	39.47
15	11	0	0	0	350	10	5	31.58
9	12	0	-1	-1	350	1	1	2.79
11	13	0	-1	0	350	1	10	16.74
2	14	1	-1	0	400	1	5	7.27
5	15	-1	0	-1	300	10	1	29.62

Table 3: Analysis of Variance (ANOVA) for % Conversion of LOH at 100 min

Sr. No.	Source	Sum of Squares	Adj.MS	D.F.	F-Value	Probability (P) > F
1	Regression	3186.0	354	9	5.58	0.036
	a. Linear	1423.9	299.83	3	4.72	0.044
	b. Square	1274.0	424.66	3	6.69	0.024
	c. Interaction	488.2	162.72	3	2.56	0.016
2	Residual Error	317.5	163.49	5		
	a. Lack-of-Fit	182.6	60.86	3	0.90	0.564
	b. Pure Error	134.9	67.44	2		
	Total	3503.5		14		

The data obtained from Eq. (3) was verified with F value and the analysis of variance (ANOVA) fitted the data into the quadratic model of RSM. These values are represented in Table 3. P values of regression, linear and square interaction coefficient are $P < 0.05$. It implies that these are significant. The observed data's statistical analysis reveals minor differences in the values of a few parameters that change the MCH's % conversion efficiency. ANOVA for the response surface quadratic model gave F value 5.58, R^2 value 0.90, and probability < 0.036 [13,26]

Graphical Evaluation

The diagnostic plot of Box-Behnken design is shown in Fig. 5. The points near to the diagonal line indicate a good fit of the model as in Fig. 5 a. This figure suggests that there is no major violation of the assumptions underlying the RSM study and hence, it confirms the normality assumptions and independence of the residuals. Fig. 5 b shows the fitted values of assumptions of constant variance. The points are scattered randomly and lie within the range of -10 to +10. Hence, it can be concluded that the developed quadratic equation was almost appropriate and it is possible to correlate this equation with the influencing variables of percentage conversion of MCH during the dehydrogenation reaction [27,28].

A response surface contour plot shows the relationship between each variable and the percentage conversion of MCH. These diagrams also help to understand the interactive effect of these variables and hence to find out the optimum conditions [11,19].

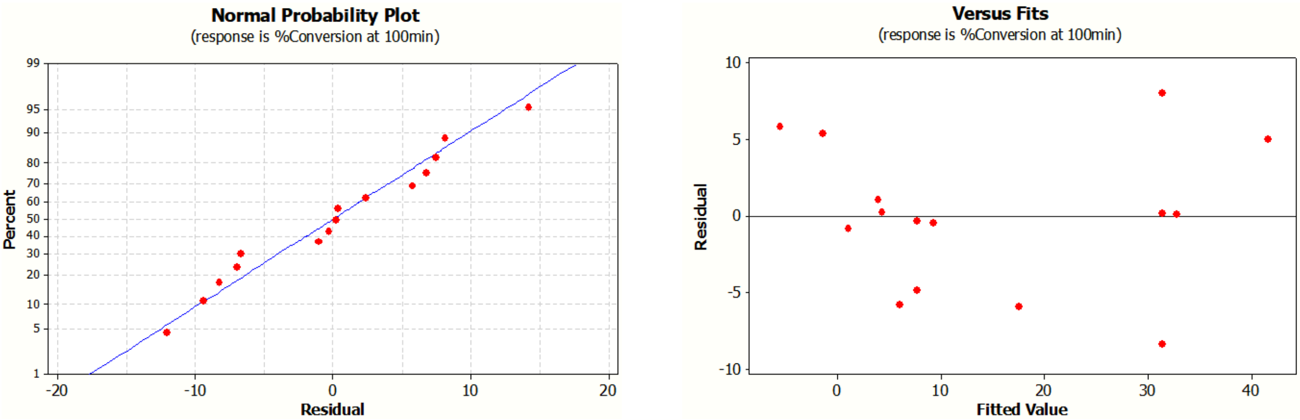

Fig. 5 a) Normal Probability Plot of the Raw Residuals, b) The Internally Studentised Residuals vs. Fitted Values Plot was Sprayed on Catalytic Surfaces

