An Experimental Design Approach to Determine Effects of The Operating Parameters on The Rate of Ru promoted Ir Carbonylation of Methanol

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Abstract—carbonylation of methanol in homogenous phase is one of the major routesfor production of acetic acid. Amongst group VIII metal catalysts used in this process iridium has displayed the best capabilities. To investigate effect of operating parameters like: temperature, pressure, methyl iodide, methyl acetate, iridium, ruthenium, and water concentrations on the reaction rate, experimental design for this system based upon central composite design (CCD) was utilized. Statistical rate equation developed by this method contained individual, interactions and curvature effects of parameters on the reaction rate. The model with p-value less than 0.0001 and R^2 values greater than 0.9; confirmeda satisfactory fitness of the experimental and theoretical studies. In other words, the developed model and experimental data obtained passed all diagnostic tests establishing this model as a statistically significant.

Keywords—Acetic Acid,Carbonylation of Methanol, Central Composite Design, Experimental Design, Iridium/Ruthenium

I. INTRODUCTION

ACETIC acid is one of the most important petrochemical products. Worldwide production of acetic acid is over 10 million tons per year [1]. This chemical is widely used for production of vinyl acetate monomer (VAM), synthesis of acetic anhydride and as a solvent for production of the purified terephthalic acid (PTA). Primarily production of acetic acid took place through aerobic fermentation of ethanol. The first commercial process to synthesize acetic acid was using organo-mercury compounds as catalysts upon oxidation of acetaldehyde. Other routes to produce acetic acid include;i) methanol carbonylation, ii) methyl formatisomerization, iii) synthesis gas to acetic acid, iv) ethane oxidation, v) oxidation of ethylene in gas phase, vi) methane carbonylation and vii) acetic acid production from methane and carbon dioxide [2]. Carbonylation of methanol in homogenous phase has the most

contribution in acetic acid production although; improvement in carbonylation of methanol in vapor phase has been successfully performed [3].

The first process for carbonylation of methanol in homogenous phase was commercialized by the BASF in 1960. This process used cobalt as catalyst and iodide as co-catalyst to produce acetic acid to perform carbonylation reaction at high temperature (250 °C) and pressure (680 bar) required. In 1973 process based upon use of rhodium catalyst and iodide co-catalyst, named Monsanto process, commercialized. This process operated at relatively mild conditions (150–200°C and 30–60bar of pressure) [4], [5].In purification stage in Monsanto process due to low CO partial pressure, rhodium catalyst participated, therefore to establish high catalyst stability and high reaction rates, high water concentration in reactor composition required. These restrictions imposed more distillation columns in the later purification stage, to remove considerable amounts of water in product stream [6]. To overcome Monsanto limitation and significant price difference between iridium and rhodium, in 1996 BP Chemicals developed Cativa process based upon iridium catalyst and iodide co-catalyst.

Dependence of carbonylation rate to process variables in the iridium is more complicated than the rhodium system. In Cativa process variables have a complex interaction between themselves as well. Carbonylation rate and selectivity in Cativa process dependedupon temperature, partial pressure of CO, concentrations of water, methyl iodide, methyl acetate, catalyst and promoter. Therefore, for optimization of the reaction conditions, studies required to investigate single and dual interaction effects of process variablesupon the carbonylation rate. Classicalexperimental methods, changing one factor at a time while otherskept constant for a multivariable system is rather time and money consuming.

In this study response surface methodology (RSM) based on central composite design (CCD) was utilized to investigate individual and dual interaction effects of such aforementioned factors upon the carbonylation rate.

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II. EXPERIMENTAL

A. Material

Methyl acetate, methyl iodide and acetic acid were obtained from the Merck Chemicals. Iridium catalyst ($IrCl_3.xH_2O$, 52.88% Ir) and Rupromoter ($Ru_3(CO)_{12}$, 47.2% Ru) were supplied from Heraeus and strem Co.'s; respectively. Carbon monoxide (99.95%) purchased from Technical Gas Service used as feedstock for carbonylation reaction.

