RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 9946

Characterization, activity and process optimization with a biomass-based thermal power plant's fly ash as a potential catalyst for biodiesel production

Prashant Kumar,[ab] Mohammad Aslam,[ac] Neetu Singh,[ab] Sunil Mittal,[d] Ajay Bansal,[b] Mithilesh Kumar Jha[b] and Anil Kumar Sarma*[a]

Received 30th October 2014
Accepted 7th January 2015

DOI: 10.1039/c4ra13475c

www.rsc.org/advances

A typical thermal power plant operated using a solid biomass mixture as fuel, which comprised 70–80% gram straw, 10–15% cotton straw, 5–10% wheat straw and leaves (2%) with a small quantity of coal (1–2%) initially used for smooth ignition, produces a residue called Biomass-Based Thermal Power Plant Fly Ash (BBTPFS). BBTPFS was investigated for composition and structural characterization using different techniques. The versatile composition of the BBTPFS was confirmed by XRF analysis that indicated the weight percent of different components *viz.* CaO (30.74%), SiO_2 (27.87%), K_2O (13.96%), MgO (6.67%), SO_3 (4.83%), Cl (3.36%), Al_2O_3 (2.83%), Fe_2O_3 (2.36%), P_2O_5 (1.34%), Na_2O (1.14%), small quantities of TiO_2, SrO, MnO, BaO, ZrO_2, ZnO, Rb_2O, Br, Cr_2O_3, CuO, NiO and As_2O_3 as active ingredients. The SEM and TEM image analysis showed the surface morphology of the BBTPFS which was found to be mixed in nature, having 1 to 500 nm range particles with meso, micro and macro porosity. BBTPFS was used as a catalyst for transesterification of *Jatropha curcas* oil having a high percentage of free fatty acids and appropriate process optimization was achieved using the Taguchi-ANOVA method. It was observed that at a temperature of 225 °C and an internal vapour pressure of 3.2 MPa in a batch reactor with 5% catalyst loading, 1 : 9 mol mol^{-1} of oil–alcohol and 3 h reaction time, the optimum yield of biodiesel obtained was ~93.9%, which is in agreement with the theoretical value. The product quality was assessed and found to conform to ASTM and EN-standards.

Introduction

Catalysis research during biodiesel production has gone forth as a new wing for the conversion of low grade vegetable oils into biodiesel at minimum efforts.[1–3] The application of heterogeneous catalysts for biodiesel production is being investigated throughout the world as evidenced from innumerable research publications and patents.[4–6] It becomes more significant economically if the catalyst applied could be generated at very low cost or these are simply waste materials derived from a renewable precursor.[3,7]

Biodiesel is produced from vegetable oils or animal fats through transesterification reaction which uses alcohols in the posture of a catalyst. The catalysts chemically coverts the molecules of triglycerides into alkyl esters known as biodiesel fuels.[8–10] The commonly used alcohols for the transesterification include methanol and ethanol. Methanol is most frequently used, due to its low cost and high activity.[11] High FFA (above 0.5%) containing oil is generally regarded as a low grade feedstock endorsed to their affinity for saponification under alkali catalyzed reaction. Therefore, high FFA containing oils is generally transesterified in two steps: first acid catalytic esterification followed by transesterification using alkali catalyst. This is a tedious process as it requires settling of the water layer in the first step followed by transesterification in the presence of an alkali catalyst in the second. A substantial amount of waste water (about 4 times the volume of biodiesel) is generated during water-wash of the acid catalytic reaction product in esterification step. The drying of the esterified mixture and subsequent use for transesterification is also a highly time consuming process. Low grade vegetable oil having high percentage of free fatty acids (FFA) or high moisture content require high temperature reaction for catalytic conversion to biodiesel in a single step as reported in a few literature recently.[12–14]

Thermal power plants are the major setup to satisfy energy demands for the producing countries.[15,16] The waste of thermal power plant (coal or biomass based) is basically ash, which are formed during combustion of solid fuels, 80% of which are real

---

[a] *Chemical Conversion Division, Sardar Swaran Singh National Institute of Renewable Energy, Kapurthala-144601, India. E-mail: anil_tu@yahoo.co.in; Fax: +91 18222555414; Tel: +91 18222555414*

[b] *Department of Chemical Engineering, Dr B R Ambedkar National Institute of Technology, Jalandhar-144011, India*

[c] *Department of Chemistry, Dr B R Ambedkar National Institute of Technology, Jalandhar-144011, India*

[d] *Centre for Environmental Science and Technology, Central University of Punjab, Bathinda-151001, India*

fine in size and known as fly ash and coarser materials that extend downwards to the bottom of the furnace known as bottom ash. Fly ash produced from the combustion of any form of biomass is referred as "bio-ash"[17] or Biomass-Based Thermal Power Plant Fly Ash (BBTPFS). The properties and composition of BBTPFS are dependent upon combustion technology (*e.g.* fixed bed or fluidized bed *etc.*) and type of biomass used in thermal power plant. BBTPFS differ from coal ashes, in particular in what feelings to its chemistry and mineralogy.[18] Almost 90 metric ton fly ash is generated per year in India. Growing amounts of solid waste produced from thermal power plants, and its administration is becoming a grave concern to the environmentalists. In India alone, only 3% of fly ash generated is used while the developed countries like Germany, 80% of the fly ash generated is being utilized.[16,19]

Most of the BBTPFS produced is either disposed of in landfill or recycled on agricultural fields or forest without any restriction.[20] BBTPFS can also be used in cement production industry.[21–23] BBTPFS volumes are enhancing globally and then as its administration cost. Thus, here in India, it is desired to increase the utilization of fly ash and to explore new fields where fly ash can be used.[24] The sulphur content of biomass is about 10 times lower than the coal and hence the BBTPFS are also expected to have lower sulphur content. Apart from environmental and solid waste management concerns discussed above, greenhouse gases are also a matter of concern that has increased drastically due to fossil fuel combustion.[10] Alternative, non petroleum based fuel is immediate need of the society to lessen CO_2 emissions and also to partially compensate the demand of oil based diesel.

