

Optimization and Packed Bed Column Studies on Esterification of Glycerol to Synthesize Fuel Additives - Acetins

Pradima J Britto[†], Rajeswari M Kulkarni, Archana Narula, Sunaina Poonacha, Rakshita Honnatagi, Sneha Shivanathan and Waasif Wahab

Department of Chemical Engineering, M. S. Ramaiah Institute of Technology, MSR Nagar, MSRIT Post, Bangalore-560054, Karnataka, India.

(Received 27 May 2021; Received in revised from 26 August 2021; Accepted 30 August 2021)

Abstract – Biodiesel production has attracted attention as a sustainable source of fuel and is a competitive alternate to diesel engines. The glycerol that is produced as a by-product is generally discarded as waste and can be converted to green chemicals such as acetins to increase bio-diesel profitability. Acetins find application in fuel, food, pharmaceutical and leather industries. Batch experiments and analysis have been previously conducted for synthesis of acetins using glycerol esterification reaction aided by sulfated metal oxide catalysts ($\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$). The aim of this study was to optimize process parameters: effects of mole ratio of reactants (glycerol and acetic acid), catalyst concentration and reaction temperature to maximize glycerol conversion/acetin selectivity. The optimum conditions for this reaction were determined using response surface methodology (RSM) designed as per a five-level-three-factor central composite design (CCD). Statistica software 10 was used to analyze the experimental data obtained. The optimized conditions obtained were molar ratio - 1:12, catalyst concentration - 6 wt.% and temperature -90 °C. A packed bed reactor was fabricated and column studies were performed using the optimized conditions. The breakthrough curve was analyzed.

Key words: Glycerol, Fuel additives, Mixed oxide catalyst, Optimization, Packed bed column studies

1. Introduction

Biodiesel has received increased attention as an alternative renewable fuel and conversion of by-product glycerol into value added chemicals has sparked immense research interest [1]. Glycerol is a promising low-cost feedstock. Value-added special and fine chemicals can be obtained from glycerol by using several catalytic processes. For instance, the selective oxidation of glycerol to glyceric acid or hydroxyacetone, dehydration to acrolein, hydrogenation to 1, 2- or 1,3-propanediol, etherification to alkyl ethers, condensation to dimers or oligomers and the acetylation/esterification of glycerol to esters [2-5]. Esterification of glycerol can be a good alternative to utilize the glycerol produced by biodiesel process. The esterification of glycerol involves a reaction between glycerol and acetic acid in the presence of catalyst to yield acetins such as monoacetin, diacetin and triacetin. Acetins have great potential as fuel additives that decrease particulate matter, carbon monoxide, emissions of unregulated aldehydes and hydrocarbons [6]. They enhance viscosity and cold flow properties when introduced in biodiesel and petroleum formulations. They are used as an antiknock additive, as a plasticizer, food additive, as a solvent in tannery, in the manufacture of explosives, and as a resource for the production of biodegradable polyesters [7,8].

Heterogeneous metal oxide catalysts are preferred over homogeneous acid catalysts as they are not corrosive and easy to separate after the reaction process [6,9,10]. Solid acid catalysts, such as ion exchange resin and heteropolyacids, exhibit poor thermal stability, poor regeneration ability and low specific area [11,12]. Metal oxides are preferred over the aforesaid catalysts as they are stable, regeneratable, inexpensive and active over a wide temperature range. CeO_2 and ZrO_2 are also promising for their (i) red-ox properties, (ii) form non-stoichiometric mixed metal oxide, (iii) thermal and high pressure stability, and (iv) reduced acid site deactivation [13,14]. Also, impregnated sulfate ions strongly influence the physiochemical characteristics of metal oxide catalysts [15]. The $\text{SO}_4^{2-}/\text{CeO}_2\text{-ZrO}_2$ combination catalyst exhibits superior catalytic activity under mild conditions. The better activity of the sulfated catalysts is due to the formation of super acidic sites on the surface of the promoted catalysts.

Statistical methods applied to reactions play an important role in planning, conducting, analyzing and interpreting data from experiments conducted. Various optimization techniques that have been employed for esterification reaction are listed in Table 1. RSM is a mathematical technique that helps in finding relationship between parameters and their response and can locate an optimum response within designated variable ranges [16]. CCD is a special type of response surface design that can fit a full quadratic model. CCD contains an embedded factorial or fractional factorial design with center points that are augmented with a group of star or axial points. Axial points are an efficient way to determine coefficients of a second-degree polynomial for the variables. CCD also tests at extreme conditions and hence gives

[†]To whom correspondence should be addressed.

E-mail: pradimabritto@gmail.com

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Table 1. Optimization methods employed for different processes

Sl. No.	Optimization Method	Parameters	Optimal conditions	References
1	RSM (3 factor 5 level CCD)	Molar ratio-2, 3, 4, 5, 6 Catalyst(KOH)loading (g) -0.25,0.5,0.75,1.0,1.25 Reaction time(min)-30,45,60,75,90	Molar ratio - 3:1 Catalyst loading (g) - 0.55 Reaction time (min) - 45	[20]
2	RSM (3 factor 5 level CCD)	For acid esterification process, H ₂ SO ₄ conc. (volume %) - 0.33, 0.5, 0.75, 1, 1.17 MoleRatio-1:0.32, 1:1, 1:2, 1:3, 1:3.68 Reaction Time (min)-9.55, 30, 60, 90, 110.45 For CuO-CaO based Transesterification process, CuO-CaO conc. (weight%)-1.32, 2, 3, 4, 4.68 Mole ratio-0.16:1, 0.3:1, 0.5:1, 0.7:1, 0.84:1 Reaction time (min) - 69.55, 90,120, 150, 170.45	For acid esterification process, H ₂ SO ₄ con (volume %) - 0.85 Mole Ratio-1:1 Reaction time (min)- 70.2 For CuO-CaO based Transesterification process, CuO-CaO conc. (weight%)-4 Mole ratio-0.3:1 Reaction time (min)-150	[21]
3	RSM (4 factor 5 level face centered CCD)	Molar ratio-2:1, 4:1, 6:1, 8:1, 10:1 Temperature (°C)-50, 55, 60, 65, 70 Catalyst (NaOH) weight (g) -0.2, 0.4, 0.6, 0.8, 1 Reaction time(min)-30, 45, 60, 75, 90	Mole ratio - 7.41:1 Temperature (°C) - 61.84 Catalyst weight (g) - 0.63 Reaction time (min) - 62.12	[22]
4	RSM (5 factor 5 level CCD)	Temperature (°C)-20, 35, 50, 65, 80 Molar ratio-1, 2, 3, 4, 5 Catalyst (Amberlyst 36) loading (g) -0.5, 1, 1.5, 2, 2.5 Feed flow rate (mL/min)-0.2, 0.4, 0.6, 0.8, 1 Pressure(bar)-0, 30, 60, 90, 120	Temperature (°C) - 30.8 Molar ratio - 2.7 Catalyst loading (g) - 1.6 Feed flow rate (mL/min) - 1.0 Pressure (bar) - 14.5	[23]
5	RSM (3 factor 3 level CCD)	Temperature (°C) -66, 80, 100, 120, 134 Molar ratio-1, 3, 5, 7, 9 Pressure(bar)-1, 41, 100, 159, 199	Temperature (°C) - 102 Pressure (bar) - 16.7 Molar ratio - 1.1	[23]
6	RSM (3 factor CCD)	Molar ratio-6:1-15:1 Catalyst (CaO) weight (g)-1to 4 Reaction time (h) - 1 to 3	Mole ratio - 10.5:1 Catalyst weight (g) - 2.5 Reaction time(h) - 3.68	[24]
7	RSM (4 factor 5 level CCD)	Molar ratio-6, 8, 10,12, 14 Catalyst (Calcium Methoxide) conc. (%) 1.5, 2, 2.5, 3, 3.5, Methanol conc. (%) - 4.5, 6, 7.5, 9, 10.5 Reaction time (min) - 30, 60, 90, 120, 150	Molar ratio - 11.6:1 Catalyst conc. - 2.83% Methanol conc. - 8.65% Reaction time (min) - 100.14	[25]
8	RSM (3 factor 3 level face centered CCD)	Mole ratio - 6:1, 9:1, 12:1 Temperature (°C) - 95, 110,125 Catalyst (sulfated alumina) weight (g) - 0.25, 0.5, 0.75	Mole ratio - 12:1 Temperature (°C) - 108.8 Catalyst weight (g) - 0.36	[26]
9	RSM (4 factor 2 level CCD)	Initial Conc. (mg/L) - 600, 1000 Bio-adsorbent dose (g/100 ml) - 0.2, 1.5 pH - 5, 12 Stirring rate (rpm) - 250, 800	Initial Conc. (mg/L) -1000 Bio-adsorbent dose (g/100 ml) - 0.2 pH Stirring rate (rpm) - 251.5	[27]
10	RSM (3 factor 5 level CCD)	Temperature (°C) - 183.2, 190, 200, 210, 216.8 Reaction time (min) -1.6, 3.0, 5.0, 7.0, 8.4 Catalyst (H ₃ PO ₄) conc. (%) - 0.33, 0.5, 0.75, 1, 1.17	Temperature (°C) - 200 Reaction time (min) - 8.4 Conc. of catalyst - 0.75%	[28]

