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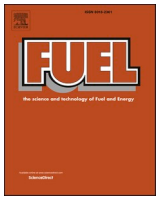

Full Length Article

Investigating biodiesel production from Chicken fat oil using bi-functional catalysts and microbubble mediated mass transfer

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ABSTRACT

Biodiesel production has been limited by slow kinetics of acid catalyzed esterification, downstream product separation before transesterification and expensive feedstock. Bi-functional catalysts can carry out esterification and transesterification simultaneously. However, an energy efficient method is still required to enhance the kinetics of esterification. Similarly, the thermodynamic equilibrium hindering the overall conversion of the esterification needs to be manipulated to increase the overall conversion of the process. The manuscript proposes a new bi-functional catalyst, 7 % Sr/ZrO_2, along with microbubble mediated injection of alcohol. The conversion of free fatty acids (FFA) and Triglycerides by bi-functional catalysts was compared with three naturally occurring bi-functional catalysts- Zwitterions. Chicken fat oil was chosen as the feedstock. Preliminary experiments were conducted to select alcohol. Experiments were designed using Response Surface Methodology. The current study shows that the use of heterogeneous catalysts and CFO as a feedstock has lucrative potentials. The rate of reaction and conversion of the process are further increased by overcoming the thermodynamic equilibrium using microbubble mediated mass transfer increasing process feasibility. Response Surface Methodology (RSM) was used to design the experiments. 7 % Sr/ZrO_2 was found to give significantly higher conversion of triglycerides as compared with the Zwitterions. However, conversion of FFA using Aspartic acid was almost similar to 7 % Sr/ZrO_2. For triglycerides and FFA, the conversion of CFO at optimize conditions using (Molar ratio = 1: 14, temperature 70 °C, and catalyst loading 1 %) was 75 % and 57 %, as compared with aspartic acid (61 % and 63 %), arginine (58 % and 73 %), and isoleucine (54 % and 39 %) respectively. Detailed comparison between other reported bi-functional catalysts showed that 7 %Sr/ZrO_2 yielded a high conversion in significantly less time. The higher performance can be attributed to the use of microbubble mediated mass transfer. The results indicate that integration of microbubble mediated mass transfer and a bi-functional catalyst can accelerate the industrial reactive separations comprising biodiesel production.

1. Introduction

Biodiesel production at the industrial level faces three major challenges. First, feed pretreatment through acid-catalyzed esterification is necessary for most commercially feasible feedstocks containing a higher amount of free fatty acids (FFA > 1 %). This means that acid pretreatment is required before the transesterification process [1]. However, acid catalysis is inherently slow and limited by equilibrium, leading to additional downstream separation steps, which increase the overall production cost [2,3]. Second, acid-catalyzed esterification exhibits slow kinetics compared to alkaline transesterification, with a speed that is approximately 4000 times slower [4]. This sluggishness is attributed to the low miscibility of reactants (feedstock and alcohols, apart from castor oil) and the production of water as a byproduct, which triggers reverse reactions and establishes a thermodynamic equilibrium [5]. Third, the debate between energy and food resources always prioritizes food, given the significant number of people worldwide experiencing malnutrition and undernourishment. This ongoing concern further

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complicates the availability and cost of biodiesel feedstock [1]. In this article, these challenges are thoroughly discussed, and plausible solutions are hypothesized. Additionally, experiments have been conducted to validate these hypotheses.

Commercially important feedstock such as waste cooking oil or animal fats are pretreated with acid catalyst to bring down the FFA content below 1 % to avoid emulsification and saponification. Conventional homogeneous acid catalysts such H_2SO_4, pTSA are preferred because of low cost and high availability. However, they incur high costs for downstream separation of glycerol, for washing and purification, and for being non-biodegradable [6]. Biodiesel production via heterogeneous catalyzed techniques has been proposed as one of the main routes as they are considered eco-friendly, product separation is more straightforward and requires no washing[7]. However, the overall conversion and rate of reaction is still low and requires high temperature and longer duration [8]. More importantly, the esterification products still needs to be separated before further processing.

Bi-functional catalysts with both basic and acidic sites can carry out esterification and transesterification simultaneously [4,9]. They eliminate the need to separate the products between esterification and transesterification, and avoid saponification. A good bi-functional catalyst having an amphoteric material can further be modified such as ZrO_2 can be modified to yield acidic sites by treating it with La_2O_3 and CaO [10]. The transesterification process is supported by the basic site while the esterification reaction is supported by the acid site. Fig. 1 illustrates the suggested reactions mechanism for the present study.

The catalyst first de-protonates the methanol to produce an alkoxide ion during the reaction. The triglyceride's carbonyl carbon is then attacked by this ion, leading to the formation of an intermediary complex. The fatty acid alkyl ester is subsequently transferred from the intermediate complex to the methanol molecule via the bi-functional catalyst's basic site, creating the final product. By protonating the triglyceride's carbonyl oxygen and facilitating the nucleophilic attack of methanol, the acid site of the bi-functional catalyst aids in accelerating the process. The acid site may also aid in preventing the production of soaps, which could decrease the final result of the biodiesel product.

Bi-functional catalysts also exist naturally in the form of Zwitterion. Zwitterions, commonly referred to as dipolar ions, are molecules that have distinct positive and negative charges on different atoms. A neutral charge is produced when these opposing charges are present in the same molecule. Amino acids are the most common example of a zwitterion. [11]. In the current study, Strontium zirconium oxide (7 % Sr/ZrO_2) was produced as a heterogonous catalyst for biodiesel synthesis and compared with zwitterions for overall conversion and rate of reaction.

Bi-functional catalysts can simplify downstream processing of biodiesel, avoiding the problem of saponification. However, esterification is still bound to have slow kinetics owing to poor miscibility of the reactants and establishment of thermodynamic equilibrium due to production of water as byproduct. Several methods have been discussed in literature to avoid these problems such as reactive distillation and various reactor configuration [12,13]. However, most of the methods are energy intensive. We have developed an energy efficient process to carry our acid catalyzed esterification using microbubble mediated mass transfer [12,14]. Alcohol, unlike conventional methods, is fed in the form of vapours using microbubble injection. The reaction is carried out at the microbubble interface where the alcohol is present in local excess as compared with oil (feedstock) pushing the reaction in the forward direction. The alcohol flux is from the bubble while the products, water and biodiesel, move inwards and towards the interface, respectively. Esters have hydrophobic tails and hydrophilic functionality, so are attracted to the microbubble interface. The bubble keeps on rising reacting with freshly available oil all the time and finally bursts at the top, removing unreacted alcohol and produced water out of the liquid system. The continuous removal of the water pulls the equilibrium in the forward direction as well. Since biodiesel has significantly higher boiling point, it condenses back into the reactor. Microbubbles rise in laminar regime, offers high surface to volume ratio [15] and surface energy as evident by reduced activation energy of esterification reaction [16].