The utilization of BBTPFS as heterogeneous catalyst for biodiesel production can be a boon to society. Recently, a fly ash supported heterogeneous catalyst derived zeolite Na-X and K-X ashes, coal fly ash loaded with KNO_3 and K_2O was reported worth production for biodiesel.[6] Apart from fly ash, boiler ash,[7] wood ash,[25] *Musa balbisiana* Colla underground stem ash[14] and *Lemna perpusilla* Torrey ash[3] *etc.* were found instrumental in the production of biodiesel. In all these potassium and sodium predominates over other metals and were reported to be the active component of catalysis process.

The objective of this study is to optimize the production of biodiesel from *Jatropha curcas* L. Oil (JCO) having high percentage of free fatty acids using BBTPFS as green catalyst. BBTPFS catalyst was fully characterized by physical–chemical means, with respect to available parameters and composition, and measured for its potency during the transesterification process. A literature search reflects that little research has been conducted using Taguchi's method for optimized production of biodiesel, but the Taguchi's method has been gaining popularity in optimizing process parameters for other engineered products. In general, the numbers of experiments increases with the growth of a number of process parameters. Instead, the Taguchi method uses a particular design of orthogonal arrays to examine the entire process parameter space with a comparatively lower activity.[26]

Furthermore, this field was intended to make utilization of the Taguchi's method and processes to maximise the yield of biodiesel (FAME) from high free fatty acid (FFA) containing JCO uses the single step transesterification method under elevated conditions. A complete picture of the fuel properties was also investigated according to the accepted standard methods and compared to ASTM D 6751 and EN 14214 biodiesel standards.

Material and methods

The JCO used for the design of experimental work was procured from an oil marketing company of Rajasthan, India. The JCO used to have acid value 18.4 mg KOH/g oil, while the initial water content was 759 ppm and used as such without further characterization as the same was properly stored and used within a month time span. Although this JCO contains different fatty acids of varying chain lengths and different degree of unsaturation, yet it has four major fatty acids, namely, 32.3% linoleic acid (C 18 : 2), 38.0% oleic acid (C 18 : 1), 16.9% palmitic acid (C 16 : 0) and 8.6% stearic acid (18 : 0).[23]

The catalyst

BBTPFS generated from the combustion of a solid biomass mainly comprised of 70–80% gram straw, 10–15% cotton straw, 5–10% wheat straw and small percentage of leaves (2%). This was compiled from a thermal power plant situated in district Bathinda of Punjab, India. The small quantity of coal (1–2%) was also employed initially for the efficient combustion of biomass as well as for the smooth operation of the thermal plant. The generated BBTPFS was stored in glass bottles after treating for an hour at 550 °C in a muffle furnace.

Characterization of catalyst

BBTPFS was characterized using XRD, XRF, BET surface area using nitrogen, thermo-gravimetric analysis (TGA), SEM and TEM.

Basicity analysis

The basic strength of the catalysts (H_) was analyzed using Hammett indicator. The basic strength of the catalysts was interpreted as being more potent than the Hammett indicator if it established a colour change but weaker if it showed no colour change. About 100 mg of the catalyst sample was shaken with a desirable amount of Hammett indicators diluted with methanol and left to equilibrate for 2 hours until no further colour change was observed. The colour of titrate was then recorded. The following Hammett indicators were used: neutral red ($H\_ = 6.8$), bromothymol blue ($H\_ = 7.2$), phenolphthalein ($H\_ = 9.3$), 2,4-dinitroaniline ($H\_ = 15.0$), 4-nitroaniline ($H\_ = 18.4$).

Crystalline phase analysis

The powder X-ray diffraction analysis (XRD) was carried out using PANalytical X'Pert Pro. The diffractometer employed Cu-Kα radiation to produce diffraction patterns from powder crystalline samples at ambient temperature. The Cu-Kα radiation was produced by Philips glass diffraction, X-ray tube with broad focus 2.7 kW type. All the samples were mounted on sample holder and the basal spacing was determined *via* powder technique.

Elemental analysis

The elemental analysis of the catalyst was performed by X-ray florescence technique with wavelength dispersive X-ray fluorescence-S8 Tiger from Bruker, Germany.

Surface area and particle size analysis

The total surface area of the catalysts was obtained by BET using nitrogen adsorption at −195.850 °C. The analysis was conducted using Micromeritics ASAP 2020 series using nitrogen adsorption/desorption analyzer.

Morphological and structural study

The scanning electron microscopy with energy dispersive X-ray detector (SEM-EDS) technique was used to obtain the information on the morphology. The morphology of the catalyst was studied using a FE-SEM QUANTA 200 FEG from FEI Netherlands. Gold coating of the samples was performed with a sputter coater.

TEM study was done with a TEM TECNAI G2 20 S-TWIN (FEI Netherlands) electron microscope. A drop of the sample suspension diluted in alcohol was put onto a holey carbon film supported by a 3 mm copper grid and then observed.

Thermal stability of the catalyst

The thermal stability of the catalyst was found with a thermogravimetric analyzer (TGA) of Perkin Elmer makes; model number STA 6000. The weight loss of the catalyst was considered within the temperature range of 30–1000 °C, and heating rate 10 °C min^{-1} and constant flow of air and nitrogen (20 ± 0.5 ml min^{-1}).

Catalyst reusability

The reusability of the BBTPFS catalysts was studied for the transesterification of JCO and was reused for five times after appropriate treatment. After each reaction, the catalyst was separated by filtration from the reaction mixture. The used catalyst was washed with acetone and then dried at room temperature. The dried catalyst was then activated in the furnace for 15 minutes at 550 °C and then used for the next batch.

