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Parametric optimization and rate laws determination for the conversion of *4-tert*-butylbenzoic acid to methyl *4-tert*-butylbenzoate

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The esterification of *4-tert*-butylbenzoic acid has been studied to produce methyl *4-tert*-butylbenzoate, having its widespread applications in the pharmaceuticals, perfumes, flavor, cosmetics, and fragrance industries. The limiting nature of the reaction is catalyzed with methane sulphonic acid, a green catalyst. The study focused on optimization of the experimental parameters to achieve higher conversion of acid with the aid of statistical analysis based on the Taguchi technique. An L_9 array, S/N ratios, and ANOVA have been used with catalyst concentration, molar ratio and time as the process parameters with acid conversion as the response variable. Parametric optimization based on Taguchi method suggest a combination of optimal parameters as 10% catalyst concentration, 5:1 methanol to acid molar ratio and 2 h at a refluxing temperature of 67°C. A kinetic investigation for the esterification is also conducted to define the rate equations that govern the overall progress of reaction and the results established that the reaction follows irreversible pseudo second order rate in the initial phase followed by the reversible second order rate. The proposed model is found to be in good agreement with the experimental results.

Keywords: Kinetic model, Methyl *4-tert*-butylbenzoate, Methane sulphonic acid, *para-tert*-butylbenzoic acid, Taguchi optimization technique, Rate constants.

The esterification reaction is an active area of research for the researchers over the decades. It is one of the basic reactions that involve in the production of a large volume of intermediates for the specialty chemical industries. Esterification is a fundamental reaction between carboxylic acid and alcohol with or without the presence of a catalyst, which produces ester and water, also known as Fischer esterification. In non-catalyzed esterification of carboxylic acids, the acid themselves act as a catalyst however the reaction is very slow to achieve equilibrium. In catalytic reaction, the proton of a catalyst is attached to the lone pair of double-bonded oxygen on the carboxylic group, which results into more reactive electrophile, that promotes nucleophilic attack of the alcohol to shape a tetrahedral intermediate[1,2]. Un-symmetry of this transitional complex eventually produces the ester. These esters can also be produced via different reaction routes viz., acid chlorides, amides, nitriles, ethers, aldehydes, ketones, acid anhydrides, unsaturated hydrocarbons, and alcohols. The esters possess a characteristic pleasant and fruity odor familiar in organic chemistry and biological materials[3]. It is used as an environmentally friendly solvent for paints, adhesive and also used as an aromatic agent for many food industries, cosmetics, pharmaceuticals, polyesters and chemical industries[4-6]. Recently, long chain mono alkyl esters have shown promising potential in fuel applications for diesel engines which are driving most of the industries[7,8].

Among different alkyl esters produced, Methyl 4-tert-butylbenzoate is a synthetic chemical of commercial importance. It is used specifically for the preparation of valuable products such as Avobenzone, 2,3-dihydrobenzofuran-3-ylacetic acid and tris(4-tert-butylphenyl) methyl chloride[9-11]. Methyl aromatics route by aerobic photo-oxidation using anthraquinone-2,3-dicarboxylic acid as an organophotocatalyst is investigated for the synthesis of methyl 4-tert-butylbenzoate[3]. Synthesis based on electrochemical oxidation of the corresponding methylbenzenes or benzaldehyde dialkyl acetals in the presence of an alkanol and of a halogenated triarylamine (tris (2,4- dibromophenyl)-amine) derivative is also reported[12]. Esterification of *para-tert*-butyl benzoic acid with methanol in the presence of acidic catalysts such as titanium sulfate, paratoluene sulfonic acid, ferric chloride, and dimethyl piperazine are also reported[13-16]. In the present study, we investigated the preparation of methyl 4-tert-butylbenzoate from *4-tert*-butylbenzoic acid using methane sulphonic acid (MSA). The study substitutes the high concentration mineral acids (H_2SO_4, HCl, HI, H_3PO_4) that are generally used to achieve a high yield of ester. These mineral acids cause several drawbacks in industrial applications such as corrosion, energy consuming product separation, and difficult and costly recovery of the product. MSA is the strong acid with less affinity for oxidizing organic compounds, less toxic and corrosive as compared to other mineral acids[17]. It is an intermediary catalyst between the sulfuric acid (H_2SO_4), and methyl sulfonyl methane ($(CH_3)_2SO_2$), in which $–CH_3$ group efficiently take up the place of $–OH$ group at each step. To achieve higher conversion of *4-tert*-butylbenzoic acid based on MSA, parametric optimization of reaction parameters has been investigated with the aid of statistical analysis based on the Taguchi technique and detailed in the later section. The investigated reaction parameter includes catalyst concentration, acid to alcohol molar ratio and time. Although the reaction rate and the conversion in esterification reactions can be enhanced by elevation of temperatures, but it is generally desired in the industrial field to develop an efficient esterification process for high yield of ester production, under mild reaction conditions and thereby investigated under refluxing methanol condition[18].

An exhaustive study has been performed on the kinetics evaluation for esterification of carboxylic acids, where Berthelot and Saint-Gilles were first one to document the esterification of acetic acid[19]. Normally, esterification initial kinetic studies are performed using stirred batch reactor on a small scale. The kinetic data along with the knowledge of the reactor configuration and the build out of a computerized simulation model for the esterification reaction are a very useful component in the optimization of esterification reactions. In spite of this, all esterification reactions still do not permit any exact mathematical treatment. Different researchers have studied the kinetics of esterification reaction of carboxylic acids using an acid catalyst. In a study of the esterification reaction of acetic acid with 2,3-butanediol in the presence of the sulphuric acid catalyst, observation stated that the reaction happens along two pairs of successive reversible reactions which were at almost equivalent speeds. Even in the early stages, these reactions do not follow simple first-, second-, or third-order equation[20]. An empirical expression was developed for a reaction between 1-butanol and acetic acid at temperature 0−120°C and the rate constant deviating 0.15 from the molar ratio of reactants, temperature, and concentration of catalyst was determined[21]. The sulfuric acid as a catalyst was utilized with 1-butanol to an acetic acid molar ratio of 3:19.6 and the concentration of catalyst to be 0.14 wt %. Berrios *et al.* have reported the kinetics of sunflower oil with methanol in the presence of H_2SO_4 catalyst, wherein it was shown that forward reaction fitted to first-order kinetics and the backward reaction to a second order kinetics[22.] Noureddini and Zhu investigated the transesterification of soybean oil with methanol representing that the experimental data is very well fitted to the second order kinetic mechanism[23].