Biodiesel can be produced from vegetable oils, animal fats, and waste cooking oils. The choice of feedstock is influenced by a number of variables, including cost, availability, and environmental impact and free fatty acid content [17]. There is a debate between fuel and food when edible-vegetable oils are utilized to make biodiesel on a wide scale[18]. Most of the nonedible oils such as Jatropha curcas, Castor, Karanja, Tobacco seed, Rice bran, Mahua, neem and rubber seed tree still requires availability of fertile land and fresh waste, and irrigation facilities apart from Jatropha Curcas and Castor which still requires semi-fertile land and some level of irrigation [1].

Animal fats like tallow and lard can be used as feedstock for the production of biodiesel. However, the biodiesel produced from them has high viscosity and hence the flow problems. Chicken Fat Oil (CFO) and Waste cooking oils (WCO) provide most lucrative options as a feedstock

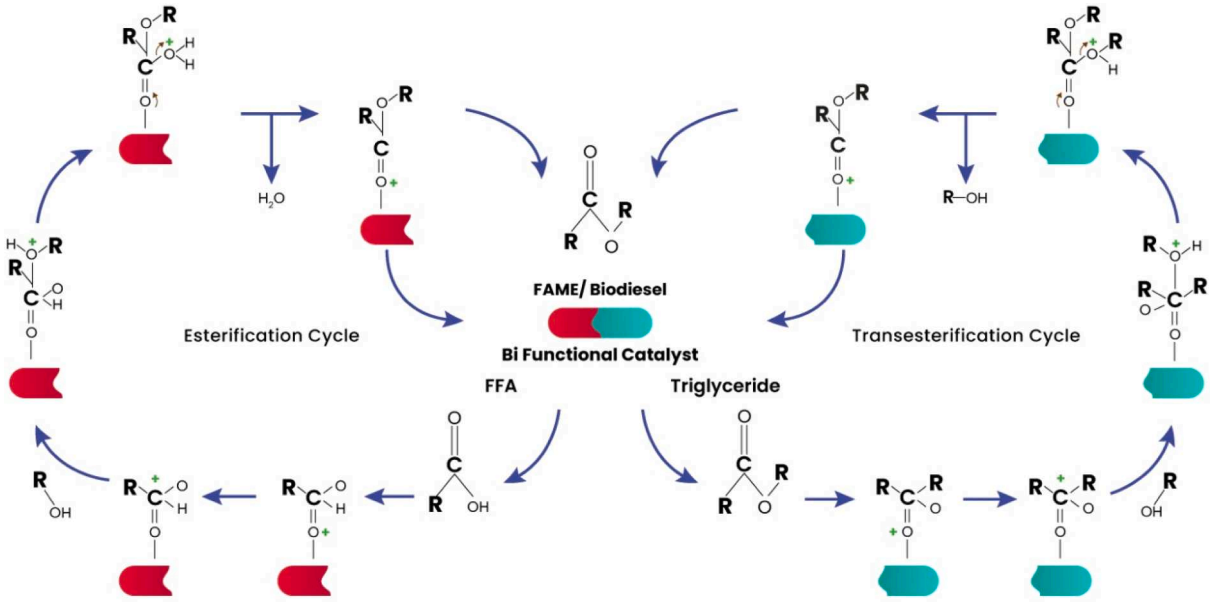

Fig. 1. Reaction mechanism for Bi-functional catalyst.

for biodiesel production. For example, WCO is three times more affordable than virgin vegetable oils [5]. However, it is not available at a single point hence its transportation cost increases the overall production cost of the biodiesel production process. However, CFO is widely available globally. Its collection is rather easier as it can be collected from any poultry processing plant in bulk and biodiesel produced by it does not have flow problems. Hence for the current study, CFO is chosen as feedstock.

Choice of alcohol (methanol or ethanol) also depends upon various factors such as higher reactivity, availability and related environmental impacts. Methanol is known to have higher conversion and rate of reaction. However, ethanol has higher availability. Conventional production of methanol, reforming and reverse water gas shift synthesis, is a fossil fuel dependent process, while ethanol is mainly produced by fermentation of sugar molasses. The choice of alcohol is also investigated in the current study.

The study provides an integrated solution to the biggest challenges of biodiesel commercialization- use of an inexpensive feedstock (CFO), overcoming the limitations of acid catalysis by using microbubble mediated mass transfer and using a bi-functional catalyst to carry out esterification and transesterification simultaneously reducing the downstream separation cost. The in-depth analysis of the parametric interaction for the biodiesel production is the other major objective of this study. The factors affecting the yield of biodiesel are FFA content, molar ratio of alcohol to oil, catalysts type and its concentration, reaction temperature and reaction time. The impact of each of these variables on biodiesel production has been thoroughly investigated [19–21]. Optimization of process parameters for biodiesel production using different catalysts are given in Table 4. Studies that correlate multiple parameters at once are rare, nevertheless. Conventional experimental design methods have a drawback that they cannot be used to study the simultaneous interaction of two or more parameters, which may provide valuable data for optimization. The Response Surface Methodology (RSM) makes it possible to produce a polynomial function that connects the response to the process variables and how they interact. This article has been divided into four sections. Section 1 deals with the introduction and scope of the manuscript. Materials and Methods are discussing in the second section. Preliminary experiments were conducted to select a suitable bi-functional catalyst (amongst a 7 % Sr/ZrO_2 and three Zwitterions) and alcohol (Methanol and Ethanol). Using selected catalyst and alcohol, experiments were designed using Response Surface Methodology. Results are discussed and analyzed in the third section. Conclusions are presented in the fourth section.

2. Materials and methods

2.1. Materials

Analytical grade FAMEs, Hexane, Zirconium (IV) Butoxide, Strontium Nitrate, Pluronic P123 Triblock Copolymer, Toluene, Isopropyl alcohol, Phenolphthalein indicator, Acetic acid, Iodic acid, Starch, Potassium Iodide, Sodium thiosulfate, Chloroform, Potassium hydroxide and Hydrochloric acid were purchased from Sigma Aldrich. CFO was purchased from a local industry in Lahore, Pakistan. Analytical grade EtOH (99 %) was purchased from DAEJUNG chemicals. All other chemicals used for catalyst synthesis and quantification were brought from Sigma Aldrich, including.

2.2. Experimental design

Conventional experimental design methods have a drawback that they cannot be used to study the simultaneous interaction of two or more parameters, which may provide valuable data for optimization [22]. The Response Surface Methodology (RSM) makes it possible to produce a polynomial function that connects the response to the process variables and how they interact [23].RSM assesses the impact of several independent factors and their interactions on the response surface of a process – in this case, biodiesel conversion for process improvement. RSM imposes a theoretically enforced model that depicts the interactions among independent parameters and responses.

