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Process optimization of *Calophyllum inophyllum*-waste cooking oil mixture for biodiesel production using *Donax deltoides* shells as heterogeneous catalyst

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Abstract

In the present work, the waste material *Donax deltoides* shells (DDS) was utilized as a heterogeneous base catalyst for biodiesel production from *Calophyllum inophyllum* oil (CIO)-waste cooking oil (WCO) mixture. Non-edible CIO possessing 65 mg of KOH g⁻¹ of acid value was mixed with WCO of low acid value in different proportions. The acid value was reduced to 33.3 mg of KOH g⁻¹ of oil by using a volumetric ratio of 1:1 and it was further reduced to 5.6 mg of KOH g⁻¹ of oil by acid catalyzed esterification process and used for biodiesel production. DDS was converted into active CaO catalyst by calcination and the catalyst characterization was performed using different instrumental techniques. The impact of calcined DDS (catalyst) concentration, reaction time and methanol to esterified oil volumetric ratio on biodiesel conversion was investigated to optimize the transesterification reaction using response surface methodology based central composite design. The biodiesel conversion was determined by proton nuclear magnetic resonance spectroscopy and a maximum biodiesel conversion of 96.5% was achieved with catalyst concentration of 7.5 wt%, methanol to oil volumetric ratio of 63.8%, reaction time of 129.3 min, stirrer speed of 450 rpm and reaction temperature of 65 °C.

Keywords: *Calophyllum inophyllum* oil, Waste cooking oil, *Donax deltoides* shells, Esterification, Transesterification, Response surface methodology

Introduction

World's energy requirement is increasing as industrial, agricultural and transport sectors are dependent on conventional energy resources [1, 2]. This ever-increasing energy demand was met by utilizing conventional fossil fuel resources which are non-renewable in nature and are getting depleted day by day. In order to overcome the fossil fuel depletion and to meet the growing fuel demands, biofuels can be a better alternative. Biodiesel is one such fuel entails alkyl esters having long chain fatty acids obtained from lipids (oils) or animal fats [3]. In addition, biodiesel is biodegradable, non-toxic, renewable, and sustainable to the environment [4, 5]. Biodiesel blended with conventional diesel fuel up to 30% can be directly used in diesel engines irrespective of any major engine alterations [6]. Soybean oil,

palm oil, and sunflower oil are few edible oils employed for biodiesel production and tested successfully in diesel engines [7, 8]. Exploiting such edible oils as feedstock leads to food versus fuel conflict and hence, non-edible feedstocks are turned out to be the pin interest for biodiesel production. Non-edible oils such as *Moringa oleifera*, *Jatropha curcas*, *Croton megalocarpus*, *Ricinus communis*, *Pongamia pinnata*, *Azadirachta indica*, *Cerbera odllam*, *Sapium sebiferum*, *Calophyllum inophyllum* were utilized as feedstock for biodiesel production [9, 10].

Among the different non-edible feedstocks, *C. inophyllum* oil (CIO) is the second most cultivated feedstock for biodiesel production [11]. *C. inophyllum* belongs to the Clusiaceae family and its native range was distributed throughout India. It shows high tolerance to brackish water, salt spray, and winds [12]. An adult plant can grow up to 20–30 m high. It bears fruits twice a year with the annual production of about 8000 fruits and its kernel

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contains 75% oil content [1, 7, 13, 14]. Hence, CIO can be exploited as a promising resource for the production of biodiesel [7, 15, 16]. Besides, 75–85% of production cost of biodiesel was attributed to the feedstock [17, 18] and hence, it is necessary to produce biodiesel economically. One such inexpensive feedstock is waste cooking oil (WCO) which is available in excess, dumped in landfills and rivers illegally [19]. To manage the WCO disposal problem and to use WCO productively, it can be efficiently employed as biodiesel feedstock. Kulkarni and Dalai [20] reviewed methods of biodiesel production from WCO and discussed quality and performance of methyl esters derived from WCO. Few other researchers also investigated the utilization of WCO as biodiesel feedstocks [19, 21–24].

In general, biodiesel synthesized via transesterification reaction necessitates a catalyst to uphold the reaction [5]. Homogeneous catalysts (NaOH and KOH) are generally exercised owing to its higher yield under mild reaction conditions and minimum reaction time [25, 26]. Conversely, exploiting such catalysts has numerous problems such as excess wastewater generated during water wash in order to remove the alkaline catalyst from biodiesel [27]. Also, it is difficult to recover the homogeneous catalyst and may corrode the pipelines and reactors. Alternatively, heterogeneous basic catalysts have shown several merits such as non-toxic, low-cost, and eco-friendly nature [24, 28]. Furthermore, it can be reused, recycled and the product (biodiesel) needs less or no water wash and also produces by-product (glycerol) with high purity [5, 19]. Hence, heterogeneous catalysts are preferred over homogeneous catalysts. Alkaline earth metal oxides can serve as solid catalyst because of its high basicity and minimal solubility in oil [29]. Calcium oxide (CaO) is one such catalyst which is non-toxic, available naturally, environmental friendly and low solubility in methanol. Utilization of seashells as a heterogeneous catalyst is an economical means of biodiesel production and also serves as an effective waste disposal strategy [5, 30, 31].

Among the various sources, sea shell derived catalyst has an excellent reusability [4]. Recently, CaO derived from *Gallus domesticus* shells [22], ostrich egg shell and chicken egg shell [21], waste scallop shell [30], white bivalve clam shell [19], *Tellina tenuis* [32], river snail shell [5], mussel shell [33], and crab shell [34] has been exploited as heterogeneous catalysts in transesterification process. *Donax deltooides* shells (DDS) is one such sea shell of bivalve type which is distributed throughout Indo-West Pacific from Andaman and Nicobar Islands to Indonesia and throughout Australia [35].