B. Experimental Procedure

Carbonylation reaction performed in 450 ml Parr hastelloy B2 autoclave, equipped with a magnetically driven stirrer with liquid injection facility and water fed cooling coils. To maintain autoclave at constant pressure, carbon monoxide supplied to the autoclave. It is reminded that in order to keep the reactor pressure constant, a sensor used to measure this parameter and then through the mass flow controllers, the necessary amounts of CO were injected into the autoclave.Carbon monoxide consumption throughout reaction recorded with a data logger. Carbonylation rate (in mole/l.h), calculated based upon consumption rate of carbon monoxide. Due to esterification of methanol by the acetic acid present as a solvent in the reactor;, methyl acetate used as substrate in batch studies. The overall reaction on this situation may be represented as (1):

$$CH_3COOCH_3 + H_2O + CO \rightarrow 2CH_3COOH \quad (1)$$
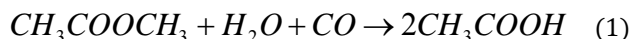
At a certain point of reaction progression, consumption of 1 mole carbon monoxide, 1 mole methyl acetate and 1 mole water was equivalent to carbonylation of one mole methanol. To calculate reaction rate cold degassed volume was used.

For carbonylation reaction runs, desired amounts of methyl acetate, methyl iodide, water and acetic acidwere placed in to the autoclave. Then autoclave sealed and was pressure tested to 35 barg with nitrogen and next flushed three times with CO up to 5 barg. This was heated to the reaction temperature with slow stirring of 150 rpm. Once reaction temperature was reached, catalyst solution ($IrCl_3$, acetic acid and water) injected in to the autoclave to initiate reaction. The reactor pressure was raised to the desired pressure and stirred upto1300 rpm.

In this work autoclave pressure was maintained constant (±5 psig) by feeding CO throughout the reactor. Reaction temperature was held constant (± 1℃) by means of heating mantle connected to temperature control system. Furthermore excess heat removed by cooling coil. At the end of the reaction,the autoclave isolated from CO feeding and cooled down to ambient temperature by a cooling coil.A schematic view of experimental setup to perform carbonylation reaction was shown in Fig.1.

C. Experimental Design

In the RSM approach the first step is to properly design experimentsin order to evaluate model parameters efficiently after performing experiments. Second step is to develop a polynomial equation to whichthe experimental data through regression is fitted. Then test correlation fitness by applying statistical criteria and finally evaluating the reaction system by the fitted model.
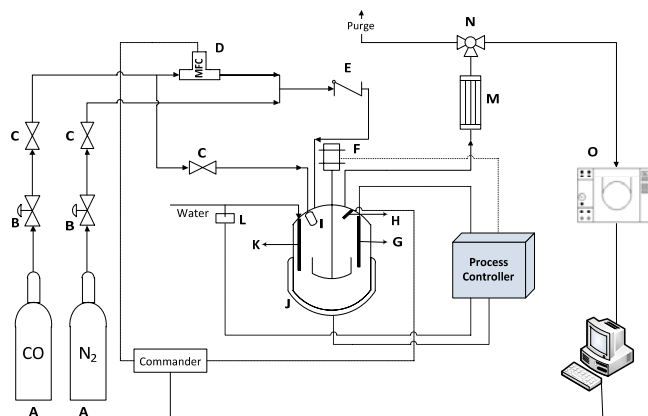

Fig.1 Schematic of the experimental setup used to perform carbonylation reaction. A: Gas cylinders, B: Regulator, C: on-off valve, D: Mass Flow Controller (MFC), E: Check valve, F: Stirrer, G: Thermocouple, H: Pressure sensor, I: Catalyst injection port, J: Mantle Heater, K: cooling coil, L: solenoid valve, M: Condenser, N: Three-way valve, O: Gas Chromatography

To develop a second order polynomial for the rate response (as (2)),central composite design (CCD) was used to statistically design experiments [7]-[9].

$$y = a_0 + \sum_{i=1}^{k} a_i x_i + \sum_{i=1}^{k} a_{ii} x_i^2 + \sum_{i}^{k} \sum_{\substack{j \\ i<j}}^{k} a_{ij} x_i x_j + \varepsilon \quad (2)$$

Where y is the predicted response, a_0 is a constant, a_i is the ith linear coefficient, a_{ii} is the ith quadratic coefficient, a_{ij} is the$i$th interaction coefficient, x_i is the independent variable, k is number of factors and ε is error. Coefficients of the model predicted through regression of the obtained experimental data. Detailsof parameter estimationsforthe model doneby these authors are reported elsewhere [7].