In the present study, we have described the preparation of methyl *4-tert*-butylbenzoate using MSA as a catalyst. The product ester is a very important intermediate, which is widely used in the organic synthesis, pharmaceutical industry, cosmetics, flavors and fragrances industries. There is a great significance to evaluate and optimize the process parameters of ester preparation due to its high demand across worldwide. In the present study catalytic esterification of *4-tert*-butylbenzoic acid with methyl alcohol produced methyl *4-tert*-butylbenzoate and water as products. The statistical analysis of reaction parameters was carried out employing Taguchi technique for the conversion of *4-tert*-butylbenzoic acid. An L_9 orthogonal array, S/N ratios, and ANOVA were used with catalyst concentration, molar ratio and time as reaction parameters and conversion of the acid as the response variable. Furthermore, using optimized parameters a kinetic evaluation was performed for the esterification reaction and an overall reaction kinetic model was developed. The experiments were conducted at different temperatures of 55, 60, 65 and 70°C with catalyst concentration 10% (w.r.to weight of acid), methanol to the acid molar ratio of 5:1 and time duration of 2 h. Kinetic rate constants were determined by experimental data and the values of activation energy were established using Arrhenius equation.

Experimental Section

Materials

4-tert-Butylbenzoic acid, anhydrous sodium sulfate and 2-propanol of purity ≥99.0% were procured from Sigma-Aldrich. Analytical grade methanol of purity

≥98% and potassium hydroxide pellets of purity ≥95% were purchased from s-d fine chemicals Ltd, Mumbai, India. Methane sulphonic acid catalyst of purity ≥98% was procured from Molychem, Hyderabad, India.

Equipment

The esterification of *para*-*tert*-butylbenzoic acid with methanol was performed ina one liter jacketed glass reactor provided with a digital overhead stirrer, which is a directly controlled model having a motor rating of 83/75 W, a max torque of 85 N cm, impeller diameter 10mm and a speed range of 200–3000 rpm. The impeller used for uniform mixing of the reaction mixture was an anchor type made of Teflon. The reactor assembly was equipped with reactor with a four necked glass top lid with provision for liquid phase temperature measurement in the reactor and periodic withdrawal of liquid samples during the reaction. The temperature measurement was done using a platinum resistance type thermocouple calibrated point to point. A Polyscience thermostat (model No. 9702) with a digital temperature controller was connected to the reactor for circulating water through the jacket of the reactor for maintaining the temperature (±0.01°C accuracy) of the reaction mixture inside the reactor. A schematic diagram of the reactor assembly is shown in Fig.1.

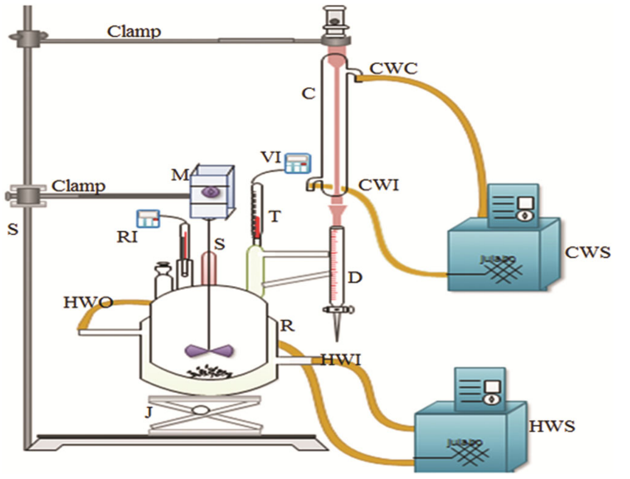


Fig. 1 — Schematic diagram of Experimental setup*:* R – Jacketed reactor, T_R – Thermowell to record reaction temperature, RI – Reaction temperature indicator, VI – Vapor temperature indicator, F – Feed inlet, C – Condenser, S – Stirrer, CWS – Cold water source, HWS – Hot water source, M - Motor, HWI – Hot water inlet stream, HWO – Hot water outlet stream, CWI – Cold water inlet stream, CWO – Cold water outlet stream, J-jack, S-stand, D-Decanter

Experimental procedure

In esterification of *4-tert*-butyltoluene to the corresponding methyl *4-tert* butylbenzoate, the optimization of the parameters was performed using MSA catalyst at various catalyst loadings (5-10 wt % w.r.to acid), acid to methanol ratios (1:4–1:6) and time (1-2 h). For optimization of the reaction parameters, *4-tert*-butylbenzoic acid (178 g) was charged to the reactor followed by addition of required quantity of methanol. The heating of the reactor, stirring and the cold water circulation in the condenser was started immediately. The reaction was conducted at methanol reflux temperature to minimize the losses of methanol for a constant mixing speed of 250 rpm. A predetermined quantity of MSA was added dropwise to the reactor. Samples were withdrawn at regular time interval. The progress of the reaction was followed by analysis of intermediate reaction samples for ester formed and acid converted using gas chromatography at different intervals of time. The kinetic evaluation was carried out at the optimized parameters of catalyst concentration, methanol to the acid molar ratio for 2 h at temperatures 55, 60, 65 and 70°C at a fixed stirring speed.

