Biodiesel Production by Esterification of Ricinoleic Acid over a Series of Synthesized Sulfated Zirconia Catalysts

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Abstract

A series of sulfated zirconia (SZ) were synthesized and evaluated for catalytic esterification of ricinoleic acid obtained from the castor oil with butanol at 110 °C. The effect of alcohols’ chain length was studied using butanol (C4), propanol (C3), ethanol (C2) and methanol (C1) at 65 °C, and reflux of corresponding alcohol boiling points. The synthesized catalysts were characterized using nitrogen porosimetry, X-ray powder diffraction, thermogravimetric analysis and Diffuse Reflectance Infrared Fourier Transform Spectroscopy. Analysis of ricinoleic conversion was performed using gas chromatography. Sulfuric acid loading improved the surface area of zirconia at a lower dose. The surface areas of the catalysts increased as the concentrations of sulfuric acid solution were increased from 0.025 to 0.10 M, after which the decline was observed. SZ obtained at 0.05 M H2SO4 (0.05SZ) gave the optimal catalytic activity compared to the other series of SZ used. The ricinoleic acid conversion decreased with increase of alcohol alkyl chain from C1-C4 at 65 °C, but increased under the reflux temperature of the corresponding alcohols, with the maximum conversion being 47% at 118 °C for the reaction involving butanol. Overall, the synthesized SZ catalysts are deployable in biodiesel production from castor oil upon optimizing other conditions.

Keywords: Ricinoleic acid; Sulfated zirconia; Biodiesel production.

Introduction

Ricinoleic acid is the major component of the castor oil extracted from the seeds of castor plant (*Ricinus communis* L.; Euphorbiaceae) (Purohit et al. 2012, Mubofu 2016). Castor oil is a naturally occurring triglyceride composed of a glycerol plus three fatty acids, of which approximately 90% of the fatty acid chains are ricinoleic acids (Sreenivas et al. 2011). The castor plant grows wildly in large quantities in tropical and sub-tropical countries, including Tanzania. Its growth requires minimal cultivation conditions, hence represents a potential second-generation biofuel feedstock. Therefore, ricinoleic acid being obtainable from such non-edible vegetable oil is considered among the promising candidates for biodiesel production.

Esterification reaction represents one of the most important reactions for the production of different useful industrial materials (Sert and Atalay 2017, Shagufta et al. 2017). Esters with low molecular weights are commonly used as fragrances or flavours, and are found naturally in essential oils. Esterification of long alkyl fatty acids from vegetable oils is a vital process
in biodiesel productions, serving as an alternative fuel source (Misi et al. 2010, Behr et al. 2012, Viele et al. 2013, Drelinkiewicz et al. 2014, Saravanan et al. 2015). Such esterification reactions are due to the weak acidity of the carboxylic acid. However, the conversion reaction takes a long time due to reversibility and reaction low rate in the absence of a catalyst (Jyoti et al. 2016). Thus, acid catalysts in esterification are crucial since the acid acts as a proton donor, hence enhancing the process (Abdoulmoumine 2010). The application of base catalysts in transesterification of oils containing a lot of free fatty acids is challenged due to the formation of soap in the process. Therefore, the use of acidic catalyst(s) in esterification is preferred in order to avoid such consequential effects (Khire et al. 2012, Arora et al. 2015, Aboelhassan et al. 2017). Esterification and other conversion reactions of ricinoleic acid using homogenous catalysts such as sulfuric acid, ruthenium and p-toluenesulfonic acid for biodiesel production and other useful products such as oleochemicals and saturated estolide esters have been reported (Salimon et al. 2011, Behr et al. 2012, Salimon et al. 2012 Narayan et al. 2017, Wang and Sun 2017). However, the use of homogenous catalysts is not environmentally friendly and consequently associated with difficulties in their separation from the products.