Process optimization is an important step in the production process to obtain the maximum biodiesel yield and conversion but it is time-devouring and laborious. Response surface methodology (RSM) is a statistical approach

to optimize the complex processes which helps to understand the interaction between the process parameters and also minimizes the number of experimental runs essential to obtain maximum conversion and also to acquire adequate data to prove that the result is statistically significant [36–39]. Several authors optimized biodiesel production using RSM techniques [24, 40–43].

The present study aimed to explore the possibility of utilizing DDS as a suitable heterogeneous alkali catalyst for methyl ester (biodiesel) production from CIO-WCO mixture. DDS was converted into the active form of CaO catalyst via calcination process. The calcined DDS was studied using Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Atomic X-ray (EDAX) spectrometry. Optimization of biodiesel process parameters using central composite design (CCD) based RSM was employed to understand the effect of reaction time, calcined DDS concentration and methanol to esterified CIO-WCO oil volumetric ratio on biodiesel conversion. The synthesized biodiesel was analyzed by proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) for determining biodiesel conversion.

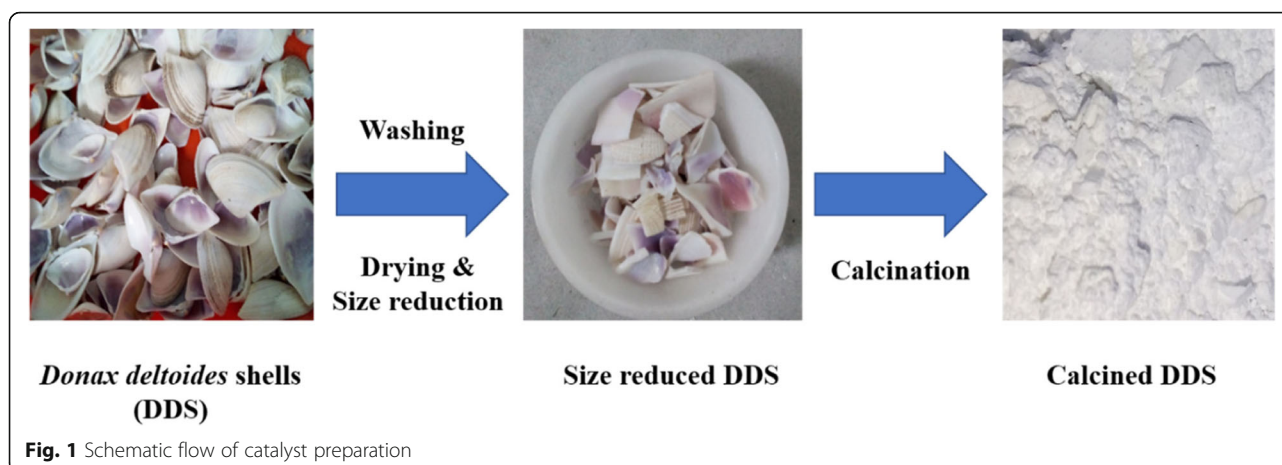
Materials and methods

Materials

DDS was collected from the sea shore of Mahabalipuram, Chennai. CIO was purchased from Tamil traders, Coimbatore, while WCO was obtained from the canteen, PSG College of Technology, Coimbatore, Tamil Nadu, India. Sulfuric acid ($\geq 97\%$), petroleum ether (40–60 °C), and potassium hydroxide ($\geq 85\%$) used in the present study were purchased from HiMedia Laboratories Pvt., Mumbai, India, while methanol, ethanol (99.9%), and phenolphthalein pH indicator solution were purchased from S.D. Fine Chemicals, Mumbai, India. Acid value of the various oil samples was determined using a standard titration method by titrating 0.1 N 95% ethanolic KOH (Burette) solution against the mixture containing 2 g of oil sample, 30 mL (equal amounts) of ethanol and petroleum ether mixture, and few drops of phenolphthalein indicator.

Catalyst preparation

DDS was washed several times with tap water and rinsed with distilled water in order to eliminate the adhered organic impurities. Cleaned DDS was dried in a hot air oven at 105 °C for 24 h and were crushed into fine particles and further subjected to calcination at 900 °C for 3 h in a programmable muffle furnace. Calcium carbonate (CaCO_3) present in the raw DDS upon calcination is converted into CaO. The calcined DDS were immediately transferred to a desiccator to avoid contact with air. The schematic workflow for catalyst preparation was shown in Fig. 1.



Catalyst characterization

SEM analysis on a Carl Zeiss (Model: Sigma V) was performed in order to analyze the surface morphology of the uncalcined and calcined DDS. EDAX was done to reveal the elemental composition of the catalyst. Formation of calcium oxide in calcined DDS was confirmed using XRD (Rigaku; Model, DMAX 2200/Ultima C) furnished with Cu K α radiation ($K_{\alpha} = 1.54 \text{ \AA}$). XPERT-3 diffractometer system was employed in order to acquire diffraction patterns with the scan range from $2\theta = 10$ to 90° , step size of 0.0130 , step time of 48.19 s and at the rate of 30 mA and 45 kV . FTIR spectroscopy on ATR-FTIR (Model: BRUKER, Germany) in scan range of $600\text{--}4000 \text{ cm}^{-1}$ was accomplished to compare the functional groups present in uncalcined and calcined DDS.

Biodiesel production

Esterification

A two-step esterification-transesterification reaction was employed since the acid value of CIO-WCO mixture was determined as $33.4 \text{ mg of KOH g}^{-1}$ of oil. Acid value reduction was performed by using 250 mL three-necked round bottom flask placed in a water bath maintained at 60°C . After esterification reaction, the acid value of CIO-WCO mixture was decreased to $5.6 \text{ mg of KOH g}^{-1}$ of oil using the optimum esterification conditions of 1:3 methanol to CIO-WCO volumetric ratio, 1% (v/v) of sulphuric acid, 90 min of reaction time and stirrer speed of 450 rpm . The excess methanol present in the esterified mixture was eliminated by heating and the resulting mixture was allowed to settle for phase separation. The bottom layer containing impurities (water and excess catalyst) was disposed and the top layer was subjected to transesterification reaction.