Analytical methods

The purity of acid was checked with Shimadzu GC-2010 using flame ionization detector (FID) fitted with ZB-5 column having 30 m length and 0.53 mm ID and confirmed by titration with KOH. During esterification, the conversion was monitored by drawing samples intermittently from the reaction mixture and analyzed. To effectively stop the reaction, samples taken from reaction mixture were immediately quenched and diluted with cold 2-propanol and anhydrous sodium sulphate was used for absorption of moisture in samples. The amount of ester formed and the reactant at the end of the experiment was estimated by the Indian Standard Method by IS: 326 (Part VIII)-1980: Determination of ester value, the content of esters and combined alcohols. The strength of MSA was determined by Indian Standard Method by IS: 326 (Part VII)-1980. The number of milligrams of KOH which is required to neutralize 1 g of sample was evaluated in the reaction mixture employing acid value. Following equations were used for the acid value and ester value determination:

$$\text{Acid value} = 56.1 \text{ x V x} \frac{\text{N}}{\text{M}} \qquad \dots (1)$$

where the V= volume of KOH solution (mL), N= normality of KOH solution, M= mass of the sample to be tested (g), 56.1 is the equivalent mass of KOH.

$$\mathrm{E.V} = \frac{56.1 \times 0.5}{\mathrm{W}}(\mathrm{Vo} - \mathrm{V1}) - \mathrm{A.V} \qquad \ldots (2)$$

where E.V = Ester value determined, V_0 = volume of HCl used for the blank test (mL), V_1= volume (mL) of HCl used for the determination, W = mass of the test sample (g), A.V= acid value determined.

Taguchi optimization technique

Taguchi method is a robust design of experiments based on orthogonal arrays. It provides a set of minimum number of experiments which will give the comprehensive details regarding the influence of all the factors on the performance parameter. This method provides less variance for the experiments with optimum settings of factor levels to investigate the effect of different factors on the mean and variance of performance[24]. Zhang *et al*. reported the importance of Taguchi design that considers multiple factors and variation caused by noise factors, which are typically ignored in the conventional DOE approach[25]. A statistical Taguchi approach has been used by several researchers to analyze the parametric effects on the esterification and trans-esterification process[26]. The present study is aimed to identify the optimal reaction conditions that yield highest *4-tert*-butylbenzoic acid conversion. The steps followed in Taguchi method are described in Fig. 2.

S/N ratio analysis

S/N ratio measures the robustness of the process, which makes the response variable insensitive to the changes caused by noise factors. In the optimization of reaction parameters, signal to noise ratio (S/N) is the objective function, which is defined as the logarithmic transformation of standard mean square deviation of desired performance, that is optimized for the desired responses. Here, signal (S) is the mean (desirable value) and noise (N) is standard deviation (undesirable value). There are different criterions for S/N ratio which can be chosen depending on the goal of the experiment as described below:

I. If goal is to maximize the response;

Larger is better is the criterion:

$$\frac{S'}{N_i} = 10\mathrm{Log}_{10}\left[\frac{1}{n_j}\sum_{j=1}^{n}\frac{1}{Y_i^2}\right] \qquad \ldots (3)$$

II. If goal is to minimize the response;

Smaller is better is the criterion:

$$\frac{S''}{N_i} = -10\mathrm{Log}_{10}\left[\frac{1}{n_j}\sum_{j=1}^{n}\frac{1}{Y_i^2}\right]$$

III. If goal is to reduce variability around the target;

Nominal is best is the criterion:

$$\frac{S'''}{N_i} = -10\mathrm{Log}_{10}\left[\frac{1}{n_j}\sum_{j=1}^{n}\left[\frac{\text{square of mean}}{\text{variance}}\right]_i\right]$$

where subscript i is the Experiment number, n is the number of replicates of experiment 'i', j is the number of replicates and Y is the response variable.

The results are presented in the form of main effect plots for S/N ratios and means, response table for S/N ratios and means in terms of delta and rank. Delta is the difference between the maximum and minimum value for each response characteristic and rank is the order of factors from the maximum effect to the little effect.

Design of Experiments

The esterification reactions of *4-tert*-butylbenzoic acid with methanol in the presence of MSA were

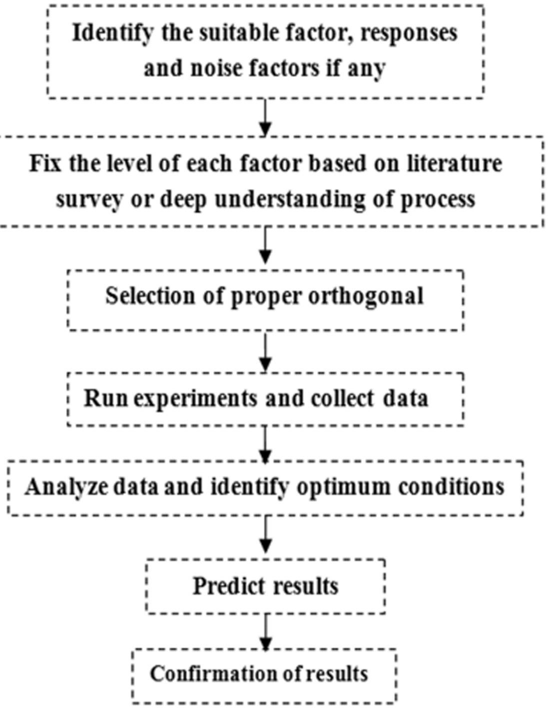


Fig. 2 — Procedure of Taguchi method

planned according to Taguchi robust design method to obtain the optimum reaction parameters for maximum conversion of acid. The three factors; catalyst concentration (X_1), the molar ratio of reactants (X_2), and time (X_3) were investigated to study the effect on the response (Y) i.e. conversion of acid. The levels of factors were fixed on the basis of preliminary experiments performed for a better understanding of the process. Three levels were considered for each factor: 5%, 7.5% and 10% (w.r.to wt acid) for catalyst concentration, 1:4, 1:5 and 1:6 for the molar ratio of acid to methanol and 1, 2 and 3 hr for time. Using statistical software, the L_9 orthogonal array of Taguchi method was generated and the set of experimental runs are reported in Table 1. According to L_9 orthogonal array, a total of 9 experiments have been carried out to get a complete picture of the effect of factors (X_1, X_2 and X_3) on the response variable (Y).

