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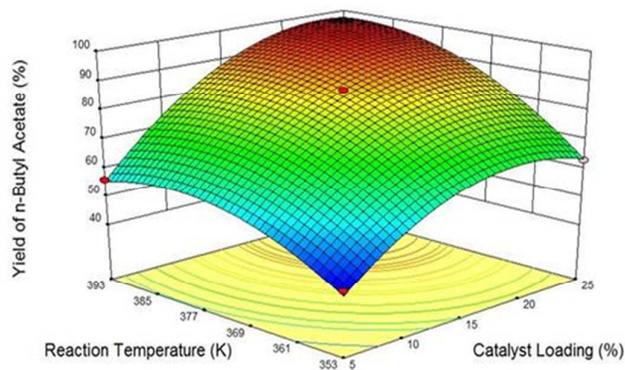


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Response surface methodology revealed that 4% (w/w) B/USY zeolite is stable (reusable for 6 cycles) and potential catalyst with 96% yield of butyl acetate.

Process Optimization by Response Surface Methodology for Transesterification of Renewable Ethyl Acetate to Butyl Acetate Biofuel Additive over Borated USY Zeolite

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Abstract

Butyl acetate, a renewable biofuel additive was synthesized by transesterification of butanol with ethyl acetate via renewable and sustainable route. Use of fermentation derived bio-butanol and bio-ethyl acetate for synthesis of butyl acetate would be more advantageous route over conventional Fischer Esterification. For the first time, a heterogeneous zeolite catalysts such as Ultra Stable Y (USY) and its modified versions obtained by borating on parent USY were used for the synthesis of butyl acetate.

Response surface methodology (RSM) was employed to optimize the process parameters for transesterification of butanol with ethyl acetate over 4% (w/w) B-USY catalyst. The influence of three crucial process variables such as catalyst loading, molar ratio, reaction temperature on yield of butyl acetate were addressed by Box–Behnken experimental design (BBD). 4% (w/w) B-USY was proved to be potential catalyst with 96% yield of butyl acetate at optimum process parameters. The 4% (w/w) B-USY catalyst was found to be reusable for 6 catalytic cycles.

Keywords: Ethyl acetate; Transesterification; Borated USY; Response surface methodology; Butyl acetate; Biofuel additive.

1 Introduction

The inevitable depletion of fossil fuel reserves and the subsequent hike in fuel price along with the environmental concerns of conventional fuels has drawn much attention of researchers to develop an industrially and environmentally benign process for production of biofuels and biofuel additives from the renewable resources. Recently, butyl acetate bearing high flash point (295 K) and very low freezing point (200 K) has been recognized as a potential biofuel additive.¹⁻³ Low freezing point (200 K) of butyl acetate improves the cold flow properties of biodiesel without significantly affecting cetane number and the mixture's heat of combustion. Moreover, its high flash point (295 K) makes it safer to use as biodiesel additive and it also makes superior than the ethyl acetate with flash point of 269 K and similar other biodiesel additives.¹⁻⁴

The process for production of ethyl acetate⁵ and butanol^{6,7} by renewable routes has been widely researched. Recent advancements in bioprocess and biotechnology has developed an environmentally benign and economically feasible fermentation process to produce butanol and ethyl acetate.^{1,8,9} Hence transesterification of this fermentation derived bioethylacetate with bio-butanol to produce bio-butyl acetate would be green process.

Transesterification of butanol with ethyl acetate can be carried out over homogeneous catalyst, but due to the well-known disadvantages of homogeneous catalysts are reinforced by environmental policies.¹ Thus, it is technological challenge to develop ecofriendly and highly active heterogeneous catalytic process for butyl acetate synthesis. Very limited literature is available on transesterification of butanol with ethyl acetate over heterogeneous catalysts.¹ To the best of our knowledge, till date, only one report is available on the heterogeneously catalyzed transesterification of butanol with ethyl acetate to synthesize butyl acetate (renewable biofuel additive).¹ Moreover, it was also recognized that there are no reports available for the transesterification of butanol with ethyl acetate over zeolites. Hence it was

thought of interest to investigate catalytic performance of USY and borated USY for transesterification of butanol with ethyl acetate. These zeolites were used because of their peculiar properties of temperature stability, porosity, surface area, acidity etc. as compared to other zeolites.

In addition to the selection of catalysts, the process optimization of the transesterification reaction is also equally important to optimize the process or operating parameters so as to identify potential catalysts for industrial application. Response surface methodology (RSM) is widely adapted for optimization of various process parameters in esterification and transesterification.¹⁰⁻¹⁶ RSM has been effectively employed for several processes involved in biodiesel production using enzyme or heterogeneous catalysts.¹⁰⁻¹⁵ Application of RSM to study the insights on influence of process parameters on butyl acetate production by transesterification of butanol with ethyl acetate has not been reported, so far.

This study explores new avenues on development of highly active, stable and cheap solid acid catalyst and process optimization by RSM for the efficient production of butyl acetate (renewable biofuel additive). For the first time, USY and borated USY are used as heterogeneous catalysts for transesterification of butanol with ethyl acetate. This research also involves application of design expert software obtaining most favorable (optimum) process parameters for the transesterification reaction with aim to achieve maximum yield of butyl acetate. The influences of three critical process parameters like catalyst loading, butanol to ethyl acetate molar ratio and reaction temperature on yield of butyl acetate were examined with Box-Behnken experimental design (BBD) of RSM and eventually an experimental mathematical equation was established to predict the correlation between the process variables. The most favorable process variables recommended by RSM were validated by

experiments. The reusability of potential catalyst at optimum process parameters is also presented.