better results for quadratic models.

Continuous flow packed-bed reactors offer significant processing advantages such as better heat and mass transfer efficiency, low maintenance, easy scale-up, continuous production with more environmental and economic benefits [17,18]. Further, using packed bed reactor, variables can be varied almost independently of each other.

The present work is mainly focused on optimizing the following factors: mole ratio of the reactants (glycerol and acetic acid), catalyst loading and the reaction temperature to maximize glycerol conversion using sulfated CeO₂-ZrO₂ metal oxide catalyst. The optimum conditions for acetylation reaction using sulfated cerium-zirconium metal oxide catalyst was determined by RSM and designed as per a five-level-three-factor CCD. Batch experiments and analysis were previously conducted for the chemical conversion of glycerol acetylation reaction using sulfated metal oxide catalysts (CeO₂-ZrO₂) and have been reported [19]. In this work, we also carried out the continuous production of acetins in a packed bed reactor using the optimized conditions.

2. Materials and Methods

2-1. Materials and synthesis of catalyst

AR grade Cerous Nitrate (Ce(NO₃)₃·6H₂O) and Zirconyl Nitrate (Zr-(NO₃)₄·5H₂O) were procured from Loba Chemie Pvt., Ltd. and used to prepare metal oxide catalyst. Urea (CO (NH₂)₂), procured from SD Fine Chemicals Ltd., was used as a reductant. Sulfuric acid (H₂SO₄) procured from Nice Chemical Pvt. Ltd., was used for sulfation of cerium-zirconium metal oxide. Acetic Acid Glacial extrapure (CH₃COOH) and Glycerol (C₃H₈O₃, LR Grade) supplied by SD Fine Chemicals Ltd, were used to carry out the esterification reaction. CeO₂-ZrO₂ metal oxide catalyst was synthesized by combustion method using metal nitrates as oxidizer and urea as reducing fuel, and the procedure is as described by Kulkarni et al. [19].

2-2. Optimization studies on glycerol esterification reaction

The esterification reaction between glycerol and acetic acid using



Fig.1. Experimental set-up for the esterification of glycerol.

metal oxide catalyst was carried in four three-necked round bottom flasks placed on independently temperature controlled magnetic stirrers (Velp Scientifica F20500420) as shown in Fig. 1. The condenser tubes provided constant water circulation to arrest reactant vapors under atmospheric pressure. The flasks were kept in separate oil baths to provide uniform heating. Stirring speed was maintained at 500 rpm throughout all experimental runs. On completion of each experimental run, a definite volume of the sample was withdrawn from the reaction mixture, centrifuged and the clear liquid was analyzed for product distribution by gas chromatography (Mayura Analytical LLP Model 1100).

2-3. Statistical analysis using design of experiments

Design of experiments (DOE) for the esterification reaction between glycerol and acetic acid was applied for optimization and to determine the main effects, quadratic effects and the interaction effects of the operating process variables: glycerol to acetic acid molar ratio (1:3 to 1:20), catalyst concentration (1 wt.% to 9 wt.%) and temperature (70 °C to 110 °C) on glycerol conversion and product selectivity. The range was chosen based on the results of our previous study [19]. Optimal reaction conditions were determined by RSM using CCD composed of 3 factors totaling 16 experiments (including one at the center point). The five level codes of these variables are $-\alpha$, -1 , 0 , $+1$, $+\alpha$, as shown in Table 2. The solution with the best desirability based on optimum glycerol conversion/Acetin selectivity was identified as the optimum parameter.

Analysis of variance (ANOVA) was performed using Statistica 10 software to find the influence of parameters on the glycerol conversion and selectivity towards formation of acetins. Significance of each term was evaluated by fitting into equations and to estimate the goodness

of fit in each case with a confidence level of 95% ($p < 0.05$). Basically, when the P (the significance probability) value of each input response is less than 0.05, the influence factor is significant.

2-4. Continuous studies

The optimized conditions obtained from RSM were further used to study the acetylation of glycerol as a continuous process. A schematic representation of the packed bed reactor system for acetin synthesis is shown in Fig. 2. The upper zone is equipped with condenser to recover any vapors and a thermometer well. The middle zone is a glass column of 3-cm ID and 40 cm length which was packed with sulfated metal oxide catalyst, beads and glass wool to facilitate effective contact of reactants with catalyst. The feed inlet was set at the top of glass column and the products were collected at the bottom. Preheated glycerol and acetic acid at molar ratio 1:12 were fed to the packed column maintained at 90 °C at a constant flow rate of 10 mL/min using peristaltic pump. Packed bed column was maintained at constant temperature. The reactor column was packed with 40 g of sulfated metal oxide catalyst (5 cm bed height). The product was collected at specific interval of time and analyzed for glycerol conversion using GC. The reaction was carried out for 15 h duration and was conducted in duplicate.

