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Process improvisation of biofuel manufacturing from misspend vegetable fat via RSM

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Abstract

The advancement of alternative fuel from inexhaustible sources has become a global concern to mitigate various multiple environmental issues and continuous rise in the fossil fuel price. Biodiesel has been established as alternative energy source to restore gasoline and motor oil in recent days. The type of catalyst used also play a key role in altering the activity of transesterification steps during the process development. We report, the synthesis of a Strontium (Sr) metal based CaO functionalized catalyst (Sr/CaO) for the said purpose which was further utilized for the manufacturing of biomassfuel from misspend vegetable fat via transesterification reactions. RSM in relation with Median Compound Sketch was used to improve the reaction conditions for maximum biodiesel yield. The yield was optimized and up to 95.3 % was attained during the process while the stimulant dose was fixed up to 1.5 % (w/v) with methanol to oil molar ratio of 9:1 at temperature 60 °C after 180 min response time.

Keywords: *Waste cooking oil, Sr/CaO catalyst, Biodiesel, Transesterification, Optimization*

1. Introduction

The escalated fossil fuel consumption in the industrial and ferriage section has led to the continuous consumption of remnant fuel reserves and significant environmental degradation worldwide. In fact, these problems can lead to a large number of predictable and unpredictable problems such as economic crisis, human health issues, etc. Besides this, the demand of transportation fuel is expected to increase by 30 percent from 124 billion litres to 202 billion litres by 2024 [1]. Moreover, the net imports of crude oil have increased from 111 MT's during 2006-07 to 202 MT's during 2015-16, with an increase of 7.08 % from 2014-15 to 2015-16 (189 MT's - 202 MT's) [2]. Because of this situation, the researchers have been putting more attention to find out clean alternative energy sources [3,4]. Over the most recent couple of decades, biomass fuel has gained notable importance both as a potential another

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fuel and as an added substance to the current oil established fills for a diesel motor. Biomass fuel reveal several quality while differentiated to that of the subsisting petroleum fuels but a portion of its properties, for example, high viscosity as compared to diesel fuel, poor cold flow properties and high NO_x emissions are significant parameters to constrain the utilization of biodiesel, too [6-8].

Conventionally, one-factor-at-a-time (OFT) technique has been extensively used to optimize process parameters but an enormous batch experiments are required, which can be a non-viable task. Hence, to enhance the process parameter efficiency, various statistical tools are used for the optimization for biodiesel synthesis. In this context, RSM in co-occurrence accompanied by Medile Compound Sketch has proven to be a promising instrument for the plan of tests and analyzing the compound result of process variables [9-11]. In the nearby study, RSM along with MCS was used to improve the reaction parameters for maximum biodiesel yield derived from misspend vegetable fat.

Substance

In this study, Misspend Vegetable Fat (MVF) was gathered from the mess of LPU hostels. The collected oil was then filtered through the cotton placed in the separating funnel in order to remove any suspended impurities and is then heated to 110 ^oC to take off any of the moisture present in the feedstock. Calcium carbonate ($CaCO_3$) and Strontium nitrate ($Sr(NO_3)_2$) was procured from Merck Pvt. Ltd. Methanol (CH_3OH), Sodium thiosulphate ($Na_2S_2O_3$), Potassium hydroxide (KOH) pellets and Sulphuric acid (H_2SO_4) has been obtained from S D Fine Chemicals Pvt. Ltd. The chemicals used during the experimental work carried out in the present investigation were of scientific category. All the aqueous mixtures were readied using Milipore water.

Methodology

Stimulant synthesis

The development has been carried out as described by Mehta et al., 2018 [12] via wet impregnation method which enhances the catalytic activity of the precursor materials. Firstly, 10g of $CaCO_3$ was calcined at 850-900°C and kept for 2 h to detach trace amount of adulterations. The CaO after calcinations method was atached to the deionized water to build suspended solution. A necessary volume of $Sr(NO_3)_2$ aqueous solution (with 0.1M) was dispersed drop by drop in CaO aq. interruptions at ambient temperature for about 1.5 h.

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However, utilizing the above as a impetus in the transelement method, the parched hard was calcined earlier at 600°C for 5h to enhance its reaction action.

Batch study of biodiesel production

The initial batch experiments to learn the result of unlike operating variables on the biodiesel production were performed using OCAT (one changeable at a time) proceed towards. The tests were conducted out in a 250 ml three-napped circular base

bottle with a backflow condenser set on the magnetic plate. The reactant blend consisting of oil, methanol and catalyst was then warmed to 65 °C for 200 min at 600 rpm. The catalyst was then taken off from the product by centrifugation at about 5000 rpm for 15 min and the resultant was allowed to settle in separating funnel for overnight to separate the supernatant layer of biodiesel. A series of washes with warm water was done and the final product sample was dried for the whole night time in an oven to remove residual moisture.