Modeling of 4-tert-butylbenzoic acid esterification reaction: Kinetic evaluation

The esterification reaction of *4-tert*-butylbenzoic acid is represented as an irreversible pseudo second order reaction ensued by a reversible second order equilibrium, described in below section. The kinetic model has been developed by accounting the acid conversion as the rate determining step. Hence, the esterification reaction is as presented in Eq.(4)

$$A + B \leftrightarrow C + D \qquad \ldots (4)$$

where A, B, C & D indicates *4-tert*-butylbenzoic acid, methanol, methyl *4-tert* butylbenzoate and water, respectively.

Pseudo irreversible reaction regime

The excess of methanol along with little product concentration in the reaction mixture and the conversion of the acid to ester follow pseudo irreversible second order reaction kinetics in the early hours of reaction mixture expressed as[27]:

$$-r_A = -\frac{dc_A}{dt} = k_1 C_A^2 \qquad \ldots (5)$$

where k_1 represents reaction rate constant for irreversible pseudo second order reaction regime. The Eq. (5) is simplified in terms of acid conversion x_A expressed as below:

$$-\frac{dx_A}{dt} = k_1 C_{Ao}(1 - x_A)^2 \ldots (6)$$

The integration of Eq. (6) yields:

$$\frac{1}{1-x_A} = f(x_1) = k_1 C_{Ao} t + c_1 \qquad \ldots (7)$$

The term on the left side of Eq. (7) is represented as a function of conversion i.e. $f(x_1)$. The straight fit of the data to time dependent Eq. (7), the slope and the intercept of the line signify the irreversible reaction rate and integral constant, respectively.

Equilibrium reaction regime

The forward and backward reaction rate follows second order kinetics, as the equilibrium of the reaction is attained[28]. Stamenkovic et al. have demonstrated the reversible second order mechanism for the forward and backward reaction[29].

$$-r_A = -\frac{dc_A}{dt} = k_2 C_A C_B - k_2^{'} C_C C_D \qquad \ldots (8)$$

where k_2 and $k_2^{'}$ are forward and reverse reaction rate constants respectively, C_B, C_C and C_D are molar concentration of methanol, *4-tert*-butylbenzoic acid and water in reaction mixture respectively. The initial concentration of methanol C_{Bo}, $C_{Co} = 0$ and

Table 1 — L_9 (3^3) orthogonal array of experiments and results.

Exp No.	X_1	X_2	X_3	X_1	X_2	X_3	Y
		Uncoded variable			Coded variable		
1	1	1	1	5	4	1	72.099
2	1	2	2	5	5	2	89.423
3	1	3	3	5	6	3	83.738
4	2	1	2	7.5	4	2	95.082
5	2	2	3	7.5	5	3	95.454
6	2	3	1	7.5	6	1	95.524
7	3	1	3	10	4	3	96.723
8	3	2	1	10	5	1	93.760
9	3	3	2	10	6	2	99.970

X_1; catalyst concentration (% w.r.to *4-tert*-butylbenzoic acid),
X_2; molar ratio of MeOH to *4-tert*-butylbenzoic acid,
X_3; time in hours,
Y; % *4-tert*-butylbenzoic acid conversion.

water $C_{Do} = 0$. Since, $C_B = C_{Ao}(M - x_A)$, $C_C = C_{Ao}x_A$, $C_D = C_{Ao}x_A$ Eq. (8) is modified as:

$$\frac{dx_A}{dt} = k_2C_{Ao}(1 - x_A)(M - x_A) - k_2^{'}C_{Ao}x_A^2 \qquad \text{... (9)}$$

where $M = C_{Bo}/C_{Ao}$ is the molar ratio of methanol to acid (5:1) and upon the integration of Eq. (9) in terms of conversion as:

$$\frac{2}{\Delta} * \ln\frac{\{2x_A(1-(1/k))-6-\Delta\}}{\{2x_A(1-(1/k))-6+\Delta\}} = f(x_2) = k_2C_{Ao}t + c_2 \qquad \text{... (10)}$$

The expression on the left side of Eq. (10) is expressed as $f(x_2)$. Where delta, $\Delta = \sqrt{36 - 20(1 - 1/k)}$, $k = k_2/k_2'$ is the equilibrium rate constant for esterification reaction and c_2 is integration constant. The equilibrium constant was determined from equilibrium conversion which is obtained experimentally by $r_A = 0$ or from the correlation, $\Delta G = -RTln(k)$. This correlation relates free energy in term of equilibrium rate constant. Moreover, equilibrium rate constant can be related to different temperatures by Van't *Hoff* equation. The slope and the intercept of Eq. (10) give the reversible forward reaction rate, k_2 and integral constant respectively. Hence, an overall generalized rate expression for the esterification of acid can be written as:

$$-r_A = \frac{C_A}{\frac{1}{k_1C_A} + \frac{1}{k_2\left(M_{BA} - \frac{M_{CA}M_{DA}}{k_2/k_2'}\right)}} \qquad \text{... (11)}$$

The above rate expression shows pseudo reaction resistance and equilibrium reaction resistance involved in the esterification reaction.

Results and Discussion

Effect of reaction parameters: Optimization using Taguchi approach

In acid catalyzed esterification reaction of *the 4-tert*-butylbenzoic acid, the goal is to maximize the acid conversion. Therefore, for the increased conversion of acid "larger is the better" criteria was chosen as the objective function.