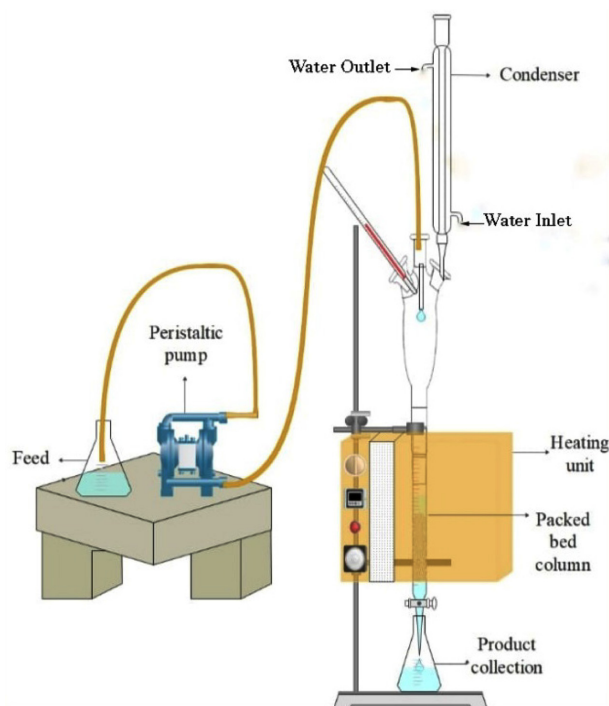


Fig. 2. Experimental set-up - column studies for the esterification of glycerol.

Table 2. Ranges and levels of operating parameters

Sl. No	Parameters	Units	$-\alpha$	-1	0	$+1$	$+\alpha$
1.	Reaction temperature	°C	70	80	90	100	110
2.	Molar ratio of glycerol to acetic acid	mol/mol	3	5	10	15	20
3.	Catalyst concentration	Wt.%	1	3	5	7	9

3. Results and Discussion

3-1. Experimental design and analysis

A total of 16 batch experiments were carried out as per DOE. The influence of the following independent variables (factors) - mole ratio of reactants, catalyst concentration and the reaction temperature - were analyzed using RSM with three factors and at five levels on glycerol conversion and the selectivity towards acetin formation. The reactions were performed randomly, as suggested by DOE to minimize error accompanying a specific order. The responses include glycerol conversion and selectivity towards mono, di and triacetin respectively. Data analysis was done using Statistica 10 software. The experimental CCD matrix and the predicted values of the response are presented in Table S1.

The input and output data (Table S1) were fitted on second-order polynomial equations (Eq. 1 to Eq. 4) which gives the functional relationship between selected factors and responses. Polynomial equations are advantageous in response surface designs in terms of flexibility and easiness in the determination of model parameters [24,29].

The model equation relates the responses Y (glycerol conversion and the selectivity towards the different esters) with main effects (X_1 , X_2 , X_3), square effects (X_1^2 , X_2^2 , X_3^2) and interaction effects (X_{12} , X_{23} , X_{13}) of process variables.

The interaction effect of factors was explained using RSM plots. Analysis of variance (ANOVA) was used as a statistical tool to fit the model. X_{12} , X_{13} and X_{23} represent the interaction between the parameter molar ratio (X_1) and temperature (X_2); molar ratio (X_1) and catalyst concentration (X_3); temperature (X_2) and catalyst concentration (X_3). The interaction effects indicate the influence of interaction of two factors on the dependent variable glycerol conversion. The interaction plot/reading implies joint effect of these factors, indicating strong/low interaction between the selected factors.

The glycerol conversion ranged from 97.420% to 100% for the experimental combination given by CCD design. The experimental data was fitted by multiple regression to construct a regression model equation to analyze and predict the optimal level for enhanced efficiency. As shown by data, the developed regression model has a satisfactory goodness of fit and confidence level. Further, the predicted value of the model is consistent with the actual value.

The fitness of the model was tested by ANOVA ($R^2=0.97$). The results of ANOVA are shown in Table S2. The model F-value and P-value were used to evaluate the significance of glycerol conversion / selectivity towards the formation of acetins. F (Fisher) value in Table S2 is the comparison of means of variance of selected samples to assess the significance of factors on yield. Larger value of F indicates greater dispersion. P (probability) value measures the compatibility of data in a hypothesis test. The larger the magnitude of F value and the smaller the P value, the more significant are the corresponding coefficients. P values less than 0.05 indicate significant model terms. Molar ratio has more effect on glycerol conversion, monoacetin and

triacetin selectivity compared to the catalyst concentration and temperature. The effect of the reaction parameters on glycerol conversion as well as the yield of monoacetin follows the order: AA/G mole ratio > catalyst weight percent > interaction between mole ratio and catalyst weight percent > reaction temperature. For selectivity towards formation of di-acetin, catalyst concentration was found to be significant and for tri-acetin formation, molar ratio, temperature and catalyst concentration were significant.

Table S1 presents the relationship between the experimental and model predicted values of glycerol conversion and selectivity toward acetins (Fig. 3). It can be seen that the values calculated from the model equations are very close to those observed in the experiments, suggesting a good validity of the proposed models. Table 3 and 4 give the optimal values of the operating parameters and the responses studied during the acetylation of glycerol, obtained using the Statistica software.

Maximizing glycerol conversion is the objective function of this study. The obtained optimized conditions were used for packed bed column studies. Glycerol conversion also indicates acetins synthesis. The product distribution is indicated by selectivity functions.

Second-order equations relating response and process variables

Glycerol Conversion

$$Y = 90.20934 + 0.68321 X_1 - 0.02158 X_1^2 - 0.00274 X_2 + 0.00044 X_2^2 + 1.90435 X_3 - 0.03346 X_3^2 + 0.00015 X_{12} - 0.02725 X_{13} - 0.01325 X_{23} \quad (1)$$

Monoacetin Selectivity

$$Y = 260.1713 - 10.3043 X_1 + 0.0910 X_1^2 - 2.6567 X_2 + 0.0047 X_2^2 - 23.0110 X_3 - 0.1038 X_3^2 + 0.0547 X_{12} + 0.4877 X_{13} + 0.1908 X_{23} \quad (2)$$

Diacetin Selectivity

$$Y = 25.02389 + 11.46220 X_1 + 0.09257 X_1^2 - 1.05036 X_2 + 0.01793 X_2^2 + 15.70652 X_3 + 1.0671 X_3^2 - 0.11125 X_{12} - 0.75275 X_{13} - 0.22225 X_{23} \quad (3)$$

Triacetin Selectivity

$$Y = -183.867 - 0.847 X_1 - 0.190 X_1^2 + 3.846 X_2 - 0.023 X_2^2 + 4.167 X_3 - 0.665 X_3^2 + 0.054 X_{12} + 0.277 X_{13} + 0.025 X_{23} \quad (4)$$

where Y = response; X_1 = molar ratio of reactants, X_2 = reaction temperature, X_3 = catalyst weight percent.

3-2. Effect of parameter on acetylation of glycerol acetylation reaction

3-2-1. Effect of temperature

Increasing temperature generally results in increased interaction between reactants/catalyst as they reduce viscosity and enhance solubility. It also improves diffusion of reactants/products in and out of the active sites. Acetylation/esterification reactions are endothermic.

