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**One Step Synthesis of Ethyl Levulinate Biofuel by Ethanolysis of Renewable Furfuryl  
Alcohol over Hierarchical Zeolite Catalyst**

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## Abstract

Ethanolysis of renewable furfuryl alcohol (FAL) to ethyl levulinate (EL) biofuel over various zeolites viz. H-ZSM-5 (microporous, medium pore), Hierarchical-HZ-5 (combination of micro- and meso pore), H-Beta (microporous, large pore) and Ultra Stable Y (USY, microporous, large pore) was studied in detail. Best of our knowledge, probably for the first time, Hierarchical-HZ-5 synthesized by desilication post-treatment has been employed as a heterogeneous catalyst for ethanolysis of FAL. The synthesized catalysts were characterized by powder X-ray diffraction (PXRD), temperature programmed NH<sub>3</sub> desorption (TPAD), Energy dispersive X-ray analysis (EDAX) etc.

Response surface methodology (RSM) with Box-Behnken experimental design (BBD) was used to investigate influence of three crucial process variables of ethanolysis such as ethanol to FAL molar ratio, percent catalyst loading and reaction temperature on EL yield. The optimization tool of design expert software was employed to obtain the optimum reaction parameters for FAL ethanolysis over Hierarchical-HZ-5 catalyst. Three intermediates of FAL ethanolysis reaction such as, ethoxymethylfuran (EMF), 4,5,5-triethoxypentan-2-one and diethyl ether (DEE) have been identified and quantified from product mixture with aid of Gas Chromatography-Mass Spectroscopy (GC-MS). Hierarchical-HZ-5 was found to be potential catalyst for ethanolysis of FAL with 73% EL yield and 26% EMF yield at optimized process parameters.

**Keywords:** Ethanolysis; Furfuryl Alcohol, Hierarchical Zeolite; Ethyl Levulinate; Biofuel.

## 1 Introduction

The practical transformation of inexpensive and renewable biomass into industrially important chemicals is one of the important technological challenges for today's researchers.<sup>1</sup> In this context, production of furfural is an important platform chemical obtained by hydrolysis and dehydration of hemicellulose has been commercialized for decades.<sup>2</sup> Hydrogenation of this biomass derived furfural leads to furfuryl alcohol (FAL). The threat of fossil fuels shortage and environmental concern is stimulating the search of alternative fuels, hence efficient conversion FAL to ethyl levulinate (EL), an important renewable oxygenate fuel additive would be sustainable green process.<sup>3-5</sup> Alkyl levulinates like EL have been already recognized as one of the top 10 biorefinery candidates in 2004 by United States Department of Energy.<sup>6,7</sup> Moreover, EL can also be used as a precursor to produce  $\gamma$ -valerolactone, which can be converted to liquid alkanes and transportation fuels.<sup>8-11</sup>

There are two pathways which can be employed to transform FAL to EL (Scheme 1): Route 1 involves two steps, first acid catalyzed hydrolysis of FAL to levulinic acid (LA). Followed by, esterification LA with ethanol over acid catalyst. It has been reported that, the hydrolysis of FAL encounters polymerization of FAL, leading to less production of LA.<sup>9,11</sup> Also, the carboxylate functional group in aqueous medium poisons the heterogeneous catalysts leading to loss in activity loss for subsequent reactions.<sup>9-11</sup> Route 2 is one step acid catalyzed ethanolysis of FAL to EL.<sup>1,9-16</sup> Ethanolysis would be an atom-economic and more beneficial compared to Route 1 (hydrolysis and esterification) as it reduces the polymerization of FAL, which ultimately gives high EL yields.<sup>5,10,11</sup> Also, one step process of ethanolysis of FAL to EL would reduce process cost, hence it would be more economical as compared to Route 1.

The ethanolysis of FAL has been reported by using strong homogeneous acids.<sup>17,18</sup> Although, strong homogeneous acids such as HCl and H<sub>2</sub>SO<sub>4</sub> find effective in the ethanolysis reaction, however they present the environmental concerns due to extremely corrosive nature

and being difficult to separate from product mixture for recycle. Hence, it is technological demand to establish environmentally sustainable process for ethanolysis of FAL by designing highly active, efficient, reusable and industrially benign heterogeneous catalyst. In this context, performances of various catalysts such as propylsulfonic acid-functionalized mesoporous silica,<sup>1</sup> functionalized silica hollow spheres,<sup>10,15</sup> acid resin,<sup>11,12</sup> zeolites<sup>12</sup>, ionic liquids,<sup>13</sup> and porous aluminosilicates<sup>14</sup> have been extensively investigated for ethanolysis. To the best of our knowledge, hierarchical H-ZSM-5 has not been reported for ethanolysis of FAL. Hence, in view of advantages of heterogeneous catalysts and to be aware of the significance and applications of FAL ethanolysis reaction from industrial as well as academic point of view, it is thought of research interest to evaluate the catalytic performance of various zeolites such as H-Beta, USY, H-ZSM-5 and Hierarchical H-ZSM-5 (Hierarchical-HZ-5) catalyst for FAL ethanolysis. These zeolites were used due to their peculiar properties of inherent acidity, porosity, surface area and temperature stability in comparison with other zeolites.

Along with catalyst selection for the FAL ethanolysis reaction, the optimization of process parameters is also utmost important to recognize industrially benign catalyst. Response surface methodology (RSM) is extensively used as an optimization software for various biomass conversion reactions such as esterification and transesterification reactions.<sup>18-22</sup> So far, RSM has not been reported for ethanolysis reaction.

The present research involves insight study on influence of process parameters for ethanolysis of FAL with the help of RSM design expert software with Box-Behnken experimental design (BBD) over Hierarchical-HZ-5, catalyst under our knowledge for the first time. The optimization tool of design expert software is used to obtain optimum process parameters for ethanolysis reaction with aim to maximize EL yield. The influences of three critical process parameters such as molar ratio (ethanol to FAL), percent catalyst loading and reaction temperature on EL yield were investigated by BBD of RSM. The correlation between

the process variables is established using experimental and mathematical equations. The optimum reaction parameters endorsed by RSM were validated by experiments. The optimized reaction parameters were used to evaluate the reusability of potential catalyst.

## 2 Results and Discussion

### 2.1 Catalyst Characterizations and Catalytic Performance

The synthesized catalysts were characterized by XRD, BET and TPO. Fig. 1 shows powder X-ray diffraction patterns of H-Beta, USY, H-ZSM-5 and Hierarchical-HZ-5 catalysts. The X-ray diffraction pattern of H-Beta shows BEA phase, USY shows typical FAU and H-ZSM-5 and Hierarchical-HZ-5 show MFI phase (Fig. 1).