Main effect plots

The effect of level of each factor on the response characteristics is showed by main effect plots for the signal to noise ratio. Main effect plots are illustrated by the characteristic average for each factor level. If the line is parallel or horizontal, it depicts no main effect present. The magnitude of main effect increases as the slope of the line increases. In the present study, it can be observed from Fig. 3, that as the catalyst concentration increases from 5-10%, S/N ratios and means increases, *4-tert*-butylbenzoic acid conversion increases and as the molar ratio of methanol to acid raised from 4 to 5 both S/N ratios and means increase but line is parallel to *x*-axis in the range of 5 to 6 molar ratio that means there is no effect of molar ratio in this range. From 1 to 2 h range the slope of the line indicates that acid conversion increases as S/N ratios and means increases. Maximum conversion happens

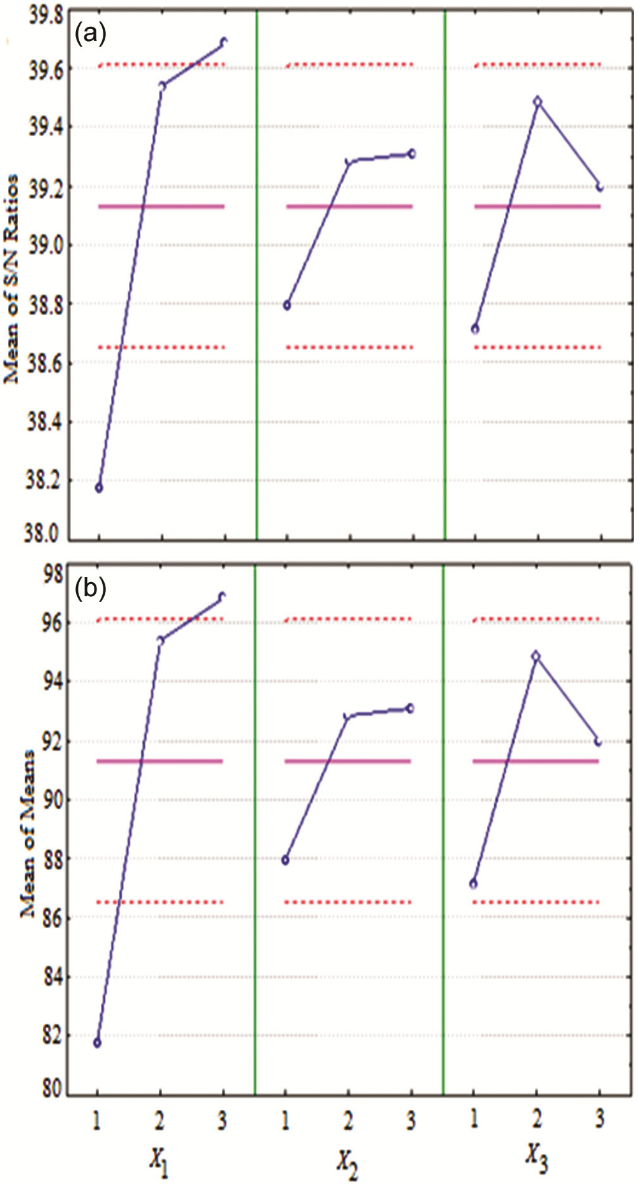


Fig. 3 — Main effect plots for esterification of *4*-tert-butylbenzoic acid (a) S/N ratios and (b) means

at 2 h of reaction and after that reaction is going into backward direction, which shows the reversible nature of the reaction.

Estimated model coefficient

In Taguchi designs, the magnitude of the factor coefficient generally shows the factor rank in the response table. The factor was ranked 1 in the response table with the coefficient having highest absolute value, with the second highest absolute value the coefficient was ranked 2 and likewise.

For the S/N ratios, it is evident from Table 2 that the catalyst concentration has the strongest effect on the response i.e., acid conversion because it has the biggest coefficient (-0.9577, 0.4137) followed by time (-0.4393, 0.3573) and the molar ratio (-0.3626, 0.1821). For means also catalyst concentration has the strongest effect on the response i.e. acid conversion because it has the biggest coefficient (-0.9577, 0.4137) followed by time (-4.184, 3.524) and molar ratio (-3.343, 1.568)

Analysis of variance

ANOVA is used to determine the relative significant effect of each factor towards response. The relative importance of each factor is specified by the sequential and adjusted sum of squares; the factor with the highest sum of squares has the maximum impact. Fischer ratio (F- test), a simple ratio of the mean of the squared deviations to the mean of the squared error; is a tool used to determine the significant effect of process factor on the response. As is evident from the Table 3 with regard to ANOVA results, it can be inferred that for S/N ratios p (0.092) < 0.1 and for means p (0.076) < 0.1, catalyst concentration is only the significant parameter at α-level of 0.10. In ANOVA table, the catalyst concentration has the largest sum of squares signifying it as the most influential operational parameter in comparison to others. An F -test was carried out for the experimental results and compared with the critical value. Based on calculated F-values, none of the parameters have statistical significance at 95% of confidence level, nevertheless, catalyst concentration contributes significantly at α-level of 0.10. It was evaluated that in the esterification reaction, catalyst concentration contributed 74.56% of the sum of the total effects followed by the time 16.38% and the contribution of MeOH to *4-tert* butylbenzoic acid ratio was 9.06% on the response variable (Y). Regression analysis was performed on the observed data of acid conversion and it was found that the model provides a good resemblance to the observed data with R^2= 0.94 using equation below:

$$\text{Conversion} = 91.31 - 9.56\ X_1\_5.0 + 4.04\ X_1\_7.5 + 5.52\ X_1\_10.0 - 3.34\ X_2\_4 + 1.57\ X_2\_5 + 1.78\ X_2\_6 - 4.18X_3\_1 + 3.52X_3\_2 + 0.66X_3\_3 \quad \ldots (12)$$

Response table for S/N ratios and means

The average of each response characteristic (S/N ratios, means) for each level of all factors is shown in response table. Delta statistics is the difference between the maximum and minimum average for each factor dependent on ranks included in table compares the

Table 2 — Estimated Model Coefficients for S/N ratios; S = 0.4592 R^2= 93.1% R^2 (adj) = 72.6% and for Means; S = 4.131 R^2= 94.2% R^2 (adj) = 76.9%.