2 Results and discussion

2.1 Catalyst characterizations

The synthesized catalysts were characterized by XRD, BET and TPO. Fig. 1 shows powder X-ray diffraction patterns of USY, 1% (w/w) B-USY and 4% (w/w) B-USY catalysts. The XRD patterns of parent USY and borated USY were found to be fully crystalline without contribution of amorphous phase and also confirmed the phase purity of synthesized catalyst samples. Osiglio and Blanco¹⁹ reported that, boric acid calcined at 593 K presents sharp peaks at 2θ of 14.8° and 27.9° , attributing to boric oxide. These peaks were not found in XRD patterns of borated USY catalysts. This implied that boric oxide was well dispersed on the USY support. The BET surface area of USY was observed to be decreased with boration due to the narrowing of pores by boron species (Table 1). The total acidities of USY and borated USY samples are depicted as Table 1. With increase in percentage boron on USY the acidity was found to be increased. The well dispersed boron species on surface of USY catalyst, as evidenced by XRD, unswervingly participate to the acidity of the catalyst, as the hydration of boron species leads to generation Brønsted acid sites.

2.2 Catalytic performance of catalysts

The catalytic performance of blank (without catalyst), USY and 1-5% borated USY catalysts at identical set of process parameters: catalyst loading of 5%, molar ratio of butanol to ethyl acetate of 4, reaction temperature of 373 K, reaction time of 0.5-5 h, speed of agitation of 400 rpm and catalysts' average particle size of 82.5 μm are represented as Fig. 2. The blank (thermal) reaction was conducted to see the effect of catalyst. It can be seen from Fig. 2 that, the maximum yield of butyl acetate was obtained at reaction time of 4 h. All the set of experiments were carried out in triplicate and had 2% error as depicted by the error

bars in the Fig. 2. The activity trend at reaction time of 4 h follows: 5% (w/w) B-USY (53%) > 4% (w/w) B-USY (52%) > 3% (w/w) USY (35%) > 1% (w/w) B-USY (18%) > USY (6%). All the borated catalysts showed higher activity than the parent USY catalyst; this can be due to higher acidity of borated USY catalysts (Table 1). The 5% (w/w) B-USY catalyst exhibited 1% higher yield of butyl acetate than 4% (w/w) B-USY catalyst. This may attributed to the multilayer formation boron species on USY at higher loading. Hence 4% (w/w) B-USY catalyst exhibiting 52% butyl acetate yield was selected as a potential catalyst. All the experiments were done in kinetically controlled regime excluding internal and external mass transfer resistances, by using average catalyst particle size of 82.5 μm and speed of agitation of 400 rpm.¹⁰

In present study, 4% (w/w) B-USY catalyst was found to be potential catalyst for the synthesis of butyl acetate. Hence, RSM design with BBD is used to investigate influence of various process parameters. The most favorable process parameter in view to maximize the yield of butyl acetate and reusability of 4% (w/w) B-USY catalyst is presented later.

2.3 Statistical analysis of RSM and influence of process parameters

2.3.1 Development of regression model equation

In the present research work, the correlation among response (yield of butyl acetate, Y) and three reaction variables (Table 2) were evaluated by using RSM. The outcomes of 17 set of experiments by BBD template are presented in Table S1 (Supporting Information). All experiments were performed in triplicate at fixed reaction time of 4 h and average value of butyl acetate yield is presented. Table S1 and Fig. 3 implied that there was no noticeable variation among the actual and predicted response values. Based on data of Table S1 and the second order quadratic model equation Eq. (1) the correlation among yield of butyl acetate (response) and the three reaction variables was regressed (in terms of original factors) by:

$$Y = +87 + 16.25X_1 + 2.25X_2 + 12.25X_3 + 0.75X_1X_2 + 4.75X_1X_3 + 8.25X_2X_3 - 12.88X_1^2 - 3.87X_2^2 - 9.87X_3^2 \quad (2)$$

Where, X_1 , X_2 and X_3 were the coded process variables for transesterification reaction, whereas Y was response of yield of butyl acetate (Table 2). Positive sign in front of linear term designates that, with an increasing the variable, the response (Y , yield of butyl acetate) increases linearly (synergistic influence), in other hand negative sign indicates antagonistic influence.^{10-12,17} In the Eq. (2), terms of X_1 , X_2 , X_3 , X_1X_2 , X_1X_3 and X_2X_3 had synergistic influence to the yield of butyl acetate (response) in contrary other terms had antagonistic influence. Percentage catalyst loading (X_1) has the strongest influence on the butyl acetate yield as the coefficient of X_1 (16.25) was the highest amongst all other variables. While, butanol to ethyl acetate molar ratio (X_2 , 2.25) has least influence on butyl acetate yield in comparison to catalyst loading (X_1) and reaction temperature (X_3). Next greatest influencing process variable was the reaction temperature (X_3), followed by interaction effects between parameter X_2X_3 and X_1X_3 . Weakest by interaction effects between parameters X_1X_2 was noticed. This can be attributed to the collective influence of process variables, similar outcomes have been noticed by other researchers.^{12,18}