A most popular second order experimental design is the central composite design (CCD) which utilized in this study. CCD is an efficient way providing sufficient amounts of information to test fitness of a model. Furthermore, the CCD did not require large number of design points; thus, reduced the cost and time needed for performing experiments. Number of experiments in CCD contains three sets including; (1) fractional factorial runs (2^{k-1}, where k is the number of factors) studying factors at -1 (minimum) and +1 (maximum) level, (2) center point runs examining factors at center point of the design space, helping in understanding of curvature and replicating them to evaluate pure errors and (3) axial or star point runs (2k, where k is the number of factor) setting all factors to 0 (*i.e.*; the center point) except one, which has the

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value +α and −α [8].

In this work Design-Expert® software (Ver. 8.0.1) were used to design experiments. CCD with $\alpha = k^{1/4}$, where k is number of factors, each of which varied over five levels used to investigate the effect of parameters on ruthenium promoted carbonylation of methanol using iridium catalystin order to acquire a good correlation model to predict the optimum reaction conditions. To reduce number of experiments, resolution V applied to experimental design. In resolution V main effects are aliased with 4-factor interactions, and 2-factor interactions are aliased with 3-factor interactions [7]. The factors picked out to investigate this reaction were: temperature, pressure, iridium, ruthenium, methyl acetate, methyl iodide concentrations and the water content. Actual and coded value for each factors investigated in this work are presented in Table I.Satisfaction degree of the polynomial equation developed through regression of (2) was evaluated by R^2 which was a measure of the amount of variation around the mean determined by the model through (3) and R_{Adj}^2 which was a measure of the amount of variation around the mean determined by experiments and adjusted for the number of terms in the model through (4); *i.e.*;

$$R^2 = 1 - \frac{SS_{residual}}{SS_{model} + SS_{residual}} \qquad (3)$$

$$R_{Adj}^2 = 1 - \frac{SS_{residual}/DF_{residual}}{\left(SS_{model} + SS_{residual}\right)/\left(DF_{model} + DF_{residual}\right)} \qquad (4)$$

Here SS is the sum of squares and DF is the degree of freedom. The statistical importance of this model was checked with adequate precision through (5) and (6), which basically is a signal-to-noise ratio; *i.e.*:

$$Adequate\ precision = \frac{\max(\hat{y}) - \min(\hat{y})}{\sqrt{\overline{V}(\hat{y})}} \qquad (5)$$

$$\overline{V}(\hat{y}) = \frac{1}{n}\sum_{i=1}^{n} V(\hat{y}) = \frac{P\sigma^2}{n} \qquad (6)$$

Here $\hat{y}$ is the predicted response, P is the number of model parameters, σ the residual mean square and n is the number of experiment. This compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination. Other criteria to check statistical significance are the F- and P-values.

TABLE I
LEVEL FOR PROCESS VARIABLES IN ACTUAL AND CODED VALUE

Independent variable	Unit	Level				
		-α (-1.63)	-1	0	+1	+α (+1.63)
A: Temperature	℃	175	179	185	191	195
B: Pressure	bar	20	23	29	35	38
C: Iridium	ppm	500	788.91	1250	1711.01	2000
D: Ruthenium	ppm	0	500.78	1300	2099.22	2600
E: Methyl Iodide	wt.%	4	6.7	11	15.3	18
F: Methyl Acetate	wt.%	12	17.39	26	34.61	40
G: Water	wt.%	6	7.93	11	14. 07	16