Term	Coeff.	SE Coeff.	T	P
		For S/N ratios		
Constant	39.1730	0.1531	255.945	0.000
X_1 5.0	-0.9577	0.2164	-4.424	0.047
X_1 7.5	0.4137	0.2164	1.911	0.196
X_2 4	-0.3626	0.2164	-1.675	0.236
X_2 5	0.1821	0.2164	0.841	0.489
X_3 1	-0.4393	0.2164	-2.029	0.180
X_3 2	0.3573	0.2164	1.651	0.241
		For means		
Constant	91.311	1.377	66.310	0.000
X_1 5.0	-9.558	1.947	-4.908	0.039
X_1 7.5	4.042	1.947	2.076	0.174
X_2 4	-3.343	1.947	-1.717	0.228
X_2 5	1.568	1.947	0.805	0.505
X_3 1	-4.184	1.947	-2.148	0.165
X_3 2	3.524	1.947	1.809	0.212

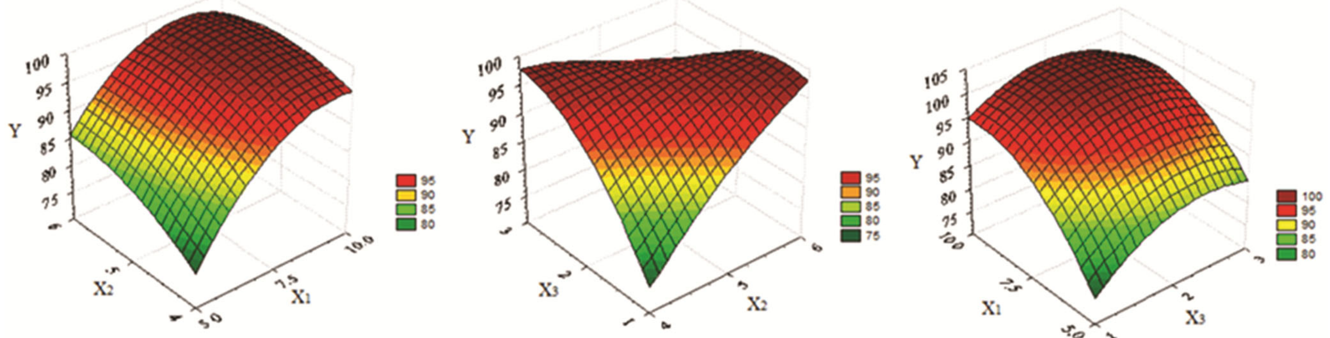
Table 3 — Analysis of Variance (ANOVA) for *4-tert*-butylbenzoic acid in L_9 orthogonal array design for S/N ratios and means.

Source	DOF[a]	Seq SS[b]	Adj MS[c]	F[d]	F_{cr}[e]	F_{cr}[f]	P	PC[g]
			For S/N ratios					
X_1	2	4.1525	2.0763	9.85	19.00	9.00	0.092	74.56
X_2	2	0.5917	0.2959	1.40	6.94	4.32	0.416	9.06
X_3	2	0.9821	0.4910	2.33	5.14	3.46	0.300	16.38
Residual error	2	0.4216	0.2108					
Total	8	6.1480						
			For means					
X_1	2	414.37	207.18	12.14	19.00	9.00	0.076	74.56
X_2	2	50.37	25.18	1.48	6.94	4.32	0.400	9.06
X_3	2	91.07	45.53	2.67	5.14	3.46	0.273	16.38
Residual error	2	34.13	17.07					
Total	8	589.94						

[a]degrees of freedom; [b]sum of squares; [c]mean square; [d]Fischer's ratio; [e]$F_{\text{at } \alpha\text{-level } 0.05}(\nu_1, \nu_2)$; [f]$F_{\text{at } \alpha\text{-level}0.10}(\nu_1, \nu_2)$ where ν_1 is the degree of freedomand $\nu_2 = (a*n - a)$, a is factor number and n is number of levels; [g]percentage contribution.

Table 4 — Response Table for S/N ratios and means for esterification reaction of *4-tert*-butylbenzoic acid.

Level	X_1	X_2	X_3	X_1	X_2	X_3
		For S/N ratios			For means	
1	38.22	38.81	38.73	81.75	87.97	87.13
2	39.59	39.36	39.53	95.35	92.88	94.83
3	39.72	39.35	39.25	96.83	93.09	91.97
Delta	1.50	0.54	0.80	15.07	5.12	7.71
Rank	1	3	2	1	3	2



(a) 3D plot: Y vs Cat. con & Molar ratio (b) 3 D plot: Y vs Molar ratio & Time (c) 3 D plot: Y vs Cat. con & Time

Fig. 4 — 3-D surface plots generated b/w *4-tert*-butylbenzoic acid Conversion (Y) vs. (X_1, X_2), (X_2, X_3), (X_3, X_4)}

relative magnitude of effects. Based on these delta values Minitab allocate ranks; rank 1 to the greater delta value, rank 2 to second greatest, and likewise. The optimum set of reaction parameters can be established with the help of the level averages in response table.

From response Table 4, the optimal operating level of parameters was found out. For both S/N ratios and means catalyst concentration at level 3 has the highest value, the molar ratio at level 2 and 3 has almost same value and time has maximum S/N ratios and means at level 2. Levels that produce the highest means and maximizes the S/N ratios results in maximum conversion. It can be observed from the level average values in response table that the S/N ratios and the means approached maximum, when the catalyst concentration was 10%, the molar ratio of MeOH to acid was 6:1 and time were 2 h. Examining the main effect plots help to come to this conclusion that 5:1 molar ratio is giving a better result than 6:1. Therefore, the optimum parameter condition to achieve our target for response characteristic was catalyst concentration of 10%, the molar ratio of 5:1 and time of 2 h. The results were also interpreted in terms of 3-dimensional surfaces and are presented in Fig. 4(a-c), which depicts that more than 60% area of the 3-D surface shows the higher conversion of acid.