Heterogeneous catalysts are preferably used over homogenous catalysts for the reasons such as easier separation and reusability (Hermida et al. 2008, Marchetti and Errazu 2008a, Yan et al. 2010, Brahmkhatri and Patel 2011). Environmentally benign modified solid acid catalysts have been successfully applied in different organic reactions including esterification (Reddy et al. 2005, López et al. 2008, Jothiramalingam and Wang 2009, Patil et al. 2011, Diamantopoulos et al. 2015). The use of solid acid catalysts for esterification reaction generally results into production of biodiesel in good yields (Marchetti and Errazu 2008b, Melero et al. 2010, Park et al. 2010, Narkhede and Patel 2013, Saravanan et al. 2014, Shagufta et al. 2017). Among heterogeneous acid catalysts, sulfated zirconia (SZ) has been found to be a good candidate due to its low cost, low toxicity, super acidic properties, good thermal stability, and non-carcinogenicity effects (Park et al. 2010). In addition, an amphoteric nature of zirconia makes it very useful and valuable in catalytic activities. Various forms of zirconia derived catalysts have been deployed in biodiesel production (Park et al. 2010, Saravanan et al. 2012, Narkhede and Patel 2013, Patel et al. 2013, Saravanan et al. 2014, Saravanan et al. 2015, Osatiashtiani et al. 2016, Shagufta et al. 2017, Guldh e et al. 2017, Booramurthy et al. 2020, Changmai et al. 2020, Rizwanul Fattah et al. 2020, Vasić et al. 2020). However, none of the sulfated zirconia had been studied for esterification of ricinoleic acid. Thus, a series of sulfated zirconia were prepared and evaluated for their catalytic activities in esterification of ricinoleic acid (C18). In an attempt to harness the biodiesel from castor oil, ricinoleic acid isolated therefrom was esterified with alcohols, including methanol (C1), ethanol (C2), propanol (C3) and butanol (C4). Studies have indicated that the conversion of the carboxylic acids to biodiesel depends on reaction parameters such as alcohol to acid molar ratios, type of catalyst used, temperature of the reaction and the chain length of the alkyl group of an alcohol (Arora et al. 2015). In previous studies, SZ catalysts were deployed in the esterification of carboxylic acids such as acetic acid, propanoic acid, hexanoic acid, lauric acid and palmitic acid with light alcohols (Osatiashtiani et al. 2016). In the present work, esterification reaction was extended to ricinoleic acid, a major constituent of castor oil and an ideal source of non-edible triglyceride. The catalytic activities of a series of the synthesized sulfated zirconia were examined at different temperatures during esterification of ricinoleic acid with different alcohols.
Materials and Methods

Materials and chemicals used

Castor seeds used as source of ricinoleic acid were collected from Dodoma region, Tanzania. Hydrochloric acid, potassium hydroxide, n-hexane, tert-butyl ether, methanol, ethanol, propanol, butanol anhydrous magnesium sulfate, sulfuric acid, zirconium hydroxide, dihexylether, and dichloromethane were bought from Sigma Aldrich and were used without further purification. In contrast, ricinoleic acid was isolated from the castor oil.

Extraction of castor oil and isolation of ricinoleic acid

Extraction of castor oil was achieved by Soxhlet extraction as per our recently reported method (Elimbinzi et al. 2020). In brief, 10 g of crushed castor seeds was placed in a thimble that was then fitted at the centre of the extractor. The castor oil was then obtained by using 250 mL of n-hexane as the extracting solvent heated at 60 °C for 2 h in a round bottom flask connected to a reflux condenser. The n-hexane vapour was condensed and passed through the thimble, then siphoned back to the flask. Roughly, 2 mL of castor oil was obtained for each 10 g of crushed castor seeds after evaporation of residual hexane. This procedure was repeated several times to obtain 200 mL from 250 g of the castor seed.

Isolation of ricinoleic acid followed the method developed by Vaisman et al. (2008) with some modifications (Elimbinzi et al. 2020), whereby 250 g of castor oil was hydrolyzed by refluxing with 60 g of potassium hydroxide in 500 mL of ethanol for 1 h. Ethanol was evaporated and the residue dissolved in 1.2 L of water followed by acidification of the mixture with concentrated hydrochloric acid to pH = 1. Tert-butyl ether (50 mL) was added to the acidified mixture to extract ricinoleic acid. The organic layer (top layer) which contained ricinoleic acid was separated from the aqueous layer using a separating funnel, washed with 2 L of warm water and dried using magnesium sulfate. The solvent was evaporated under vacuum using rotary-evaporator to afford ricinoleic acid.