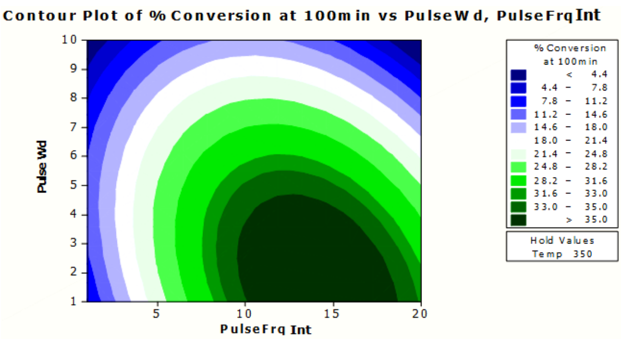

Fig. 6: Response Surface Contour Plot Showing Interaction between Pulse Width and Pulse Frequency Interval

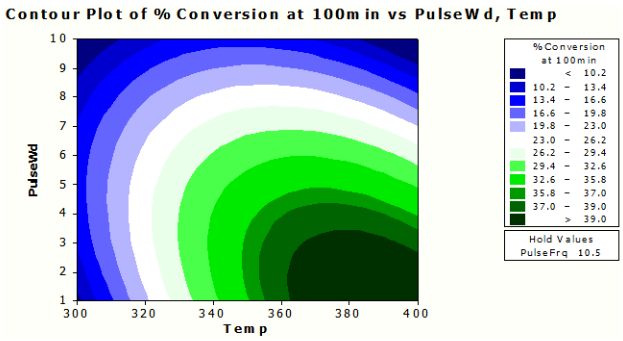

Fig. 7: Response Surface Contour Plot Showing Interaction Between Pulse Width and Temperature

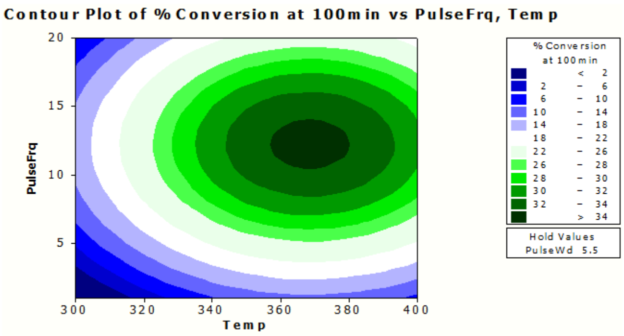

Fig. 8: Response Surface Contour Plot Showing Interaction Between Temperature and Pulse Frequency Interval

Fig. 6 shows the percentage conversion of MCH at 100 minutes as a result of the interaction between the pulse width of the reactant and pulse frequency interval of the reactant with one variable kept constant i.e. temperature, maintained at a constant value 350 °C. The percentage conversion efficiency of MCH increased along with the pulse frequency interval up to a pulse frequency interval of 18 sec, but after that, the percentage conversion efficiency started to decline. This may be because there is a significant time gap of more than 18 s between each pulse of reactant, so less reactant was sprayed on the catalytic surface. Hence, there was less interaction between the reactant and catalyst which affected the dehydrogenation reaction. It was shown that the dehydrogenation reaction was less efficient at increasing pulse widths, which may be due to the formation of a liquid pool on the catalytic surface area as during high pulse width at a time more reactant [29,30].

The internally studentized residuals vs. fitted values plot were sprayed on catalytic surfaces. It is clear from Fig. 6 that percentage conversion efficiency at 350°C increased up to 18 sec of pulse frequency interval and 4.5 ms of pulse width beyond that this efficiency decreased.

The interaction between temperature versus pulse width and temperature versus pulse frequency interval are shown in Fig. 7 and Fig. 8.

In Fig. 7 pulse frequency interval was constant at 10.5 s where it was observed that as the temperature increased