2.3.2 Analysis of variance (ANOVA)

Statistical analysis based on the analysis of variance (ANOVA) was employed for fitting second order quadratic model. Table S2 (Supporting Information) represents all the model terms for all responses obtained by RSM. At confidence level of 95%, the F-value of the model of 323.96 and with very low probability value ($p < 0.001$) implied that the model fitted was highly significant. This also implied that regression model used was the reliable to predict the yield of butyl acetate. The probability values <0.05 ($p < 0.05$) designate significant model terms.¹⁸ In present case X_1 , X_2 , X_3 , X_1X_2 , X_2X_3 , X_1^2 , X_2^2 and X_3^2 are significant model terms. The statistical significance data corresponding to individual

parameter in Table S2 revealed that, linear term of catalyst loading (X_1) and reaction temperature (X_3) has significant influence on the butyl acetate yield owing to the high F-value and low p-values. The quadratic term of catalyst loading (X_1), F-value 407.14 was observed to be more important than the reaction temperature (X_3), F-value 239.51 and the molar ratio (X_2), F-value 36.88. Moreover, the consequence of interaction between molar ratio and reaction temperature (X_2X_3) also influenced the butyl acetate yield expressively (F-value 232.63) as is specified by the p-value ($p < 0.0001$).

2.3.3 Model fitting

The regression equation (Eq. (1)) and coefficient of determination (R^2) were used to evaluate the suitability/fit of model. A high value of the coefficient of determination ($R^2 = 0.9976$) vindicated an exceptional association among the independent process variables, which also intended that the second order model was precise and at least 99.76% of the variability in the data could be elucidated by the model. The predicted R^2 (R^2 -predicted = 0.9617) was in equitable covenant with the adjusted R^2 (R^2 -adjusted = 0.9945) and was observed to be very adequate to specify the high implication of the model. Adequate precision (the signal to noise ratio) > 4 is suitable. In present investigation, adequate precision ratio of 56.76 an acceptable signal and proved the ability of model to navigate the design space. In addition, a moderately lesser value of the coefficient of variation ($CV = 1.76\%$) implied that the model possessed a superior accuracy and the experiments performed were reliable. In present model, a minimum of 3 Lack of Fit degrees of freedom (Df) and 4 Df for 'Pure Error' ensured a validity of 'Lack of Fit' test (Table S2).

These statistical tests along with statistical model fit summary, high determination coefficient, lack of fit tests and with a consecutive model sum of squares indicated that, the nominated model to be reasonable for predicting the response (yield of butyl acetate). This model was further employed to obtain most favorable (optimum) process variables for

transesterification reaction aiming to maximize the yield of butyl acetate and to make the process economical and industrially benign.

2.3.4 Influence of process variables on yield of butyl acetate

In order to investigate the individual and interactive effects of process variables on the yield of butyl acetate, three-dimensional response surface plots and two-dimensional contour (interaction) plots were drawn (Figs. 4-6). The three-dimensional surfaces are the graphical illustration of the regression equation (Eq. 2) and each contour curve (two dimensional) represented the combinations of two test variables with the other one maintained at its level of zero (central value). It has been reported that, the circular contours denotes the negligible interaction between the corresponding variables.^{10-13,17,18} On the contrary, the elliptical contours symbolize the significant interactions amongst the relevant variables. The influence of correlation among catalyst loading and molar ratio (Fig. 4), molar ratio and reaction temperature (Fig. 5) and catalyst loading and reaction temperature (Fig. 6) at constant reaction time of 4 h are indicated by 3D response surface plots and 2D contour plots.

As can be seen in Fig. 4, with increase in loading of 4% (w/w) B-USY catalyst from 5-25% at constant molar ratio (6:1) and reaction temperature (373 K), the yield of butyl acetate found to be increased from 52 to 85%. This is attributed to the increase in catalyst loading makes avail of more catalytically active acid sites for the transesterification reaction (Table 1). This reveals that formation of butyl acetate from ethyl acetate involves a more active acid site demanding step. The butyl acetate yield was also observed to be proportional to catalyst amount used; revealing that the reaction proceeds through a pure heterogeneous mechanism. Also, as specified by low p-value (< 0.0001) (Table S2), the catalyst loading is highly significant for transesterification reaction. With increase in molar ratio (butanol : ethyl acetate) from 2:1 to 6:1 at constant catalyst loading of 25%, reaction time of 4 h and reaction temperature of 373 K, the yield of butyl acetate was observed to be slightly increased from 85

to 90%. More dilution of reactants with increase in the molar ratio at limited catalyst active sites would not increase the product formation markedly. This implied that the molar ratio has low influence (p-value of 0.0018) as compared to catalyst loading (p-value of < 0.0001) on yield of butyl acetate, indicating that higher yield of butyl acetate could be obtained with lower molar ratio. Hence, to avoid cost associated with separation of unreacted butanol from final product mixture and to make the process industrially benign, low molar ratio should be preferred. However, the interaction effect between molar ratio (X_2) and catalyst loading (X_1) was found to be insignificant with shape of two dimensional contour curve circular (Fig. 3) and with high p-value (0.2896) of X_1X_2 interaction term (Table S2).

The influence of interaction between molar ratio and reaction temperature at constant catalyst loading of 15% and reaction time of 4 h is shown as Fig. 5. The significant interaction effect of molar ratio and reaction temperature was exhibited by ellipse mound shape of two dimensional contour curves (Fig. 5) and as was also evident from low p-value (0.0002) of X_1X_3 interaction term (Table S2). With elevating temperature the yield of butyl acetate was observed to be linearly increased. This was in agreement with the Arrhenius law, a higher temperature results in a higher rate of transesterification leading to higher yield of butyl acetate.²⁰ The reaction temperature was found to be highly influencing parameter on the yield of butyl acetate and this was also evident from low p-value (< 0.0001) (Table S2).