Preparation of sulfated zirconia (SZ) catalysts

A series of sulfated zirconia (SZ) catalysts with different sulfate ion loading were prepared as previously described by Osatiashtiani et al. (2016). The procedure involved impregnating 50 g of Zr(OH)4 (MEI chemicals XZO-880/01) with 50 mL of sulfuric acid solution of molarity 0.025–0.25 M. The mixture was stirred for 5 h at ambient temperature, filtered and dried overnight at 80 °C and then calcinated at 550 °C for 3 h. The prepared series of sulfated zirconia catalysts were termed as 0.025SZ, 0.05SZ, 0.1SZ, 0.25SZ corresponding to molarity of the acid used. The catalysts were stored and used without further pre-treatment.

Characterization of sulfated zirconia catalysts

N2 porosimetry was performed on a Quantachrome Nova 4000 porosimeter, with BET surface area calculated over the range of P/Po = 0.03–0.19, in which a linear relationship was maintained. Pore size distributions were obtained using BJH model to the desorption branch of the isotherm. Structural order with phase identification was evaluated by means of X-ray powder diffraction (XRD) on a Bruker D8 Advance diffractometer using the Cu Kα line in the range 2θ = 10–80° with a step size of 0.04°. Thermogravimetric analysis (TGA) was used to determine thermal stability of the synthesized catalysts. The TGA was performed using PerkinElmer Pyris 6 thermal analyzer between 40 and 800 °C (ramp rate 10 °C/min) under flowing N2 (30 ml/min). Functional group analysis was done by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) conducted in air using a Thermo Nicolet 6700 FTIR spectrometer. A well-mixed sample containing 25 mg of catalyst powder and 225 mg KBr were prepared and compressed into the sample holder. KBr was used for a background correction.
Evaluation of catalytic performance

Batch esterification was performed at 110 °C using a Radleys Carousel Reactor Station. 150 mmol of butanol, 5 mmol of ricinoleic acid (C18) with 0.5 mmol of dihexyl ether (used as an internal standard) and 100 mg of the SZ series were added to the reactor station. Esterification of ricinoleic acid with other alcohols (methanol, ethanol and propanol) was done using the same quantity of catalysts at 65 °C and the reflux temperature for ethanol, propanol and butanol based on the boiling points of the respective alcohol. Samples of the reaction mixture were collected periodically, filtered and diluted with dichloromethane prior to analysis using gas chromatography (GC). The reaction was monitored using a Varian 450-GC equipped with 1079 programmable, direct on-column injector and Phenomenex ZB-1 HT Inferno 15 m × 0.53 mm × 0.15 μm capillary column. All catalytic profiles were recorded as an average of 3 injections per sample. Conversions were reported based on the change in the concentrations of the ricinoleic acid, with initial rates calculated over the first hour of the reaction. Turnover frequencies (TOF) were determined from the initial reaction rate which was normalized to the acid site loadings as determined by propylamine adsorption/thermogravimetric-mass spectroscopy (TGA-MS).

Results and Discussion

Materials characterisation

Porosity properties of the unmodified zirconia and sulfated zirconia were obtained using N$_2$ porosimetry at 77 K. The BET method was used to study the surface area while the BJH approach was used for pore volume and diameter analyses. All samples exhibited type IV isotherm with hysteresis loop as presented in Figure 1. This indicated capillary condensation of the mesoporous materials. The BET graphs showed straight lines for unmodified zirconia and sulfated zirconia. The BET surface area was observed to increase with the concentration of sulfuric acid solution used to load sulfate ranging from 0.025 to 0.1 M. This was ascribed to changing from less-porous zirconia (unmodified) to a more porous material, supporting the formation of mesoporous sulfated zirconia after calcination. Such increase in the surface area of sulfated zirconia due to the formation of porous surface involving the sulfate species and the supporting oxides is phenomena well reported (Reddy et al. 2006). However, a decrease of the surface area was observed at higher concentration of sulfuric acid as indicated in Table 1. This was attributed to a tendency of the excess SO$_4^{2−}$ to block some of the pores that significantly reduces surface area of the catalyst (Reddy et al. 2006), hence a postulate for the observed unordered pattern. For instance, the surface area of unmodified zirconia, 82 m$^2$/g, when impregnated with sulfuric acid increased to 164 m$^2$/g at 0.1 M and eventually declined to 154 m$^2$/g at 0.25 M. The shift in hysteresis loop from 0.65–0.8 to 0.43–0.6 P/P$_o$ was observed with increasing the concentration of sulfuric acid loading. Such shift could be due to an increase of sulfate loading resulting to a decrease in the average pore volume and diameter. For example, BJH pore diameter declined from 6.6 nm of unmodified zirconia to 3.4 nm for materials loaded with 0.025–0.25 M of sulphuric acid. On the other hand, the pore size distribution was affected as the concentration of the acid was changing. This could be due to the induction of additional microporosity caused by higher acid loading, hence damaging mesoporosity (Osatiashtiani et al. 2014). The textural properties of a series of SZ catalysts synthesized using different acid loading concentration are summarised in Table 1.