With increase in temperature from 70 to 110 °C, it was found that monoacetin formation was suppressed, while selectivity to higher esters was promoted (Table S1). The results obtained suggest that at

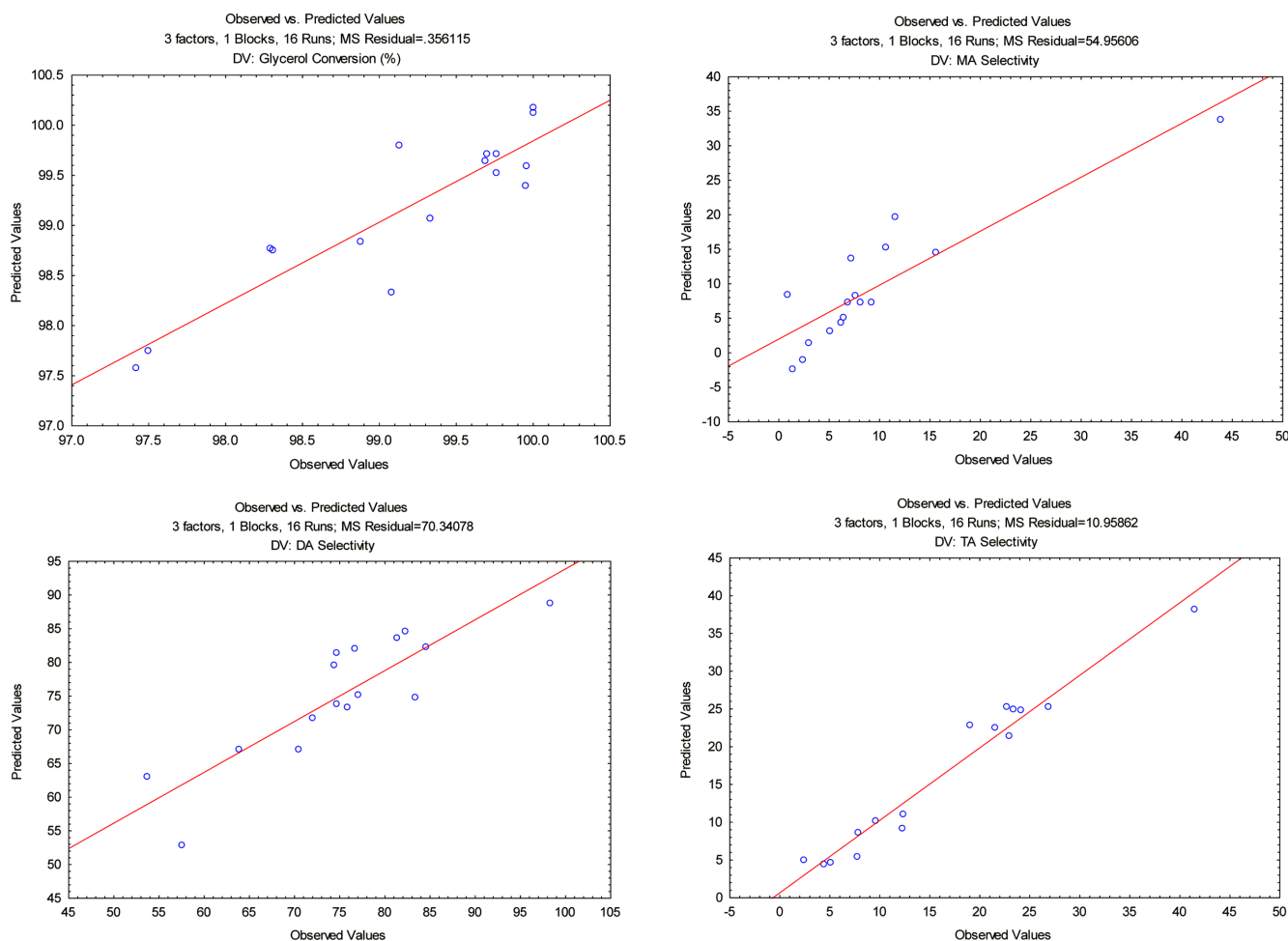


Fig. 3. Observed and predicted values for the esterification of glycerol.

Table 3. Optimum values

Factors	GC	MA	DA	TA
Molar Ratio	12.44801 \approx 12	10.1089	8.84975	20.8596
Temperature ($^{\circ}$ C)	88.62124 \approx 90	101.3013	85.90398	112.5905
Catalyst (wt%)	5.84147 \approx 6	5.998	4.70776	9.611

Table 4. Values of Response studies

Responses	Values (%)
Glycerol Conversion	99.795
Monoacetin Selectivity	4.1975
Diacetin Selectivity	66.056
Triacetin Selectivity	29.945

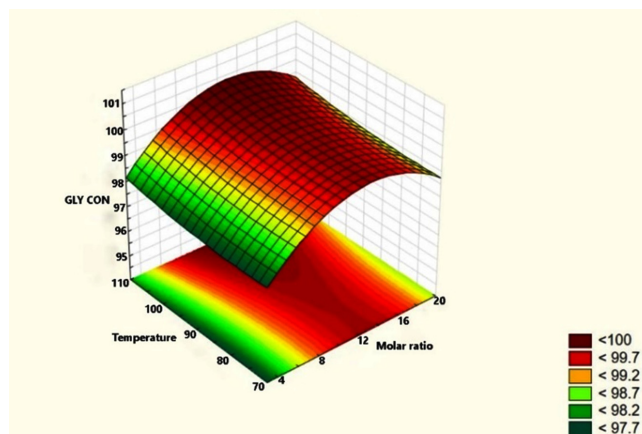
a higher temperature, mono and diacetin are converted to triacetin through consecutive reaction, increasing selectivity towards triacetin formation. The slight drop in selectivity towards diacetin was due to the conversion of more diacetin to triacetin. Glycerol conversion increased with increase in temperature due to the conversion of glycerol to mono, di and triacetin. Higher temperature is known to support triacetin formation and at the same time alter/shift the equilibrium towards the formation of reactants [30,31].

3-2-2. Effect of molar ratio

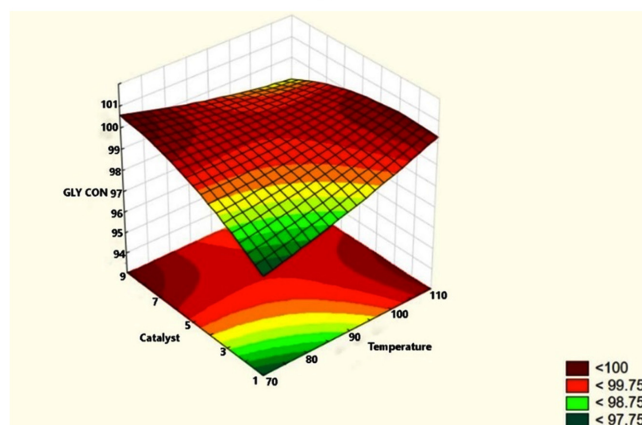
Esterification of glycerol is an equilibrium-limited reaction with acetic acid, and hence high glycerol conversion can be attained only when one of the reactants is taken in excess [30]. Glycerol conversion was found to increase with increase in acetic acid concentration in the feed (Table S1). Monoacetin selectivity was found to decrease with increase in AA/gly molar ratio. Esterification of glycerol is a reversible reaction and hence excess availability of acetic acid in the reaction mixture drives the reaction towards the formation of di and tri-acetins [31].