Fig. 6 represents the influence of catalyst loading and reaction temperature on the yield of butyl acetate in 3D response surface and 2D interaction plot at constant molar ratio (butanol to ethyl acetate) of 4:1 and reaction time of 4 h. It is an obvious from Fig. 6 that, at any designated value of reaction temperature from 353 to 393 K, the yield of butyl acetate increased proportionally with catalyst loading. The influence of individual term and interaction term of reaction temperature and catalyst loading perceived to be highly

significant on yield of butyl acetate, which was also supported by low p-value (< 0.0001) (Table 4).

From this study, catalyst loading and reaction temperature were found to be most contributing terms while molar ratio was least significant term for the transesterification reaction. However, the interaction between catalyst loading and molar ratio has no influence on the response (Y, yield of butyl acetate). Hence, it is highly crucial to develop most favorable reaction parameters for transesterification of ethyl acetate with butanol over 4% (w/w) B-USY in view to obtain maximum yield of butyl acetate.

2.3.5 Obtaining most favorable process parameters by RSM and model validation

The most favorable process variable for transesterification of ethyl acetate with butanol over 4% (w/w) B-USY were achieved with numerical technique (numerical algorithm) built in the Design-Expert[®] Version 8.0.7.1 software. The numerical method examines the design space by the developed model in the analysis to find factor settings that meet the goal of maximizing the percentage yield of butyl acetate (response). The three independent process parameters (Table 2) were fixed in the range among low (-1) and high (+1) while the response (yield of butyl acetate) was set to maximum value.²¹ The most favorable (optimum) parameters including the predicted and experimental yield of butyl acetate are presented in Table 3. The experimental value of yield of butyl acetate showed in table is an average of three independent experiments (Table 3). Yield of butyl acetate of 96% is in fine agreement with the predicted value, with a moderately trivial error of 1.6%. Thus the experimental error is fewer than $\pm 5\%$, hence the projected statistical model was suitable to predict the yield of butyl acetate by transesterification of butanol with ethyl acetate over 4% (w/w) B-USY.

2.4 Reusability of catalyst

The reusability of 4% (w/w) B-USY catalyst was evaluated for transesterification of butanol with ethyl acetate at the most favorable process parameters obtained by RSM design (Table 3). After each catalytic run, the catalyst from product mixture was separated by centrifugation and used for proceeding cycle without any post-treatment. The 4% (w/w) B-USY catalyst was perceived to be firm for five catalytic cycles (fresh and four reuses) with 96% yield of butyl acetate (Fig. 7). Thereafter, for the sixth cycle marginal decrease in yield of butyl acetate (96-94%) was observed. This implies that the 4% (w/w) B-USY catalyst is highly active, reusable and stable and has a potential of further application.

2.5 Merits of present method

Recent findings revealed that butanol and ethyl acetate can be produced by economically viable fermentation process.^{2,8,9} Hence, heterogeneously catalyzed transesterification of fermentation derived bio butanol with bioethylacetate would be a viable process for production of butyl acetate, a renewable biofuel additive. The byproduct obtained in this process, ethanol, can be once more used to produce ethyl acetate which get reused again for transesterification.^{2,5} This method of production of butyl acetate from fermentation derived reactants would be clean and green in devoid of the drawbacks associated with the widely used Fischer and Speier esterification.²² Also, this process does not demand superior grade (acetic acid resistant) stainless steel equipment and it is also lacking of waste water (formed as product) removal complications and severe adulteration (linked with the usage of homogeneous catalysts).

In this perspective, the current process of using of 4% (w/w) B-USY catalyst for production bio-butyl acetate from fermentation source would be environmentally and economical viable process offering additional principles of green chemistry and engineering with prospective welfares regarding high catalytic activity (96%, yield of butyl acetate) at

milder operating parameters, high catalyst stability (reusable for 6 catalytic cycles) (Fig. 7), renewable and clean synthetic route and devoid of waste byproducts.

3 Conclusions

Transesterification of butanol with ethyl acetate to butyl acetate (biofuel additive) was studied over modified zeolites. The outcomes achieved in current research discloses that 4% (w/w) B-USY zeolite is highly active, stable (reusable for 6 cycles) and potential catalyst for production of high yields (96%) of butyl acetate.

The RSM with BBD quadratic model ($R^2 = 0.9976$) revealed that catalyst loading and reaction temperature are the most significant parameters for transesterification while molar ratio (butanol to ethyl acetate) is the least significant. The present method for the synthesis of butyl acetate over 4% (w/w) B-USY catalyst is clean and sustainable, follows the principles of green chemistry and engineering.

4 Experimental section

4.1 Materials

Ultra Stable Y (USY) zeolite having $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 30 was procured from Zeolyst, USA. Ethyl acetate (99.8%), butanol (99%) and H_3BO_4 were obtained from Sigma–Aldrich (Sigma, St. Louis, USA).

4.2 Catalyst synthesis and characterization

Typically, 60.0 g of USY catalyst was taken into a 1000 ml round bottom flask and then 600 ml of a 0.64% H_3BO_4 solution in water was added. The said mixture was refluxed at 363 K for 1 h under magnetic stirring. Then solvent was evaporated using rota vapor (353 K). The material thus obtained was in white powder form and subjected for the stepwise calcinations in presence of nitrogen at 593 K for 5 h. A calcined material was then obtained with a 1% boron content and designated as 1% (w/w) B-USY. Similarly, other borated USY

catalysts were prepared with boron content of 3% (w/w) B-USY and 4% (w/w) B-USY and 5% (w/w) B-USY.

Powder X-ray diffraction patterns of synthesized catalyst were recorded on X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) using $\text{CuK}\alpha$ radiation at a scanning rate of 0.0671/s in the 2θ ranging from 5 to 50° (Fig. 1).