Fig. 2 depicts the N<sub>2</sub> physisorption isotherms of H-ZSM-5 and Hierarchical-HZ-5 catalysts. The isotherm of the parent H-ZSM-5 shows a plateau starting at a very low relative pressure (type I), the characteristic of microporous zeolite structures. On the other hand the N<sub>2</sub> isotherms of Hierarchical-HZ-5 represents hysteresis loop at higher P/P<sub>0</sub> value attributed to type I and type IV isotherms which suggests the presence of both micro and mesoporosity in Hierarchical-HZ-5 catalyst. Physico-chemical properties of all catalysts is represented in Table 1. Hierarchical-HZ-5 showed higher BET surface area, pore volume, pore diameter and acidity as compared to parent H-ZSM-5, this is attributed to removal of silicon from the framework without complete destruction of the lattice.<sup>23</sup> Fig. S1 (Supporting Information) represents the surface morphology of H-ZSM-5 and Hierarchical-HZ-5 observed under FE-SEM. FE-SEM demonstrated that, the overall size and morphology of alkali treated Hierarchical-HZ-5 zeolite was not significantly affected.

Catalytic performances of USY, H-Beta, H-ZSM-5 and Hierarchical-HZ-5 catalysts were assessed for ethanolysis of FAL to EL at identical set of reaction parameters: molar ratio (ethanol to FAL) of 8:1 and catalyst loading of 10 wt. % of FAL, reaction temperature of 373 K and reaction time of 2 h (Fig. 3). Three intermediates such as ethoxymethylfuran (EMF),

4,5,5-triethoxypentan-2-one and diethyl ether (DEE) have been identified and quantified from product mixture with aid of GC-MS and GC. Hierarchical-HZ-5 was found to be most active amongst the studied catalysts. The overall trend of EL yield obtained was USY (5%) < H-Beta (8%) < H-ZSM-5 (13%) < Hierarchical-HZ-5 (19%). Hierarchical-HZ-5 (micro- and meso pore) was observed to be more active as compared to microporous medium pore (H-ZSM-5) and microporous large pore (H-Beta and USY) zeolite. The activity trend obtained was the cumulative effect of physico-chemical properties such as surface area, pore volume and acidity of catalyst (Table 1). The removal of silicon by desilication in Hierarchical-HZ-5 increases the total acidity, which led increased EL yield, as this reaction is acid driven. Hierarchical-HZ-5 was also observed to be higher in surface area, pore volume than parent HZSM-5, which increases the accessibility of active sites in the Hierarchical-HZ-5. Amongst the evaluated catalysts, Hierarchical-HZ-5 was found to be potential catalyst for ethanolysis of FAL. This comparison amongst micro-medium, micro-large and micro-meso porosity confirmed that the ethanolysis of FAL required both micro-meso porosity, which helps to convert intermediate into desired products. Hence, in view to maximize EL yield, RSM design with BBD was implied to investigate the influence of various process parameters for an ethanolysis FAL to EL over Hierarchical-HZ-5. Also, the optimized process parameters for maximum EL yield and reusability of Hierarchical-HZ-5 catalyst is presented later.

The ethanolysis of FAL was studied over Hierarchical-HZ-5 with varying reaction time. Fig. 4 shows the progress in yield of EL, EMF, 4,5,5-triethoxypentan-2-one and DEE with respect to reaction time. It has been observed that at initial reaction time up to 2 h, the formation of 4,5,5-triethoxypentan-2-one was more as compared to EL, however after reaction time of 3.5 h, the DEE and 4,5,5-triethoxypentan-2-one were no longer observed in the reaction product. This is attributed to utilization of 4,5,5-triethoxypentan-2-one and DEE in formation of EL. The EMF was observed in reaction product even after 4 h with 49 % yield. The results

obtained about the product distribution are in consistent with the reported literature.<sup>11,13</sup> EL yield reached at its maximum value of 41% at reaction time of 4 h and thereafter it remained unchanged. Hence, reaction time of 4 h with 41% EL yield and 49% EMF yield was considered as optimum reaction time and used in all further experiments.

## 2.2 Statistical analysis of RSM and influence of process parameters

### 2.2.1 The Model Fitting and Statistical Analysis

The ethanolsis of FAL to EL over Hierarchical-HZ-5 was optimized through RSM approach. The seventeen designed experiments in order to optimize three process parameters in the BBD were represented in Table S1 (Supporting Information). Table S1 and Fig. 5 implied that there was no noticeable variation among the actual and predicted response values.

By applying the multiple regression analysis on the experimental outcome, the responsive variable (Y) and the three test variables were related in terms of coded factors by second-order polynomial Eq. (1):

$$Y = +54 - 8X_1 + 12X_2 + 3.25X_3 + 4.25X_1X_2 + 0.25X_1X_3 + 2.75X_2X_3 - 2.12X_1^2 - 0.13X_2^2 + 0.38X_3^2 \quad (1)$$

Where  $X_1$ ,  $X_2$  and  $X_3$  are the coded process variables for ethanolsis and Y indicates the response (EL yield) (Table 2).

Statistical testing of regression equation was performed by analysis of variance (ANOVA) and Fisher  $F$ -test (Table S2). At 95% of the confidence level, the model  $F$ -value of 207.86 with very low probability value ( $p < 0.001$ ) indicated that the model was reliable to predict the yield of EL. The predicted  $R^2$  ( $R^2$ -predicted = 0.9404) was in reasonable agreement with the adjusted  $R^2$  ( $R^2$ -adjusted = 0.9915). Adequate precision (the signal to noise ratio)  $> 4$  is desirable. In present study, the adequate precision ratio of 58.35 meant an adequate signal and hence model could be employed to navigate the design space. In addition, a low value of the coefficient of variation (CV = 1.88%) demonstrated high degree of precision and great deal



of experimental reliability. Furthermore, in present model, a minimum of three Lack of Fit degrees of freedom (Df) and four Df for 'Pure Error' confirmed a validity of 'Lack of Fit' test (Table S2). The above statistical analysis implied that the model is adequate to predict the EL yield (Y) within the scope of the variable investigated.

The  $p$ -values less than 0.05 ( $p < 0.05$ ) indicate the model term is significant.<sup>19-21</sup> In present study, linear term of catalyst loading ( $X_2$ ,  $F$ -value = 1152) was found to be more important than molar ratio ( $X_1$ ,  $F$ -value = 512 and reaction temperature ( $X_3$ ,  $F$ -value = 84.5). The interaction between molar ratio and catalyst loading ( $X_1X_2$ ,  $F$ -value = 72.25) has more influence on response (Y) than the catalyst loading and reaction temperature ( $X_2X_3$ ,  $F$ -value = 30.25). However, the interaction between molar ratio and reaction temperature ( $X_1X_3$ ) is not significant, owing to low  $F$ -value of 0.25 and high  $p$ -value of 0.63. Moreover, the quadratic term of molar ratio ( $X_1^2$ ) with  $p$ -value of 0.003 is significant term, while  $X_2^2$  and  $X_3^2$  are not significant terms ( $p > 0.05$ ).

#### 2.2.4 Analysis of the Response Surface Plots

For better visualization of the statistically significant process parameters depicted from ANOVA, the three-dimensional (3D) response surface plots and two dimensional (2D) contour curves were represented as Fig. 6-8. These types of plot represent the effect of two process parameters on response (EL yield) at one time while other one variable is maintained at its zero level (central value). All these experiments were performed at constant reaction time of 5 h. The influence of correlation among catalyst loading and molar ratio (Fig. 6), molar ratio and reaction temperature (Fig. 7) and catalyst loading and reaction temperature (Fig. 8) at constant reaction time of 4 h are indicated by 3D response surface plots and 2D contour plots.