The biodiesel yield (%) was calculated as follows:

$$\text{Biodiesel yield (\%)} = \left[\frac{\sum P_i - \sum PI}{\sum PI} \times \frac{W_i}{W} \times 100\right], \qquad (1)$$

Where, $\sum P_i$ is the integrated peak area from $C_{6:0}$ to $C_{24:1}$, $\sum PI$ is the integral peak area for the methyl heptadecanoate, W is the weight (mg) of the sample and W_i is the weight (mg) of the internal standard.

Design Statistics

The experimental data obtained from the design was used to find out the regression coefficients of second order polynomial equation to measure the optimum response value as expressed in the Eq. (1). In this equation, y is the predicted response; β_o, β_j, β_{ij} *and* β_{jj} are constant coefficients; X_i *and* X_j are the coded independent variables or factors and ε is the random error. The regression coefficient of quadratic equation and response surface has been generated by Design Expert version 7.0, State ease Inc. Minneapolis, USA. The coefficient of determination R^2 was used to find out the quality of fit of the polynomial equation and regression coefficients and then it was checked by F-test and t-test respectively [4]. The response surface methodology was used to find out the optimum value of selected variables (Table 1).

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum \sum_{i<j} \beta_{ij} X_i X_j + \sum_{j=1}^{k} \beta_{ij} X_j^2 + \varepsilon \qquad \textbf{(1)}$$

The process parameters that have been considered in the biodiesel production were

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considered in terms of coded values with different levels in order to study the effect during various reaction conditions.

Table 1 Independent variables for CCD design

Independent Variables		Levels	Levels	Levels
		-1	0	+1
Catalyst dose	% w/v	1.0	1.5	2.0
M:O molar ratio		6	9	12
Reaction temp	°C	50	60	70
Reaction time	min	60	180	200

Results and discussion

The physico – chemical properties of the procured WCO for the present work are shown in the Table 2. As shown in the Table 2, the acid value of procured WCO is higher than prescribed limit. So, it has to be reduced prior to its use for biodiesel production.

Table 1 Physico–chemical properties of WCO compared with reported literature

	(%) of composition	
Property	**WCO (this study)**	**WCO[a]**
Acid value (mg of KOH/g)	4.2	0.24
FFA content (in terms of oleic)	2.1	0.12
Density (kg/m^3)	914.45	918
Kinematic Viscosity (cSt)	36.17	39.78
Flash point ($^{\circ}$C)	182	-
Calorific value (MJ/kg)	36.79	-

[a]Atapour et al. 2014

Experimental design

The interactive effect of process variables on the percent yield of synthesized biofuel have been analyzed by statistical tool RSM. A targeted number 30 experiments were performed as per the design grid obtained from CCD.

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Table 3 Central Composite Design matrix

Run	X_1	X_2	X_3	X_4	Actual biodiesel yield	Predicted biodiesel yield
1	-1.00	-1.00	-1.00	-1.00	10.4	9.05
2	1.00	-1.00	-1.00	-1.00	15.61	15.63
3	-1.00	1.00	-1.00	-1.00	25.24	25.99
4	1.00	1.00	-1.00	-1.00	30.18	29.50
5	-1.00	-1.00	1.00	-1.00	12.06	12.25
6	1.00	-1.00	1.00	-1.00	36.8	36.60
7	-1.00	1.00	1.00	-1.00	38.52	36.88
8	1.00	1.00	1.00	-1.00	58	58.16
9	-1.00	-1.00	-1.00	1.00	31.88	32.69
10	1.00	-1.00	-1.00	1.00	36.54	35.71
11	-1.00	1.00	-1.00	1.00	45.58	43.31
12	1.00	1.00	-1.00	1.00	42.48	43.27
13	-1.00	-1.00	1.00	1.00	59.24	57.45
14	1.00	-1.00	1.00	1.00	78.02	78.24
15	-1.00	1.00	1.00	1.00	74.8	75.76
16	1.00	1.00	1.00	1.00	94.6	93.48
17	-2.00	0.00	0.00	0.00	20.8	22.23
18	2.00	0.00	0.00	0.00	46.46	46.53
19	0.00	-2.00	0.00	0.00	15.56	16.29
20	0.00	2.00	0.00	0.00	47.7	48.47
21	0.00	0.00	-2.00	0.00	27.5	28.13
22	0.00	0.00	2.00	0.00	80.68	81.55
23	0.00	0.00	0.00	-2.00	19.28	19.91