III. RESULTS AND DISCUSSION

Perturbation plot shows comparison between all factors at a selected point in the design space. Perturbation plot for the carbonylation rate was shown in Fig.2. The rate response is drawn by changing only one factor over its range while others held constant. The plot demonstrates the effect of all factors at center point in the design space (*e.g.*; temperature of 185℃, pressure of 29 bars, Iridium contentof 1250 ppm, Ruthenium concentration of 1300 ppm, Methyl iodide contentof 11 wt.%, Methyl acetate concentration of 26 wt.% and water content of 11 wt.%). The comparatively flat line of methyl iodide shows insignificance effect of this factor on the reaction rate in the design space considered. All factors except water concentration have positive effect on the rate (*e.g.*; evencoefficient of methyl iodide is very low in(3) yet it is of positive effect). This might be concluded from this Equation, where all linear terms have positive signs, except water. By comparison of coefficients of the aforementioned factors in that equation, significant parameters on the rate response were determined in the order of: temperature, pressure, ruthenium, iridium and methyl acetate. It might be seen from(3) and perturbation plot, pressure and water concentration had curvature effect. Reaction rate approximately increased linearly with the temperature and concentrations of iridium, ruthenium and methyl acetate in the considered design space.

To evaluate effects of process variables on the reaction rate in carbonylation reaction, experiments performed based upon design matrix of central composite design with six replicated points (*i.e.*; total number of experiments were 50 runs). To minimize effect of uncontrolled factor, experiments were performed in random sequence. After evaluation of experimental results, a quadratic function for reaction ratewas obtained by utilizing Design-Expert® 8.0.1.

To estimate coefficient of polynomial, the least square procedure was applied, and then based upon fitted surface response surface, analysis were performed. The quadratic equation based upon coded value, for the reaction rate undertaken is:

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$Y_1 = 22.48 + 3.52A + 3.36B + 2.49C + 3.20D - 8.432 \times 10^{-3}E + 1.52F - 2.83G - 1.87AC - 1.56AE - 1.96AF + 1.5AG + 2.15BD + 1.75BE - 1.04CD - 1.89CG - 1.03DE - 1.47EG - 3.30B^2 - 2.95G^2$ (7)

Statistical importance of the generated model evaluated by the F-test (*i.e.*; Fisher test) was calculated by the Model Mean Square divided by the Residual Mean Square, for analysis of variance (ANOVA). Results of ANOVA for reaction rate were presented in Table II. ANOVA results from the Table II confirmed this correlation may indeed be applied to the designed space. The F-value for the ratewas 21.05, thus, forthe rate response there is only a 0.01% chance that a "Model F-value" this large could occur due to noise. Very low probability value for both correlations(p-value < 0.00001) implies these are significant for 95% confidence interval (*i.e.*; p-value less than 0.05 indicate significance). Insignificant terms in models has p-value greater than 0.10, such terms may be droppedout manually from the correlation to enhance regression quality. For the rate response, AB, AD, BC, BF, BG, CF, CE, DF, DG, EF, FG, A^2, C^2, D^2, E^2, F^2 and E terms were determined to not be significance in the model in the design space considered and were removed from it. It is noteworthy that, in spite of E term had p-value greater than 0.10, it was kept in the respective correlation since some interaction effects involving E had significant co-effects on the rate response.

II for the rate response,the p-value for lack of the fit test is greater than 0.05, thus not significant. Adequate precision for the rate response was 17.58. This value is greater than 4, thus, the statistical criterion established for such model is significant for the described process. Goodness of the predicated values for the response by the model was measured by the predicted R-square. For an adequate model predicted, R-square was within 0.2 of the adjusted R-square. From Table II, the fact revealed that the rate response passed this conditionsuccessfully.

Predicted versus actual plot for the rate response was shown in Fig.3. As may be seen from thisFigure the values predicted by the model and results obtained from experimentsplaced very closely to the diagonal line due to their low differences. Furthermore, coefficients determined for therate responseswereclose to unity ($R^2 = 0.93$). Thisfurther supportedthe fact that there was a good fit between the actual and predicted values.