Fig. 6 represents the effects of molar ratio (ethanol to FAL) and catalyst loading (wt. % of FAL) on EL yield at reaction temperature of 393 K and reaction time of 5 h. It can be seen from Fig. 6 that at constant molar ratio of 4 with increase in loading of Hierarchical-HZ-5

catalyst from 10 to 30%, the EL yield increased from 53 to 68%. In contrary, with same rise in catalyst loading (10-30%), the EMF yield decreased from 45 to 26%. The lower catalyst loading (10%) showed less activity (53% EL yield and 45 % EMF yield), indicating the need of catalytically active acid sites for levulinate ester formation. The catalyst loading of 30% provides more catalytically active acid sites which help in converting intermediates such as EMF to EL (Table 1). The EL yield is found to be proportional to catalyst amount used which indicates that the reaction follows pure heterogeneous mechanism. Moreover, as indicated by low p-value ( $< 0.0001$ ) (Table S2), the catalyst loading is significantly influencing process parameter in ethanolsis of FAL. However, with increase in molar ratio of ethanol to FAL from 4:1 to 12: 1 at constant catalyst loading of 30%, the EL yield decreased from 68 to 59% and EMF yield increased from 26 to 36%. The higher dilution of FAL at identical catalyst acid sites leads to more formation of the intermediate EMF due to partial polymerization of FAL. This implies that the higher yield of levulinate ester (EL) can be obtained at lower molar ratio, which would save operating, equipment and energy cost associated with the separation of unreacted ethanol from final product mixture making the process industrially benign. The interaction effect of catalyst loading and molar ratio on EL yield was found to be significant with shape of 2D contour curve ellipse mound and the low p-value ( $< 0.0001$ ) of the interaction term ( $X_1X_2$ ) (Table S2).

The influence of molar ratio and reaction temperature on EL yield at a constant catalyst loading of 20% and reaction time of 5 h is depicted as Fig. 7. With increase in reaction temperature from 373 to 413 K at constant molar ratio of 4:1, the EL yield increased from 57 to 62%. This is attributed to increase in rate of polymerization of FAL to EL at elevated temperature. However, the interaction between reaction temperature and molar ratio has no influence on EL yield which is also indicated by high p-value (0.6324) of interaction term ( $X_1X_3$ ) (Table S2).

Fig. 8 shows effect of different catalyst loading (%) and reaction temperature on the EL yield in 3D surface response and 2D interaction plots at identical molar ratio of 8:1 and reaction time of 5 h. It is obvious from the figure that at any designed quantity of catalyst loading from 10 to 30%, the EL yield was found to be increased proportionally with reaction temperature. At fixed reaction temperature of 413 K, with increase in catalyst loading from 10 to 30%, the EL yield increased from 43 to 73%. The individual terms of catalyst loading ( $X_2$ ) and reaction temperature ( $X_3$ ) with  $p$ -value of  $< 0.0001$  have more significant effect on EL yield than the interaction term  $X_2X_3$  with  $p$ -value of 0.0009 (Table S2).

### 2.2.5 Multiple response optimization of FAL ethanolsis and model validation

The optimum process parameters for ethanolsis of FAL over Hierarchical-HZ-5 catalyst were obtained by using numerical algorithm built in the Design-Expert® Version 8.0.7.1 software. The three independent reaction parameters depicted in Table 2 were set in the range among low (-1) and high (+1) while the EL yield (response) was set to be at maximum value.<sup>18,19</sup> Table 3 shows the predicted and experimental EL yield at optimized process parameters. EL Yield of 73% is in fine agreement with the predicted value (73.4%), with the experimental error less than  $\pm 5\%$ . This implied that the proposed RSM statistical model valid and accurate to predict EL yield.

### 2.3 Reusability of catalyst

The optimized process parameters summarized in Table 3 were used to evaluate the reusability of Hierarchical-HZ-5 catalyst for ethanolsis of FAL. The catalyst was separated by filtration from product mixture and used for next catalytic run. Hierarchical-HZ-5 catalyst was found to be stable for three reaction cycles (fresh and two reuses) with same 73% EL yield and 26% EMF yield (Fig. 9). Thereafter, for the fourth cycle the EL yield decreased marginally from 73% to 70%. Four times used Hierarchical-HZ-5 catalyst was characterized by XRD (Fig. 1) and EDAX. The XRD pattern of used Hierarchical-HZ-5 in Fig. 1 indicated slight

decrease in intensity of peaks as compared to fresh Hierarchical-HZ-5. This is attributed to the deposition of reaction intermediates to catalyst surface. However, four times used Hierarchical-HZ-5 was found to be still crystalline with no amorphous contribution. The elemental analysis of used Hierarchical-HZ-5 by EDAX showed Si/Al ratio of 30, indicating no further desilication of catalyst during the reaction. This indicates that the Hierarchical-HZ-5 catalyst is stable, highly active and has a potential of its application.

Song et al.,<sup>10</sup> used arylsulfonic acid functionalized hollow mesoporous carbon spheres (ArSO<sub>3</sub>H-HMCSs) for ethanolysis of FAL to EL. They reported EL yield of 81.3% at ethanol to FAL molar ratio of 60:1 and reaction temperature of 393 K. Use of excess amount of ethanol would be uneconomical in large scale process.<sup>10</sup> Wang et al.,<sup>13</sup> reported 90% EL yield with 1,3-bis(sulfopropyl)1H-imidazol-3-ium hydrogenosulfate ionic liquid. However, ionic liquids have known limitations such as not easy to separate and reuse. Neves et al.,<sup>14</sup> used various porous aluminosilicates for ethanolysis of FAL to EL. They reported Al-TUD-1 zeolite with 80% EL yield at 60 equivalent of ethanol, reaction temperature of 413 K and reaction time of 24 h and 30 wt. % of catalyst.<sup>14</sup> Use of longer reaction time of 24 h would lead to increase in the process cost.

The current process of catalytic synthesis of EL biofuel by ethanolysis of renewable FAL over Hierarchical-HZ-5 catalyst would be environmentally and industrially benign in perspective of high catalytic activity (73% EL yield) and high catalyst stability (3 cycles) (Fig. 9), renewable synthetic route and devoid of waste byproducts.

### 3 Conclusions

Hierarchical- HZ-5 zeolite was synthesized by alkali treatment to H-ZSM-5, which improves the catalyst physicochemical properties such as surface area, acidity and create mesoporosity in addition to micropores. This improved catalyst was used for the one step ethanolysis of renewable FAL to EL biofuel. The reaction parameters were optimized by using

RSM design with BBD. The optimized process parameters were validated with experimental. The proposed RSM statistical model was validated well with accuracy of 99.45%.

Hierarchical-HZ-5 zeolite gave maximum catalytic activity of 73% EL yield and 26% EMF yield, with three times catalyst reusability. The present process of FAL ethanolysis over Hierarchical-HZ-5 follows green chemistry principles such as renewable and sustainable routes and minimization of byproduct formation.

