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State-of-the-art novel catalyst synthesised from waste glassware and eggshells for cleaner fuel production

Ala’a H. Al-Muhtaseb a,*, Farrukh Jamil b,*, Ahmed I. Osman c,*, Myo Tay Zar Myint d, Htet Htet Kyaw e, Rashid Al-Hajri a, Murid Hussain b, Mohammad N. Ahmad f, Mu Naushad g

a Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman
b Department of Chemical Engineering, COMSATS University Islamabad (CUI), Lahore Pakistan
c School of Chemistry and Chemical Engineering, Queens University Belfast, Belfast, Northern Ireland, UK
d Department of Physics, College of Science, Sultan Qaboos University, P.O Box 36, 123 Al-Khoud, Muscat, Oman
e Nanotechnology Research Center, Sultan Qaboos University, P.O Box 33, 123 Al-Khoud, Muscat, Oman
f Department of Chemical Engineering and Advanced Energy, Faculty of Engineering and Architecture, American University of Beirut, Lebanon
g Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

Keywords: Novel catalyst, Waste glass, Waste eggshells, Biodiesel, Optimisation

ABSTRACT

Biodiesel is regarded as an environmentally friendly alternative fuel. The current research synthesises novel heterogeneous catalysts derived from waste (lab glassware and eggshells) and utilised for biodiesel production. Beef fat, abundantly available worldwide, is used as an oil feedstock and then converted into biodiesel, an environmentally friendly fuel. The synthesised catalyst consists of precursor silica dioxide (treated waste glassware) and calcium oxide (calcined from eggshells) that have been modified by impregnating cerium oxide to increase activity. The catalyst is characterised to ensure its suitability for the reaction to produce methyl esters (biodiesel) from animal fat, and biodiesel production is then tested. Characterisation revealed the suitability of the catalyst for the intended application, followed by a comprehensive parametric study to optimise the reaction conditions, including process temperature, time, methanol to oil molar ratio, and catalyst loading. According to the parametric study, the optimal conditions are as follows; process temperature (70 °C), time (100 min.), methanol to oil molar ratio (11) and catalyst loading (3 wt%), where the optimum biodiesel yield was 95.29 wt %. Furthermore, the produced biodiesel is then characterised to report its fuel properties and compared to standards (ASTM6751 & EN14214) which revealed its suitability as a potential alternative fuel. The reusability of the catalyst is also determined. The results indicated that it could be reused up to five times without a noticeable decrease in its reactivity. Based on the results, it can be concluded that synthesised catalysts from such waste materials are a viable option for commercial biodiesel production.

1. Introduction

Fossil-derived fuels are the key sources of energy production, transportation, and domestic consumption [1]. The current scenario regarding the availability of fuels derived from fossil sources is alarming. It is anticipated that they might withstand for the next two decades until they will reduce to a minimum level [2,3]. Environmental issues resulting from the excessive use of fossil fuels in the transportation or industrial sectors are an additional crucial factor frequently overlooked in developing countries [4,5]. Moreover, security issues in petroleum-rich nations cause price increases and availability problems. As a result of these factors, researchers considered alternative sources. Biomass is the most suitable feedstock for biofuel production because it can be transported and stored without difficulty [6,7]. Moreover, when biomass is directly combusted as a fuel source in different industrial applications, it has been reported that 50–60 % of the total energy content is wasted on the environment [8]. Therefore, biomass should be used to produce biofuels.

Biofuels derived from biomass may exist in gaseous, liquid, and solid states [9]. Liquid oil is considered the most suitable fuel source, with several advantages over other renewable sources. It can be stored, transported, and used for vehicles and energy production [10,11]. Due to its low energy and high density, oil derived from biomass cannot be utilised directly as a fuel. Therefore, bio-oil derived from biomass must
be processed before use as a fuel, and transesterification is one of the most suitable biofuel techniques for oil derived from biomass [12,13]. Biodiesel is the biofuel derived from the transesterification of bio-oil, and its energy content is comparable to diesel derived from fossil fuels [14,15]. Biodiesel, a combination of methyl esters, has been reported to be of similar quality to fossil diesel [16,17].