Transesterification

Transesterification was performed using a 250 mL three-necked round bottom flask with a temperature

indicator fitted on a side arm and a chilled water condenser fitted on another side arm while mechanical stirrer was inserted in the middle arm. Transesterification reaction was studied to investigate the effect of catalyst concentration, methanol to esterified CIO-WCO volumetric ratio and reaction time on methyl ester conversion. For all experimental runs, temperature and stirrer speed was maintained at 65°C and 450 rpm respectively. Once the reaction is completed, the transesterified mixture was heated to remove excess methanol followed by filtration using Whatman No. 1 filter paper (Pore size: $11 \mu\text{m}$) to remove the catalyst from the reaction mixture. The resulting transesterified mixture was allowed to settle overnight for clear phase separation. High dense bottom layer containing glycerol was discarded whereas the top layer containing fatty acid methyl esters (biodiesel) was examined for biodiesel conversion using $^1\text{H-NMR}$ (Model: Bruker Avance 300 MHz). CDCl_3 was used as a solvent. Percentage biodiesel conversion was determined using the equation given by Knothe [44] as shown in Eq. (1).

$$\% \text{ Biodiesel conversion} = 100 * \frac{2A_{\text{ME}}}{3A_{\alpha\text{CH}_2}} \quad (1)$$

where % Biodiesel conversion is the percentage conversion of CIO-WCO to methyl esters, A_{ME} is the integration value of the methoxy protons of the methyl esters and $A_{\alpha\text{CH}_2}$ is the integration value of the α -methylene protons.

Optimization of the transesterification process

Design of experiments

CCD based RSM was applied to study the impact of three independent transesterification parameters such as calcined DDS concentration, methanol to esterified CIO-WCO volumetric ratio and reaction time on biodiesel conversion. The range and levels of the transesterification variables are presented in Table 1. A total of 20 experimental runs were generated with 2^3 factorial

Table 1 Range and levels of independent variables

Name	Symbols	Units	(−) α	Low	Middle	High	(+) α
Catalyst concentration	A	wt%	4.64	6	8	10	11.36
Methanol to oil ratio	B	% (v/v)	55.18	62	72	82	88.82
Reaction time	C	Min	99.55	120	150	180	200.45

experiments, 6 axial points, and 6 center points. The effect of independent parameters on biodiesel conversion was analyzed by the second-order polynomial equation as shown in Eq. (2).

$$\begin{aligned} \% \text{ Biodiesel conversion} = & \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 AB \\ & + \beta_5 AC + \beta_6 BC + \beta_7 A^2 \\ & + \beta_8 B^2 + \beta_9 C^2 \end{aligned} \quad (2)$$

where A, B, and C are the coded parameters considered for optimization. β_0 represents constant value. The terms β_1 , β_2 , and β_3 represent the linear coefficients. The terms β_4 , β_5 , and β_6 represent the interaction coefficients with β_7 , β_8 , and β_9 representing the quadratic coefficients.

Results and discussion

Catalyst characterization

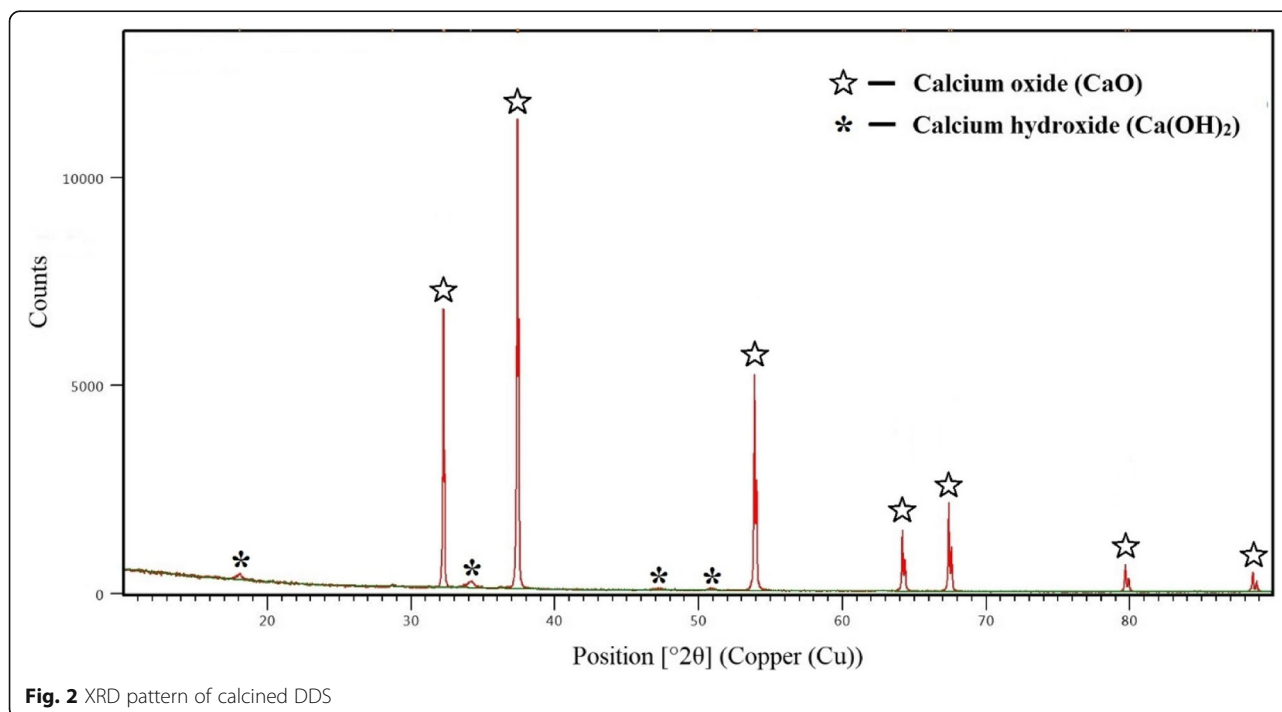
XRD analysis

XRD pattern of calcined DDS is represented in Fig. 2. The apexes at 2θ of 32.2, 37.4, 53.9, 64.2, 67.4, 79.7, 88.6° correspond to CaO. The obtained result shows similarity with