For experimental design Box-Behnken Design (BBD) is applied to design the trials in the current investigation as there are more than two factors and the design requires fewer runs than other factorial designs, BBD is used [24]. BBD also employs points at the center points of the cubical design borders and center, with three levels for each component (1, 0, +1). Instead, then making predictions at extreme ends and pairings of all factors, it does it at the centre of the factor space. The equation is used to plan experiments in BBD.

$$N = 2m \times (m.1) + d \tag{1}$$

where d is the number of main points and M indicates the total number of study parameters.

Three factors and four central points are investigated through BBC. A (molar ratio-1:5 to 1:30), B (catalyst dosage 0 g to 2 g wt.% of CFO), and C (Temp 70 °C) are the three independent variables as shown in **Table SI** and the regression equation are as follow:

$$\begin{aligned} FFA\ Conversion = {} & +33.09722 + 5.36111 \times A + 46.83333 \times B - 1.19167 \\ & \times C - 0.066667 \times AB - 0.020000 \times AC + 0.100000 \\ & * BC - 0.117778 \times A^2 - 16.87500 \times B^2 + 0.008333 \times C^2 \end{aligned} \tag{2}$$

In order to determine the maximal biodiesel conversion from CFO, a total of 16 experiments were carried out. The fit summary statistics are employed to choose the model and briefly describing the experimental outcomes. To determine how well the proposed model fits, an ANOVA statistical analysis is employed. ANOVA is also used to determine the components' main and interactive effects. The P and F-value test was used to determine the significance of the study's factors. Furthermore, this is not the first study for biodiesel production using RSM. However, it is first study that where RSM has been used to design the experiments and investigate parametric interaction between the biodiesel production using CFO as a feedstock, a bi-functional catalyst and integrating it with a microbubble mediated mass transfer.

2.2.1. Chicken fat oil Extraction

Chicken fat was washed with water and dried before heated conventionally to extract the oil from it. A vessel containing 5 kg of cleaned chicken fat was heated in a (Bio-Base China) oven for 6 h at 110 °C. The melted fats were filtered to separate liquid from solid residue. The oil was stored at 4 °C for further processing. CFO was characterized for acid value, FFA%, density and viscosity as shown in Table 1 and its composition are shown in Table 2.

2.2.2. Catalyst preparation

Zirconium (IV) butoxide and strontium nitrate ($Sr(NO_3)_2$) are utilized as precursors to make mesoporous catalysts. The schematic presentation of the process is shown in Fig. 2.

5.0 g of Pluronic P123 triblock copolymer is dissolved in 50.0 mL of 99.5 % anhydrous EtOH and stirred for 4 h at room temperature. Separately, 80 mmol of zirconium (IV) butoxide (80 wt% solution in 1-butanol) was dissolved in 20 mL of 60–70 % nitric acid and 50 mL of EtOH (anhydrous). Once dissolved, a specific amount of (7 wt% of zirconium (IV) butoxide) strontium metal solution (1.0 M) is added to a

Table 1
Properties of Chicken Fat Oil Extraction.

Acid value	37.5 mg KOH/g
FFA	19 %
Density	925 kg/m^3
Viscosity	44.2479 m^2/s

Table 2
Composition of fatty acid in CFO.

Fatty acid	Composition (%)
Palmitic acid	2.09
Palmitoleic acid	10.40
Octadecatetraenoic acid	5.51
Linoleic acid	15.30
Arachidic acid	39.40
Linolenic acid	7.02
Docosatetraenoic acid	5.65
Lignoceric acid	14.63

flask and stirred for 2 h. The pH was maintained at 12 using a 2 M NaOH solution. The solution is heated for 4 h with slow stirring. The two solutions were then blended. The mixed solution was stirred for 5 h at room temperature. The solvent is evaporated in the oven at 100 °C for 24 h without stirring. The catalyst was calcined for 5 h in an air furnace at 550 °C. Preliminary studies were carried out by varying amounts of combination of Sr and ZrO_2. 7 % Sr loading produced the highest biodiesel conversion. As a result, 7 % Sr was used as an optimized concentration of in the study.

2.2.3. *Experimental setup*

The schematic diagram of the entire assembly is given in Fig. 3. Methanol was boiled in a two-neck 500 cm^3 round bottom flask using a heating mantle. The sintered borosilicate glass reactor was attached to the flask as shown in Fig. 3. The sintered borosilicate had a pore size of 16 to 50 μm. For each set of experiments, oil and catalyst are pre-mixed and combined for 40 min using a magnetic stirrer set to 400 rpm at 70 °C before pouring it into the glass reactor. The reactor does not require stirring because the reaction mixture is well mixed because of microbubbles. The system's temperature is kept at 70 °C. The reaction was stopped after the set amount of alcohol, according to the molar ratio, has been evaporated and passed through the reactor.

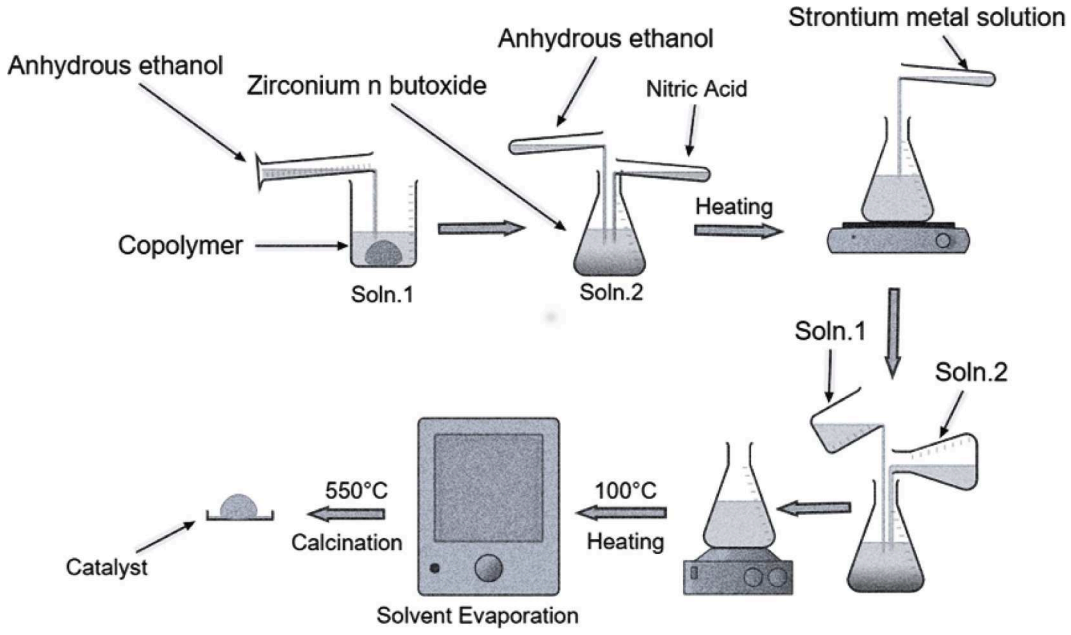

Fig. 2. Step-by-step synthesis of Strontium zirconium oxide (7% Sr/ZrO_2).