Design of experiment for the optimization of transesterification process

Orthogonal arrays were used with the help of Taguchi's method for experimental purpose. In this work, the effect of four parameters, *i.e.* the molar ratio of alcohol to oil, reaction time, catalyst concentration and reaction temperature for the production of JCO biodiesel were optimized. These variables were named to have larger effects on the production of biodiesel made from other feedstock.[27] We have taken to encompass all the grades in the present study because based on different oil resources and catalyst, the degree of importance of each optimal condition is very different.[28] A five level, *i.e.* L-25 experimental model was picked out and experimentally studied. The diversity factors were studied by crossing the orthogonal array of the control parameters, as indicated in Tables 1 and 2. L-25 refers to a Latin square and the experiment number. The numbers in Table 1 indicate the levels of the parameters.

Table 1 Design of experiments, with four parameters at five-level, for the production of JCO methyl esters

			Levels				
Parameters	Unit	Symbol	1	2	3	4	5
Catalyst loading	%	A	1	2	3	4	5
Molar ratio	Mol.	B	1 : 3	1 : 6	1 : 9	1 : 12	1 : 15
Reaction time	(Minutes)	C	60	90	120	150	180
Temperature	°C	D	150	175	200	225	250

In this study, Minitab 16 software was used to examine the results and optimize the experimental parameters for the automatic design and analysis of Taguchi experiments for determining the command variables.

Statistical analysis of results

Signal-to-noise ratio. The Taguchi orthogonal array, is an audio concept of signal-to-interference ratio (*S*/*N*), utilized to figure the impact of noise components on the reaction. As such, noise factors are elements that cannot be handled during the running of the experimentations. These factors cause variations in the response data and to be considered for analysing the results. The *S*/*N* was defined as the least difference in response that design should be observed as statistically significant to the measured standard deviation of the reaction. The signal was set at 10% of the mean value of the JCO biodiesel content.

Analysis of variance (ANOVA). ANOVA was used to analyze the experimental data obtained to ascertain the significance of each factor on the response. Combining ANOVA with the Taguchi approach gives a systematic approach for optimization of parameters with reference to their performance. The *F*-value in ANOVA signifies the validity of the null hypothesis. The *F*-test was accomplished by calculating the corresponding *P*-value in the *F*-value distribution curve. The null hypothesis is rejected if the *P*-value for a factor is less than 0.05 (5%), and the factor is considered to significantly affect the response, *i.e.* the percentage biodiesel yield in this experiment.

Catalytic activity analysis during transesterification reaction. Transesterification reaction was carried in a High Pressure High Temperature (HPHT) Bench Top Batch of 1.8 L capacity (Amar Equipments Company, Mumbai, India). The transesterification reaction was performed by varying temperature, oil to methanol molar ratio, reaction time and catalyst loading as suggested by Minitab 16 software. The speed of the impeller was set at 550 RPM. Initially no pressure was applied to the reactor, which increased up to 4.31×10^6 Pa by increasing internal vapor pressure at 250 °C. The produced samples were collected after rapid cooling of the reactor using its integrated cooling system. Then, samples were taken by opening the sampling bottom

Table 2 Orthogonal array used to design experiments with four parameters at five-levels, L-25 (5**4)

S. no.	Catalyst loading (%)	Molar Ratio	Reaction time (min)	Temperature (°C)	Biodiesel yield (%)	Error	*S*/*N* ratio
1	1	3	60	150	29.73	0.11	29.46
2	1	6	90	175	36.95	0.18	31.35
3	1	9	120	200	42.50	0.92	32.57
4	1	12	150	225	48.057	0.66	33.64
5	1	15	180	250	53.61	0.40	34.58
6	2	3	90	200	48.83	0.08	33.77
7	2	6	120	225	54.38	0.18	34.71
8	2	9	150	250	59.93	0.44	35.55
9	2	12	180	150	55.45	0.76	34.88
10	2	15	60	175	58.44	0.23	35.33
11	3	3	120	250	66.25	0.27	36.42
12	3	6	150	150	61.77	0.07	35.81
13	3	9	180	175	68.99	0.00	36.78
14	3	12	60	200	70.31	0.32	36.94
15	3	15	90	225	75.87	0.58	37.60
16	4	3	150	175	75.32	0.84	37.54
17	4	6	180	200	80.87	0.10	38.16
18	4	9	60	225	82.19	0.42	38.30
19	4	12	90	250	87.74	0.68	38.86
20	4	15	120	150	83.25	0.48	38.41
21	5	3	180	225	85.74	0.80	38.66
22	5	6	60	250	86.76	0.78	38.77
23	5	9	90	150	89.58	0.31	39.04
24	5	12	120	175	89.80	0.75	39.06
25	5	15	150	200	92.35	0.49	39.31
Mean *S*/*N* ratio							**36.22**

value. The samples collected from the reactor were allowed to settle in a ventilator before analysis. The heavy weight catalyst settled at the rear of the reactor and collected first. The oily phase was subsequently changed to the rotary vacuum evaporator (Heydolph, Germany Make) to separate un-reacted methanol at 45–50 °C and 2.25×10^3 Pa. The samples were then centrifuged to separate the catalyst, glycerin (GL) and biodiesel. The upper layer of the centrifuged sample consists of the oily phase (biodiesel), the lower one of the glycerine, while in the centre, between the oil and the glycerine phase appears the catalyst. The catalyst was later washed using petroleum ether and methanol to remove the bound ester in dispersed phase and glycerol.

Biodiesel analysis by GC. The biodiesel prepared was analyzed using Agilent make Gas Chromatograph (GC). The methodology used for analysis of biodiesel is similar as per our previous report[14] *i.e.* as per EN 14103 specifications for % conversion of ester while EN 14106 for analysis of monoglyceride, diglyceride and free glycerol.

Fuel characteristic analysis of the FAME. The fuel properties of the biodiesel obtained were analysed using appropriate ASTM D 6751 and EN 14214 standard procedure specified for B100 biodiesel stocks.

Results and discussion

Characterization of BBTPFS catalyst

The basicity of the BBTPFS catalyst was found to be in the range of $9.3 < H\_ < 15.0$. This catalyst was found stronger than the weakest indicator phenolphthalein ($H\_ = 9.8$) that established a colour change from pink to colourless. However, it is weaker than the strongest indicator *i.e.* 2,4-dinitroaniline ($H\_ = 15.0$) as no colour change was observed.