Nitrogen isotherms (adsorption and desorption) of synthesized catalysts were obtained at low temperature (77 K) with Beckman Coulter SA 3100 analyzer (CA, USA). The calcined sample was degassed at 573 K for 10 h prior to measurements. The specific surface area is calculated using Brunauer-Emmett-Teller (BET) method (Table 1).

Acidity of catalyst was measured by temperature programmed desorption of ammonia (TPD- NH_3) with Micromeritics AutoChem (2910, USA) (Table 1). These experiments were performed in a gas-flow system equipped with thermal conductivity detector (TCD). Prior to the measurements, the freshly calcined catalyst sample was dehydrated at 423 K in high purity (99.995%) helium flow (50 mL min^{-1}) for 1 h. The temperature was then reduced to 343 K and NH_3 was permitted to adsorb by exposing catalyst sample to a gas stream encompassing of 10% NH_3 in helium for 1 h. The sample was then flushed with helium for another 1 h. The NH_3 desorption was performed in helium flow (50 mL min^{-1}) by rising the temperature up to 873 K at heating rate of 10 K min^{-1} .

4.3 Reaction of transesterification and analysis

The USY (parent) and different percentage (1-5%) borated USY catalysts were used for transesterification of butanol with ethyl acetate to obtain butyl acetate (renewable biofuel additive). The butanol, ethyl acetate and catalyst were sequentially added into 50 mL two-necked round bottom glass flask fortified with a reflux condenser, a magnetic stirrer and a thermometer. The temperature accuracy of $\pm 0.5 \text{ K}$ was maintained with an electric-heated thermostatic oil bath. The reaction is allowed to run for desired time (1-5 h) at the set

temperature (353–393 K) and after completion of reaction the catalyst from liquid product mixture was removed by centrifugation.

The obtained liquid product mixture was analyzed with gas chromatography (GC) Chemito GC-1000, capillary column, BP-1 (50 m length and 0.3 mm width) equipped with Flame Ignition Detector (FID) within programmable temperature range of 313 K to 473 K by using with Nitrogen as a carrier gas. The GC-MS (Agilent-5977-AMSD) was used to confirm the reaction products.

4.4 Box–Behnken experimental design

RSM with Design-Expert[®] Version 8.0.7.1 (Stat- Ease, Inc., Minneapolis, USA) was used to design the experiments for the reaction parameters used for the transesterification of butanol with an ethyl acetate over 4% (w/w) B-USY catalyst to synthesize butyl acetate biofuel additive. The RSM design with three process variables was performed to gain the optimum process parameters for transesterification reaction. The three independent process variables selected were percentage catalyst loading (X_1), butanol to ethyl acetate molar ratio (X_2) and reaction temperature (X_3). The variables and their coded and uncoded values are presented in Table 2. The percentage yield of butyl acetate (Y) was selected as response/target parameter.

The 3^3 Box-Behnken experimental design (BBD) involving 17 set of experimental runs consisting of 12 factorial points and 5 center points were performed.^{10-12,17,18} These fully randomized experiment formulations consist of all possible combinations of the independent variables at all levels.

The interaction between process variables and maximization of response (Y) was performed by second-order quadratic model.¹⁰⁻¹²

$$Y = \alpha_0 + \sum_{i=1}^n \alpha_i X_i + \sum_{i=1}^n \alpha_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^n \alpha_{ij} X_i X_j$$

(1)

(1)

Where, Y is the percentage yield of butyl acetate (response variable). The parameters X_i and X_j are independent process variables. The terms of α_o , α_i , α_{ii} , α_{ij} are the regression coefficient, the linear term and squared term for the process variable i and the interaction terms among variables i and j , respectively. The n is the total number of variables (in this case, $n = 3$) used to study influence on the yield of butyl acetate. Each process variable was coded into levels -1, 0 and +1 and shown in Table 2.

The polynomial equation was used to correlate the response and experimental levels of each factor. The central composite rotatable design was employed to obtain second-order regression coefficients (R^2). Its significance of coefficient of regression was evaluated by the value of F-test.

The most favorable process parameters for transesterification were achieved by investigating the three dimensional (3D) response surfaces, two dimensional (2D) contour plots and computing the regression equation.

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Figure captions:

- Fig. 1** Powder X-ray diffraction patterns of USY, 1% (w/w) B-USY and 4% (w/w) B-USY catalyst.
- Fig. 2** Catalytic performance of synthesized catalysts for transesterification of ethyl acetate with butanol at catalyst loading of 5%, molar ratio (butanol to ethyl acetate) of 2:1 and reaction temperature of 373 K.
- Fig. 3** Plot of actual versus predicted values of butyl acetate yield over 4% (w/w) B-USY catalyst.
- Fig. 4** Response surface and contour plot for synthesis of butyl acetate as a function of molar ratio and catalyst loading at reaction time of 4 h and reaction temperature of 373 K.
- Fig. 5** Response surface and contour plot for synthesis of butyl acetate as a function of molar ratio and reaction temperature at reaction time of 4 h and catalyst loading of 15%.
- Fig. 6** Response surface and contour plot for synthesis of butyl acetate as a function of catalyst loading and reaction temperature at reaction time of 4 h and molar ratio (butanol to ethyl acetate) of 4:1.
- Fig. 7** Reusability of 4% (w/w) B-USY catalyst for the synthesis of butyl acetate at most favorable process parameters: molar ratio of 4:1, catalyst loading of 20%, reaction time of 4 h and reaction temperature of 383 K.