Either edible or non-edible bio-oil can be produced from biomass; however, the palatable source can be a source of fuel versus food controversy [4,18]. To avoid this controversy, non-edible sources and agricultural waste are considered feedstock for bio-oil extraction, which is then used to produce biodiesel [5,19]. Economically, non-edible biomass or agricultural waste is advantageous for biofuel production. However, the non-edible biomass or agricultural waste has several disadvantages, including a high acidic oil content. High acidity presents FFA, which must be treated before transesterification, thereby increasing the cost of biodiesel production [20,21]. Thus, it is essential to seek out feedstocks that produce oil with a low FFA content and are abundant to produce biodiesel for commercial applications [22,23]. Biodiesel derived from biomass has several advantages over fossil fuels, including biodegradability, renewable and sustainable nature with high energy content [24,25]. In addition, it has been reported that biodiesel can be used directly as fuel in engines and generators without any modification, demonstrating its potential as a fuel source [26,27]. Several non-edible feedstocks, such as animal fat, rubber seed, palm waste glass, the waste glass produced SiO$_2$, which is used as a precursor for catalyst synthesis, according to [14,15]. Biodiesel, a combination of methyl esters, has been reported to be of similar quality to fossil diesel [16,17].

In the presence of basic catalysts, triglycerides are transesterified to produce biodiesel. Initially, alkali hydroxides were used as catalysts that tend to be in a homogeneous phase with oil and alcohol reactants [29,30]. Even though the homogeneous catalysts process is relatively fast and conversion is also high, there are several disadvantages to using homogeneous catalysts [31,32]. Homogeneous catalysts are inseparable from products, which increases the cost of both the product and the process. This can be avoided by employing a heterogeneous catalyst that is recoverable and reusable [33,34]. Several heterogeneous catalysts, including alkaline earth metal oxides, have been directly or indirectly considered for biodiesel production. They offer both advantages and disadvantages [35,36]. The primary objective of considering heterogeneous catalysts was recovery and reuse, which contributed to the economic viability of biodiesel. However, heterogeneous catalysts for biodiesel production can be more cost-effective when the catalyst is derived from waste and discards [6,37]. Agricultural waste is a carbon source which is used as a precursor for catalyst synthesis, according to several studies [38–40]. Considering waste material as a source for catalyst synthesis with active metal modification can thus be viewed as a viable strategy for producing cost-effective product biodiesel [41,42].

In the current work, the precursor for the catalyst was derived from waste glass. The waste glass produced SiO$_2$ after treatment and modification with the egg’s outer shells (CaO). The pristine precursor (CaO-SiO$_2$) modified with active transition metal “cerium oxide, CeO$_2$” produced highly active catalyst sites for the transesterification step of oil to biodiesel. This work is novel of its kind. The synthesised catalysts were characterised by several techniques such as XRD, SEM, EDX, BET, TPD and XPS. Thus, the synthesised novel catalyst is used for biodiesel production from beef tallow. The biodiesel is then analysed based on ASTM6751 and EN14214 standards, which assure its suitability for fuel use.

2. Materials and methodology

2.1. Materials

Beef fat was collected local market in Muscat, and eggshells were collected from a university café. Before grinding, they were washed with water, and the internal sticky layer was removed. The waste glass was gathered from all labs in the engineering college at Sultan Qaboos University. The outer layer of eggshells in powdered form is collected and dried. Cerium nitrate and methanol were bought from Merck.

2.2. Catalysts synthesis and analysis

A novel heterogeneous catalyst is synthesised, consisting of SiO$_2$ processed from waste glass. The waste glass powder is passed from thermal treatment in a muffle furnace at 750 °C, and the treated powder is then collected from the furnace, followed by acidic treatment to get the pure form of SiO$_2$. Pristine SiO$_2$ is taken as a base material for a novel catalyst to be synthesised. Further on, eggshells that were expected to be calcium carbonate were impregnated with pristine SiO$_2$ in different concentrations such as xCaO-SiO$_2$ (x = 5, 10, 15 & 20 %). The samples of catalysts were named as SiO$_2$ (CS-0), 5 %CaO-SiO$_2$ (CS-1), 10 %CaO-SiO$_2$ (CS-2), 15 %CaO-SiO$_2$ (CS-3) and 20 %CaO-SiO$_2$ (CS-4). The impregnated catalyst samples were calcined in a muffle furnace at 650 °C for four hours with a heating rate of 3 °C/min. The optimised catalyst (CS-3) sample was then modified by active metal Ce and thermal treatment at 650 °C for four hours with a heating rate of 3 °C/min. The final sample of catalyst modified by Ce is called Ce-CS-3 and is collected and stored in an airtight container to avoid contamination.