The XRD patterns of the synthesized catalysts show that unmodified zirconia portrayed the presence of a mixture of monoclinic and tetragonal phase, while the sulfated zirconia exhibited prominent lines due to a tetragonal phase. This indicates that the impregnation of sulfate ions into zirconia strongly influenced the phase modification from thermodynamically more stable monoclinic phase to metastable tetragonal
phase. This is well noticeable from the diffractograms in Figure 2, with the characteristic peaks corresponding to tetragonal zirconia (around $2\theta = 30^\circ$, $35^\circ$) becoming more intense than that of unmodified exhibiting monoclinic zirconia phase (around $2\theta = 28^\circ$, $31^\circ$) corroborating previous observations (Reddy et al. 2006, Adamski et al. 2007, Shi et al. 2016). The increase in the concentration of sulfuric acid solution during acidification of zirconia increased the phase transformation. Thus, addition of sulfate ions significantly changed the properties of zirconia.

![Figure 1: Isotherms (a) and pore size distribution (b) of unmodified and sulfated zirconia at different concentrations.](image)

**Table 1:** Textural properties of zirconia and SZ catalysts at different acid loading concentrations

<table>
<thead>
<tr>
<th>ID</th>
<th>[H$_2$SO$_4$]/ M</th>
<th>Surface area/m$^2$ g$^{-1}$</th>
<th>Pore diameter/ nm</th>
<th>Pore volume/ cc g$^{-1}$</th>
<th>Acid loading/ mmol g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>0.0</td>
<td>82</td>
<td>6.6</td>
<td>0.45</td>
<td>0.22</td>
</tr>
<tr>
<td>0.025SZ</td>
<td>0.025</td>
<td>132</td>
<td>3.4</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>0.05SZ</td>
<td>0.05</td>
<td>131</td>
<td>3.4</td>
<td>0.40</td>
<td>0.75</td>
</tr>
<tr>
<td>0.10SZ</td>
<td>0.10</td>
<td>164</td>
<td>3.4</td>
<td>0.33</td>
<td>1.30</td>
</tr>
<tr>
<td>0.25SZ</td>
<td>0.25</td>
<td>154</td>
<td>3.5</td>
<td>0.31</td>
<td>1.51</td>
</tr>
</tbody>
</table>

![Figure 2: Wide angle XRD patterns for unmodified and sulfated zirconia.](image)
TGA and DTG analysis for zirconia and SZ series as indicated in Figure 3, showed a weight loss at around 100 °C which is attributed to the loss of water adsorbed on the surface of the catalyst. Another peak was observed at around 500–650 °C indicating a possible decomposition of sulfate ion coordinated to zirconia, while the weight loss observed above 650 °C was linked to the decomposition of sulfonyl group from the surface of the catalyst. It should be noted that calcination at higher temperatures leads to a change from ionic to covalent character with S=O bond, accounting for the observed two regimes associated with surface sulfate losses in TGA. The latter bond type is responsible for strong acidic active sites generated on the SZ catalytic surfaces (Signoretto et al. 2005, Reddy et al. 2006). The intensity of the DTG peaks increased with the concentration of sulfuric acid used to impregnate zirconia. Weight loss was only observed at around 100 °C for unmodified zirconia confirming there was no sulfate in zirconia before functionalization. In the DTG plot, a peak at around 650 °C was observed for all SZ series. This was attributed to the decomposition of sulfate attached in zirconia. Generally, TGA analysis portrayed good thermal stability for all synthesized solid supports and their derived catalysts.