calcined angel wing shell [4], obtuse horn shells [25], bivalve clam shells [45], mussel shells [46], golden snail shells [47] and lobster shells [48]. The highly confined intensity peaks of DDS (calcined) represent the CaO presence and high crystallinity of the sample [33]. Minor peaks at 18.1, 34.2, 47.2 and 50.9° represent the presence of Ca(OH)₂ due to the interaction of CaO with the residual moisture present in the air [30, 45]. Temperature acts a major part in the transformation of CaCO₃ to CaO [25]. The absence of peaks at 26.2, 33.1, 37.8, 45.8, and 52.4° represents the absence of CaCO₃ in calcined DDS which confirms the complete transformation of calcium carbonate to calcium oxide [47].

FTIR analysis

Figure 3 shows FTIR spectra of DDS (uncalcined and calcined). For uncalcined DDS, distinct peaks were noticed at 707, 859, 1476, and 2345 cm^{−1} while for calcined DDS, the characteristic peaks were identified at 868, 1413, 1472, and 3637 cm^{−1}. The absorption band appeared in uncalcined DDS at 707, 859 and 1476 cm^{−1} indicates the in-plane, out-of-plane vibration and asymmetric stretching modes of CO₃^{2−}, respectively [49]. For calcined DDS, the band at



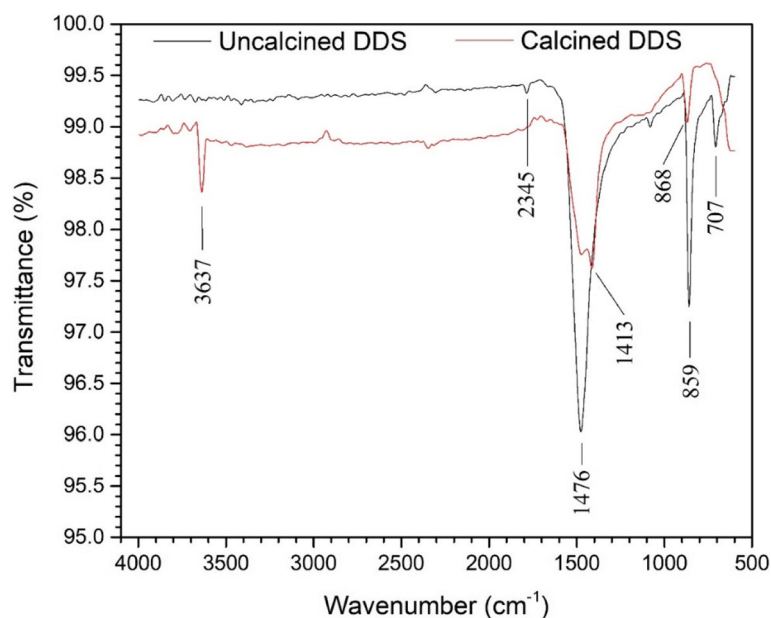


Fig. 3 FTIR spectra of calcined and uncalcined DDS

around 1413 cm^{-1} represents bending vibration of O-Ca-O group [48] and the band at 868.8 cm^{-1} for calcined DDS represents shift of CO_3^{2-} molecules to higher energy [45]. The band around 3637 cm^{-1} in calcined DDS was attributed to -OH group asymmetric stretching vibration of calcium hydroxide which may arise owing to the interaction of calcined DDS to surrounding air [50].

SEM and EDAX analysis

Figure 4a and b display the surface morphology of uncalcined and calcined DDS. The uncalcined DDS shown

in Fig. 4a shows relatively smooth and undistorted flat surface while the calcined DDS illustrated in Fig. 4b shows that particles are highly irregular in shape and are seen as aggregates. Similar morphological changes were reported in obtuse horn shells [25], lobster shells [48], angel wing shell [51], and clam shell [52]. During calcination (900°C -3 h), the undistorted structure of uncalcined DDS transformed into porous clumsy-like structure clearly indicates that calcination at higher temperature is appropriate for complete transformation of CaCO_3 to CaO [51]. Elemental composition of DDS