The composition analysis using XRF confirms the presence of CaO (30.74 wt%), SiO_2 (27.87 wt%), K_2O (13.96 wt%), MgO (6.67 wt%), SO_3 (4.83 wt%), Cl (3.36 wt%), Al_2O_3 (2.83 wt%), Fe_2O_3 (2.36 wt%), P_2O_5 (1.34 wt%), Na_2O (1.14 wt%), trace amounts of TiO_2, SrO, MnO, BaO, ZrO_2, ZnO, Rb_2O, Br, Cr_2O_3, CuO, NiO and As_2O_3. The composition has been found to be almost identical to the ash used in the cement industry. CaO is present in highest percentage in BBTPFS catalyst. CaO and SiO_2 dominate the major proportions and more than 50% of the compositions of the BBTPFS catalyst comprised with these two. Both are highly active, as indicated in the literature, SiO_2 as Sorbent while CaO to facilitate transesterification. Due to the high CaO content, the ashes are classified as Class C [17–19, 26]. Even K_2O, MgO, Al_2O_3 and some of the compounds present in less amount (such as Na_2O, TiO_2, SrO and ZnO *etc.*) are proven heterogeneous catalyst for biodiesel production.[14,30]

For BBTPFS catalyst XRD analysis (Fig. 1) ascertains the presence of sharp peaks of CaO, $CaCO_3$, mullite (mainly aluminum oxide (Al_2O_3), silicon oxide (SiO_2) and calcium silicate (Ca_2SiO_4)), at 2θ in between 20–21, 23–24, 27–31, 39–44, 47–52 and 57–58 of crystalline phases, respectively.[18] It has been found that the surface area of the catalyst is 4.0953 $m^2\ g^{-1}$, total pore volume 0.004863 $cm^3\ g^{-1}$ for pores smaller than 207.365 Å (radius) at P/P_o equal to 0.9004 and pore size expressed as average pore radius is equal to 47.5 Å.

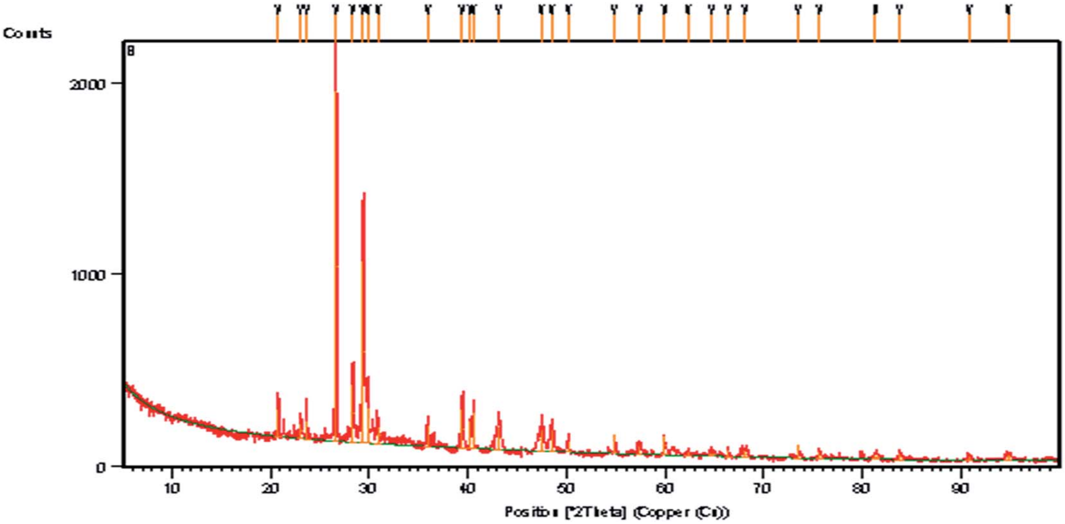
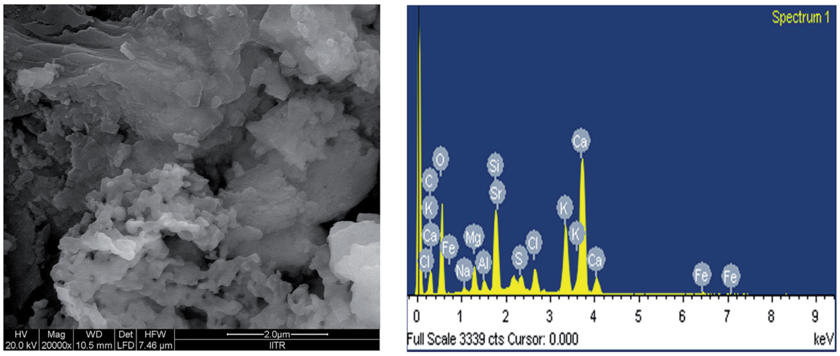


Fig. 1 XRD pattern of BBTPFS showing different crystalline phases at specific 2θ and identification of the components.



(a) (b)

Fig. 2 SEM analysis of BBTPFS to depict the surface morphology.

The SEM-EDX analysis (Fig. 2) of the BBTPFS catalyst was conducted and confirmed the presence of C, O, Mg, Al, Si, P, S, Cl, K, Ca and Fe. The typical elemental composition of the BBTPFS catalyst has been represented in Table 3. The Fig. 2a showed that the BBTPFS particles have irregular shape, like the one reported by Rajamma *et al.*[18] and revealed the presence of voids or pores distributed over the BBTPFS catalyst surface[31] having mesoporosity, micro porosity and macro porosity.