TABLE II
ANALYSIS OF VARIANCE FOR THE REACTION RATE RESPONSE

Source	Sum of squares	DF	Mean square	F value	p-value prob> F
For Y_1					
Model	2685.25	19	141.33	21.05	< 0.0001
Residual	201.42	30	6.71		
Lack of fit	187.76	25	7.51	2.75	0.1314
Pure error	13.65	5	2.73		
Cor total	2886.67	49			

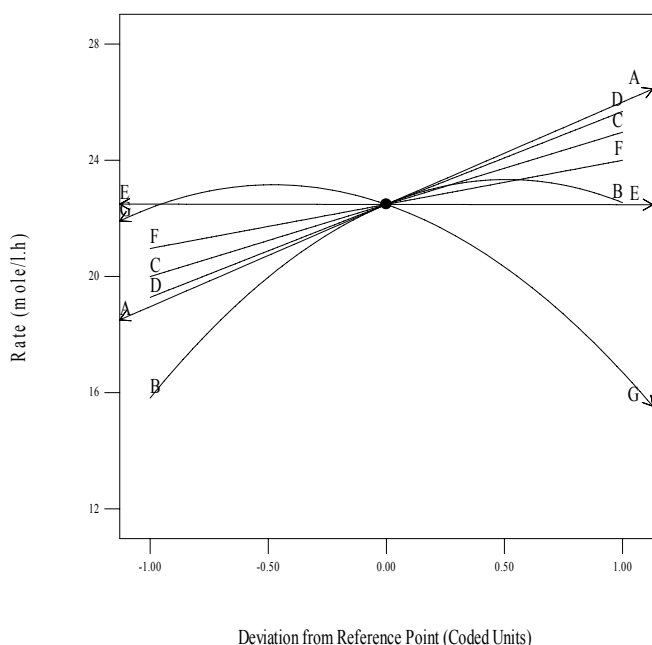$R^2 = 0.9302$, Adj-$R^2 = 0.8860$, Pre-$R^2 = 0.8308$, Adequate precision= 17.585

Fig.2 Perturbation plot for the rate response (A: Temperature, B: Pressure, C: Iridium, D: Ruthenium, E: Methyl iodide, F: methyl acetate and G: Water contents)
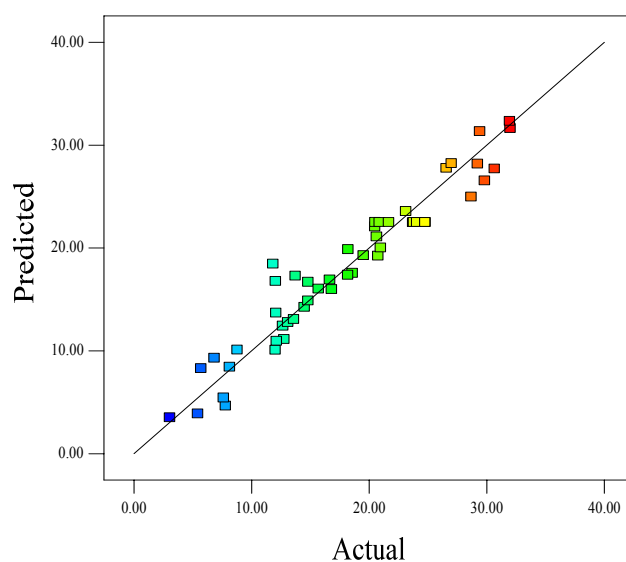
Fig.3 The actual versus predicted values for the reaction rate

Comparison between the residual error and pure error was done with "lack of the fit" test. As may be seen from the Table

If points in a normal probability plot followed a straight linethat would indicate the residual(*i.e.*; difference between the observed and predicted values) follow normal distribution.Internally studentized residual is the residual divided by the estimated standard deviation of that residual

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which is ameasure of the number of standard deviations separating the actual and predicted values.Results are shown in Fig.4 led to conclusion that there was no apparent problem with the normality and no serious violations in the assumptions that errors arenormally distributed and independent of each other.