## 4 Experimental section

### 4.1 Materials

Ultra Stable Y (USY) zeolite (Si/Al = 15) was procured from Zeolyst, USA. Ethyl levulinate (99.8%) and furfuryl alcohol (98%) were obtained from Sigma Aldrich (USA). Ethanol (99.9%) was obtained from Cympran Gludt BV, Belgium. H-Beta, H-ZSM-5, Hierarchical-HZ-5 catalysts were synthesized at Catalyst Pilot Plant, CSIR-NCL, Pune (India).

### 4.2 Catalyst synthesis and characterization

Reported procedures were used to synthesize H-Beta (Si/Al = 8),<sup>24</sup> and H-ZSM-5 (Si/Al = 37).<sup>25</sup> Hierarchical-HZ-5 was obtained by following method 10 g of H-ZSM-5 was mixed with 300 mL 0.2 M aq. NaOH in a flask and kept at 338 K for 30 min. Then, this zeolite sample was subjected to threefold ion exchange with aq. 0.1M ammonium nitrate (in the proportion of 10 mL g<sup>-1</sup> of product for 5 h at 338 K). Finally, the sample was transformed into proton form by calcinations in air at 823 K for 5 h.

The phase purity of all catalyst samples was confirmed by powder X-ray diffraction patterns, which were recorded on X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) using CuK $\alpha$  radiation at a scanning rate of 0.0671/s in the 2 $\theta$  ranging from 5 to 50° (Fig. 1). Low temperature (77 K) nitrogen isotherms (adsorption and desorption) of H-ZSM-5 and Hierarchical-HZ-5 catalysts were recorded with Beckman Coulter SA 3100 analyzer (CA, USA) (Fig. 2). The calcined sample was degassed at 573 K for 10 h prior to the

measurements. The specific surface area and pore diameter of synthesized catalysts was calculated using Brunauer-Emmett-Teller (BET) and Barrett–Joyner–Halenda (BJH) method respectively (Table 1). Energy dispersive X-ray analysis (EDAX) was used to determine the Si/Al ratio of the synthesized catalysts (Table 1). The overall acidity of synthesized catalysts was measured by Temperature Programmed Ammonia Desorption (TPAD) using a Micromeritics AutoChem (2910, USA) equipped with thermal conductivity detector (Table 1). The surface morphology of H-ZSM-5 and Hierarchical-HZ-5 was observed by Field Emission Scanning Electron Microscope (FE-SEM, HITACHI, Model-S4800 type II) (Fig. S1, Supporting Information).

### 4.3 Catalytic Evaluation and Product Analysis

All the experiments were performed under reflux in 50 mL two-necked round bottom flask equipped with condenser, a magnetic stirrer and thermostatic oil bath. The reaction was allowed to run for set time (1-5 h) at the set temperature (373–413 K) and after completion of reaction the flask was cooled with cold water to stop the reaction. The catalyst from liquid product mixture was removed by centrifugation.

The liquid reaction feed and product were analyzed by using GC, Varian-CP-3800, capillary column, SPB-5 (30 m length, 0.25 mm I.D. and 0.25  $\mu\text{m}$  film thickness) with nitrogen as a carrier gas and Flame Ignition Detector (FID) in programmable temperature range of 353 to 553 K. The products were quantified by an external standard method based on the average peak area of each product under three parallel GC measurements of each experiment. The concentrations of FAL, EMF and EL in product mixture were calculated based on the standard curve obtained using an authentic samples with an analytical error of  $\pm 2\%$ . The reaction products were also confirmed by GC–MS (Agilent-5977-AMSD). All the experiments were carried out in duplicate and the average values with an error of  $\pm 2\%$  were reported.

### 4.4 Experimental Design with Box–Behnken and Optimization by RSM

RSM with Design-Expert<sup>®</sup> Version 8.0.7.1 (Stat- Ease, Inc., Minneapolis, USA) in combination with Box-Behnken design (BBD) was used to perform experimental design for ethanolsis of FAL to EL biofuel over Hierarchical-HZ-5 catalyst. RSM was developed to obtain optimum process parameters for ethanolsis of FAL in view to maximize the EL yield. Three independent process variables were employed to design the experiments, namely molar ratio of ethanol to FAL ( $X_1$ ), percent catalyst loading ( $X_2$ ) and reaction temperature ( $X_3$ ). The percent yield of EL ( $Y$ ) was the response/target parameter of this design.

The  $3^3$  Box-Behnken experimental design (BBD) containing 17 set of experimental runs comprising 12 factorial points and 5 center points were performed.<sup>19-21</sup> The second-order quadratic polynomial equation for the EL yield ( $Y$ ) could be described by Eq. (2):<sup>21</sup>

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j \quad (2)$$

Where,  $Y$  is the value of predicted response (percentage EL yield). The  $X_i$  and  $X_j$  are the uncoded independent variables. The terms  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are the intercept coefficient (offset), the linear effect term, the squared effect term and interaction effect term, respectively. The  $k$  is total number of independent variables (in this case,  $k = 3$ ) used to study influence on the EL yield. Each process variable was coded into levels -1, 0 and +1 and shown in Table 2.

The adequacy of each factor of response was checked by analysis of variance (ANOVA). 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. Fisher  $F$ -test in form of F-value was employed to investigate fitness of experimental model.

The  $P$ -value test also used to justify the significance of process parameters on the response (yield of EL biofuel). The smallest  $P$ -value indicates the significantly influencing

parameter on the response. The optimum process parameters for the ethanolysis of FAL to EL over Hierarchical-HZ-5 were obtained by exploring 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, H-Beta, H-ZSM-5, Hierarchical-HZ-5 and used Hierarchical-HZ-5 catalyst.
- Fig. 2** N<sub>2</sub> adsorption-desorption isotherms of H-ZSM-5 and Hierarchical-HZ-5 catalysts.
- Fig. 3** Catalytic performance of various zeolites for ethanolysis of furfuryl alcohol (FAL) at reaction conditions: molar ratio (ethanol to FAL) of 8:1 and catalyst loading of 10 wt.% of FAL, reaction temperature of 373 K and reaction time of 2 h.
- Fig. 4** Influence of reaction time on ethanolysis of FAL over Hierarchical-HZ-5 at reaction conditions: molar ratio (ethanol to FAL) of 8:1 and catalyst loading of 10 wt.% of FAL and reaction temperature of 373 K.
- Fig. 5** Plot of actual versus predicted values of EL yield over Hierarchical-HZ-5 catalyst.
- Fig. 6** Response surface (3D) and contour (2D) plot of EL yield as a function of molar ratio (ethanol to FAL) and catalyst loading at reaction temperature of 393 K and reaction time of 4 h.
- Fig. 7** Response surface (3D) and contour (2D) plot of EL yield as a function of molar ratio (ethanol to FAL) and reaction temperature at catalyst loading of 20% and reaction time of 4 h.
- Fig. 8** Response surface (3D) and contour (2D) plot of EL yield as a function of catalyst loading (%) and reaction temperature (K) at molar ratio (ethanol to FAL) of 8:1 and reaction time of 4 h.
- Fig. 9** Reusability of Hierarchical-HZ-5 catalyst for ethanolysis of FAL at reaction conditions: molar ratio (ethanol to FAL) of 6:1 and Catalyst loading of 30 wt.% of FAL, reaction temperature of 413 K and reaction time of 4 h.
- Scheme 1.** Acid-catalyzed transformation of furfuryl alcohol (FAL) to ethyl levulinate (EL) biofuel.