The structural information of the catalyst was studied from the TEM (Fig. 3); that varies from single nanometric range to

Table 3 Elemental composition of the BBTPFS catalyst

Element	Weight%	Atomic%
C	16.89	26.72
O	41.92	49.80
Mg	4.10	3.20
Al	1.51	1.06
Si	9.97	6.75
P	1.14	0.70
Cl	1.92	1.03
K	14.07	6.84
Ca	7.57	3.59
Fe	0.91	0.31
Total	**100.00**	**100.00**

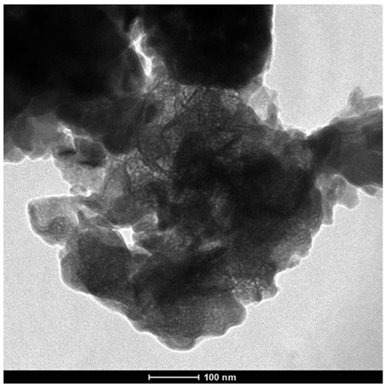


Fig. 3 TEM analysis of BBTPFS catalyst at 100 nm scale.

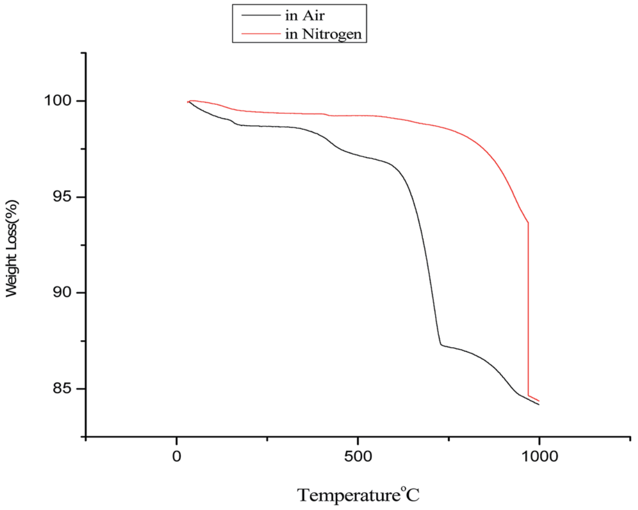


Fig. 4 Thermo Gravimetric Analysis (TGA) graph of BBTPFS under constant nitrogen and air flow to differentiate %wt loss with increasing temperature.

500 nm range, showing a homogeneous mixture of uneven materials. The nano size, structural dimension and active components of the BBTPFS catalyst provided effective surfaces to their catalytic efficacy during transesterification of triglyceride, irrespective of the FFAs present in the oil.

The thermogravimetric analysis (TGA) of the BBTPFS catalyst is shown in Fig. 4, which has been plotted within the temperature range (30–1000 °C), to determine the weight loss with respect to temperature. It is obvious from the Fig. 4 that the catalyst losses its moisture due to dehydration in the temperature ranges of 30–150 °C, devolatilization and then gradual decomposition of the BBTPFS has been observed thereby releasing small molecules. Moreover, it is also noted that 15% losses are visible during the thermal decomposition of the catalyst in both the N_2 and air medium. CaO which represents 30% of the BBTPFS catalyst displays a high thermal stability at any temperature within the prescribed limit of the TGA.[29,31]

Catalytic activity

It is obvious from the XRF analysis that the BBTPFS catalyst consists of both acidic and alkaline nature species which enhances the acid–base catalyzed transesterification reaction. The acidic and alkaline species are still not present in equivalent proportions in BBTPFS catalyst which practically makes it of alkaline nature. During the transesterification reaction under elevated temperature and pressure, water produced as the byproduct from the free fatty acid esterification, reacts with SO_3, P_2O_5, K_2O, Na_2O and produces H_2SO_4, H_3PO_4 and KOH, NaOH respectively, *in situ* that further accelerates the transesterification reaction significantly to achieve the desired product with higher yield *i.e.* over all yield of biodiesel was enhanced.[30,32,33]

$$K_2O + H_2O \rightarrow 2KOH$$

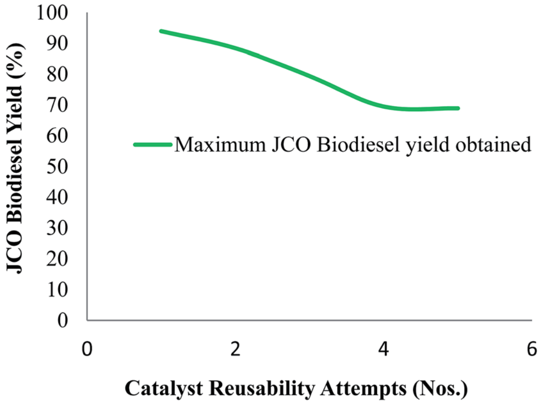


Fig. 5 The effect of catalyst reusability on JCO biodiesel yield (%).

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

$$Cl_2 + H_2O \leftrightarrow HCl + HOCl$$

Nevertheless, this too causes negative impacts of deactivation of catalysts after first usage because the catalytic surface partially decomposed. Thus, activation of the catalyst is an inevitable step before reuse. Due to its efficient activity a single step transesterification becomes feasible for high FFA containing JCO.

Moreover, the reusability of the BBTPFS catalysts was studied for the transesterification of JCO and was reused for five times as shown in Fig. 5, after appropriate treatment of the catalyst in Muffle furnace at 550 °C for 15 minutes. It has been clearly observed Fig. 5 that the efficiency of the catalyst was reduced more than 5% in first two batches, while the efficiency of the catalysts was reduced from 9–10% in the third and fourth successive batches. Nevertheless, there has been observed a negligible decrease in efficiency in the final batch. Hence, the catalyst can be recycled up to five times, however after activation at 550 °C, successively, with the decrease in the efficiency not exceeding more than 25%.