**Figure 3**: TGA (a) and DTG (b) plots for unmodified and sulfated zirconia.
DRIFTS analysis as depicted in Figure 4, was carried out to confirm the functional groups present in the unmodified zirconia and sulfated zirconia catalysts. The absorption bands at 1026–1069, 1143 and 1222–1243 cm\(^{-1}\) are considered as characteristic peaks from S-O stretching of the coordinated \(\text{SO}_4^{2-}\) on the surface of sulfated zirconia (SZ). S=O stretching band attached to the metal oxide surface was observed at 1389 cm\(^{-1}\). The broad peak observed at 3375 cm\(^{-1}\) was assigned to O-H stretching band of adsorbed water on the surface of both modified and unmodified zirconia. 

![Figure 4: The DRIFT spectra of unmodified and sulfated zirconia.](image)

**Esterification reaction**

**Catalysts activity**

The activity of unmodified and a series of sulfated zirconia catalysts were evaluated for esterification reactions. The synthesized series of SZ were first evaluated for the esterification of ricinoleic acid with butanol at 110 °C to evaluate the impact of sulfate impregnation on zirconia, the results of which are presented in Figure 5 and Table 2. The SZ catalysts (0.025SZ, 0.05SZ, 0.10SZ and 0.25SZ) showed higher conversion of ricinoleic acid compared to unmodified zirconia (ZrO\(_2\)) indicating increased catalytic performance by sulfate impregnation. As seen in Figure 5 and Table 2, optimum acid sites attained when 0.05 M sulfuric acid was impregnated to zirconia led to higher conversion and initial reaction rate compared to other concentrations of sulfuric acid used. This observation could be associated with the increase in loaded acid active sites as the concentration of sulfuric acid increased up to the maximum plateau at which the monolayer was fully covered. The rate limiting step in esterification reaction is the nucleophilic attack of alcohols to the carbonium ion formed through proton donation to the acid (Srilatha et al. 2009 Vieira et al. 2013, Osatiashtiani et al. 2016). Therefore, the increase of acid site strength across a series of SZ had a positive impact on the efficiency of the carbonium ion formed. Table 2 provides the summary of esterification of ricinoleic acid with butanol at 110 °C over a series of SZ catalysts.

**Table 2: Esterification of ricinoleic acid with butanol over different catalysts at 110 °C**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>6 h conversion (%)</th>
<th>Initial rate (mmol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO(_2)</td>
<td>22.0</td>
<td>0.4</td>
</tr>
<tr>
<td>0.025SZ</td>
<td>29.1</td>
<td>0.4</td>
</tr>
<tr>
<td>0.05SZ</td>
<td>43.3</td>
<td>0.6</td>
</tr>
<tr>
<td>0.10SZ</td>
<td>36.8</td>
<td>0.4</td>
</tr>
<tr>
<td>0.25SZ</td>
<td>37.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 5: Reaction profiles of ricinoleic acid conversion with butanol at 110 °C.

Effect of alcohol chain length in esterification of ricinoleic acid

Esterification of ricinoleic acid with alcohols of different chain lengths (C1-C4; i.e., methanol, ethanol, propanol and butanol) was carried at 65 °C to investigate the effect of alcohol carbon chain length over unmodified zirconia and a series of SZ. Figures 6 and 7 illustrate the conversion profiles of the ricinoleic acid with different alcohols at 65 °C for all catalysts investigated. The decrease in conversion of ricinoleic acid was observed as the chain length of the alcohol increased. For instance, ricinoleic acid conversions were 35, 28, 23 and 20% when methanol, ethanol, propanol and butanol were used, respectively for esterification using 0.05SZ (optimally performing catalyst) at 65 °C as indicated in Figure 8 and Table 3. Thus, the smaller the alcohol carbon chain the higher the conversion of the ricinoleic acid. This is in good agreement with previous studies (Saravanan et al. 2012, Osatiashtiani et al. 2016). Such reactions involve generation of nucleophilic species during deprotonation of the alcohol OH group which attack the carbocation to generate a tetrahedral intermediate which eventually form ester by dehydration. The observed low reactivity with increase of alcohol carbon chain is attributed to steric effect and polarity. Increasing alkyl chain length improves electron-donating properties which destabilize protonated transition state, explaining the consequential decrease in esterification rate (Osatiashtiani et al. 2016, Keshav et al. 2018).