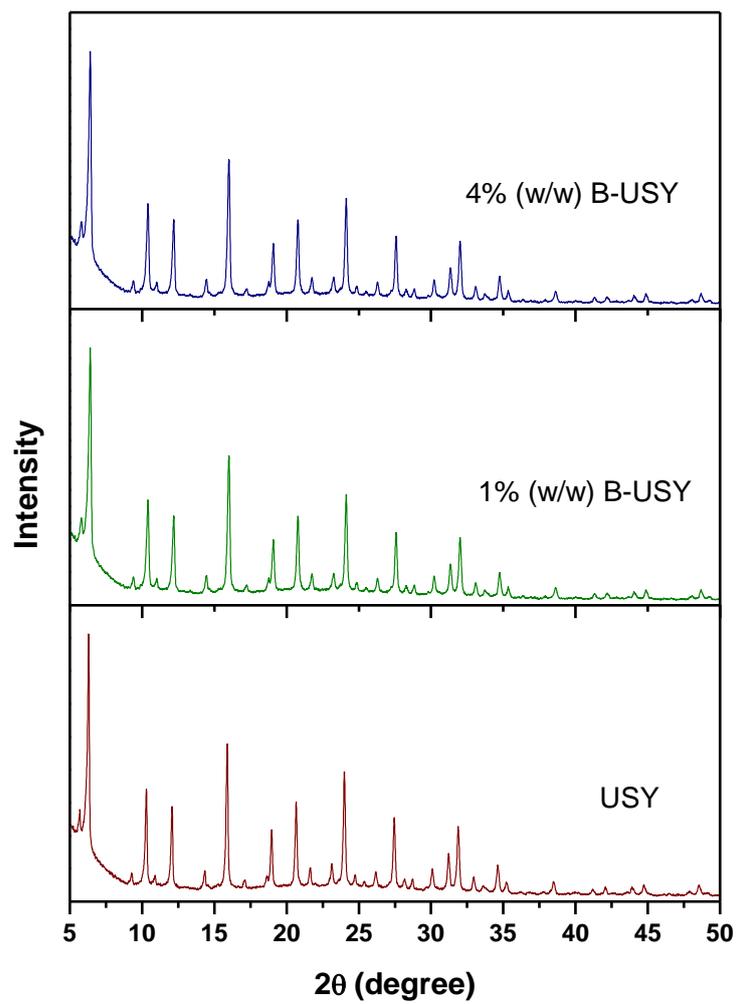


Fig. 1

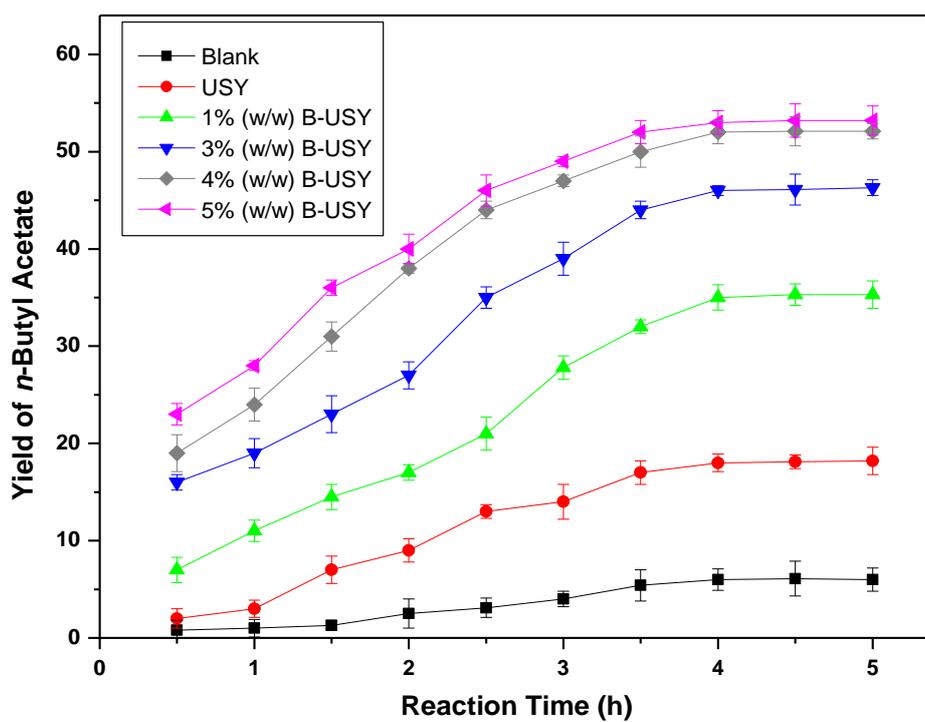