Process optimization by orthogonal arrays using Taguchi's method

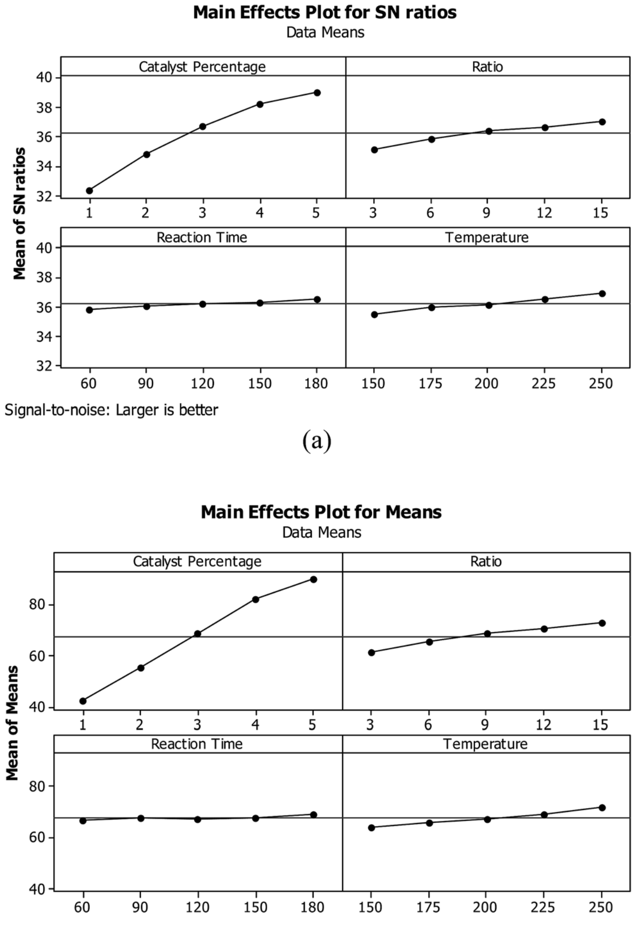
The Taguchi method can be employed for the optimization of factor combination and to determine possible factor interactions to ensure a robust design for the process of biodiesel production. The Taguchi method provided a systematic and efficient mathematical platform to analyse and optimise process parameters using only a few well-defined experimental sets.[34] Analysis of variation (ANOVA) was used to optimise the results from Taguchi method and to fetch the proportional importance of each parameter. ANOVA results predicted catalyst concentration as the most effective parameter for output of biodiesel with the BBTPFS catalyst (Table 4).

Table 4 Analysis of variance[a]

Source	DF	SS	MS	F	P
Regression	4	8026.0	2006.5	397.27	0.000
Residual error	20	101.0	5.1		
Total	24	8127.0			

[a] The SS of parameter added together with SS of residual error to form residual error SS(pooled). Significant at 95% confidence level: F (0.05, 2, $4)^{1/4}$ × 6 (F-test). DF indicates degree of freedom. SS and MS indicate sum of square and mean square respectively.

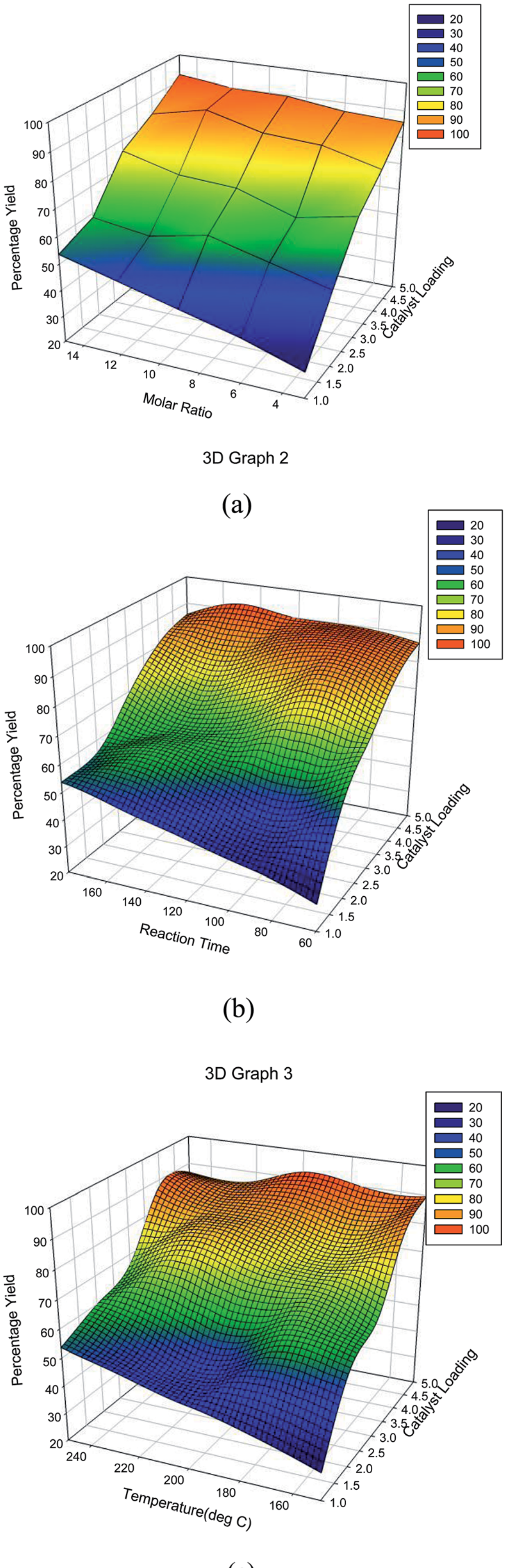
Signal-to-noise (S/N) ratio is the most important tool used in the Taguchi robust parameter design. The S/N ratio can be used to evaluate the deviation from the target of a quality characteristic and variation of a system as shown in Fig. 6a. The higher the S/N ratio is, the more robust the system will be.[35] Three attributes of quality characteristics were defined by Taguchi. Based upon their characteristics, the S/N ratios are of three different types, *i.e.* smaller-the-better, larger-the-better and nominal-the-better. The S/N ratio, with a larger-the-better characteristic can be expressed equally:



(a)

(b)

Fig. 6 (a) Main effects plot for S/N ratio of process variables. (b) Main effects plot for means of process variables.