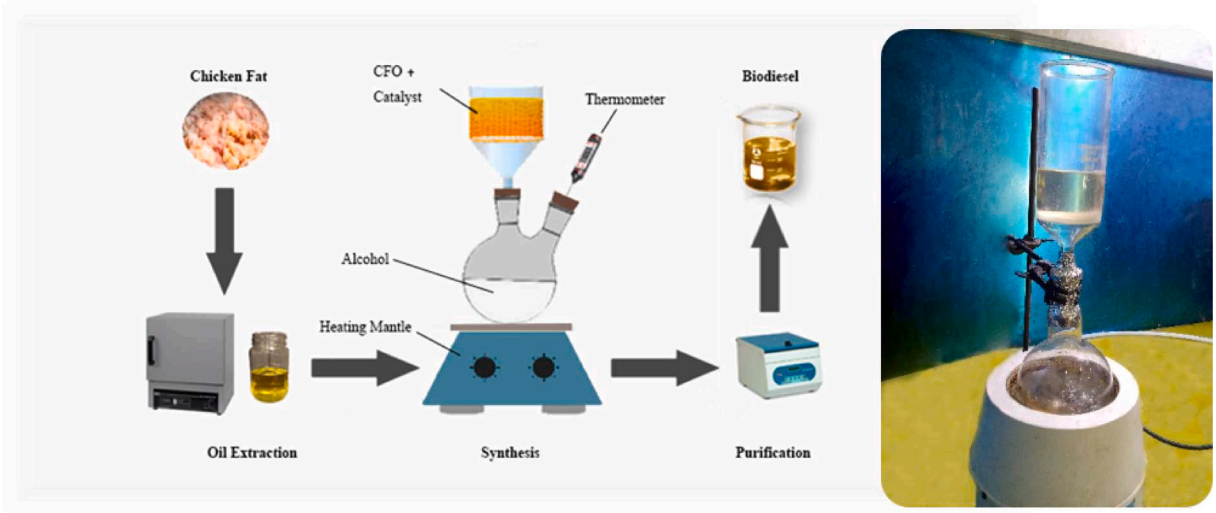

Fig. 3. Detailed illustration of biodiesel production using microbubble technology.

2.2.4. Biodiesel purification and washing

After the experiment, all samples are centrifuged at 5000 rpm for 5 min to recover the catalyst. Afterward, biodiesel mixture is thoroughly washed with ultrapure water (Biobase Water purification system, China). The biodiesel layer is separated using a separation flask. This process is repeated several times for the complete removal of impurities. Samples are dried in Bio Base China Oven at 100 °C to remove all water and kept at 4 °C for further analysis. To estimate the standard error, all experiments were repeated three times.

2.3. Biodiesel analysis

2.3.1. FFA and triglyceride analysis

To determine the FFA content in biodiesel AOCS standard method was used by using the following Eq (3) and (4) [25,26].

$$\mathbf{AV}\left(\frac{\mathbf{mgKOH}}{\mathbf{gbiodiesel}}\right) = \frac{(\mathbf{A}-\mathbf{B})\times\mathbf{N}\times 56.11}{\mathbf{W}} \quad (3)$$

$$\mathbf{FFA}(\%) = 0.506\times\mathbf{AV} \quad (4)$$

Where AV = acid value, A = volume of KOH used for titration (ml), B = volume of KOH used for blank titration (ml), N = Normality of KOH, and W = mass of biodiesel (g). Triglyceride was determining by the iodometric-periodic acid method conducted according to the AOCS Official Method Ca14-56.

3. Results and discussion

3.1. Catalyst Characterization

The FTIR spectrum of 7 % Sr/ZrO_2 is shown in Fig. 4 The spectrum of zirconia shows a broad peak band in the region of 3,700–3400 cm^{-1}, which is attributed to asymmetric stretching of –OH groups. The band at 900 cm^{-1} is associated with ZrO. The peak at 1623 cm^{-1} corresponds to the Carbonyl (C = O) group due to SrO_2 in the catalyst. The bending vibration of the C H bands is what causes the weak absorption bands at 1603 cm^{-1} and 1318 cm^{-1} [27].

The catalyst's pore size distribution is depicted in Fig. 5. The pore size and surface area are determined using Brunauer-Emmett-Teller (BET) adsorption technique and presented in Table 3. Catalyst pore size shows mesoporous structure with sizes ranging from 3 nm to 11 nm [4].

The analysis of the nitrogen content adsorbed at a relative pressure (p/p°) of 0.9933 is used to estimate the total pore volume under the assumption that there would be negligible external surface adsorption compared to pore adsorption. By using the t-plot approach, the pore surface area and pore volume are determined [4].

The XRD diffractograms of synthesized Sr/ZrO_2 are shown in Fig. 6.

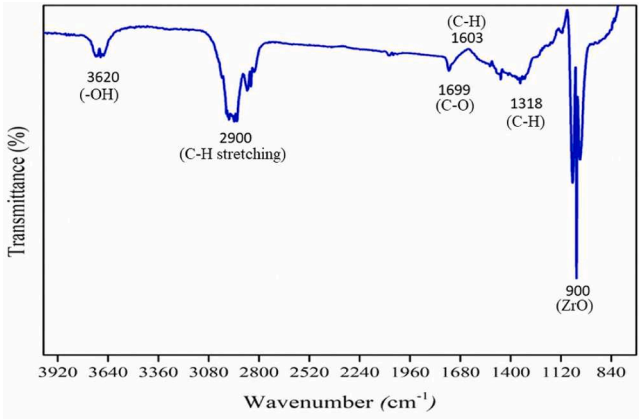

Fig. 4. Characterization of Sr/ZrO_2: FTIR.

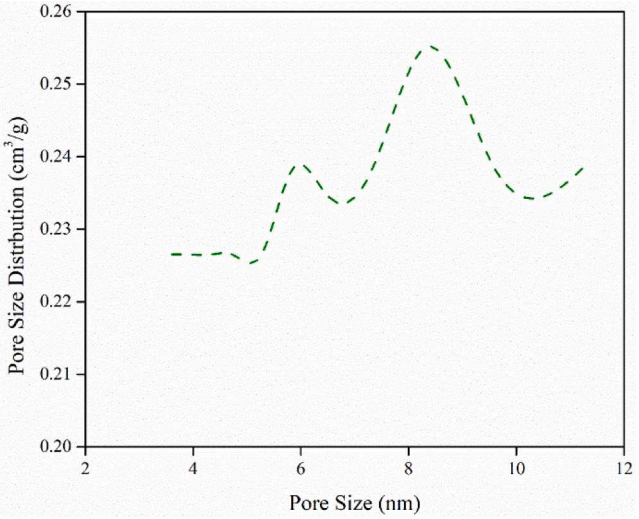

Fig. 5. Characterization of Sr/ZrO_2: BET analysis.