The high conversion in case of 5:1 molar ratio than 6:1 was mainly due to the excess water formed during the initial hours of reaction that gradually deactivates the strength of the catalyst. Moreover, Liu *et al.* suggested that the decreased activity of the catalytic protons is due to the favored solvation by water over methanol[1]. The concentration of protonated acid decreases due to solvation with water, which inhibits the production of esters. Owning to reversible nature of esterification reaction, duration of 2 h was enough to reach its highest conversion rate of acid with sufficient catalyst concentration of 10%. Conversion of acid was predicted 99.9% for the optimum parameters. The experiment was conducted for optimum parameters and conversion was obtained 98.8%. The result confirms that the esterification reaction was well represented by the model Eq. (12)**.**

Modeling of 4-tert-butylbenzoic acid esterification reaction: Kinetic evaluation

The achieved optimized conditions were employed for the kinetic evaluation of *4-tert*-butylbenzoic acid esterification reaction. The composition profile of acid conversion in the esterification reaction in respect of time for varying temperatures 55, 60, 65 and 70°C is illustrated in Fig. 5. It was observed that the time and temperature significantly affect the composition profile of acid conversion to ester formation in the reaction mixture.

The conversion of acid with reaction time is defined by the proposed kinetic model Eq (9)**.** The kinetic model assumes the irreversible pseudo second order reaction, which is distant from the equilibrium and approaching equilibrium demonstrated by the reversible second order model. It is observed that for the initial hours (~ 40 min), the reaction follows irreversible pseudo second order reaction given by Eq. (5) and presented in Fig. (6a). Subsequently, the reaction follows reversible second order reaction given by Eq. (8) shown in Fig. (6b) at all the temperatures studied. The experimental data well fitted to the proposed reaction mechanism in the aforesaid state regime.

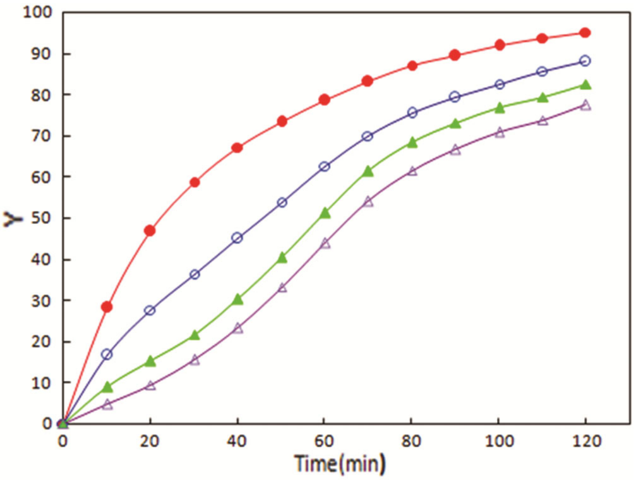


Fig. 5 — Composition profile of acid catalyzed esterification of *4-tert*-butylbenzoic acid (Y) to methyl *4-tert*-butylbenzoate w.r.to time at different temperatures △ 55°C; ▲ 60°C; ○ 65°C; ● 70°C

The reaction rate constants for the esterification of acid based on irreversible pseudo second order reaction and reversible second order reaction at temperatures are presented in Table 5**,** which was evaluated from the slopes of linear curves. It can be observed from the table that as the temperature increases, the esterification rate also increases and highest rate was achieved at a reaction temperature of

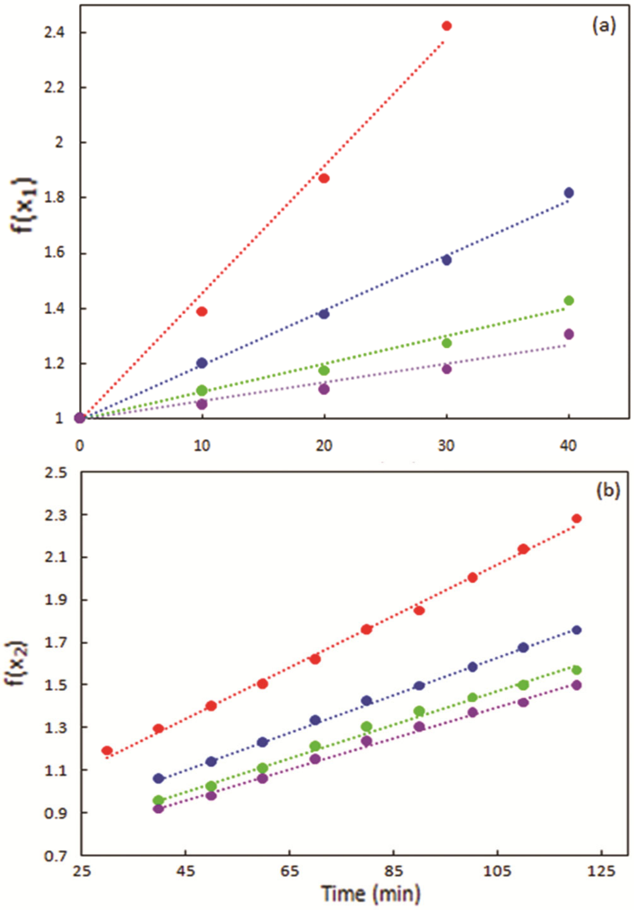


Fig. 6 — Fitted values (dotted lines) and experiment data (solid symbols) during esterification of *4-tert*-butylbenzoic acid (a) irreversible pseudo second order reaction (b) reversible second order reaction at temperatures ● 70°C; ● 65°C; ● 60°C; ●55°C

Table 5 — Rate constants $(dm^3/kmol/min)$ and activation energy, $E_a(kJ/mol)$for different reaction regime at different temperatures

T(°C)	Pseudo irreversible second order		Reversible second order			
	k_1	E_a	k_2	E_a	$k_2^{'}$	E_a
55	2.957	119.6	3.087	30.49	0.042	87.96
60	4.391		3.430		0.064	
65	8.609		3.830		0.097	
70	19.957		5.130		0.175	

70°C. Further, with the increase in temperature from 55°C to 70°C, the pseudo reaction rate, k_1 almost becomes six folds in the early phase of reaction thereafter, in the reversible reaction regime, the forward rate constant, k_2 dominates over backward reaction rate, nevertheless backward reaction rate, $k_2^{'}$ of equilibrium controlled regime significantly affected by shifting the temperature from 55°C to 70°C. The temperature dependence of rate constants in chemical reaction mixture is determined using Arrhenius equation as:

$$k = A.exp\left(\frac{-E_a}{RT}\right) \qquad \text{... (13)}$$

where A denotes pre-exponential factor, E_a is activation energy and R is the gas constants. Figure 7 shows the Arrhenius plot of the temperature dependence of irreversible pseudo reaction rate, k_1 reversible forward rate, k_2 and reverse reaction rate. The irreversible pseudo second order reaction rate shows highest activation energy in the reaction regime and is temperature sensitive. The highest temperature, 70°C, was the most favorable in the temperature range under investigation.