(a)

(b)

(c)

Fig. 7 Effects of various factors on transesterification reaction, (a) molar ratio, (b) reaction time and (c) reaction temperature.

Table 5 Regression analysis. The regression equation is; percentage yield = 5.38 + 12.2catalyst percentage + 0.937ratio + 0.0149reaction time + 0.0771temperature[a]

Predictor	Coef.	SE coef.	T	P
Constant	5.377	3.178	1.690	0.006
Catalyst percentage	12.194	0.318	38.370	0.000
Ratio	0.938	0.106	8.850	0.000
Reaction time	0.015	0.011	1.400	0.004
Temperature	0.077	0.013	6.060	0.000

[a] $S = 2.24740$ $R_{\mathrm{Sq}} = 98.8\%$ $R_{\mathrm{Sq}}(\mathrm{adj}) = 98.5\%$.

Table 6 Sequential model sum of squares[a]

Source	DF	Seq SS
Catalyst percentage	1	7178.7
Temperature	1	147.1
Molar ratio	1	425.8
Reaction time (minutes)	1	21.6

[a] DF: degree of freedom, Seq SS: sequential model sum of squares.

Table 7 Fuel properties of JCO biodiesel

Properties	Biodiesel standard	JCO biodiesel
Density at 15 °C (g cm^{-3})	0.875–0.900	0.852
IBP/FBP (°C)		310/480
Distillation characteristics: (%recovery@330, 360, 365, 370, 427 °C)	90% 360	20.0 40.0 80.0 90.0 99.6
Flash point, (°C)	120	112 °C
Calorific value (MJ kg^{-1})	37.25	39.15
Viscosity@40 °C (mm^2 s^{-1})	2.5–6	4.98
Acid value (mg KOH per g)	0.50	1.88
Cetane no.	47.0	48.5
Rams bottom carbon residue (wt%) max	0.300	0.273
Copper strip corrosion	3	1a
Water and sediment content (mg kg^{-1}) max	500	800
Pour point °C max	Winter +3 and summer +15	6
Oxidation stability at 110 °C, h, min	6	0.74
Sulphur content (mg kg^{-1}) max	15	4.9
Iodine value (gI$_2$ per 100 g) max	120	81.9
Sodium mg kg^{-1}	5	<1
Potassium mg kg^{-1}	5	<1
Total (Na + K) mg kg^{-1}	5	
Free glycerol (%) max	0.2	0.155
Monoglycerides (%) max	0.8	0.014
Diglycerides (%) max	0.2	0.000
Triglycerides (%) max	0.2	0.010
Total glycerol (free plus bound) (%) max	0.25	0.179
Sulfated ash (%) mass max	0.02	0.01
Total contamination	24	22

$$\eta_{ij} = -10\log\left(\frac{1}{n}\sum_{j=1}^{n}\frac{1}{{y_{ij}}^2}\right) \tag{1}$$

where y_{ij} is the ith response of the jth experiment, n is the total number of tests.

The S/N ratios for the twenty five sets of experiments are likewise presented in Table 2. The average yield of JCO biodiesel and the S/N ratio were 67.44% and 36.22, respectively. The mean S/N ratio, which was estimated from the gist of the parameters and the interactions at assigned levels, was the average of all the S/N ratios of a set of control parameters at a paid level as indicated in Table 2. The donation of an experimental parameter was estimated from the maximum difference in the values between the mean S/N ratios and means as shown in Fig. 6b. The order of influence of the parameters in terms of the yield of JCO biodiesel was: A (catalyst concentration) > B (molar ratio) > D (reaction temperature) > C (reaction time). The effects of S/N ratios (Fig. 6a) and the effects of means (Fig. 6b) are in concordance with the above trend.

Biodiesel production was observed as optimum at 225 °C, 5% catalyst concentration (w/v); and 1/9 oil/methanol molar ratio, average yield of JCO biodiesel and the S/N ratio were 93.93% and 39.99, as ascertained from the Taguchi's method. The effects of various factors on transesterification reaction, molar ratio, reaction time and reaction temperature have been presented in Fig. 7a–c respectively, that describes their 3D variation with respect to each other correlating with wt% yield of biodiesel.

This had been experimentally confirmed with 94% biodiesel yield in less than three hours in the presence of BBTPFS catalyst. The equation obtained from regression analysis (Tables 4 and 5) is as listed beneath:

$$\text{Percentage yield} = 5.38 + 12.2\text{catalyst percentage} + 0.937\text{ratio} + 0.0149\text{reaction time} + 0.0771\text{temperature} \tag{2}$$

This equation signifies that the variable quantities required for the reaction to produce biodiesel could be optimized and catalyst plays the vital role during the reaction to proceed at a better rate (Table 6).

Fuel property analysis of the biodiesel

JCO biodiesel obtained as per suggestion of Taguchi's Method using Minitab 16 software was analyzed using appropriate ASTM and European standards after purification (Table 7). The products were found as per specification. The free fatty acids were reduced to 0.94% from 9.2% originally present in the oil. The fuel properties of the biodiesel obtained are as enlisted in Table 7. These values clearly demonstrate that the biodiesel obtained can be used as substitute of petroleum diesel without further treatment. Leaching of sodium and potassium ion was almost negligible (<1 mg kg^{-1}) in the biodiesel obtained. Hence no further treatment was needed.

Conclusion

BBTPFS catalyst was found instrumental in the production of Biodiesel from high FFA containing JCO. The catalyst acts on two stages, first, the reduction of free fatty acids to ester (esterification) at elevated temperature and pressure; conversion of triglycerides to esters and glycerol in the second. The outcomes show that the process parameters effect the transesterification reaction according in following order: A (catalyst concentration) > B (molar ratio) > D (reaction temperature) > C (reaction time). An optimized parameter combination for the maximum JCO biodiesel production was generated utilizing the signal-to-interference (S/N) ratio and was found at 225 °C, 5% Catalyst concentration (w/v); and 1/9 oil/methanol molar ratio in 3 hours. This can definitely offer a pathway for efficient utilization of BBTPFS as catalyst for transesterification of oils having high FFA contents, such as used frying oils also. Further, extended studies will be embraced in all the uncovered area such as detail active acidic and basic sites, surface deactivation of catalyst during the reaction and reusability for large scale biodiesel production in the future scope of employment.