All catalyst samples were characterised by several techniques, which include phase determination by X-ray diffraction, using PAN analytical, Xpert PRO instrument, USA, equipped with rotating anode and Cu Ka radiation, surface morphology and elemental composition of the fabricated catalysts were observed by field emission scanning electron microscopy (Jeol, JSM 7800F, Japan) equipped with EDX detector (Oxford instrument, U.K.). BET analysis was carried out for the catalyst samples using ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA. The binding energy was determined using X-ray photoelectron spectroscopy (ScienTa Omicron, Germany). The catalyst’s acid and basic sites were determined by temperature program desorption TPD using Thermo Finnigan TPDRO 1100 Series. Thus, results obtained from all techniques tend to predict its suitability for methyl esters production.

2.3. Biodiesel production and analysis

Beef fat (oil) processed in the presence of synthesised novel catalysts in two neck reaction vessels. The reaction vessel is fitted as a thermostated jacket, and control reaction temperature while the reaction mixture is continuously stirred with a magnetic stirrer. The oil is poured into the reaction vessel and heated once the desired temperature is achieved based on the reaction parameters mentioned in Table 1. A premixed solution of methanol and catalyst is poured into the reaction vessel. The reaction mixture is continuous stirring for the desired time, and once the reaction time is over stirrer is stopped along with this heater. The mixture is allowed to cool, and the cooled mixture is centrifuged at 5000 rpm to remove the catalyst; once it has been done, the mixture is poured into a separating funnel and allowed to stay there for 24 h. The mix in the separating funnel separates into two distinct layers from which the upper layer is referred to as biodiesel and the bottom as glycerol. The bottom layer of glycerol is separated, and the remaining layer of biodiesel is washed with warm water to remove any water-soluble impurities. Water content from biodiesel is removed using.

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>The ranges defined for independent variables based on what the detailed parametric study is conducted for biodiesel production.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst loading (wt. %)</td>
<td>Minimum</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>40</td>
</tr>
<tr>
<td>Methanol to Oil molar ratio</td>
<td>5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>50</td>
</tr>
</tbody>
</table>
sodium sulfide beads, and finally, the biodiesel product is ready for application. Gas chromatography-mass spectroscopy GC-MS analysed the biodiesel samples using Perkin Elmer Clarus 600 fixed with DB-Wax column.

3. Results and discussion

3.1. Phase determination by XRD analysis

All catalyst samples are analysed through the XRD technique. The resultant diffraction lines of each sample are shown in Fig. 1. The diffraction lines representing waste glass treated by a thermo-chemical approach show quite a broad single diffraction peak between 15 and 30’, which is related to the JCPDS library (46-1045), which was noticed that represents the existence of pure silica dioxide [43]. So, based on these spectra, it can be found that waste glass that might have other components is removed either by acid leaching or calcination. Further on, waste glass silica dioxide modified by impregnating eggshell-derived lime in different quantities can be seen in Fig. 1. Each spectrum shows that modified silica-dioxide catalysts are crystalline due to sharp peaks. The diffraction peaks at 32.10°, 37.28° and 53.71° represent the presence of pure CaO, and the results were compared with the JCPDS library (37–1497) [12,13,15]. As the quantity of lime increased, the diffraction peak strength started increasing, which can be attributed to the fact that CaO might start appearing on the surface of the precursor, which got detected when X-rays were showered on samples. Similarly, when the cerium oxide is impregnated onto an optimised catalysts sample (CS-3), additional diffraction peaks were present at 28.38°, 33.01° and 47.28° in spectra, representing the presence of CeO2 and results were compared with JCPDS library (34-0394). The results for each catalyst sample showed definite diffraction peaks of all desired components, which confirmed the successful Synthesis of novel catalysts.

3.2. Surface morphology by FESEM and EDX

The surface morphology of synthesised catalysts was determined by scanning electron microscopy (SEM), and for qualitative analysis, EDX was also done for each catalyst sample, as shown in Fig. 2. It can be observed from the image (Fig. 2a) representing the pure silica dioxide that particles do not possess any definite shape, and EDX shows the existence of silica and oxygen. So, based on EDX results compared to XRD spectra of pure silica dioxide, it is consensus that it consists of pure silica dioxide. Further on, when precursor (SiO2) was impregnated with lime, it was found to have bonded with each other; moreover, it was also observed that pores were also present. EDX results show the presence of each component existence.