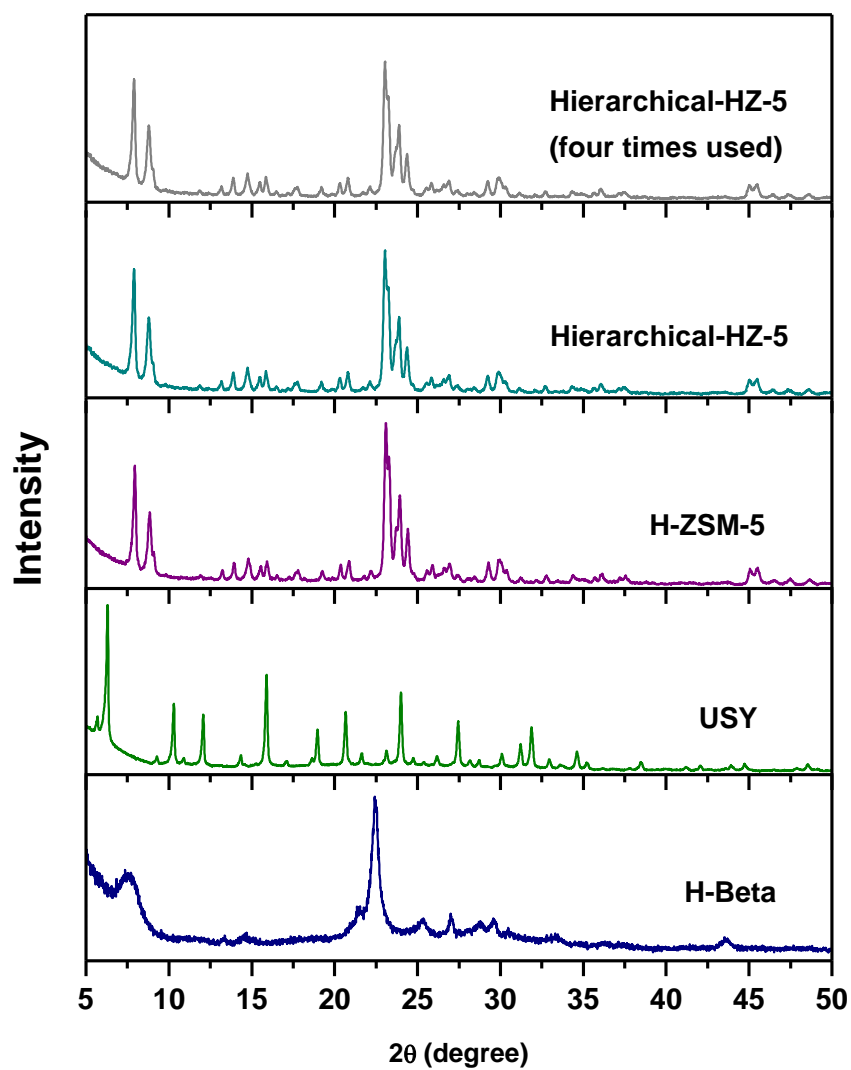


Fig. 1

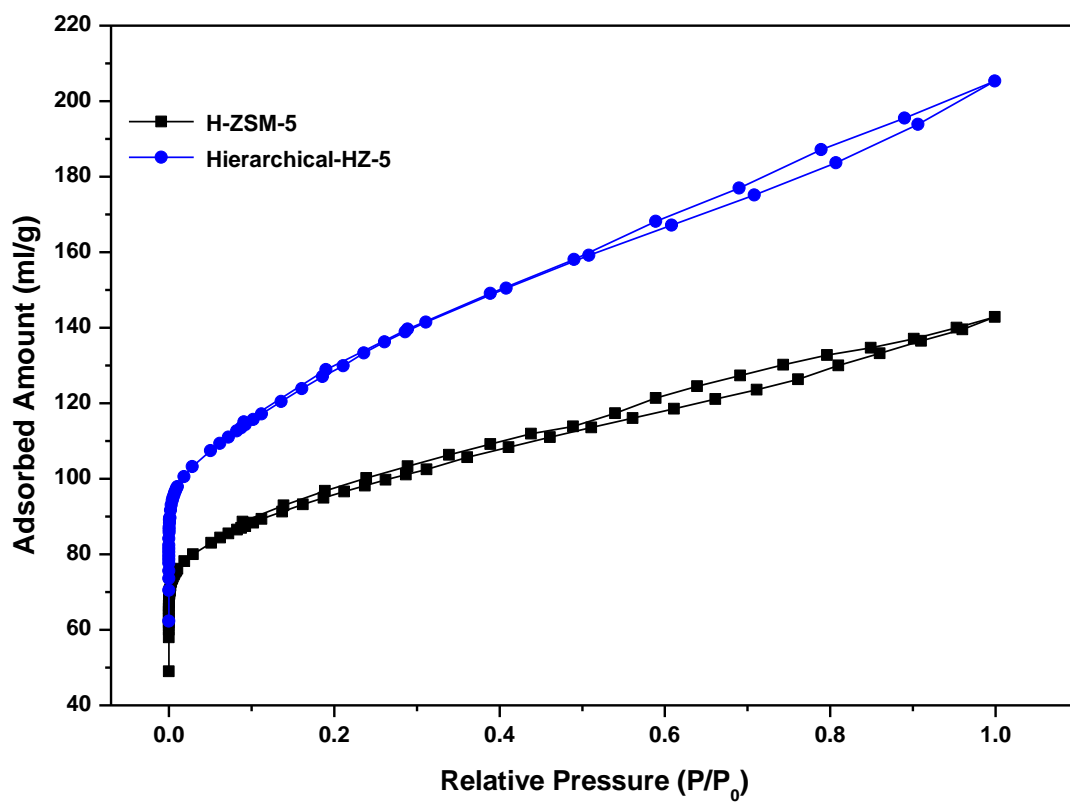


Fig. 2

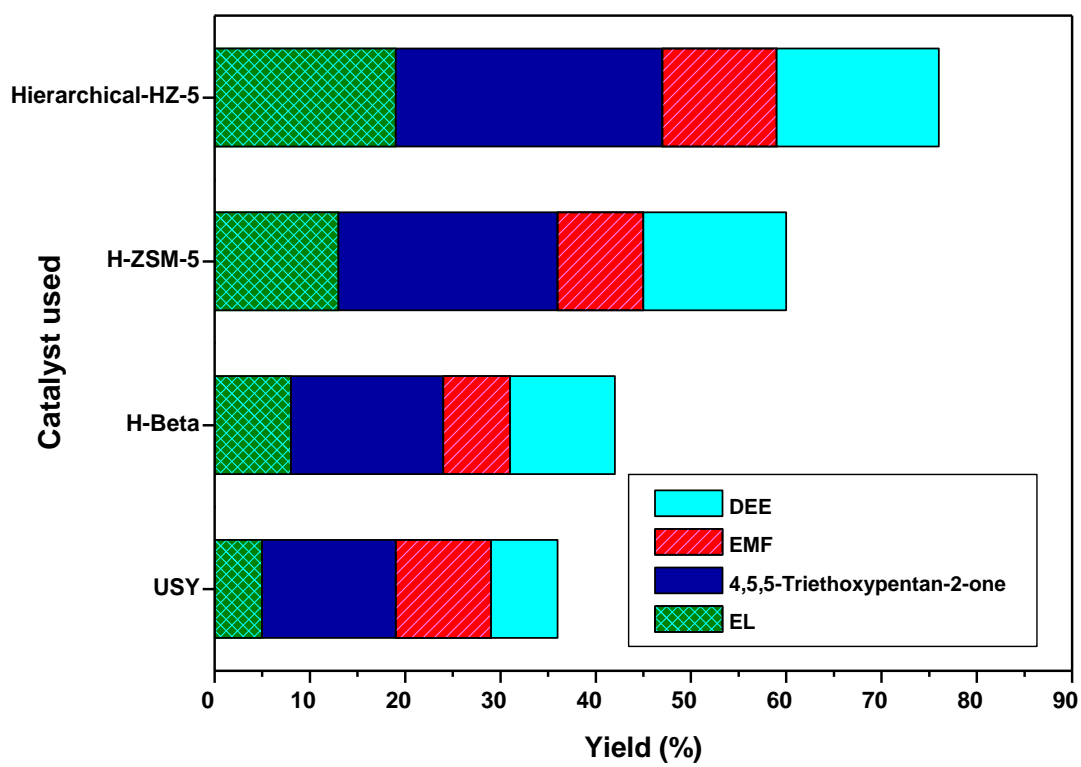