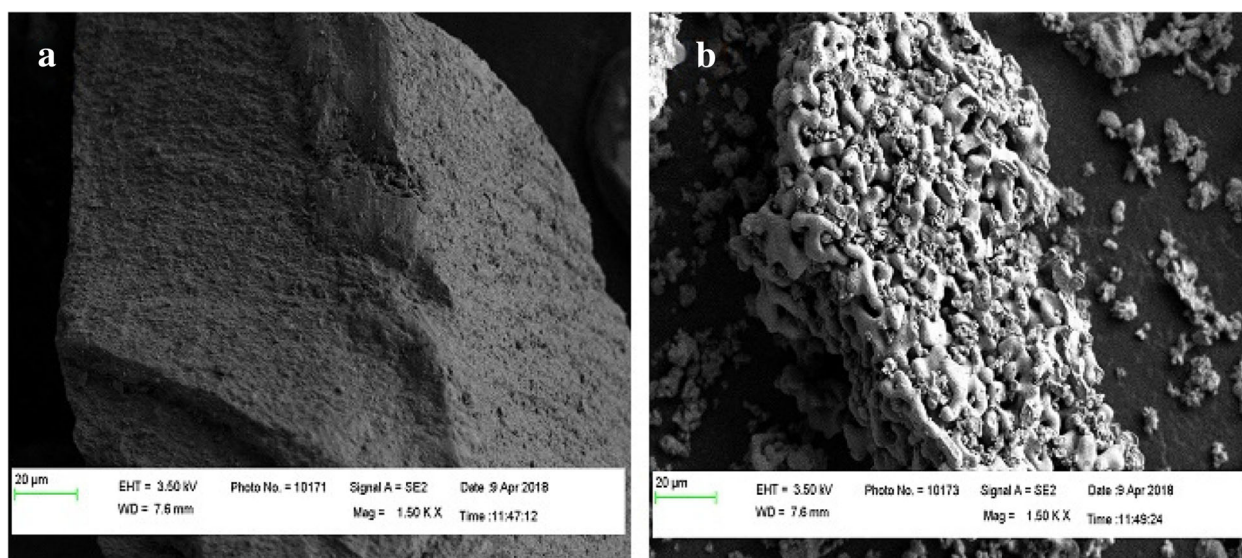


Fig. 4 SEM image of (a) uncalcined DDS and (b) calcined DDS

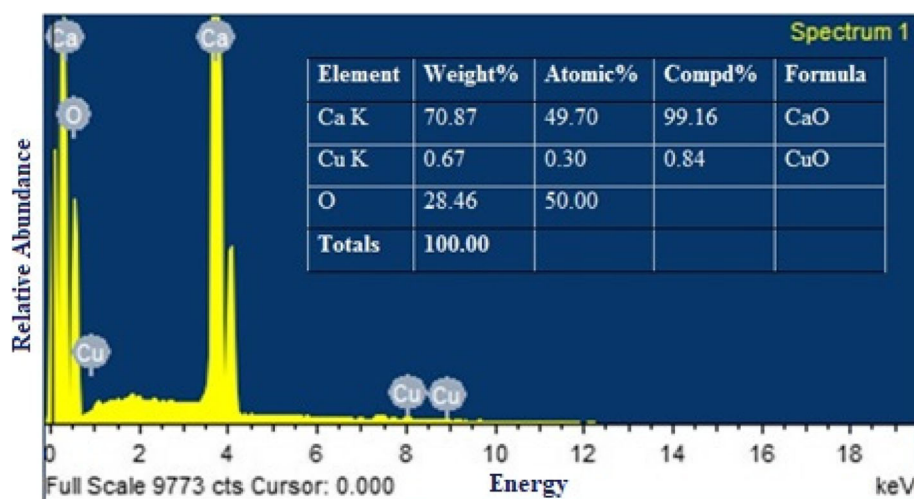


Fig. 5 EDAX analysis of calcined DDS

derived catalyst was analyzed using EDAX with the result presented in Fig. 5. From EDAX, it is evident that calcium is the major component present in the DDS.

Physicochemical properties of CIO and WCO

The acid value of the raw CIO and WCO were determined as 65 mg of KOH g⁻¹ of oil and 0.25 mg of KOH g⁻¹ of oil respectively. Physicochemical properties of crude WCO and CIO are represented in Table 2. In the present work, methyl ester production via esterification followed by transesterification process was carried out. Different proportions of WCO and CIO were mixed and its corresponding acid value was tabulated (Table 3). The acid value of raw CIO:WCO 50:50 v/v was 33.4 mg of KOH g⁻¹ of oil and was subjected to esterification which reduced the acid value to 5.6 mg of KOH g⁻¹ of oil. Transesterification of esterified mixture further diminishes the acid value to <0.5 mg of KOH g⁻¹ of oil.

Optimization of biodiesel production

Central composite design based RSM

To maximize biodiesel conversion through transesterification process and to analyze the relationship between methanol to esterified CIO-WCO volumetric ratio, reaction time and calcined DDS concentration, RSM-CCD was employed in this study. Table 4 shows the CCD matrix for the biodiesel production from CIO-WCO mixture. The results of CCD were subject to multiple regression analysis initially. It is noticed that the selected model (quadratic) is well suitable for analysis since it is not aliased. ANOVA shown in Table 5 represents that the model is statistically significant since it shows smaller p-value and larger F value. The predicted values are in accordance with experimental values and this emphasizes the better correlation among the input factors and the methyl ester conversion. The predicted R² = 0.9349 and adjusted R² = 0.9862 shows that the quadratic model is appropriate to predict the biodiesel conversion. The coded equation for methyl ester conversion is presented in Eq. (3).

Table 2 Physicochemical properties and fatty acid composition of CIO and WCO

Properties	Waste cooking oil	<i>Calophyllum inophyllum</i> oil	Mixture of WCO and CIO (50–50%)
Acid value = (mg of KOH g ⁻¹ of oil)	0.25	65	33.4
Density at 27 °C (kg m ⁻³)	918	929	922
Kinematic viscosity at 40 °C (mm ² s ⁻¹)	26.0	59.3	40.6
Saponification value (mg of KOH g ⁻¹)	193	382	292
Palmitic acid (%)	10.1	22.3	17.1
Oleic acid (%)	84.6	55.0	57.3
Linoleic acid (%)	–	17.0	15.5
Stearic acid (%)	–	4.4	4.2
Others (%)	5.3	1.4	6.0

Table 3 Different blends of CIO and WCO and its corresponding acid values

S. No	<i>Calophyllum inophyllum</i> oil (%)	Waste cooking oil (%)	Acid value (mg of KOH g ⁻¹ of oil)
1	100	0	65.0
2	75	25	44.6
3	50	50	33.5
4	25	75	15.4
5	0	100	0.3

Biodiesel conversion (%) = + 76.46 – 3.38 * A – 10.75

* B – 4.94 * C – 4.56 * AB

+ 1.73 * AC + 17.92

* BC – 15.09 * A² – 0.0876

* B² – 0.9202 * C²

(3)

where A, B, and C represent the coded forms of DDS concentration (wt%), methanol to esterified CIO-WCO volumetric ratio and reaction time (min). The term AB, AC, and BC represents the interaction terms between the parameters. Terms A², B², and C²

represent the quadratic effects of the independent parameters.