Figure 6: Reaction profiles of ricinoleic acid conversion with methanol (a) and ethanol (b) at 65 °C.
Effect of temperature in esterification of ricinoleic acid

The effect of temperature during esterification of ricinoleic acid was evaluated based on the boiling points of different alcohols used over a series of SZ catalysts. The results are presented in Figures 9–10 and Table 3. It was shown that increase in temperature enhances the conversion of ricinoleic acid when reacted with selected series of alcohols, C2-C4, compared to the same reaction undertaken at 65 °C. All evaluated catalysts showed an increase in performance as the temperature of the reaction was raised to the boiling points of the respective alcohols (ethanol, propanol and butanol) as indicated in Table 3. The increases in the conversion of ricinoleic acid using 0.05SZ catalyst with change in temperature of were 37, 40 and 47% for ethanol, propanol and butanol, respectively. For instance, the conversion of ricinoleic acid with butanol increased from 43.3 to 47.3% when the temperature changed from 110 to 118 °C (Figure 10). This supports the fact that, esterification reaction is an endothermic reaction, hence a temperature dependent reaction (Sert and Atalay 2017, Han et al. 2019). Therefore, increase in temperature favours the conversion of ricinoleic acid. This is due to the fact that the number of collisions increases as the temperature of the reactions increases because of the increase in molecules’ kinetic energy. Therefore, the conversion of limiting step reagent is raised by decreasing the activation energy and hence accelerating the forward reaction of the esterification process. The increase in temperature during esterification of ricinoleic acid increased the conversion, in agreement with previous work in which ethanolysis of ricinoleic acid under homogeneous ruthenium catalyst attained high conversion of up to 99% when temperature increased from 25 to 90 °C (Behr et al. 2012).
Effect of temperature on turnover frequency and catalyst activity

Turn over frequency (TOF), which is a measure of the instantaneous efficiency of a catalyst, was determined for esterification of ricinoleic acid by varying alcohols over a series of SZ at 65 °C and reflux point for respective alcohols. Temperature had effect on the TOF and the activity of the catalyst. Figure 11 shows the activity changed as the temperature of the reaction was changed from 65 °C to reflux of each alcohol used. The TOF and activity of the...
catalyst increased with increase in temperature for ethanol, propanol and butanol to their corresponding reflux temperature as shown in Figures 12 and 13.

Figure 11: Activity for esterification of ricinoleic acid by varying alcohols over a series of sulfated zirconia at 65 °C (a) and at reflux point for respective alcohols (b).

Figure 12: TOFs for esterification of ricinoleic acid by varying alcohols over a series of sulfated zirconia at reflux point.

Figure 13: TOFs and activity esterification of ricinoleic acid by varying alcohols at reflux temperature of ethanol, propanol, and butanol.

Conclusion
The production of biodiesel using ricinoleic acid as a feedstock and a series of SZ catalysts was undertaken. The synthesized series of SZ were used to esterify ricinoleic acid with butanol at 110 °C. The effects of temperature and alcohol carbon chain length were studied at 65 °C and their corresponding reflux temperatures. The decrease in acid conversion
was observed with increase of alcohol carbon chain from methanol (C1) to butanol (C4). The increase in the conversion was observed as the reaction temperature was raised to alcohols’ reflux temperature. Impregnation of zirconia improved the activity of the catalysts as sulfated zirconia displayed good catalytic activities compared to unmodified zirconia. The highest conversion (47%) of ricinoleic acid was attained through esterification with butanol at 118 °C (reflux temperature) for 6 h. 0.05SZ catalyst exhibited the highest conversion during the reaction compared to other series of SZ catalysts used in this study. The synthesized SZ catalysts were active for esterification reaction of ricinoleic acid, thus deployable in the biodiesel production. However, further optimization studies of these catalysts preparations and reaction conditions are recommended to improve the biodiesel yield.

Declaration of competing interest
The authors declare that there are no competing interests regarding this work.

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Reddy BM, Sreekanth PM and Lakshmanan P