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24	0.00	0.00	0.00	2.00	78	78.87
25	0.00	0.00	0.00	0.00	41	41.49
26	0.00	0.00	0.00	0.00	41	41.49
27	0.00	0.00	0.00	0.00	42.5	41.49
28	0.00	0.00	0.00	0.00	42.42	41.49
29	0.00	0.00	0.00	0.00	41	41.49
30	0.00	0.00	0.00	0.00	41	41.49

The regression analysis (RA) was implemented and quadratic polynomial equations were developed. Then different process parameters were taken in terms of code parameters for the expectation to get optimal reaction conditions (Eq. 2). As per the equation, the individual running parameters having coefficients with positive esteem will have synergistic impact on percent conversion, whereas coefficients with negative esteem indicate hinders the biodiesel yield [13,14].

$$Biodiesel\ Yield\ (\%) = 41.49 + (6.08x_1) + (8.05x_2) + (13.35x_3) + (14.74x_4)$$

$$-(0.77x_1 * x_2) + (4.44x_1 * x_3) - (0.89x_1 * x_4) +$$

$$(1.92x_2 * x_3) - (1.58x_2 * x_4) + (5.39x_3 * x_4) -$$

$$(1.78x_1^2) - (2.28x_2^2) + (3.34x_3^2) + (1.98x_4^2) \qquad (2)$$

The data obtained from CCD matrix was then evaluated further for the statistical significance by studying analysis of variance (ANOVA). While contemplating the impact of certain specific variant, with the increase in F-value and SS, the noteworthiness of the analogues term rises. It has been evident from the Table 2 that value of F factor of the deduced model is 549.00 along with value of probability factor < 0.0001 and high value of sum of squares (13579.75).

Table 2 ANOVA table for

Source	**SS**	**D.O.F**	**Mean square**	**F value**	**p value**	
Model	13579.75	14	969.98	549.00	< 0.0001	*significant*

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x_1 - Catalyst dose	886.10	1	886.10	501.52	< 0.0001	
x_2 – M:O	1554.13	1	1554.13	879.62	< 0.0001	
x_3 –Reaction temp	4279.74	1	4279.74	2422.29	< 0.0001	
x_4 –Reaction time	5214.72	1	5214.72	2951.48	< 0.0001	
x_1x_2	9.41	1	9.41	5.33	0.0357	
x_1x_3	315.86	1	315.86	178.77	< 0.0001	
x_1x_4	12.66	1	12.66	7.16	0.0173	
x_2x_3	59.10	1	59.10	33.45	< 0.0001	
x_2x_4	39.97	1	39.97	22.62	0.0003	
x_3x_4	464.73	1	464.73	263.03	< 0.0001	
x_1^2	86.59	1	86.59	49.01	< 0.0001	
x_2^2	142.18	1	142.18	80.47	< 0.0001	
x_3^2	305.66	1	305.66	173.00	< 0.0001	
x_4^2	107.07	1	107.07	60.60	< 0.0001	
Residual	26.50	14	1.77			
Lack of Fit	23.66	10	2.37	4.16	0.0646	not significant
Pure Error	2.85	5	0.57			
Cor Total	13606.25	29				

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$R^2 = 0.977$	Adj $R^2 = 0.975$					

The obtained results is in accordance with the graph of perturbation for process variables (Fig. 1), which depicts that C and D factor has the steepest curve which indicates that biodiesel yield has significant affectability to change in the corresponding factor.