Table 3
Structural Properties of Catalyst.

Catalyst	Surface area [a] (m^2/g)	BJH Area [b] (m^2/g)	BJH Volume [c] (cm^3/g)	BET Pore Diameter [d] (nm)	BJH Pore Diameter [e] (nm)
7 wt% ZrO2	119.80	117.34	0.2154	8.97	8.21

The crystal structure of pure ZrO_2, observed to be monoclinic. Since there is no peak broadening in the Sr/ZrO_2 catalyst after 4–5 h of calcination at 550 °C, the ZrO_2 crystal structure is sustained. The XRD pattern of Sr/ZrO_2 mostly showed monoclinic ZrO_2 as the parent structure's peaks, with Sr/ZrO_2 peaks also present at 31.750°. The analysis shows that the addition of Sr metal in ZrO_2 increases the amphoteric behavior of ZrO_2, which increases both the basic and acidic active sites of the catalyst. The presence of both acidic and basic sites in 7 % Sr/ZrO_2 facilitate both esterification and transesterification [28].

Fig. 7 depicts the synthesized catalyst's scanning electron microscopy (SEM) images. The sample shows the agglomeration of the particles.

3.2. Process optimization

3.2.1. Effect of EtOH and MeOH on biodiesel production

In the current study, EtOH and methanol are both used. Due to its reactivity and high equilibrium conversion, methanol is the preferable alcohol. However, it is limited by low mass transfer rates in the transesterification reaction due to its poor solubility in oil due to relatively higher polarity from shorter carbon chains. Because EtOH is more soluble in oil than MeOH, the mass transfer limitation between oil, alcohol, and catalyst is minimized. The obtained yield of biodiesel from EtOH and methanol can be seen in Fig. 8. The maximum FFA conversion of EtOH was 51 % and for MeOH was 58 %. Similarly, 10 % more triglyceride are converted using methanol. The results indicate that the EtOH yield was relatively low as compared to methanol. However, considering the non-dependence of EtOH production on fossil fuels and higher availability, it was selected for further study.

3.3. Effect of conventional and synthesized catalysts

Experiments are performed using different catalysts, under the same nominal conditions, to investigate the effect of natural and synthetic

Table 4
Comparison of the current study with other catalysts used for biodiesel production.

Catalyst	Catalyst loading (wt. %)	Temperature (°C)	Time (min)	Conversion (%)	Reference
ZrO_2/SiO_2	10	125	180	76.9	[29]
CaO/SiO_2	8	60	60	91	[30]
KF/Al_2O_3	3	60	480	90	[31]
Lipase A from Candida antarctica	5.5	30	1320	94.6	[32]
Li-Al HTA	3	65	60	83	[33]
Li/ZrO_2	3	65	180	98.2	[34]
La-dolomite	7	65	180	98	[35]
7 % Sr/ZrO_2	1	70	20	(TGs: 75) (FFA: 58)	**This study**
$C_4H_7NO_4$	1	70	25	(TGs: 61) (FFA: 73)	**This study**
$C_6H_{14}N_4O_2$	1	70	25	(TGs: 63) (FFA: 54)	**This study**
$C_6H_{13}NO_2$	1	70	25	(TGs: 48) (FFA: 39)	**This study**

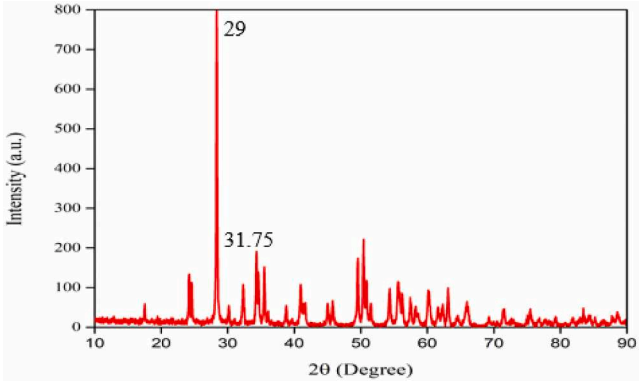

Fig. 6. Characterization of Sr/ZrO_2: XRD analysis.

catalysts on biodiesel production, as shown in Fig. 9. Experiments were performed using three Zwitterions; aspartic acid, arginine, isoleucine and one synthetic catalyst Sr/ZrO_2. For Aspartic acid, Arginine, Isoleucine and Sr/ZrO_2 overall triglyceride conversion was found to be 61 %, 63 %, 48 % and 75 % respectively. It is important to note the conversion profile is similar for all catalysts conversion of triglycerides. However, the conversion 7 %Sr/ZrO_2 is significantly higher as compared to the Zwitterion ions because of its higher acid/basic character and larger number of available active sites [4]. Using the Sr/ZrO_2 catalyst enhanced the yield of biodiesel by up to 75 %. ZrO_2 is amphoteric and possesses both basic and acid-active sites. The active site further strengthens by modifying it with Sr, which tends to increase the catalyst activity. The conversion of FFA for 7 % Sr/ZrO_2 is approximately 79 %. Aspartic acid also provided similar conversion for FFA as well. This could be explained on the stronger acidic character of Aspartic acid. On the other hand, Isoleucine and Arginine gave 35 % and 50 % FFA conversion respectively.

An analysis of various catalysts and operational parameters such as time of reaction, temperature and overall all conversion is provided as a comparison in Table 4. It could be seen that several catalysts have been used so far at various operational conditions. Highest conversion was provided of 98 % was reported by Ibrahim et al., [24]. However, the reaction was completed in 180 min. The catalyst loading (1 %) in the current study was significantly less as compared with the other studies. Similarly, both the time and temperature used in the current study is significantly lower than the other reported studies. This higher rate of reaction and overall conversion can be attributed to the use of microbubbles. Microbubbles provide higher surface area. More importantly due to smaller radius, as governed by Young-Laplace law, the inside pressure can increase significantly resulting is higher temperature of the vapors. This results in higher surface energy which enhances the rate of the reaction and reduces the activation energy.

3.4. ANOVA Analysis

The F-value of 9.68 indicates the model to be significant. A large F-value is extremely unlikely to be caused by noise, with a 0.60 % probability. The Table 5 indicates how the quadratic model's accuracy is further evaluated by the correlation coefficient (R^2), adjusted R^2, and anticipated R^2. R^2 values near 1 show that actual data effectively fits the model's predictions. R^2 is 0.9355 in this case, according to the quadratic model. The modified R^2 of 0.8389 is relatively close to the projected R^2 of 0.0910; the difference is more than 0.2. This is sufficient precision for a signal-to-noise ratio measurement. It is preferable to have a ratio of more than 4. The signal-to-noise ratio of 9.6786 indicates that the signal is adequate.