Similarly, for each sample, the particle does not possess any definite shape, and due to thermo-chemical treatment, it can be observed that the catalyst became porous. It has been reported earlier that acid treatment causes the leaching of certain elements, which causes the pores to be created in pristine precursors and reactions that involve reactants with a longer chain and higher molecular weight should be treated in porous catalysts [11]. SEM and EDX results were also in consensus with XRD analysis which showed the presence of each component. Thus, it can be concluded that porous catalysts are successfully synthesised, which will be used for biodiesel production.

3.3. Catalysts’ surface chemistry

The surface and sub-surface chemistry and elemental composition of the synthesised catalysts were observed using the XPS technique. Fig. 3a shows the survey spectrum of the catalysts where the main peaks of the expected elements such as Si 2p, C 1s, O 1 s, Ca 2p, and Ce 3d peaks were detected, which confirmed the successful impregnation of CaO and metal Ce modification. For the Ce-CS-3 catalyst, extra peaks at B.E. values between 880 and 915 eV can be assigned to the Ce 3d peak. Similarly, for each sample, the particle does not possess any definite shape, and due to thermo-chemical treatment, it can be observed that the catalyst became porous. It has been reported earlier that acid treatment causes the leaching of certain elements, which causes the pores to be created in pristine precursors and reactions that involve reactants with a longer chain and higher molecular weight should be treated in porous catalysts [11]. SEM and EDX results were also in consensus with XRD analysis which showed the presence of each component. Thus, it can be concluded that porous catalysts are successfully synthesised, which will be used for biodiesel production.

3.4. Physiochemical analysis

The synthesised catalysts were analysed through the BET technique to determine the physicochemical properties, including surface area, pore-volume, and diameter. The results of the BET analysis are shown in
Table 2 for each catalyst sample. It can be observed that pristine silica-oxide possesses a definite surface area which increases when impregnated with CaO in different proportions. The increment in surface predicts that adding CaO particles got attached to the precursor, which increased the area exposed to reactants. The increased surface area will lead to better exposure of active sites to reactants [31,33]. A similar trend was observed for pore diameter and volume: by increasing CaO quantity, they increased till SC-3 (15 wt% CaO). Still, when the amount of CaO increased beyond 15 wt% CaO, the pore volume and diameter decreased. The decrement in pore volume and diameter can be related to an additional amount of active material after a specific limit (15 wt%), which may be stuck into precursor pores, leading to less exposure to active site reactants. Each sample of catalysts possesses a pore diameter higher than the 5.8 nm reported diameter of the triglyceride molecule [33]. This represents that synthesised catalyst will expose proper pore channels for efficient conversion of reactants to products without any mass transfer limitation. Further on, when CS-3 (15 wt% CaO-SiO$_2$) was modified with active metal oxide (CeO$_2$), the surface is got increased, tending that it is adequately bonded with precursor and will allow more surface area, which will lead to exposure to more active sites with reactants leading to higher product yield.

3.5. Active sites determination by TPD

The temperature-programmed desorption (TPD) technique has been adopted to analyse the presence of active sites in synthesised novel heterogeneous catalysts. Carbon dioxide TPD, which involves the adsorption and desorption of CO$_2$ at high temperatures, tends to give the quantitative analysis of basic sites (negative) present in the material. The results of CO$_2$-TPD concerning temperature are shown in Fig. 4a. It has been observed that pristine SiO$_2$ precursors gave two peaks in desorption patterns, the first at 200 °C, which represents weak basic sites.
and the second, which is quite broad, 530–720 °C, represents strong basic sites. Strong basic sites are referred to strong Lewis bases, which can donate pairs of electrons [12]. Further on, adding CaO to the precursor tends to increase the strength of both peaks, which can be referred to as the addition of basic sites. It can be seen that the peak became broader (Fig. 4a) at lower temperatures, 150–350 °C representing weak basic sites, along with that peak representing strong basic sites was also broader as compared to the precursor; a however slight shift in the peak was observed. Moreover, a similar trend was observed for each catalyst with increased CaO on the precursor. For CS-3 and CS-4, it can be seen that along with broader peaks of weak basic sites, small shoulder peaks were observed, which can be attributed to weak basic sites of two different natures. Similarly, modified sample CS-3-Ce tends to give a broad peak of 80–350 °C, consisting of two shoulder peaks on either side of the main peak. The presence of shoulder peaks at different temperatures represents the presence of basic sites with different natures [31]. So, it can be concluded that the precursor initially has a very minimal amount of basic sites, either weak or strong. However, the addition of CaO increased the strength of basic sites of both strengths weak and strong. Moreover, CeO₂ gave additional basic sites to modified precursors.