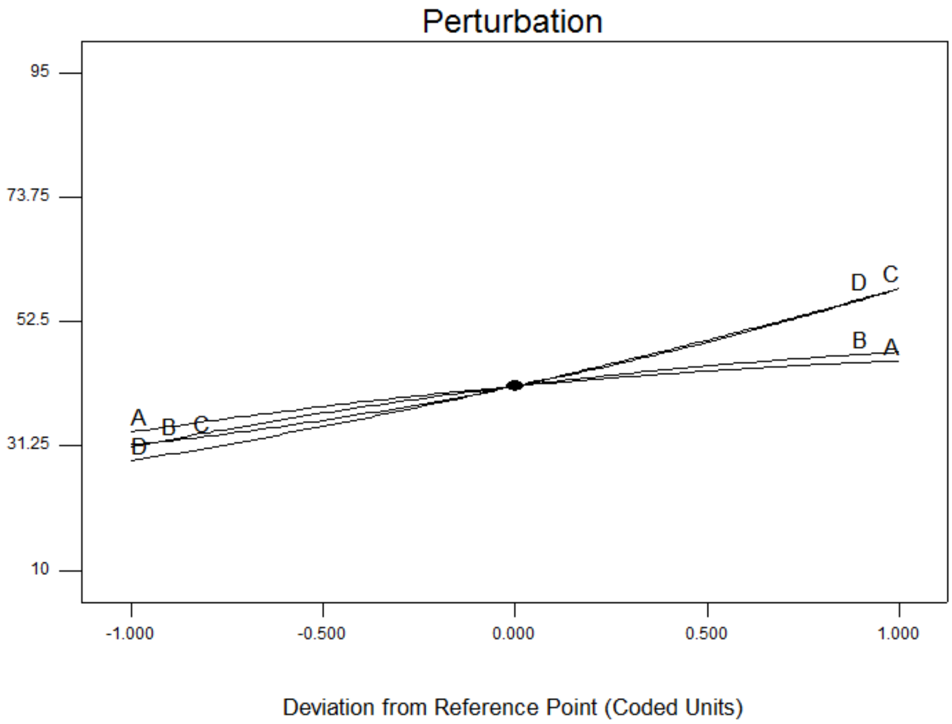

Fig. 1 Perturbation plot

Fig. 2 represents the connection between predicted vs actual values of biodiesel generation from WCO utilizing synthesized Sr/CaO as base heterogeneous catalyst. The calculated actual data is the percent biodiesel yield that was deliberated by Eqn. (1) whereas the anticipated (Predicted) values have been calculated with Eqn. (2).

It tends to be seen from the below plot is majority of the predicted values of the design matrix were near to that of the actual values. Therefore, this plot verifies the reliability for produced regression framework, which can be effectively used as a effective tool to predict for evaluating the optimal transesterification reactions [15].

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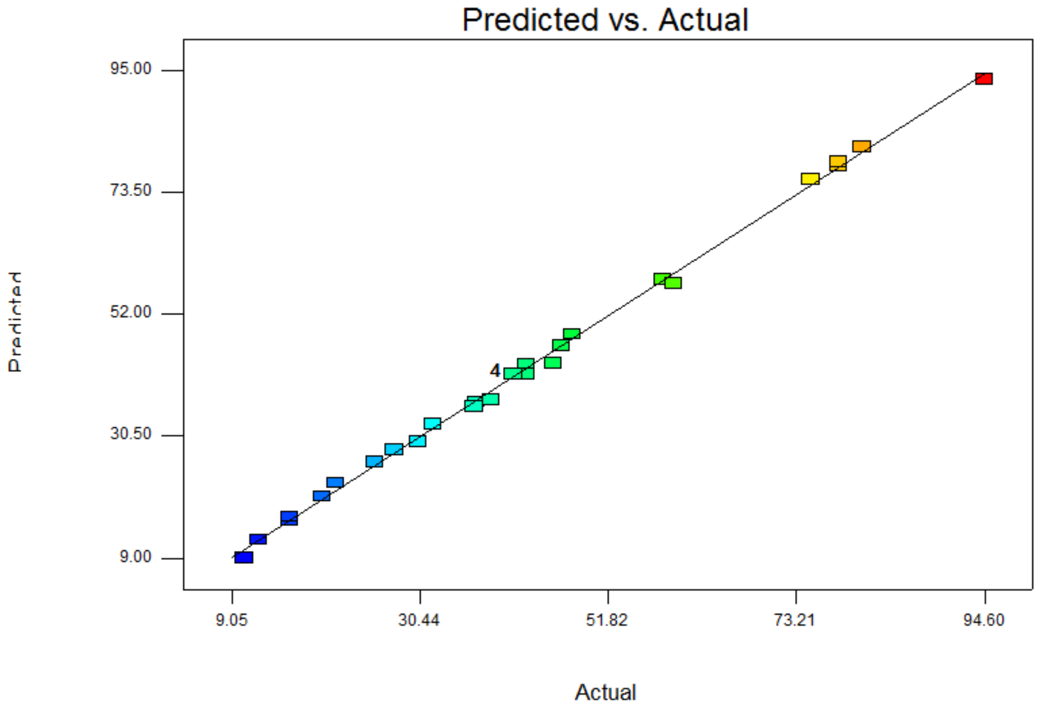

Fig. 2 Predicted vs. Actual plot

Conclusion

In the present work, Sr/CaO has been synthesized via wet impregnation method. Waste cooking oil (WCO) has been used for the production of biodiesel in the presence of strontium-functionalized calcium oxide (Sr/CaO) as base heterogeneous catalyst. In order to evaluate the combined effect of process variables on percentage biodiesel yield, statistical optimization was carried out by RSM. The highest yield of 95.3 % was obtained when the catalyst dose was 1.5 % (w/v) at methanol (9 molar) to oil (1 molar) ratio at 60 °C undergoing 180 min duration.

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