3-2-3. Effect of catalyst concentration

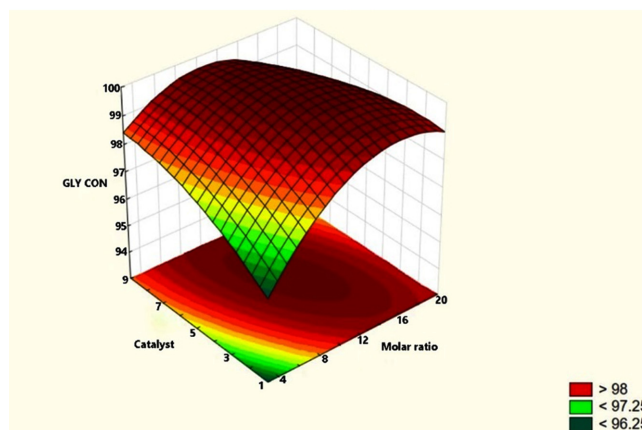
Acetin formation was found to increase with increase in catalyst concentration due to increased active sites. At the initial stage, an increase in catalyst concentration accelerated the rate of reaction and enhanced product formation. But with further increases in catalyst



(i)



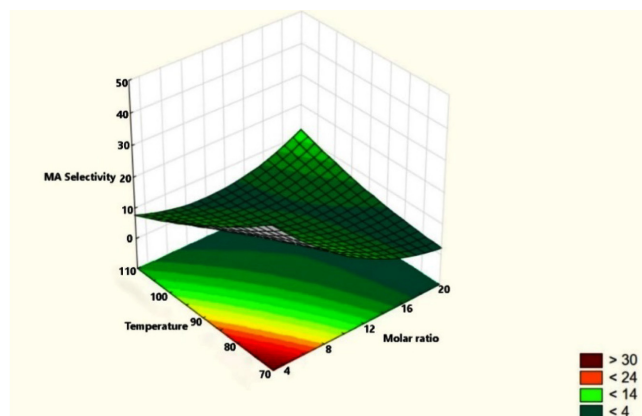
(ii)



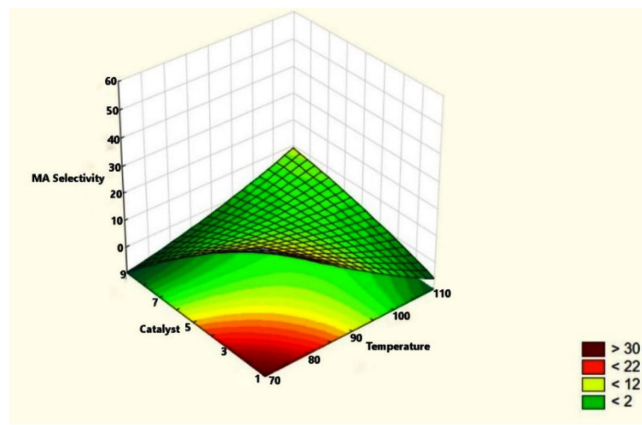
(iii)

Fig. 4. Surface response for the glycerol conversion evaluated against the variables (i) molar ratio/temperature, (ii) temperature/catalyst, (iii) molar ratio/catalyst.

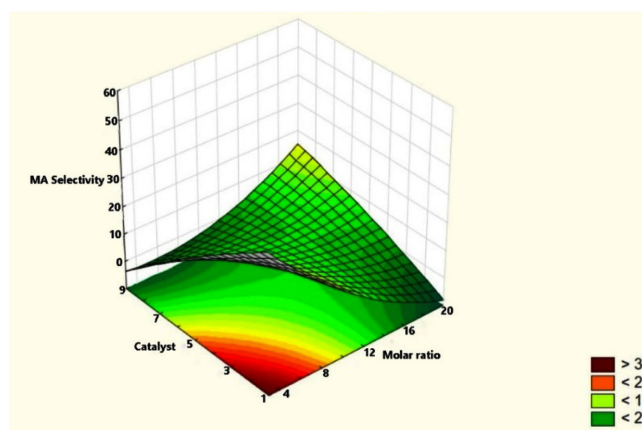
concentration, the particles tend to agglomerate, reducing the accessibility of the reactants at the catalyst surface. The active sites situated on the surface of agglomerates actively participate in product formation and hinder transfer rates to active sites situated within [32]. The selectivity of mono and diacetin was found to decrease with increase in the catalyst concentration, whereas triacetin selectivity increased with increase in catalyst concentration.



(i)



(ii)



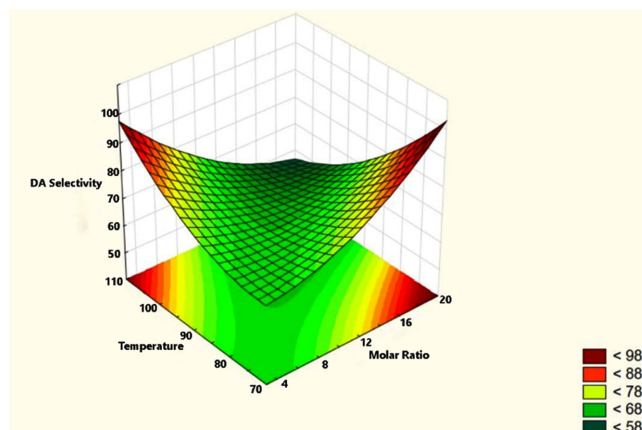
(iii)

Fig. 5. Surface response for the monoacetin selectivity evaluated against the variables (i) molar ratio/temperature, (ii) temperature/catalyst, (iii) molar ratio/catalyst.

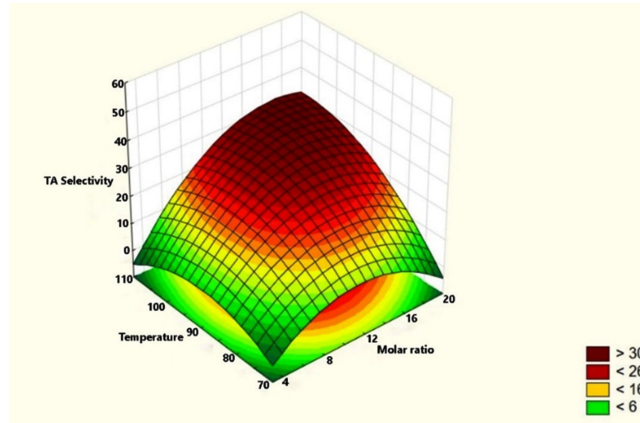
Response surface plots (Fig. 4-7) indicate the interaction effect of the (i) acetic acid /glycerol molar ratio and temperature, (ii) temperature and catalyst on glycerol conversion and product selectivity, and (iii) acetic acid/glycerol molar ratio and catalyst.