Fig. 3

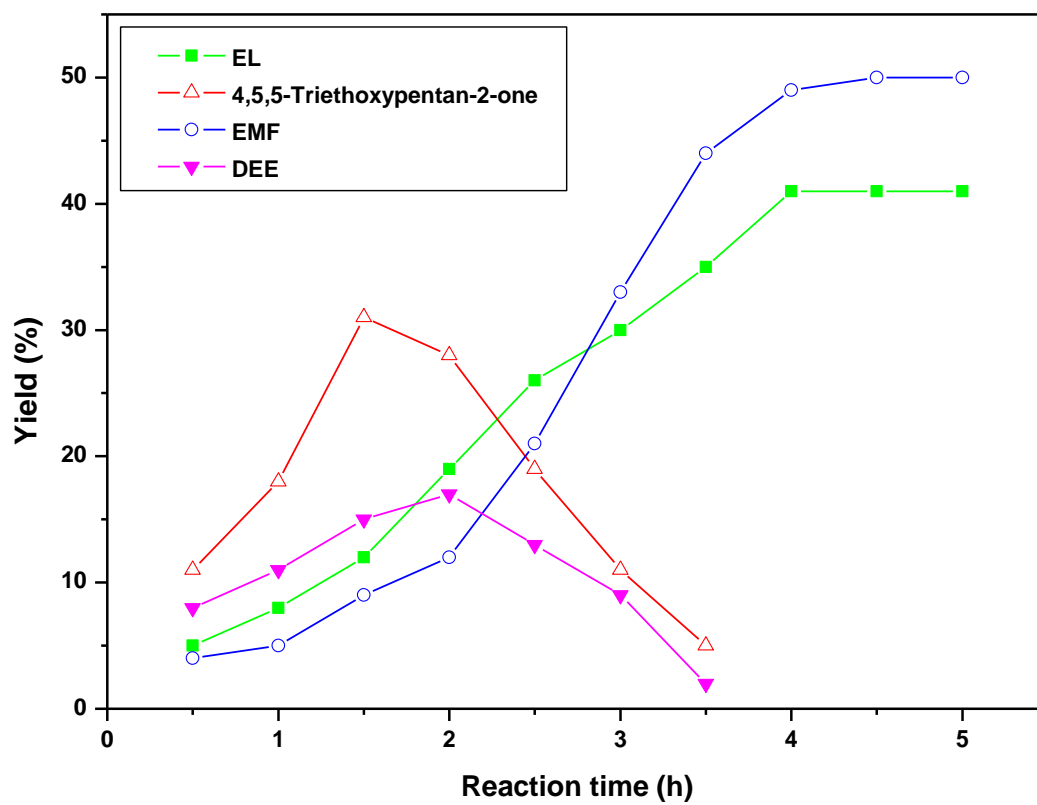
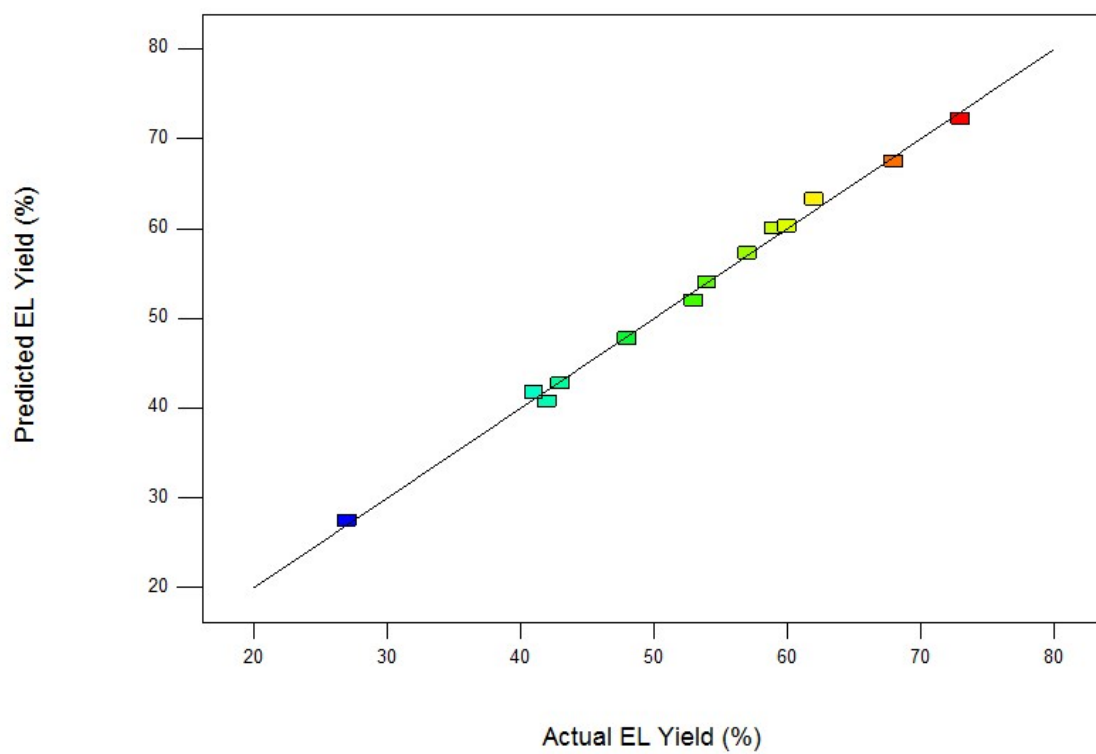
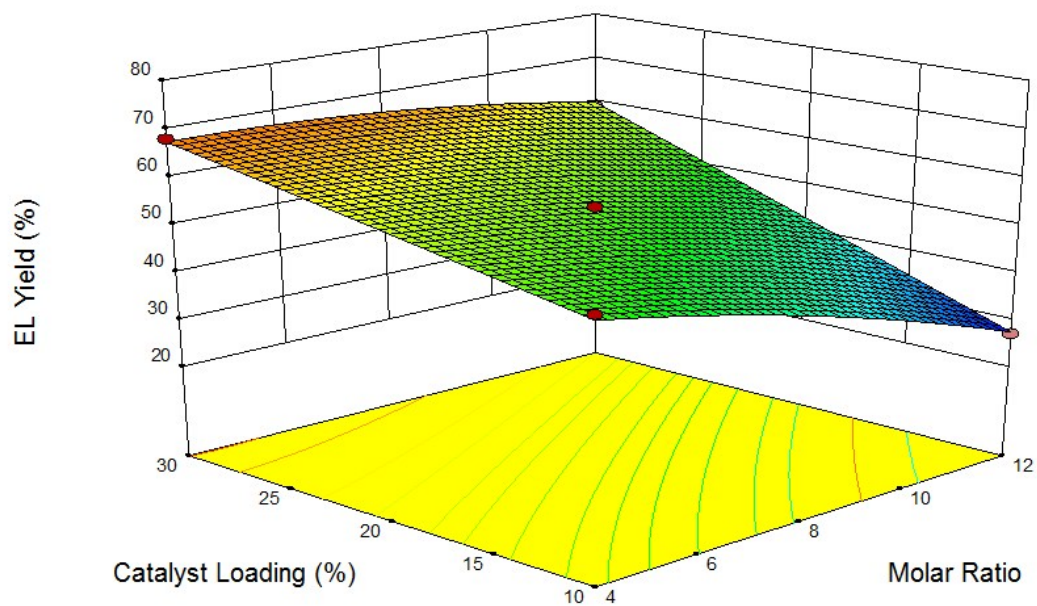