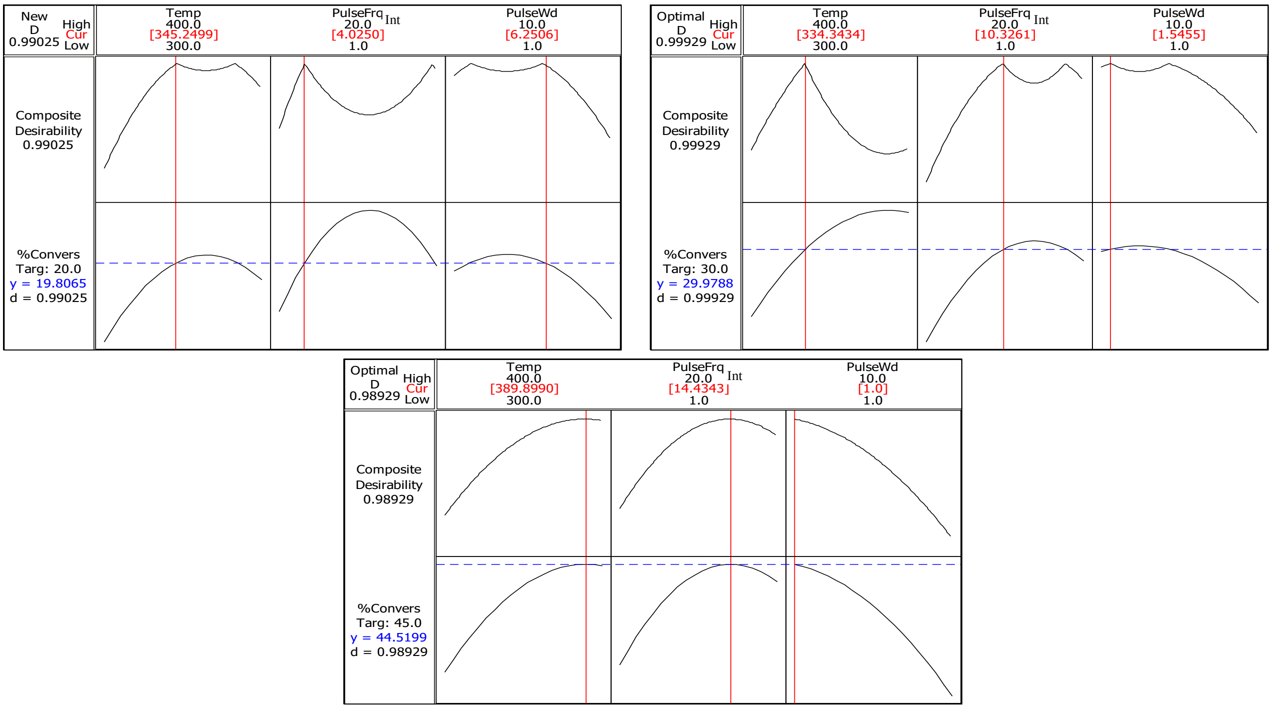

Fig. 9: Variable Parameters for a) 20% b) 30% c) 45% Conversion of MCH During Dehydrogenation Reaction.

up to a certain extent, the percentage conversion efficiency of MCH also increases and during this period pulse width is between 1 to 3 ms. Beyond a certain limit of temperature and pulse width; efficiency gets decreased this may be due to the reason that with high pulse width liquid pool formation takes place on the catalytic surface area and with very high temperature; before the actual interaction between reactant and catalytic surface reactant get started evaporating due to high temperature i.e. less interaction period between reactant and catalyst. Fig. 8 indicates the interaction between temperature and pulse frequency interval at a constant pulse width 5.5 ms. As the temperature increases the efficiency of the percentage conversion of MCH increases and this was also applicable to the pulse frequency interval of the reactant. The temperature range is between 350 to 380°C and the pulse frequency interval range between 11 to 14 sec shows good efficiency of percentage conversion i.e. this range is the best interaction range when the pulse width is constant 5.5 ms. Above this interaction range, efficiency of results decreases due to the facts which we already discussed in earlier figures for high frequency and high temperature.

Model Validation Studies

For the verification of Box-Behnken model and proposed regression, six more sets of experiments were carried out with different combinations of the three independent variables. Percentage conversion efficiency was found out from encoded values of process variables and model equation. For the desirable percentage conversion of MCH, required reaction parameters were identified from the model validity graphs [4,31,32]. Fig. 9 a, b and c are examples of model validity graphs where we targeted 20%, 30% and 45% MCH conversion during the dehydrogenation reaction respectively. These graphs show the required variable parameters for desirable percentage conversion of MCH during dehydrogenation reaction [33,34].

In Fig. 9a, we targeted 20% conversion of MCH during dehydrogenation reaction, and to achieve this result we obtained desirable parameters from the validity graph i.e. 345 °C temperature, 4 sec pulse frequency interval, and 10 ms pulse width. The temperature curve shows a positive slope which indicates that if the temperature increases then percentage conversion also increases. The positive slope of the frequency-time curve indicates that if the frequency period is enhanced then it has a positive effect on percentage conversion [13,35]. But both of these curves show a negative slope after a specific point which may be due to the that; at very high high-temperature reactant gets evaporated before the actual interaction between the reactant and catalyst secondly if a very huge time gap

Table 4: Experimental Conditions for Model Validation with Corresponding Predicted and Observed Responses