3-3. Continuous packed bed reactor study

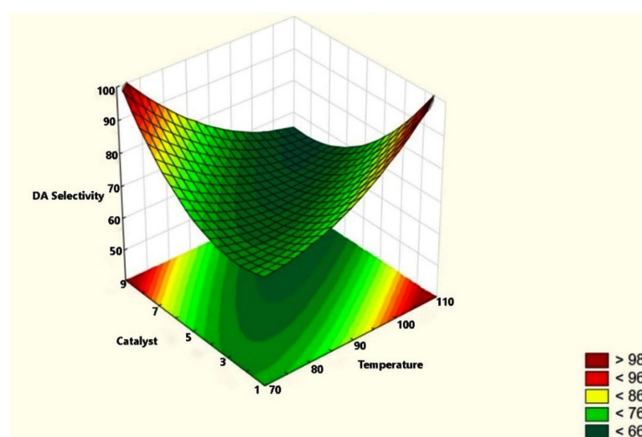
Several studies on batch reactor for glycerol esterification reaction



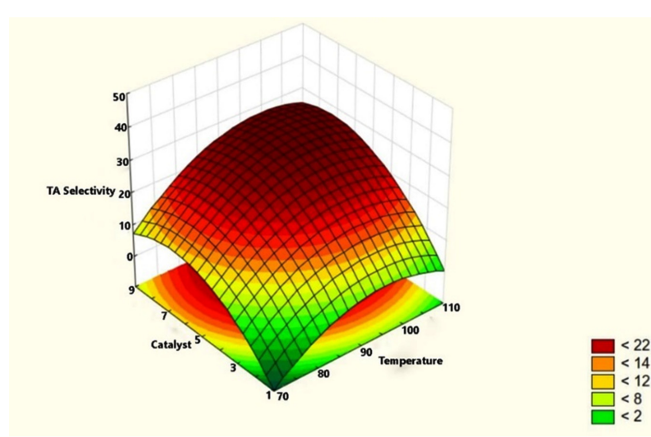
(i)



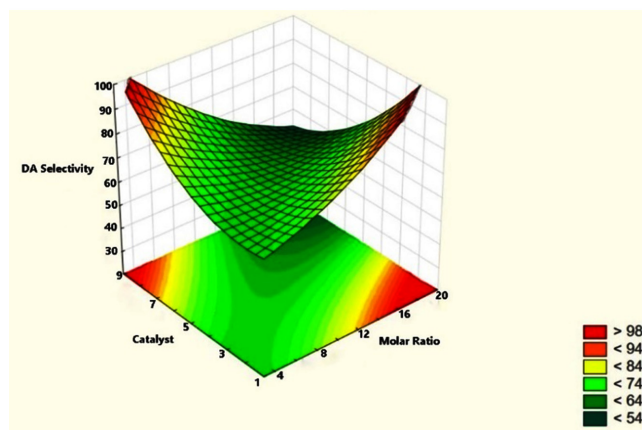
(i)



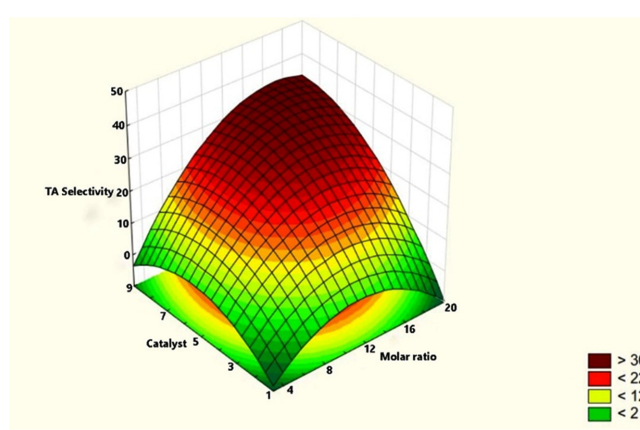
(ii)



(ii)



(iii)



(iii)

Fig. 6. Surface response for the diacetin selectivity evaluated against the variables (i) molar ratio/temperature, (ii) temperature/catalyst, (iii) molar ratio/catalyst.

Fig. 7. Surface response for the triacetin selectivity evaluated against the variables (i) molar ratio/temperature, (ii) temperature/catalyst, (iii) molar ratio/catalyst.

have been reported in literature. In a batch reactor, reactants react in the presence of a suitable catalyst for sufficient time to achieve equilibrium. However, for practical operation of scale up study, continuous packed bed reactors are preferred. The advantage of continuous packed bed reactor study is continuous interaction of reactants to facilitate conversion of bulk volume of glycerol using a fixed amount of catalyst. Packed bed reactors are easy to operate,

give good yield, are energy efficient, easier to regenerate packed catalyst and easier to scale up from batch system.

The column performance is analyzed in terms of the breakthrough curve. A breakthrough curve was obtained by plotting the ratio of C_t/C_i against time for a given condition, where C_i and C_t are initial glycerol concentration and glycerol concentration at any given time t . The breakthrough curve is shown in Fig. 8. Breakthrough point (t_b)

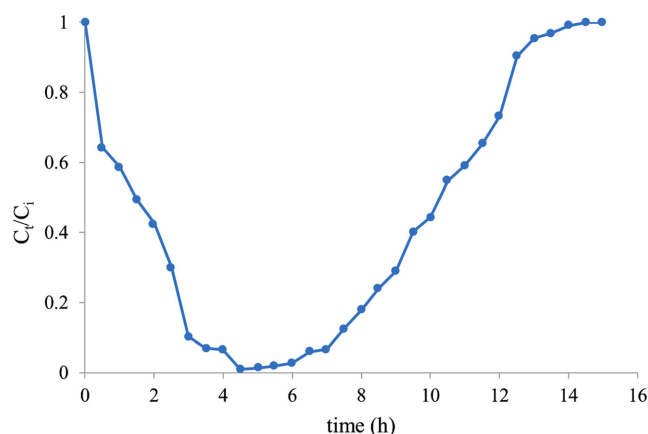


Fig. 8. Break-through curve on acetin synthesis in a packed bed continuous reactor.

was 7.5 h, evaluated from the curve and it is a point in terms of time where the outlet glycerol concentration reached 10% of inlet glycerol concentration. Exhaustion time was 13h, the time at which glycerol concentration increased to 95% of inlet glycerol concentration. Production rate of acetins in packed bed reactor was found to be 75 g/h when compared to that of batch reactor with 2.5 g/h. Hence, a packed bed column is advantageous when compared to batch system for esterification reaction.

4. Conclusion

A glycerol esterification reaction was carried out over sulfated $\text{CeO}_2\text{-ZrO}_2$ metal oxide catalyst. The catalyst was prepared by combustion method and sulfated by impregnation of sulfuric acid. The influence of various parameters such as acetic acid to glycerol (G/AA) mole ratio, catalyst concentration and temperature was studied to evaluate the conversion of glycerol and selectivity towards the formation of acetins. Two sets of batch experiments were conducted and the experimental conditions were designed as per CCD. The process parameters - mole ratio of reactants, catalyst weight percent and reaction temperature were - optimized. It was also observed that the effect of the reaction parameters on glycerol conversion followed the order: Gly/AA mole ratio > catalyst weight percent > interaction between mole ratio and catalyst weight percent > reaction temperature. The optimized conditions were determined by RSM using the Statistica 10 software and are a molar ratio of 1:12, catalyst concentration of 6 wt% and temperature 90 °C.