Model validity of esterification of 4-tert-butylbenzoic acid

The kinetic model (Eq. (11)) proposed in the present study for the esterification of acid was verified with the experimental results by evaluating the percentage of conversion of acid based on the following equations:

$$x_A = \frac{k_2 c_{Ao} t - 1 + c_1}{k_2 c_{Ao} t + c_1} \; ; 0 \le t \le t_1 \qquad \text{... (14)}$$

$$x_A = \frac{0.5\Delta}{(1-(1/k))} \frac{(1+e^{(0.5k_2 \Delta C_{A0} t + 0.5\Delta c_2)})}{(1-e^{(0.5k_2 \Delta C_{A0} t + 0.5\Delta c_2)})} + \frac{3}{(1-(1/k))} ; t \ge t_1 \qquad \text{... (15)}$$

where Eqs. (14) & (15) are expressed as irreversible pseudo second order reaction regime and reversible second order equilibrium reaction regime, respectively. According to above-mentioned equations, Fig. 8. depicts the comparison of data from the kinetic model with experimental results at 60, 65 and 70°C, methanol to the acid molar ratio of 5:1 and time of 2 hrs and catalyst concentration 10%. The relative percentage deviation between calculated and experimental acid conversion values at temperatures 60, 65 and 70°C were 0.92, 0.54 and 0.45 for pseudo second order reaction and 0.38, 0.16

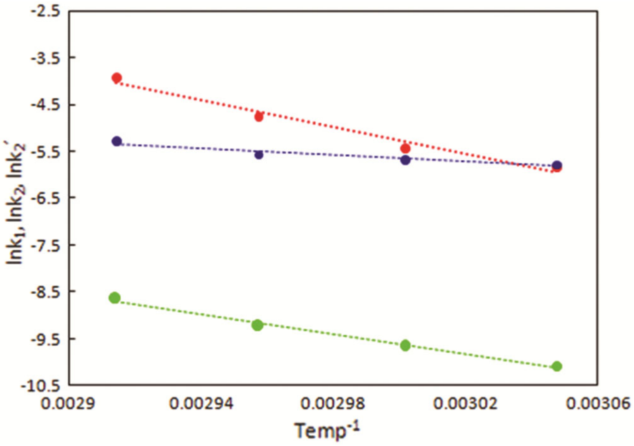


Fig. 7 — Arrhenius plot for temperature dependency of irreversible pseudo reaction rate, k_1 (●); reversible forward rate, k_2 (●); reverse reaction rate, $k_2^{'}$ (●)

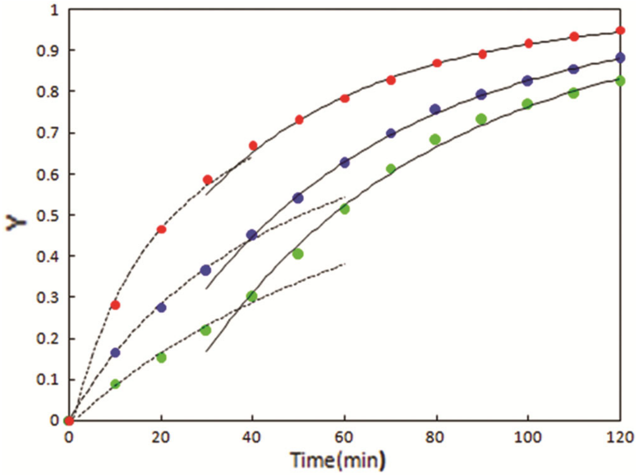


Fig. 8 — Comparison of proposed kinetic model; irreversible pseudo second reaction regime (- - -); reversible second order reaction regime (-) and experimental data ● 70°C; ● 65°C; ● 60°C during esterification of *4-tert*-butylbenzoic acid

and 0.14 for irreversible second order reaction, respectively. There is a good agreement between experimental and simulated kinetic data for the esterification of acid to ester. Hence, in the presence of the catalyst MSA, this model gives a reliable expression and represents the overall kinetics of esterification reaction of the acid with methanol.

Reusability of the catalyst

From the industrial perspective, catalyst properties such as its activity as well its reusability are of much importance[30]. The catalyst is recovered after the reaction to be recycled in esterification process, to know if the catalyst would tend towards poisoning with the loss of catalytic activity during the reaction. It was observed that MSA catalyst can be recycled consecutively 5- 6 times with no significant loss in activity. A number of cycle recovery results to a very little drop in activity, showing constancy and withholding capability of this useful environmental friendly catalyst. The decrease in catalytic activity after a number of consecutive runs can contribute to catalyst deactivation due to poisoning by water[31].

Conclusion

Based on the observations, it can be concluded that the catalyst concentration is the most influencing parameter followed by time and molar ratio. The optimal parameters for *4-tert*-butylbenzoic acid esterification obtained within the experimental ranges studied are catalyst concentration 10% w.r.to wt of acid), methanol to the acid molar ratio of 5:1 and time of 2 hrs. Under these conditions, a maximum acid conversion of ~98.8% could be achieved. Finally, the results are verified by the confirmation run. The kinetics of the acid esterification process was studied at optimises conditions obtained by Taguchi design at temperatures (55-70°C) for 5 K interval. The kinetics of the process was explained by the fast irreversible pseudo second order in the earlier initial phase of the reaction, subsequently slow reversible second order reaction approaching equilibrium. The variation in *4-tert*-butylbenzoic acid conversion with time was adequately reflected by the proposed kinetic model. Experimental data was well correlated to the model prediction. The MSA, an environment-friendly catalyst can be reused with no significant loss in activity.

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