Acknowledgements

The first author acknowledges Dr B R Ambedkar NIT Jalandhar for the PhD Fellowship and SSS-NIRE for the platform of experimental works. The authors are also thankful to the concerned authority of IOCL, Faridabad for carrying out some of the quality tests of biodiesel and Dr V K Srivastava, IIT Roorkee, for determining the BET surface area, pore size and pore volume of the catalyst. First author expresses special thanks to Mr Amit Lal Researcher NIT Jalandhar for his help during the application of Taguchi's Method.

References

1 P. Zhang, Q. Han, M. Fan and P. Jiang, *Fuel*, 2014, **124**, 66–72.
2 S. Niju, K. M. Meera, S. Begum and N. Anantharaman, *RSC Adv.*, 2014, **4**, 54109–54114.
3 A. P. S. Chouhan and A. K. Sarma, *Biomass Bioenergy*, 2013, **55**, 386–389.
4 H. Kazemian, B. Turowec, M. N. Siddiquee and S. Rohani, *Fuel*, 2013, **103**, 719–724.
5 M. A. K. I. M. Rizwanul Fattah, H. H. Masjuki and M. A. Wakil, *RSC Adv.*, 2014, 17787–17796.
6 S. L. Danlin Zeng, W. Gong, H. Chena and G. Wanga, *RSC Adv.*, 2014, **39**, 20535–20539.
7 W. W. S. Ho, H. K. Ng and S. Gan, *Bioresour. Technol.*, 2012, **125**, 158–164.
8 D. Madhu, B. Singh and Y. C. Sharma, *RSC Adv.*, 2014, **4**, 31462–31468.
9 Y. Morikawa, X. Zhao and D. Liu, *RSC Adv.*, 2014, **4**, 37878–37888.
10 E. Akbar, N. Binitha, Z. Yaakob, S. K. Kamarudin and J. Salimon, *Green Chem.*, 2009, **11**, 1862–1866.
11 C. L. Chen, C. C. Huang, D. L. Tran and J. S. Chang, *Bioresour. Technol.*, 2012, **113**, 8–13.
12 Z. J. Jie Xu, L. Lia and T. Fang, *RSC Adv.*, 2014, 23447–23455.
13 V. Vadery, B. N. Narayanan, R. M. Ramakrishnan, S. K. Cherikkallinmel, S. Sugunan, D. P. Narayanan and S. Sasidharan, *Energy*, 2014, **70**, 588–594.
14 A. K. Sarma, P. Kumar, M. Aslam and A. P. S. Chouhan, *Catal. Lett.*, 2014, **144**, 1344–1353.
15 G. Tao, Z. Hua, Z. Gao, Y. Chen, L. Wang, Q. He, H. Chen and J. Shi, *RSC Adv.*, 2012, **2**, 12337–12345.
16 M. R. Senapati, *Curr. Sci.*, 2011, **12**, 1791–1795.
17 A. Jaworek, T. Czech, A. T. Sobczyk and A. Krupa, *J. Electrost.*, 2013, **71**, 165–175.
18 R. Rajamma, R. J. Ball, L. A. C. Tarelho, G. C. Allen, J. A. Labrincha and V. M. Ferreiraa, *J. Hazard. Mater.*, 2009, **172**, 1049–1060.
19 V. C. Pandey, P. C. Abhilash and N. Singh, *J. Environ. Manage.*, 2009, **90**, 2943–2958.
20 S. Jala and D. Goyal, *Bioresour. Technol.*, 2006, **97**, 1136–1147.
21 S. Maschio, G. L. Tonello Piani and E. Furlani, *Chemosphere*, 2011, **85**, 666–671.
22 B. Carrasco, N. Cruz, J. Terrados, F. A. Corpas and L. Pérez, *Fuel*, 2014, **118**, 272–280.
23 T. C. Esteves, R. Rajamma, D. Soares, A. S. Silva, V. M. Ferreira and J. A. Labrincha, *Materials*, 2012, **26**, 687–693.
24 J. Kalembkiewicz and U. Chmielarz, *Resour., Conserv. Recycl.*, 2012, **69**, 109–121.
25 M. Sharma, A. A. Khan, S. K. Suri and D. K. Tuli, *Biomass Bioenergy*, 2012, **41**, 94–106.
26 H. H. M. M. I. Arbab, M. Varman, M. A. Kalam, H. Sajjada and S. Imtenana, *RSC Adv.*, 2014, 37122–37129.
27 H. V. Lee, R. Yunus, J. C. Juan and Y. H. T. Yap, *Fuel Process. Technol.*, 2011, **92**, 2420–2428.
28 S. Z. Hassan and M. Vinjamur, *Chem. Eng. Sci.*, 2014, **110**, 94–104.
29 A. N. Öktea and D. Karamanis, *Appl. Catal., B*, 2013, 538–552.
30 A. P. S. Chouhan and A. K. Sarma, *Renewable Sustainable Energy Rev.*, 2011, **15**, 4378–4399.
31 R. Rajamma, R. J. Ball, L. A. C. Tarelho, G. C. Allen, J. A. Labrincha and V. M. Ferreira, *J. Hazard. Mater.*, 2009, **172**, 1049–1060.
32 R. Chakraborty, S. Bepari and A. Banerjee, *Bioresour. Technol.*, 2011, **102**, 3610–3618.
33 K. Motokura, M. Tada and Y. Iwasawa, *J. Am. Chem. Soc.*, 2009, **131**, 7944–7945.
34 M. J. Climent, A. Corma, S. Iborra and M. J. Sabater, *ACS Catal.*, 2014, **4**, 870–891.
35 S. Z. Hassan and M. Vinjamur, *Chem. Eng. Sci.*, 2014, **107**, 290–301.