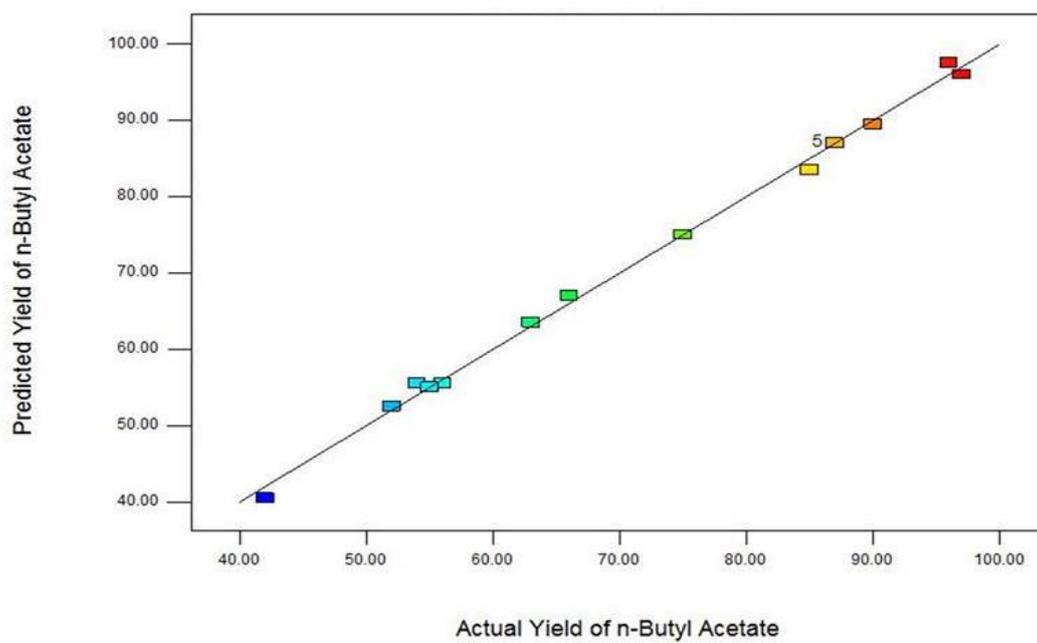
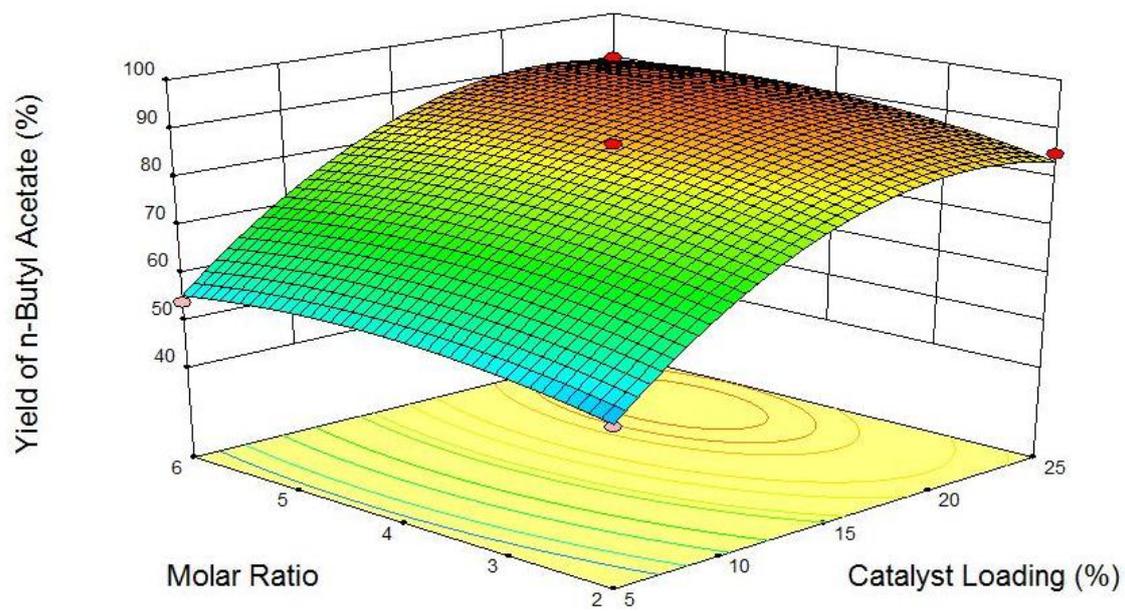