Fig.5 showed the internally studentized residuals and the predicted reaction rate. It tests the assumption of constant variance. As shown in this Figure, points have scattered random pattern and all values of the predicted rate lied between -3 and +3 of standard deviation. ThisFigure also indicated that there was not any apparent problem with the rate response.
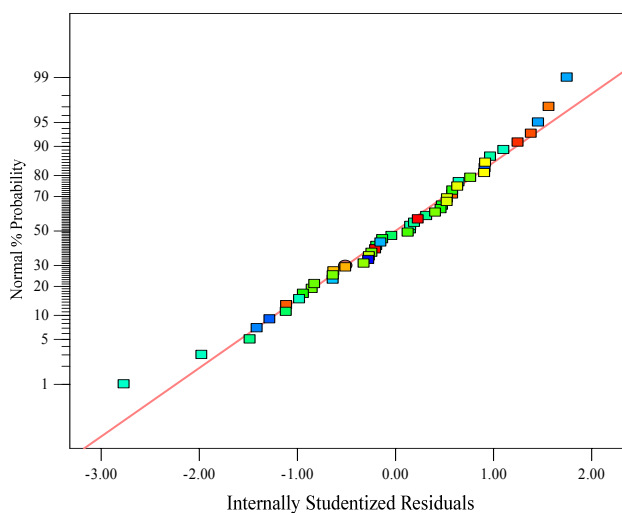
respectively. The external studentized residuals werethemeasure of how many standard deviations the actual value deviated from the predicted value after deleting aforementioned effects in (7). Most of the standard residuals should lie in the interval of ±3.50 and any observation with a standardized residual outside of this interval is potentially unusual with respect to its observed response.Fig.6 and Fig.7, the external and internalstudentized residual values below the interval of ±3.50 indicated that the approximation of the fitted model with the carbonylation rate response was satisfactory.

Fig.4The internally studentized residuals and normal % probability plot for the Rate response

Fig.6 The internally studentized residuals plot determinedfor the carbonylation rates
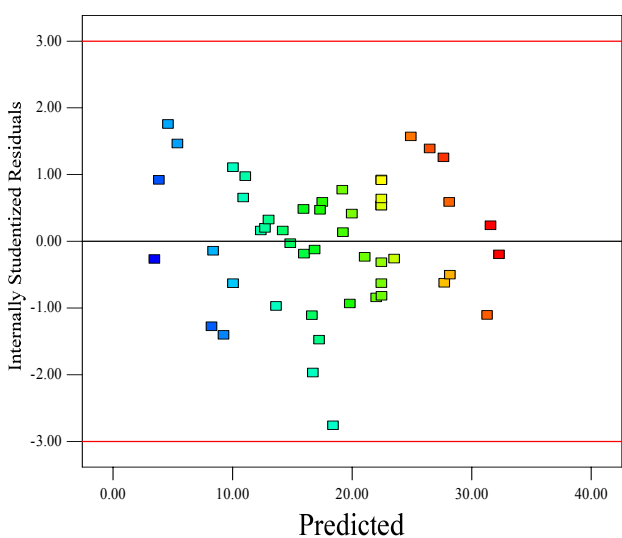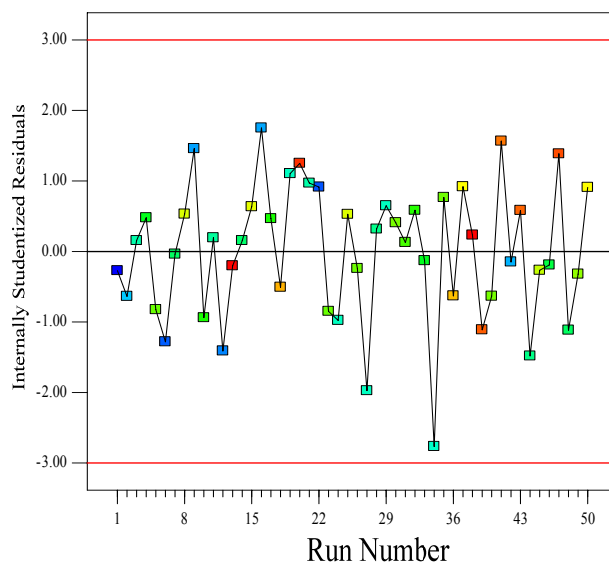