Impact of calcined DDS concentration and methanol to esterified CIO-WCO ratio on methyl ester conversion

Figure 6a presents the impact of DDS concentration and methanol to esterified CIO-WCO volumetric ratio on methyl ester production with time being fixed constant as 150 min. Increase in the conversion of oil to methyl esters was perceived with increased catalytic concentration and decreased with increased methanol to esterified CIO-WCO volumetric ratio. The higher amount of DDS enhanced the rate of reaction and hence higher reaction rate is achieved at a shorter reaction time [21]. At 8 wt% DDS and 62%

Table 4 CCD matrix for the biodiesel production from CIO-WCO mixture

Run	A: Catalyst concentration wt%	B: Methanol to oil ratio % (v/v)	C: Reaction time min	Experimental biodiesel conversion %	Predicted biodiesel conversion %
1	4.64	72	150	38.8	39.5
2	8	72	150	76.7	76.5
3	6	82	180	67.0	68.8
4	11.36	72	150	29.1	28.1
5	10	62	180	48.2	51.2
6	10	82	180	59.1	56.4
7	6	82	120	49.1	46.3
8	8	72	99.6	83.0	82.2
9	10	62	120	95.0	93.4
10	8	55.18	150	95.1	94.3
11	6	62	120	91.6	94.5
12	8	72	150	76.7	76.5
13	10	82	120	23.9	27.0
14	8	72	150	76.7	76.5
15	8	72	150	76.2	76.5
16	8	72	150	75.8	76.5
17	8	88.82	150	57.7	58.1
18	8	72	150	76.5	76.5
19	8	72	200.5	65.0	65.6
20	6	62	180	48.2	45.3

Table 5 ANOVA table for transesterification process

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8140.50	9	904.50	151.37	< 0.0001	significant
A-Catalyst concentration	155.87	1	155.87	26.09	0.0005	
B-Methanol to oil ratio	1578.11	1	1578.11	264.10	< 0.0001	
C-Reaction time	333.72	1	333.72	55.85	< 0.0001	
AB	166.44	1	166.44	27.85	0.0004	
AC	23.91	1	23.91	4.00	0.0734	
BC	2568.65	1	2568.65	429.87	< 0.0001	
A ²	3281.85	1	3281.85	549.23	< 0.0001	
B ²	0.1106	1	0.1106	0.0185	0.8945	
C ²	12.20	1	12.20	2.04	0.1835	
Residual	59.75	10	5.98			
Lack of Fit	59.04	5	11.81	82.63	< 0.0001	
Pure Error	0.7145	5	0.1429			
Cor Total	8200.25	19				

R²–0.9927; Adj. R²–0.9862; Pred. R²–0.9349

methanol to esterified CIO-WCO volumetric ratio, methyl ester conversion was about 87%. Increasing the volumetric ratio from 62 to 82% reduced the methyl ester conversion (65%). This clearly implies that methanol has an inverse relation with biodiesel conversion. Excess methanol leads to difficulty in separation because it increases the glycerol solubility in product phase [37]. Increasing DDS concentration beyond 9 wt%, decreased conversion was found due to the meagre diffusion among oil, methanol and solid DDS phases while using an excess amount of catalyst. A similar trend was reported with CaO derived from chicken and ostrich egg shells for biodiesel production from WCO [21] and for CIO-WCO mixture using KOH as a catalyst [53]. From ANOVA table, it was found that the interactive effect between calcined DDS concentration (A) and methanol to esterified CIO-WCO ratio (B) on methyl ester conversion is significant since the p-value (0.0004) was found to be much less than 0.05.

Impact of calcined DDS concentration and reaction time on methyl ester conversion

Figure 6b illustrates the impact of catalyst concentration and reaction time on the conversion of CIO-WCO to methyl esters. At 6 wt% calcined DDS and 120 min reaction time, methyl ester conversion was found to be 70%. Conversely, a minor decline in conversion (57%) was seen when the time was increased to 180 min. Besides, increasing catalyst concentration beyond 8 wt% and holding the time at 150 min, the methyl ester conversion was around 76%. However,

increasing the time resulted in decreased methyl ester conversion (70%). At 10 wt% calcined DDS loading and 120 min transesterification time, 60% conversion was achieved. Furthermore, increasing the transesterification time from 120 to 180 min exhibited decreased conversion (54%). From the Fig. 6b, it was observed that between 7 and 8 wt% of catalyst concentration and transesterification time of 120 min, maximum methyl ester conversion (81%) was achieved. This clearly indicated that excess reaction time resulted in decreased biodiesel conversion [54]. From ANOVA table, it was observed that the interactive effect between calcined DDS concentration (A) and reaction time (C) on methyl ester conversion is insignificant since the p-value (0.0734) was found to be slightly greater than 0.05.

Impact of methanol to esterified CIO-WCO oil ratio and reaction time on methyl ester conversion

Figure 6c represents the impact of methanol to esterified CIO-WCO volumetric ratio and reaction time on methyl ester conversion. At a minimum level of methanol to esterified CIO-WCO volumetric ratio and reaction time, a maximum methyl ester conversion was observed. Besides, increasing the methanol ratio decreases the methyl ester conversion. This clearly indicates that methanol to esterified CIO-WCO volumetric ratio has greater impact on methyl ester conversion. Also, the use of excess methanol has a negative impact on biodiesel conversion. Similar observations were reported by Ezekannagha et al. [43] on the transesterification process of lard oil optimized using RSM-CCD. From ANOVA table, it was evident that the interactive effect between methanol to esterified CIO-WCO ratio (B)