Fig. 2

**Fig. 3**

**Fig. 4**

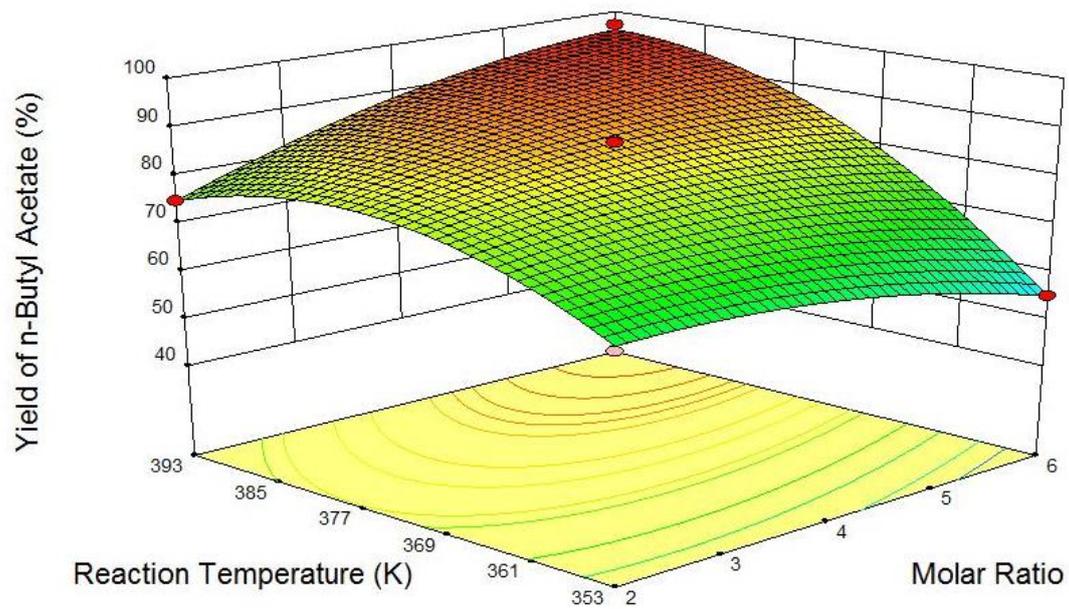
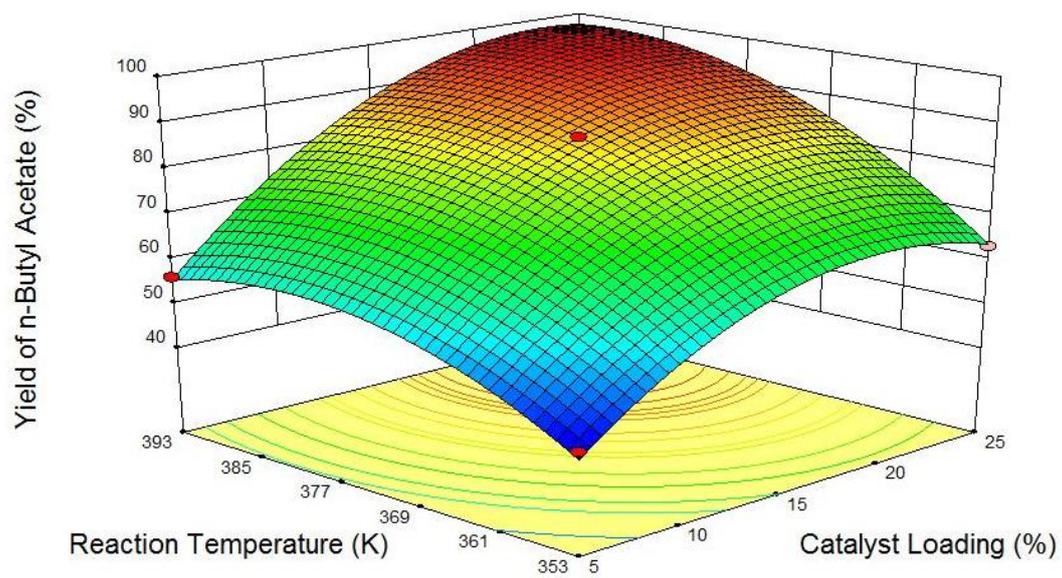


Fig. 5

**Fig. 6**

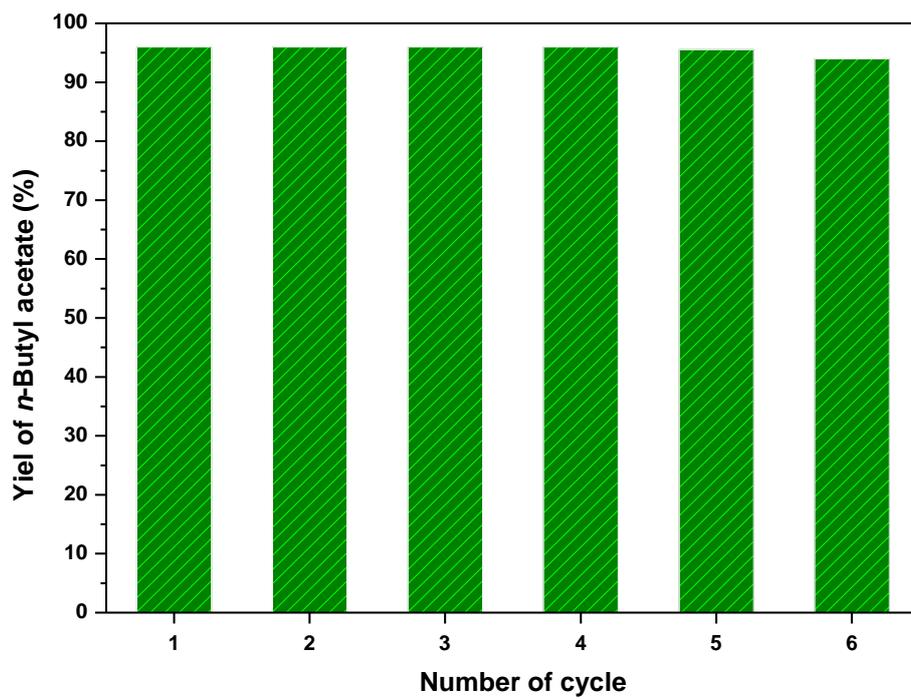


Fig. 7

Table 1 Physico-chemical properties of catalysts.

Catalyst	BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	Total Acidity ($\mu\text{mol g}^{-1}$)
USY	839	378
1% (w/w) B-USY	790	511
3% (w/w) B-USY	771	587
4% (w/w) B-USY	765	640
5% (w/w) B-USY	753	662

Table 2 Selected variables and coded levels used in the Box-Behnken design.

Variables	Symbol	Coded levels		
		-1	0	+1
Catalyst Loading (wt. % of ethyl acetate)	X ₁	5	15	25
Molar Ratio (butanol to ethyl acetate)	X ₂	2	4	6
Reaction Temperature (K)	X ₃	353	373	393

Table 3 Most favorable process parameters for trans-esterification of ethyl acetate with butanol over 4% (w/w) B-USY for reaction time 4 h and validation model adequacy.

Process parameters	Catalyst loading, X₁ (wt. %)	Molar ratio (butanol to ethyl acetate), X₂	Reaction temperature, X₃ (K)	Yield of Butyl acetate, Y (%)
Predicted	19.7	4.3	383.3	97.6
Experimental	20	4	383	96