Model significance is suggested by the model's F-value of 21.37. The probability of noise producing an F-value this high is only 0.07 %. Table 6 shows how the quadratic model's accuracy is further evaluated by the correlation coefficient (R^2), adjusted R^2, and anticipated R^2. R^2 values near 1 show that actual data effectively fits the model's predictions. R^2 is 0.9697 in this case, according to the quadratic model. The modified R^2 of 0.9244 is relatively close to the projected R^2 of 0.6360; the difference is more than 0.2. This is sufficient precision for a signal-to-noise ratio measurement. It is preferable to have a ratio of more than 4.

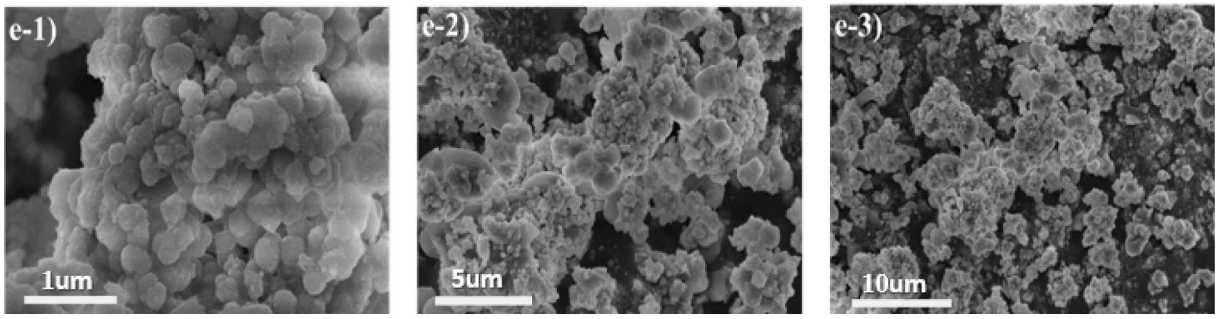

Fig. 7. Characterization of Sr/ZrO_2: e-1 to 3 SEM analysis.

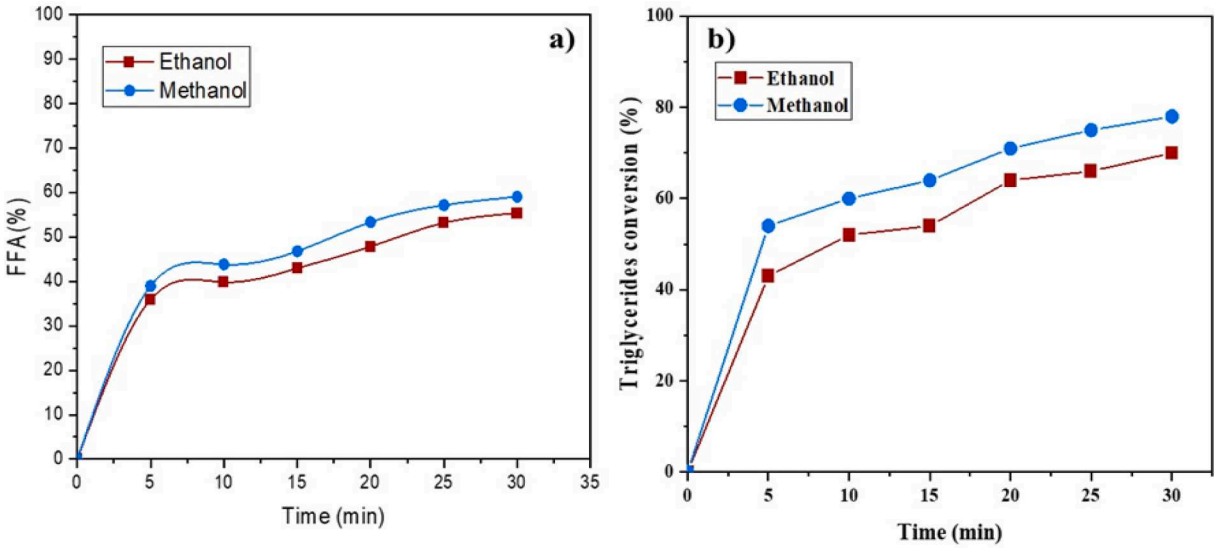

Fig. 8. Effect of EtOH and MeOH on yield a) FFA b) Triglycerides Conversion.

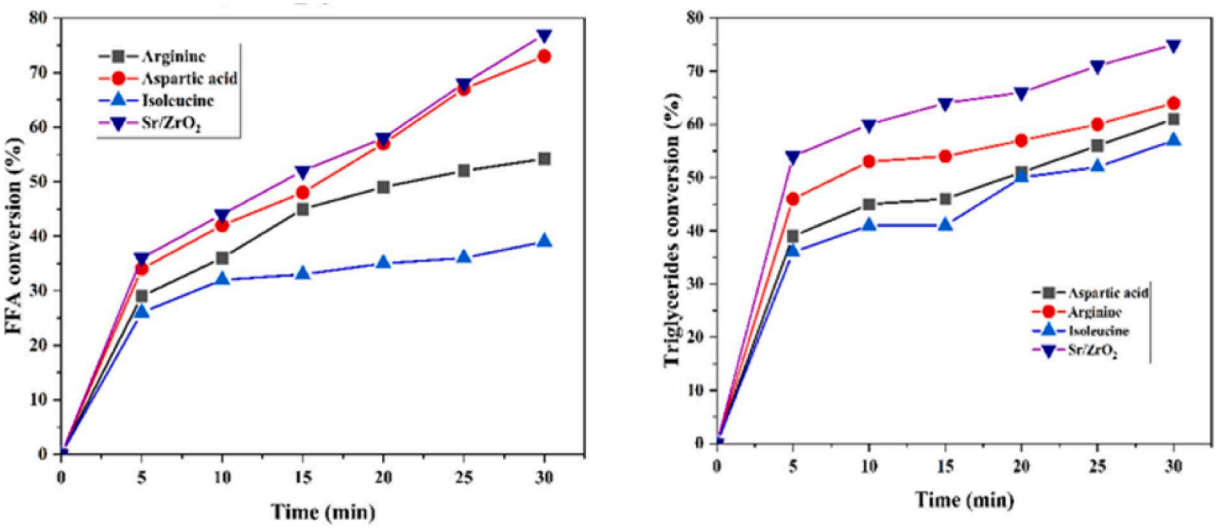

Fig. 9. Conversion of Biodiesel diesel a) FFA% b) Triglycerides.

Table 5
ANOVA for response 1 quadratic surface model.

Std. Dev.	7.58	**R^2**	0.9355
Mean	46.19	**Adjusted R^2**	0.8389
C.V. %	16.41	**Predicted R^2**	0.0910
		Adeq Precision	9.6786

Table 6
ANOVA for response 2 quadratic surface model.

Std. Dev.	6.28	**R^2**	0.9697
Mean	49.50	**Adjusted R^2**	0.9244
C.V. %	12.68	**Predicted R^2**	0.6360
		Adeq Precision	12.441

The signal-to-noise ratio of 12.441 indicates that the signal is adequate.