Additional Experiment Number	Reaction Temp. (°C)	Pulse Freq. Int. (sec)	Pulse width (ms)	Predicted % Conversion of MCH	Experimental % Conversion of LOH	% Difference
1	345	4	6	19.80	19.13	3.38
2	364	4	4	24.99	26.80	7.24
3	334	10	1	29.97	32.60	9.10
4	370	12	5	34.97	36.80	5.2
5	383	10	2	39.99	37.92	5.17
6	389	14	1	44.51	46.36	4.1

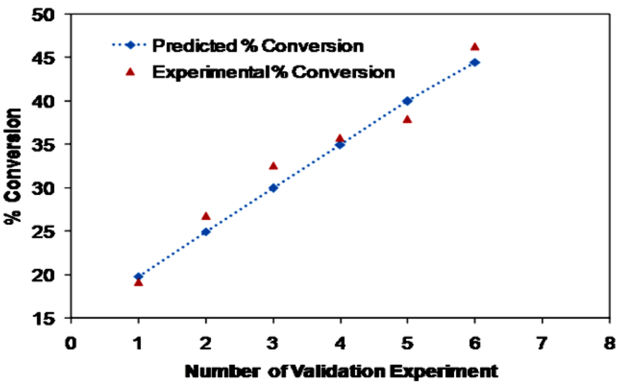

Fig. 10: Comparison between Additional Validity Experimental Results with Predicted Results

is there after each frequency then very less amount of reactant get interacted with catalyst [7,8,30]. The negative slope of pulse width indicates that due to high pulse width, liquid pool formation takes place on the catalytic surface which affects the activity of the catalyst. Fig. 9b shows 30% conversion of MCH at 334°C temperature, 10 s frequencies and 1 ms pulse width here we observed positive slopes for temperature and frequency and negative slopes for pulse width these conditions are the same as we discussed in Fig. 9a.

In Fig. 9c, we targeted 45 % Conversion of MCH during dehydrogenation which was our optimized condition from Box-Behnken trial experiments. Here we observed the peak points of all the reaction parameters [4-6,36]. The temperature curve shows a positive slope up to c.a. 390°C after that it shows a negative slope this may be due to that at a very high-temperature reactant started evaporation before the actual interaction with the catalyst which affects the percentage conversion of MCH. The pulse frequency interval curve shows a negative slope after 14 s, which indicates that a long time gap after each pulse decreases the percentage conversion of reactant. The negative slope of pulse width after 1 ms shows that at high pulse width, there is a chance of liquid pool formation which affects the activity of the catalyst or that pool is act as a barrier between reactant and catalyst and hence, percentage conversion of reactant get decreases [37].

Table 4 presents the expected percentage conversion of MCH, the parameters required for targeted results and the actual experimental results. Under optimum conditions, the percentage conversion of MCH was found to be 46.36% which was very close to the expected value given by the proposed model i.e., 45% Conversion of MCH where independent variables were fixed at temperature 389°C, pulse frequency interval 14 sec and pulse width 1 ms. Fig. 10 shows the results of all the validity experiments with predicted percentage conversion and actual experimental percentage conversion of methylcyclohexane during dehydrogenation reaction by using 5 wt% Pt/ACC. This graph indicates that the proposed quadratic model gives a satisfactory fit to the additional experiments of validation [38].

CONCLUSIONS

ANOVA analysis explains the proposed regression model with independent variables based on Box-Behnken design. This model involves R^2 and R^2_{adj} correlation coefficients of 0.90 and 0.74 respectively. With the aid of RSM, it has been determined from the present findings that the best parameters for LOH percentage conversion are 389°C temperature, 14 sec pulse frequency interval, and 1 ms pulse width, where 44.51% MCH conversion is expected. This was confirmed with the actual experimental value 46.36 % conversion of MCH during dehydrogenation by using a 5 wt% Pt/ACC catalyst. The validation experiments suggested the accuracy of the developed model with Box-Behnken design. The overall study confirms that Box-Behnken design combined with RSM can be efficiently used for the optimization of reaction conditions of the spray pulse reactor during the dehydrogenation of LOH. It is also useful to study independent variables as well as to study the interactive effect of these variables to maximize the percentage conversion of LOH. Here, we achieved our objective that optimization of reaction conditions concerning temperature, pulse width and pulse frequency interval of spray pulse reactor which is used for dehydrogenation of LOH with the help of methylcyclohexane as a reactant and 5 wt% Pt/ACC catalyst. This method proves to be an efficient and time-saving technique for studying the effect of various parameters on the reactor system and reaction. This approach to optimization for LOH dehydrogenation may also be applied to the reaction's other parameters, such as catalyst weight, reactant choice, and catalyst choice. It also explains the interactive effect of these parameters due to which optimization of the whole process was possible.

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