The future work of this project is in extending the results obtained for process scale-up pilot scale. Flow reactor with different configurations, catalyst surface modification etc., can be explored for this esterification reaction. The economic feasibility of the process should also be looked into.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Notations

AA	: Acetic Acid
C_i	: Initial Glycerol concentration
C_t	: Glycerol concentration at time (t)
CCD	: Central Composite Design
DA	: Diacetin
DOE	: Design of Experiments
Gly	: Glycerol
GC	: Gas Chromatography
MA	: Monoacetin
RSM	: Response Surface Methodology
TA	: Triacetin
t_b	: Break-through point

Acknowledgments

We are grateful to VGST (GRD-691) and MSRIT for supporting this study.

References

1. Aghbashlo, M., Tabatabaei, M., Rastegari, H., Ghaziaskar, H. S. and Shojaei, T. R., "On the Exergetic Optimization of Solketal-acetin Synthesis as a Green Fuel Additive Through Ketalization of Glycerol-derived Monoacetin with Acetone," *Renew. Energ.*, **126**, 242-253(2018).
2. Sato, S., Sakai, D., Sato, F. and Yamada, Y., "Vapor-phase Dehydration of Glycerol Into Hydroxyacetone over Silver Catalyst," *Chem. Lett.* **41**, 965-966(2012).
3. Aruna, S. T. and Mukasyan, A. S., "Combustion Synthesis and Nanomaterials," *Curr Opin Solid St M*, **12**, 44-50(2008).
4. Gandarias, I., Arias, P. L., Fernández, S. G., Requies, J., El Doukali, M. and Güemez, M. B., "Hydrogenolysis Through Catalytic Transfer Hydrogenation: Glycerol Conversion to 1, 2-propanediol," *Catal. Today*, **195**, 22-31(2012).
5. Ozbay, N., Oktar, N., Dogu, G. and Dogu, T., "Conversion of Biodiesel by-product Glycerol to Fuel Ethers Over Different Solid Acid Catalysts," *Int. J. Chem. React. Eng.*, **8** (2010).
6. Gonçalves, C. E., Laier, L. O., Cardoso, A. L. and da Silva, M. J., "Bioadditive Synthesis from $\text{H}_3\text{PW}_{12}\text{O}_{40}$ -catalyzed Glycerol Esterification with HOAc Under Mild Reaction Conditions," *Fuel Process Technol.*, **102**, 46-52(2012).
7. Costa, I. C., Itabaiana Jr, I., Flores, M. C., Lourenço, A. C., Leite, S. G., de M. e Miranda, L. S. and de Souza, R. O., "Biocatalyzed Acetins Production Under Continuous-flow Conditions: Valorization of Glycerol Derived from Biodiesel Industry," *J. Flow Chem.*, **3**, 41-45(2013).
8. Pradima, J. and Kulkarni, M. R., "Review on Enzymatic Synthesis of Value Added Products of Glycerol, a by-product Derived from Biodiesel Production," *Resource-Efficient Technologies*, **3**, 394-405(2017).
9. Melero, J. A., van Grieken, R., Morales, G. and Paniagua, M., "Acidic Mesoporous Silica for the Acetylation of Glycerol: Synthesis of Bio Additives to Petrol Fuel," *Energy & Fuels*, **21**, 1782-

- 1791(2007).
10. Ferreira, P., Fonseca, I. M., Ramos, A. M., Vital, J. and Castanheira, J. E., "Esterification of Glycerol with Acetic Acid Over Dodecamolybdophosphoric Acid Encaged in USY Zeolite," *Catal Commun.*, **10**, 481-484(2009).
 11. Wang, S. and Guin, J. A., "Silica-supported Sulfated Zirconia: a New Effective Acid Solid for Etherification," *Chem. Commun.*, **24**, 2499-2500(2000).
 12. Mallick, S. and Parida, K. M., "Studies on Heteropoly Acid Supported Zirconia II. Liquid Phase Bromination of Phenol and Various Organic Substrates," *Catal Commun.*, **8**, 889-893(2007).
 13. Ifrah, S., Wie, L. I., Buisette, V., Denaire, S. and Marques, R. M. J. C., U.S. Patent Application No. 16/096, 279, (2019).
 14. Shah, P. M., Day, A. N., Davies, T. E., Morgan, D. J. and Taylor, S. H., "Mechanochemical Preparation of Ceria-zirconia Catalysts for the Total Oxidation of Propane and Naphthalene Volatile Organic Compounds," *Appl. Catal. B. Environmental*, **253**, 331-340(2019).
 15. Reddy, P. S., Sudarsanam, P., Raju, G. and Reddy, B. M., "Selective Acetylation of Glycerol over CeO_2 -M and $\text{SO}_4^{2-}/\text{CeO}_2$ -M (M= ZrO_2 and Al_2O_3) Catalysts for Synthesis of Bioadditives," *J. Ind. Eng. Chem.*, **18**, 648-654(2012).
 16. Kulkarni, R. M., Shetty, K. V. and Srinikethan, G., "Optimization of Nickel (II) and Cadmium (II) Biosorption on Brewery Sludge Using Response Surface Methodology," *In Materials, Energy and Environment Engineering*, 121-127(2017).
 17. Salvi, H. M., Kamble, M. P. and Yadav, G. D., "Synthesis of Geraniol Esters in a Continuous-flow Packed-bed Reactor of Immobilized Lipase: Optimization of Process Parameters and Kinetic Modeling," *Appl. Biochem. Biotech.*, **184**, 630-643(2018).
 18. Nanda, M. R., Yuan, Z., Qin, W., Ghaziaskar, H. S., Poirier, M. A. and Xu, C. C., "A New Continuous-flow Process for Catalytic Conversion of Glycerol to Oxygenated Fuel Additive: Catalyst Screening," *Appl. Energ.*, **123**, 75-81(2014).
 19. Kulkarni, R. M., Britto, P. J., Narula, A., Saqline, S., Anand, D., Bhagyalakshmi, C. and Herle, R. N., "Kinetic Studies on the Synthesis of Fuel Additives from Glycerol Using CeO_2 - ZrO_2 Metal Oxide Catalyst," *Biofuel Research J.*, **7**, 1100(2020).
 20. Niju, S., Raj, F. R., Anushya, C. and Balajii, M., "Optimization of Acid Catalyzed Esterification and Mixed Metal Oxide Catalyzed Transesterification for Biodiesel Production from Moringa Oleifera Oil," *Green Process Synth.*, **8**, 756-775(2019).
 21. Yesilyurt, M. K., Arslan, M. and Eryilmaz, T., "Application of Response Surface Methodology for the Optimization of Biodiesel Production from Yellow Mustard (*Sinapis alba* L.) Seed Oil," *Int. J. Green Energy*, **16**, 60-71(2019).
 22. Aghbashlo, M., Tabatabaei, M., Jazini, H. and Ghaziaskar, H. S., "Exergoeconomic and Exergoenvironmental co-optimization of Continuous Fuel Additives (acetins) Synthesis from Glycerol Esterification with Acetic Acid Using Amberlyst 36 Catalyst," *Energ. Convers. Manage.*, **165**, 183-194(2018).
 23. Usman, B. and Garba, A. A., "Application of Central Composite Design (CCD) in the Optimisation of Parameters for the Production of Biodiesel from Cattle Fat Using CaO as Solid Base Catalyst," *In A Conference paper presented at the Yusuf Maitama Sule University, Kano, Faculty of Science 3rd Annual International Conference at Kano, Nigeria* (2017).
 24. Chumuang, N. and Punsuvon, V., "Response Surface Methodology for Biodiesel Production Using Calcium Methoxide Catalyst Assisted with Tetrahydrofuran as co Solvent," *J. of Chemistry* (2017).
 25. Arun, P., Pudi, S. M. and Biswas, P., "Acetylation of Glycerol Over Sulfated Alumina: Reaction Parameter Study and Optimization Using Response Surface Methodology," *Energ. Fuel*, **30**, 584-593(2016).
 26. Sadhukhan, B., Mondal, N. K. and Chatteraj, S., "Optimization Using Central Composite Design (CCD) and the Desirability Function for Sorption of Methylene Blue from Aqueous Solution Onto Lemna Major," *Karbala International J. of Modern Science*, **2**, 145-155(2016).
 27. Mendonça, A. D. M., Siqueira, P. M., Souza, M. M. V. M. and Pereira Jr, N., "Optimization of Production of 5-Hydroxymethylfurfural from Glucose in a Water: Acetone Biphasic System," *Brazilian J. Chem. Eng.*, **32**, 501-508(2015).
 28. Carley, K. M., Kamneva, N.Y. and Reminga, J., Response Surface Methodology; School of Computer Science, Carnegie Mellon University: Pittsburgh, PA; CASOS Technical Report CMUISRI-04-136(2004).
 29. Liao, X., Zhu, Y., Wang, S. G. and Li, Y., "Producing Triacetyl-glycerol with Glycerol by Two Steps: Esterification and Acetylation," *Fuel Process Technol.*, **90**, 988-993(2009).
 30. Gao, X., Zhu, S. and Li, Y., "Graphene Oxide as a Facile Solid Acid Catalyst for the Production of Bioadditives from Glycerol Esterification," *Catal. Commun.*, **62**, 48-51(2015).
 31. Tao, M. L., Guan, H. Y., Wang, X. H., Liu, Y. C. and Louh, R. F., "Fabrication of Sulfonated Carbon Catalyst from Biomass Waste and Its Use for Glycerol Esterification," *Fuel Process Technol.*, **138**, 355-360(2015).
 32. Setyaningsih, L., Siddiq, F. and Pramezy, A., Esterification of Glycerol with Acetic Acid over Lewatit Catalyst," *In Matec Web of Conferences*, **154** 01028(2018).