Fig. 4

**Fig. 5**

**Fig. 6**



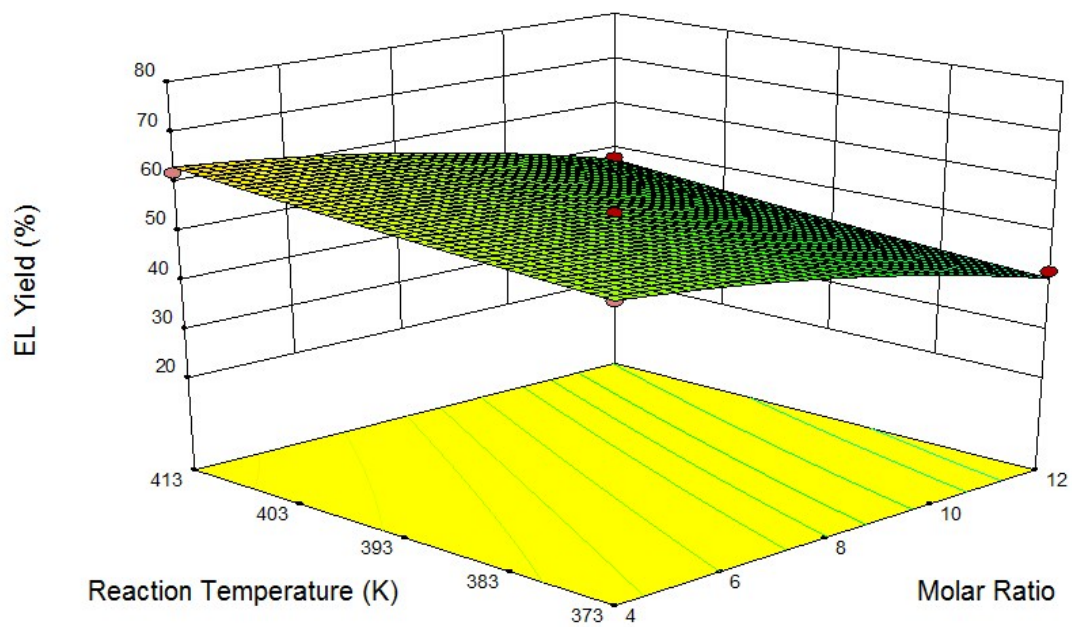


Fig. 7

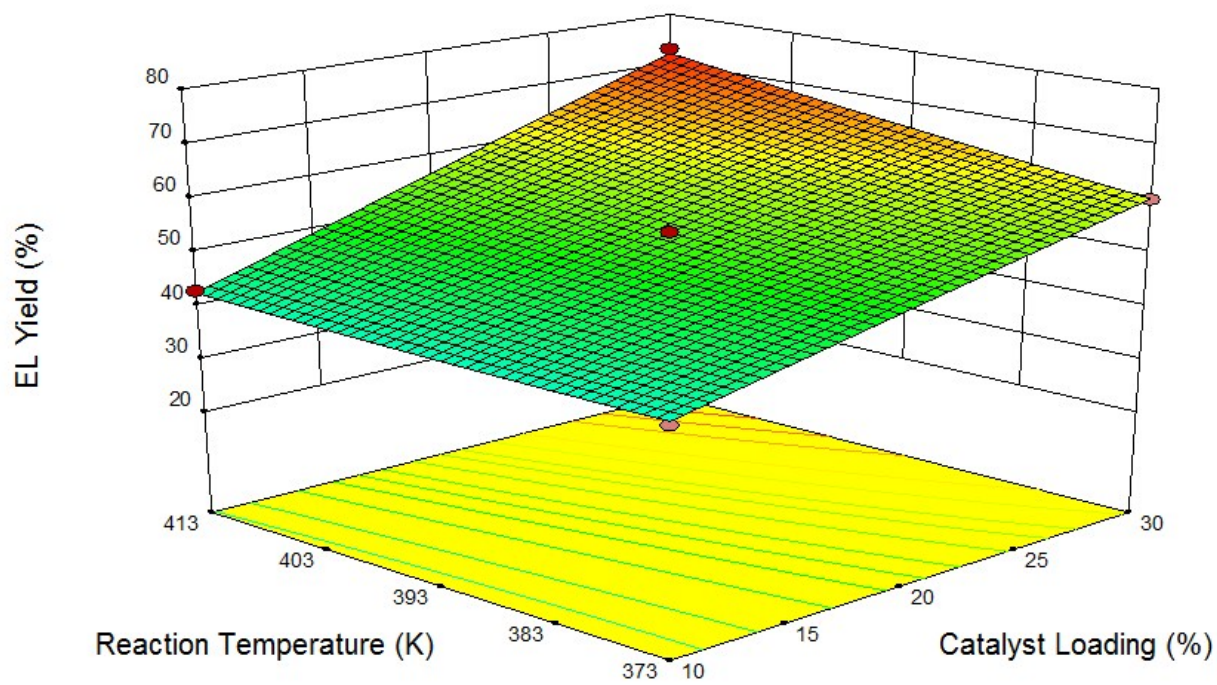


Fig. 8

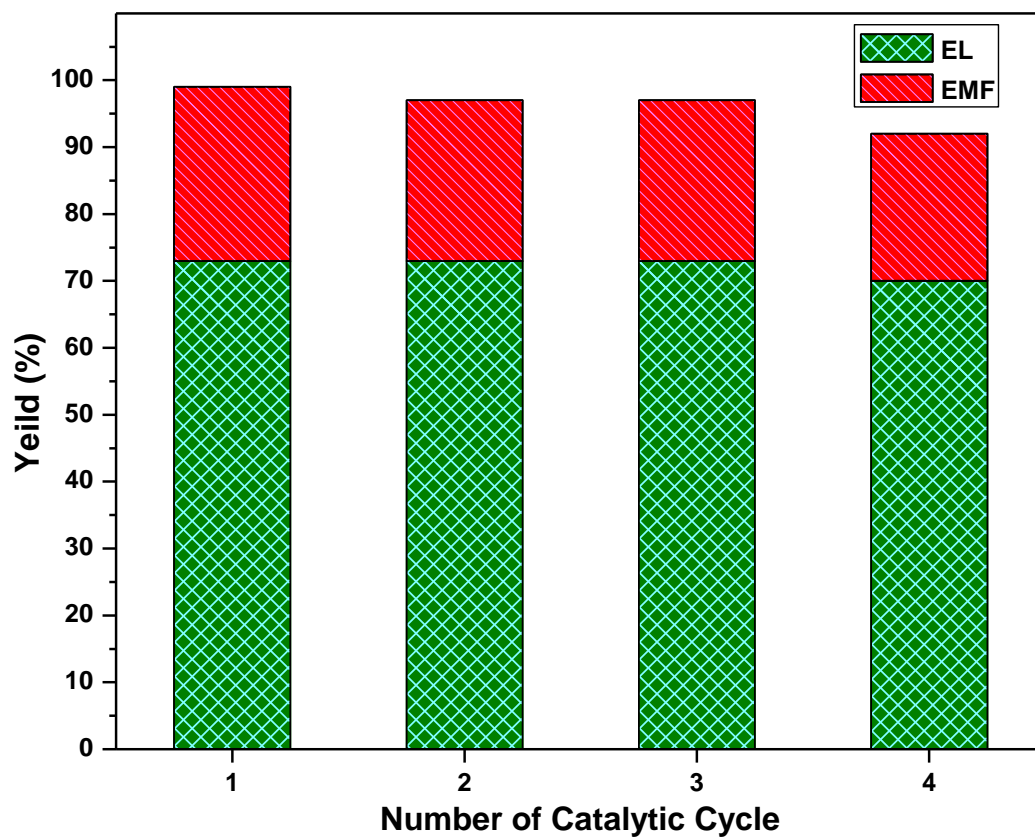
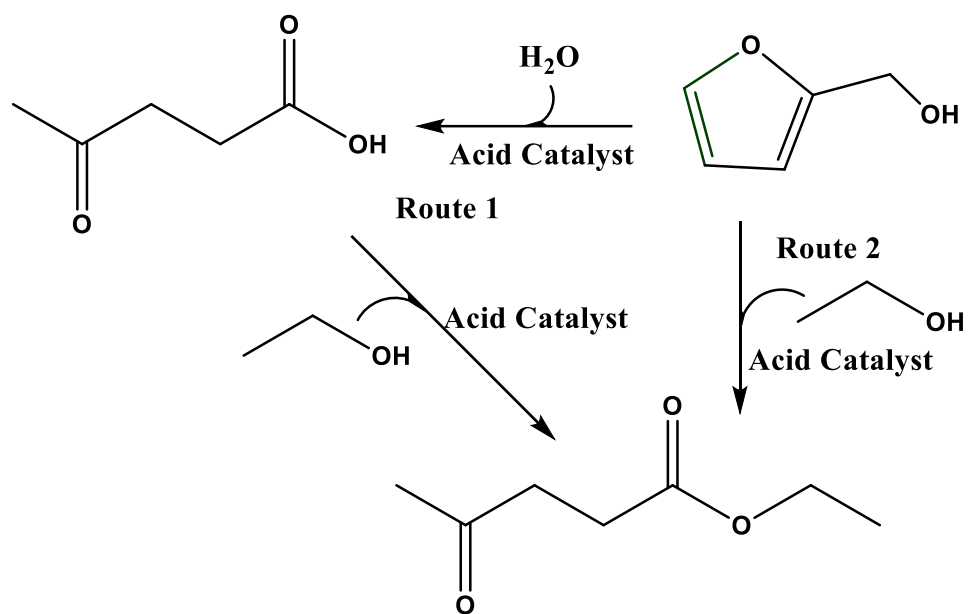


Fig. 9



Scheme 1

**Table 1** Physico-chemical properties of catalysts.

Catalyst	Si/Al ratio <sup>a</sup>	S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>P</sub> <sup>c</sup> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>P</sub> <sup>d</sup> (Å)	Total Acidity <sup>e</sup> (mmol g <sup>-1</sup> )
USY	15	773	0.42	7.2	0.38
H-Beta	8.8	560	0.38	6.4	0.54
H-ZSM-5	37	300.8	0.17	5.5	0.51
Hierarchical-HZ-5	30.15	427.6	0.31	29.78	0.73

<sup>a</sup>Si/Al ratio was estimated by EDAX; <sup>b</sup>Surface area (S<sub>BET</sub>) was calculated by Brunauer-Emmett-Teller equation; <sup>c</sup>Pore volume (V<sub>P</sub>) was determined from single point desorption isotherm at  $P/P_0 = 0.9$ ; <sup>d</sup>Pore diameter (D<sub>P</sub>) was calculated using Barrett-Joyner-Halenda desorption branch of the isotherm; <sup>e</sup>Total acidity was determined with ammonia TPD.

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

Variables	Symbol	Coded levels		
		-1	0	+1
Molar Ratio (Ethanol to FAL)	X <sub>1</sub>	4	8	12
Catalyst Loading (%)	X <sub>2</sub>	10	20	30
Reaction Temperature (K)	X <sub>3</sub>	373	393	413

**Table 3** Most favorable process parameters for ethanolysis of FAL over Hierarchical-HZ-5 zeolite for reaction time 4 h and validation model adequacy.

<b>Process parameters</b>	<b>Molar ratio (ethanol to FAL), <math>X_1</math></b>	<b>Catalyst loading (wt. %), <math>X_2</math></b>	<b>Reaction temperature, <math>X_3</math> (K)</b>	<b>EL Yield, Y (%)</b>
Predicted	5.7	29.9	412.4	73.4
Experimental	6	30	413	73