In Fig. 10 the actual and anticipated values of the experimental data are presented using RSM-generated correlations. The quadratic model is significant for predicting the responses of the independent variables because the actual results in the plot are close to the anticipated ones.

3.5. Combined effects of catalyst loading and molar ratio on conversion

The interactive relationship between the molar ratio and catalyst loading on the response surface is shown in a 3D graph in Fig. 11 with all other variables held constant at their midpoints. When the catalyst loading is increased from 0 to 1 g wt.% of oil, the conversion increases rapidly[21]. Catalyst concentration increases and improves CFO protonation. The conversion and reaction rate of producing biodiesel increases with increasing protonation degree. Because the catalyst begins to decompose, the conversion reduces at the maximum catalyst loading. This reduces the conversion rate and also alters the color of the biodiesel. The conversion rate increases slightly when the alcohol to CFO's molar ratio increases. One argument is that alcohol evaporates as bubbles, which enables unreacted alcohol to leave the body. Since the temperature of the reactor is set higher than the boiling point of alcohol, the effect of the molar ratio is negated. Only a minute amount of alcohol remains in the system even when the molar ratio increases.

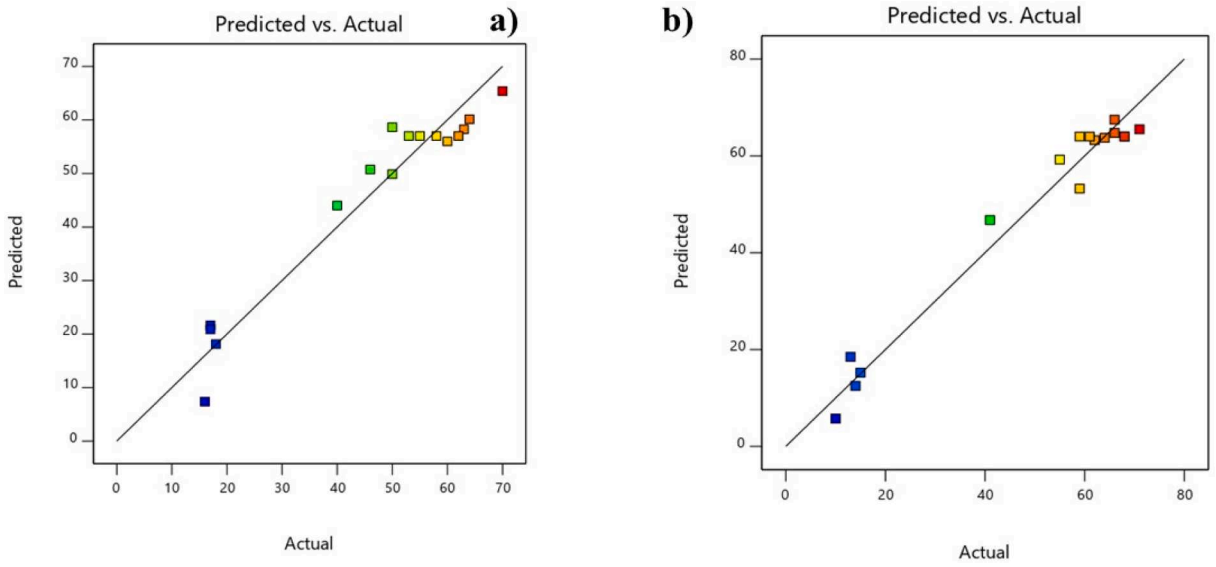

Fig. 10. Actual Vs predicted plots for the production of biodiesel by RSM.

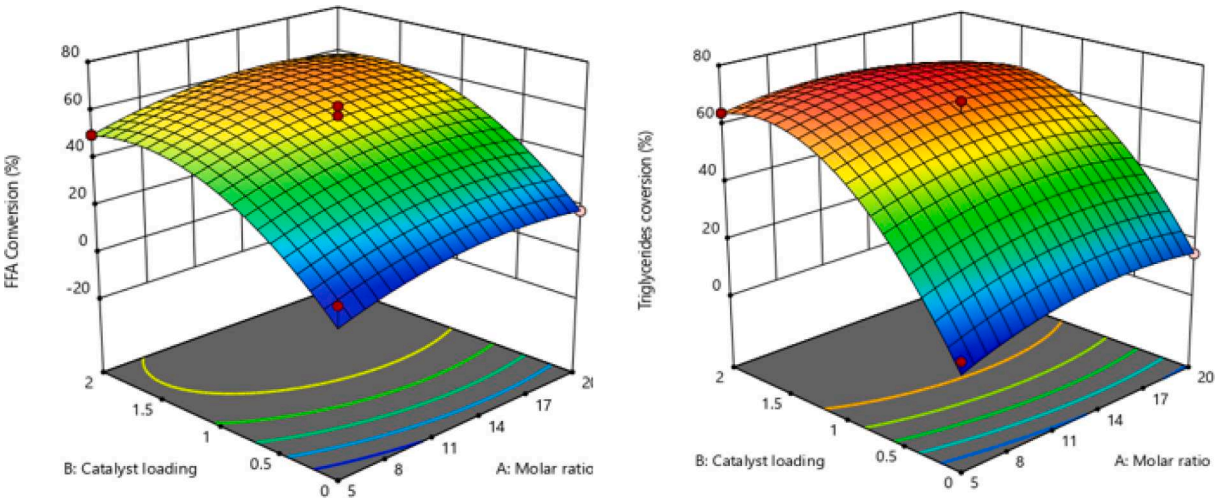

Fig. 11. Combined effect of catalyst loading and molar ratio on conversion.

3.6. The combined effect of molar ratio and temperature on conversion

In Fig. 12 the influence of temperature and molar ratio on the response surface is plotted in three dimensions while all other variables are kept constant at their midpoints. The rate of reaction can be accelerated by increasing the temperature. Increasing the temperature, on the other hand, raises the expense of the biodiesel generation process [36]. The results indicate that there is no significant change in the overall conversion of biodiesel production by increasing temperature. It seems that under all reaction circumstances, the reactor's temperature is higher than the alcohol's boiling point. When the bubble rises, they react with CFO, and unreacted alcohol leaves the system, which does not affect the overall conversion of the process. However, the high-temperature system shows higher conversion at the start of the reaction. The conversion rate increases slightly when the alcohol to CFO's molar ratio increases.

3.7. The combined effect of temperature and catalyst loading on the conversion

In Fig. 13 a 3D plot depicting the interaction between temperature and catalyst loading on the response surface is shown while maintaining the center values of all other variables. The conversion dramatically rises as catalyst loading is raised from 0 g to 1 g wt.% of oil. The findings show that a temperature rise boosted biodiesel conversion. Additionally, the 3D Figure shows that increasing the catalyst loading has little to no impact on the process' conversion after a certain point. Because of this, 1 wt% of CFO should be used as the catalyst concentration.