Authors

Pradima J Britto: (Ph. D)., Research Scholar, Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India; pradimabritto@gmail.com

Dr. Rajeswari M Kulkarni: Ph. D., Associate Professor, Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India; rmkulkarni@msrit.edu

Dr. Archana Narula: Ph.D., Professor and Head, Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India; archna_71@yahoo.com

Sunaina Poonacha: Student., Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India; sunaina.poonacha@yahoo.co.in

Rakshita Honnatagi: Student., Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India, hrkulkarni98@gmail.com

Sneha Shivanathan: Student., Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India; snehashivanathan137@gmail.com

Waasif Wahab: Student., Department of Chemical Engineering, M S Ramaiah Institute of Technology, MSR Nagar, Bangalore, 560-054, India; waasifkaruthedath@gmail.com

Appendix

Table S1. Design matrix for CCD with experimental and predicted values

	Molar Ratio (X ₁)	Temperature (X ₂)	Catalyst wt% (X ₃)	Experimental				Predicted			
				X _{Gly} (%)	S _{MA} (%)	S _{DA} (%)	S _{TA} (%)	X _{Gly} (%)	S _{MA} (%)	S _{DA} (%)	S _{TA} (%)
1	5	80	3	97.420	43.860	53.730	2.400	97.5760	33.70834	62.98976	4.93788
2	5	80	7	99.330	7.590	84.560	7.840	99.0700	8.31534	82.32476	8.60163
3	5	100	3	99.080	15.590	76.670	7.730	98.3310	14.54034	82.08476	5.38663
4	5	100	7	98.290	6.200	81.410	12.370	98.7650	4.40934	83.63976	11.06538
5	15	80	3	99.950	8.104	82.260	9.630	99.3941	7.23947	84.54262	10.14049
6	15	80	7	99.130	2.960	74.670	23.350	99.9981	1.35447	73.76762	24.89924
7	15	100	3	100.00	2.390	74.640	22.960	100	4.20814	74.38762	21.40424
8	15	100	7	99.760	0.890	57.580	41.510	99.5231	8.38647	52.83262	38.17799
9	3	90	5	97.500	11.540	83.380	5.070	97.7496	19.61686	74.84500	4.69550
10	20	90	5	98.880	6.440	72.030	21.520	98.8386	5.13754	71.69977	22.49764
11	10	70	5	99.690	10.630	77.110	12.240	99.6454	15.25060	75.16381	9.16332
12	10	110	5	100.00	5.080	75.890	19.020	100	3.11460	73.32381	22.89082
13	10	90	1	98.310	7.240	98.350	4.400	98.7544	13.63560	88.75381	4.42832
14	10	90	9	99.956	1.360	74.450	24.100	99.5924	1.38040	80.53381	24.86582
15	10	90	5	99.700	6.840	70.440	22.710	99.7088	7.28800	67.07024	25.29256
16	10	90	5	99.764	9.200	63.860	26.890	99.7088	7.28800	67.07024	25.29256

Table S2. ANOVA for the Quadratic Model for Acetylation of Glycerol

	Glycerol Conversion			MA Selectivity			DA Selectivity			TA Selectivity		
	Std Error	F	P	Std Error	F	P	Std Error	F	P	Std Error	F	P
Molar Ratio (X ₁)	0.42789	14.27	0.0092	5.3155	7.05	0.037	6.0132	0.93	0.371	2.37365	72.99	0.0001
Molar Ratio (X ₁ ²)	0.00759	8.092	0.0293	0.0942	0.93	0.371	0.1066	0.75	0.418	0.04209	20.279	0.0040
Temperature(°C)(X ₂)	0.27234	0.6469	0.4518	3.3832	2.68	0.152	3.8276	0.048	0.833	1.51077	17.195	0.006
Temperature (°C) (X ₂ ²)	0.00146	0.0910	0.773	0.0182	0.06	0.803	0.0206	0.76	0.416	0.00812	8.14	0.029
Catalyst concentration (wt.%) (X ₃)	1.04180	1.97	0.209	12.9418	4.66	0.074	14.6417	1.208	0.313	5.77917	38.11	0.0008
Catalyst concentration (wt.%) (X ₃ ²)	0.03658	0.83	0.395	0.4545	0.05	0.826	0.5142	4.307	0.083	0.20295	10.747	0.0168
1L by 2L (X ₁₂)	0.00422	0.002	0.972	0.0524	1.08	0.337	0.0593	3.519	0.109	0.02341	5.33	0.0602
1L by 3L(X ₁₃)	0.02110	1.66	0.24	0.2621	3.46	0.112	0.2965	6.44	0.044	0.11704	5.616	0.0555
2L by 3L(X ₂₃)	0.01055	1.577	0.25	0.1310	2.11	0.195	0.1483	2.247	0.1845	0.05852	0.185	0.6819