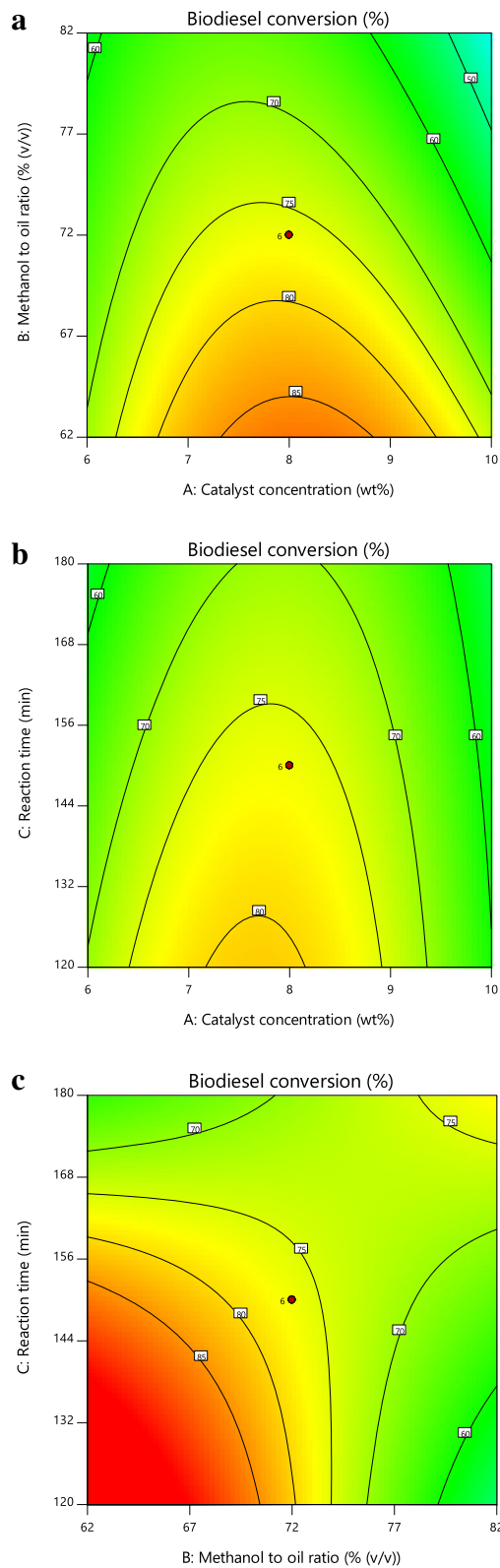


Fig. 6 Effect of parameters on biodiesel conversion (a) catalyst concentration and methanol to oil volumetric ratio, (b) catalyst concentration and reaction time, and (c) methanol to oil volumetric ratio and reaction time

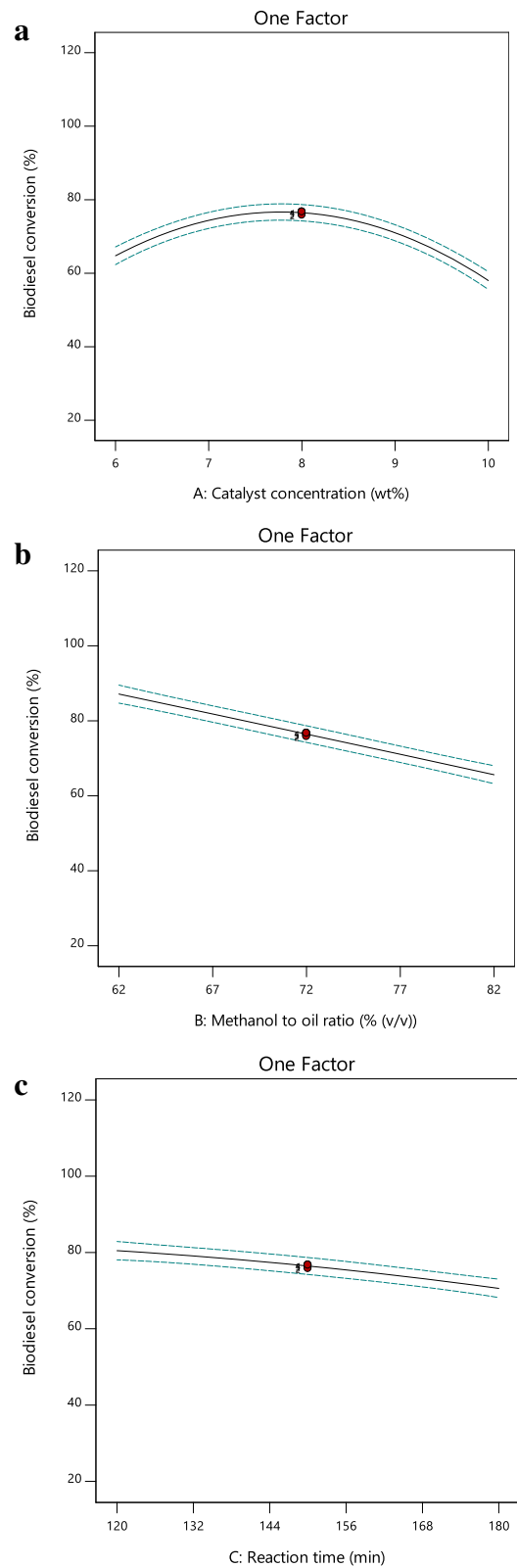


Fig. 7 Effect of individual parameters on methyl ester conversion (a) catalyst concentration, (b) methanol to oil volumetric ratio, and (c) reaction time

and reaction time (C) on methyl ester conversion is highly statistically significant since the p-value (<0.0001) was found to be very minimum. Furthermore, the graphs presented in Fig. 7a, b and c show the individual parameter effect such as calcined DDS concentration, methanol to esterified CIO-WCO ratio, and reaction time on the methyl ester conversion. The synthesized DDS catalyst concentration was varied from 6 to 10 wt% as shown in Fig. 7a and it was observed that the catalyst concentration significantly improved the methyl ester conversion up to 8 wt%. Further, increase in the catalyst concentration reduces the methyl ester conversion which can be attributed to the poor mass transfer occurrence in the transesterification reaction due to the high solid loading. However, methanol to oil ratio plays a highly significant role in methyl ester conversion due to its low p-value (<0.0001) and very high F-value (264) followed by reaction time ($p=0.0001$ and $F=56$) and catalyst concentration (p -value of 0.0005).