4. Conclusions

Biodiesel production was investigated using a synthetic bi-functional catalyst 7 % Sr/ZrO_2 and compared with Zwitterions (Aspartic Acid, Isoleucine and Arginine). The use of Bi-functional catalysts is complemented by the use of microbubble mediated mass transfer of alcohol vapours. 7 % Sr/ZrO_2 demonstrated higher conversion for both FFA and Triglycerides than Zwitterions. For triglycerides and FFA, the conversion of 7 % Sr/ZrO_2 was 75 % and 57 % respectively, as compared 61 %, 63 %, and 58 % and 73 %, 54 and 39 % of aspartic acid, arginine and isoleucine respectively. To optimize the process parameters and investigate interactions between them, experiments were designed using RSM. Catalyst loading, temperature and molar ratio was investigated as

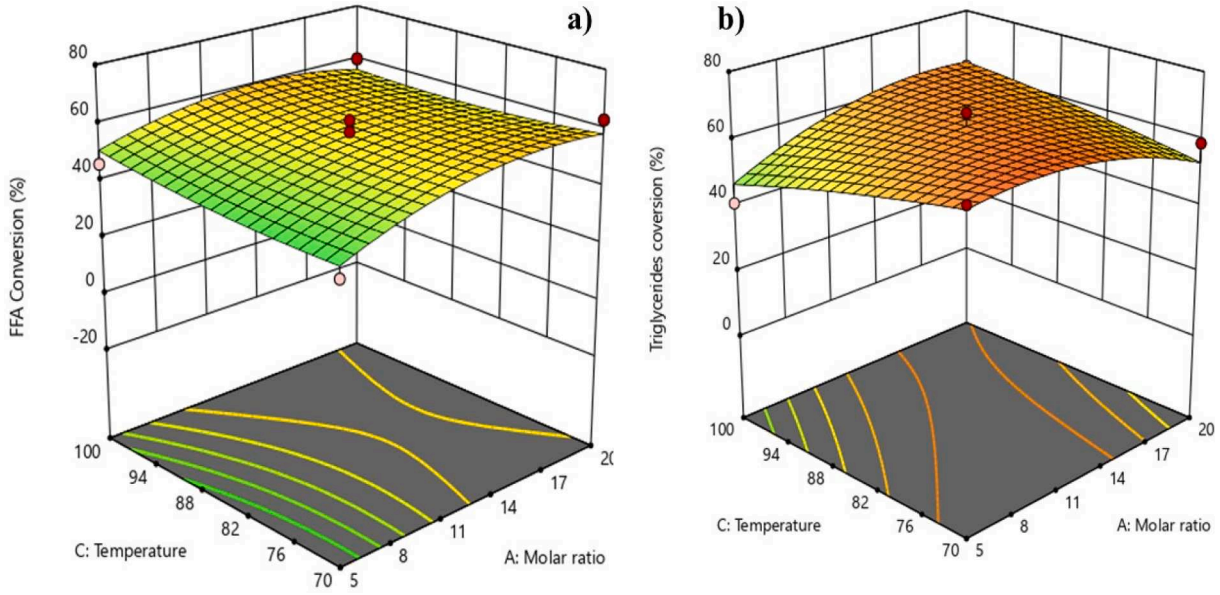

Fig. 12. Combined effect of molar ratio and temperature on conversion.

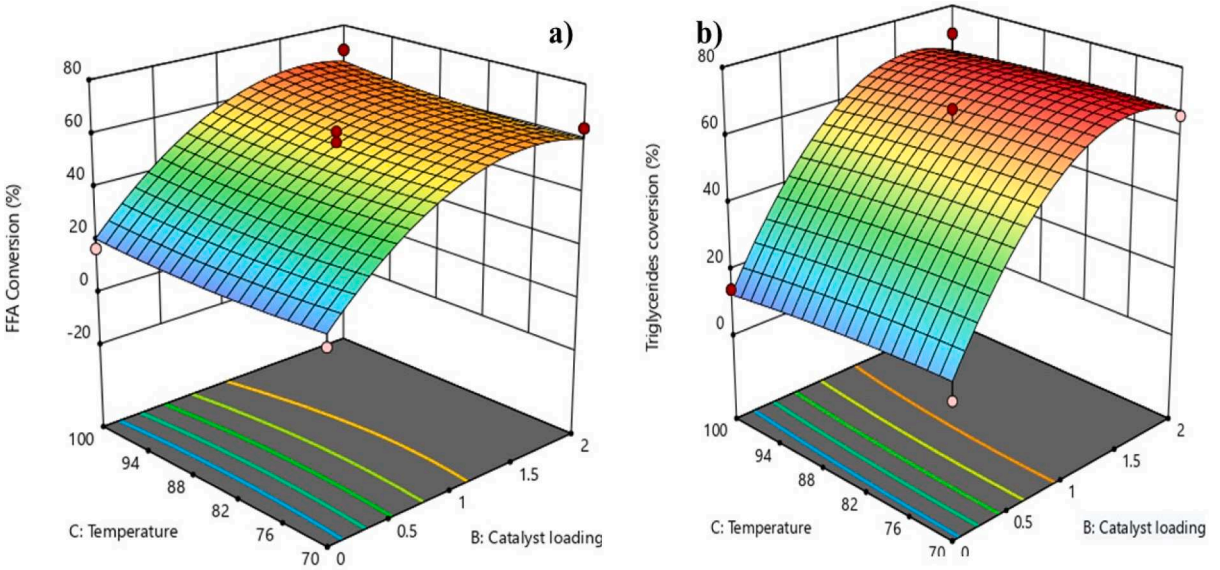

Fig. 13. Combined effect of catalyst loading and temperature on conversion.

process parameters. For both FFA and Triglyceride conversion, catalyst loading and temperature was found to be most significant parameters. For triglycerides and FFA, the conversion of CFO at optimize conditions using (Molar ratio = 1: 14, temperature 70 °C, and catalyst loading 1 %) was 75 % and 57 %, as compared with aspartic acid (61 % and 63 %), arginine (58 % and 73 %), and isoleucine (54 % and 39 %) respectively. The comparison with other reported studies related to bi-functional catalysts demonstrated that the current integrating 7 %Sr/ZrO_2 with microbubble mediated mass transfer technology resulted in higher conversion of triglycerides and FFAs in shorter period of time and at a relatively low temperature. The results indicate that integration of microbubble mediated mass transfer and a bi-functional catalyst can accelerate the commercialization of biodiesel production.

CRediT authorship contribution statement

Maryam Asif: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **Fahad Javed:** Writing – review & editing, Investigation, Conceptualization. **Muhammad Younas:** Investigation, Formal analysis. **Mazhar Amjad Gillani:** . **William B. Zimmerman:** . **Fahad Rehman:** .

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2023.130125.

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