Fig.5 The predicted rate and internally studentized residuals plot
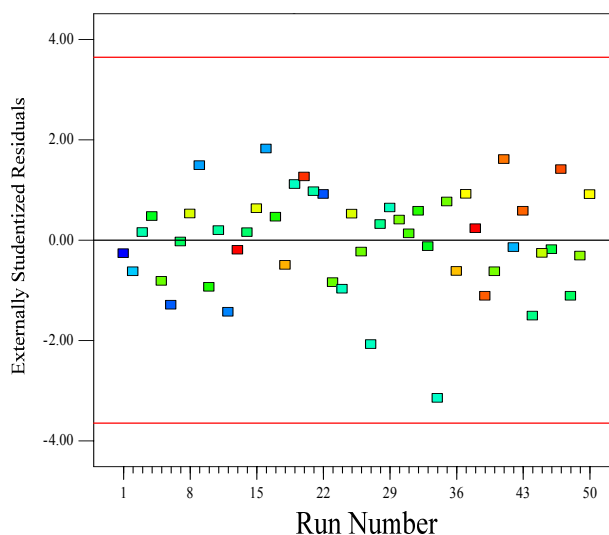
Fig.7 The externally studentized residuals plot determined for the Carbonylation Rates

The external and internalstudentizedresidual plots for the carbonylation rateswere shown in Fig.6 and Fig.7;

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TheBox-Cox plot provides a guideline for selecting the correct power law transformation ($y' = y^\lambda$). The software utilizedin this research recommended transformation based upon the best lambda value, which is found at the minimum point of the curve generated by the natural log of the sum of squares of the residuals. If the 95% confidence interval around this lambda included 1, then the software does not recommend a specific transformation. As shown in Fig.8,the Box-Cox plot for data obtained in this research did not require any transformation, because λ=1 was located in the 95% confidence interval.
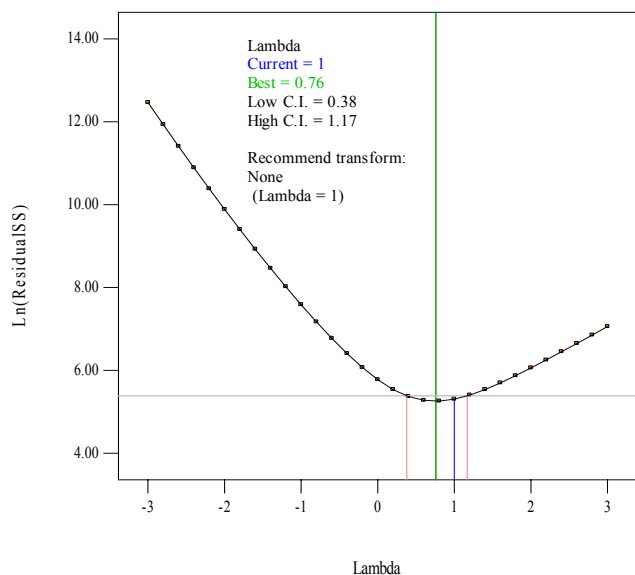

Fig.8 The Box-Cox plot for the rate data in this work

IV. CONCLUSION

In this study experimental design approach based upon central composite design was used to investigate effectsof parameters like iridium, ruthenium, methyl iodide, methyl acetate and water concentrations as well as, temperature and pressure on the carbonylation rate of methanol. It was demonstrated that an increase in all factors except water and methyl iodide contents would enhance the reaction rate. Furthermore, influence order of importance of aforementioned factors on the reaction rate was shown to be as follow: temperature, pressure, ruthenium, water, iridium and methyl acetate concentrations. In addition, methyl iodide concentration did not display any significant effect on the reaction rate. Furthermore, in the reaction rate correlation,a square effect of water and pressure were pronounced. Ultimately, a second order polynomial for prediction of the reaction rate was developed which only containedsignificant effectswith p-values less than 0.1. P-values for the model less than 0.0001 conditions confirmed this quadratic model fitted the obtained experimental rate data properly. Inaddition,the "lack of fit" test for this model was not significant (p-value greater than 0.1). This model and experimental data pass all diagnostic tests, establishing it as statistically significant. This study showed how one may utilize statistical means to carefully study effects of parameters both individually and in dual interactions form and paves down the road for optimizing the reaction rate conditions currently under investigation by these researchers.

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