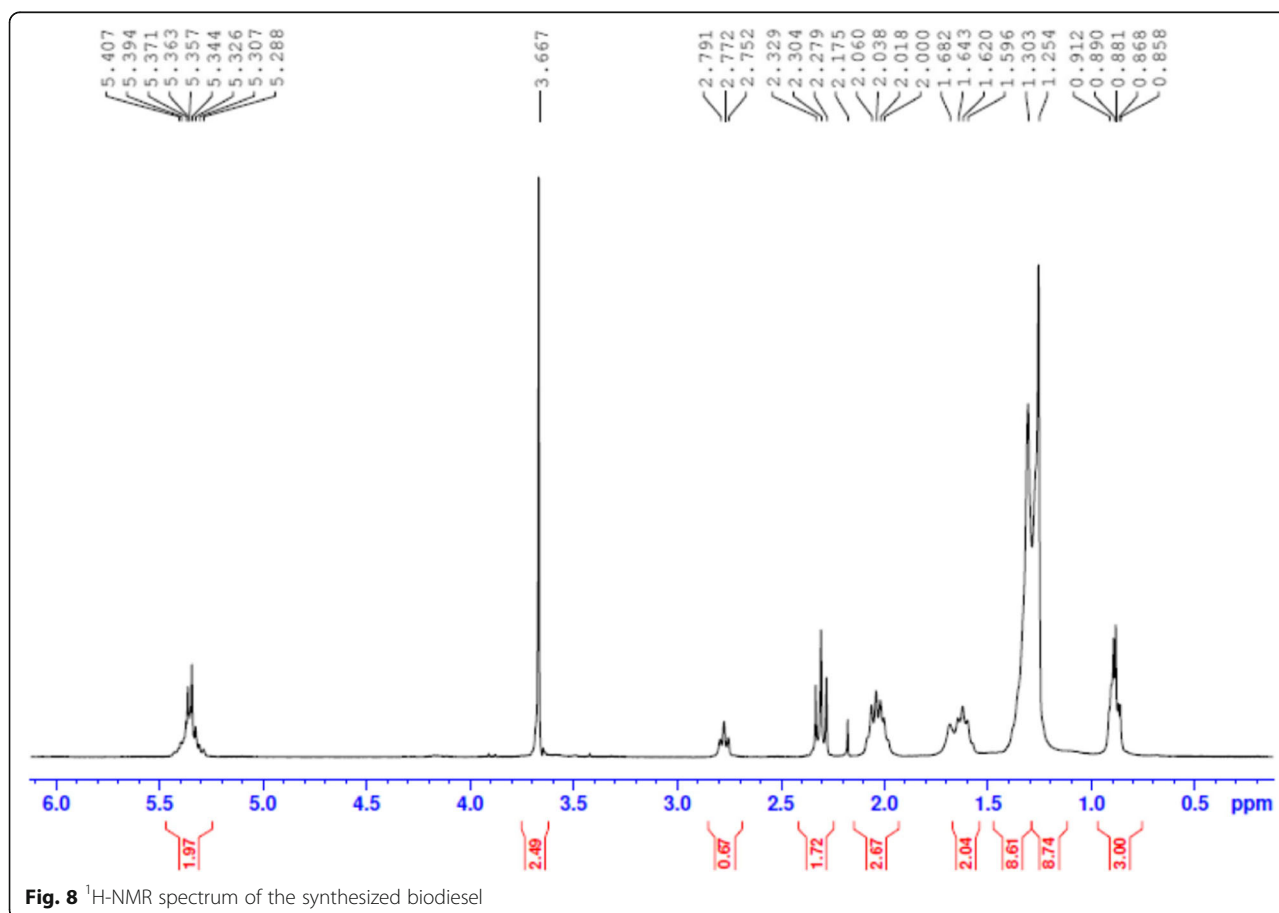
¹H-NMR spectrum of CIO-WCO derived methyl esters

The ¹H-NMR spectrum of the CIO-WCO derived methyl esters is presented in Fig. 8 and the corresponding

biodiesel conversion evaluated by Eq. (1) was determined as 96.5%.

Conclusions

In the present study, DDS derived CaO was employed as a cost effective heterogeneous catalyst for methyl esters production from CIO-WCO via transesterification process. Utilizing low-cost WCO as feedstock makes biodiesel production more economical and also prevents illegal landfilling thereby creating a safe environment. Also, the mixing of WCO with non-edible oil like CIO will act as a potential feedstock owing to the limited prevalence of CIO throughout the year. Blending of CIO with WCO at different proportions was evaluated to lower the acid value and the opted CIO-WCO (1:1 volumetric) mixture showed a moderate acid value of 33.4 mg of KOH g⁻¹ oil. Further, to diminish the acid value of CIO-WCO mixture, the esterification reaction was executed using sulphuric acid as homogeneous catalyst and the acid value was further decreased to 5.6 mg of KOH g⁻¹ of oil. In transesterification process, the effect of transesterification time, volumetric ratio of methanol to esterified CIO-WCO and calcined DDS concentration on biodiesel conversion was investigated using CCD of



RSM. The ANOVA analysis indicated that the volumetric ratio of methanol to esterified CIO-WCO had a greater impact on methyl esters conversion. ¹H-NMR results revealed the maximum experimental methyl esters conversion of 96.5% at a catalyst concentration of 7.5 wt%, methanol to esterified (CIO-WCO) oil volumetric ratio of 63.8%, reaction time of 129.3 min, stirrer speed of 450 rpm and transesterification temperature of 65 °C. The observed experimental methyl esters (biodiesel) conversion results were in agreement with the predicted biodiesel conversion of 97.5%.

Acknowledgments

SN is grateful to Science and Engineering Research Board (SERB), New Delhi, India for Early Career Research Award (ECR) and MB is thankful to SERB for the award of Junior Research Fellowship (JRF).

Authors' contributions

All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Received: 2 September 2018 Accepted: 21 February 2019

Published online: 06 May 2019

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