The ammonia TPD was done to define the acidic sites (positive)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-0</td>
<td>84.32</td>
<td>0.011</td>
<td>21.58</td>
</tr>
<tr>
<td>CS-1</td>
<td>85.51</td>
<td>0.272</td>
<td>29.87</td>
</tr>
<tr>
<td>CS-2</td>
<td>88.74</td>
<td>0.291</td>
<td>37.51</td>
</tr>
<tr>
<td>CS-3</td>
<td>99.91</td>
<td>0.327</td>
<td>41.28</td>
</tr>
<tr>
<td>CS-4</td>
<td>100.56</td>
<td>0.328</td>
<td>38.79</td>
</tr>
<tr>
<td>CS-3-M</td>
<td>108.35</td>
<td>0.321</td>
<td>40.47</td>
</tr>
</tbody>
</table>

Fig. 3. (a) XPS survey spectrum of synthesised catalysts, namely (CS-0 to CS-4 and Ce-CS-3) (b) High-resolution O 1 s scan of synthesised catalysts (c) Quantitative analysis of main components present on synthesised catalysts surface.

Fig. 4. TPD results for synthesised catalysts from waste glass, eggshells, and cerium oxide where (X) CO₂-TPD for pristine SiO₂ (a), pristine SiO₂ modified with lime derived from eggshells (b-e), and (e) precursor (CaO-SiO₂) modified with cerium oxide and (Y) NH₃-TPD for pristine SiO₂ (a), pristine SiO₂ modified with lime derived from eggshells (b-e) and precursor (CaO-SiO₂) modified with cerium oxide (e).
present in the synthesised catalysts, which involves adsorption and desorption of ammonia with temperature variation. The trend of NH3-TPD for each catalyst sample is shown in Fig. 4b. It can be observed that precursors derived from treated waste glass SiO2 possess weak acidic and acidic solid sites. As the precursor is modified with lime thus, no definite changes in peaks were observed. This can be related to the fact that SiO2 can act as acidic oxide as it can emit a pair of electrons and vice versa; by adding lime (basic nature) to the precursor, no noticeable change in peak strengths was observed. So, it can be concluded that synthesised catalysts possess both acidic and basic, referred to as bifunctional catalysts.

3.6. Catalyst evaluation

The activity of synthesised novel catalysts is evaluated by converting animal fat to methyl esters. The activity of each catalyst based on methyl esters (biodiesel) yield is shown in Fig. 5. Based on the catalyst characterisation, it can be evaluated that due to the crystalline phase and proper pore channels of porous synthesised catalysts, they can support the biodiesel production reaction. Moreover, active sites were present in all catalyst samples regardless of their quantity which varies due to modification. So, it can be observed that pristine silica dioxide (CS-0) derived from treated waste glass powder can help produce methyl esters from animal fat; however, the yield is relatively low. The low yield relates to the TPD analysis of catalyst, which was that pristine silica dioxide has very few active sites.

Further on, as the CS-0 was modified with impregnation of calcium oxide (CaO), the yield tended to be higher as it kept increasing until the quantity of calcium oxide increased up to 15 wt%. Higher biodiesel yield due to modification of pristine silica dioxide with lime can be related to CaO’s high basic nature promoting the biodiesel reaction. Moreover, it was also observed and reported that the active sites increased upon adding CaO to CS-0. From BET results, it was clear that proper pore channels were present to offer the interaction between reactants and active sites, which tended to give higher biodiesel yield. Furthermore, when the quantity of CaO increased beyond 15 wt%, the biodiesel yield decreased slightly compared to biodiesel yield when less CaO was impregnated to CS-0. The decrement in biodiesel yield can be attributed to several facts, including blockage of some active sites and less interaction of reactants, which gave less biodiesel yield. So, it can be concluded that basic active sites are good up to a certain level, decreasing biodiesel yield when exceeded. Meanwhile, the best catalyst among all samples is CS-3 which possesses an optimised number of active sites.

3.7. Parametric study

Before the parametric study, the catalyst consisting of silica oxide as a precursor derived from modified waste glass impregnated with eggshell-derived lime in different ratios was evaluated to sort the best possible catalyst. The most suitable catalyst (CeO2-15 %CaO-SiO2 (CS-3)) for biodiesel yield is modified with basic cerium oxide. Further, the modified catalyst was used for biodiesel production and optimising the process. The process was optimised based on four operating parameters: catalyst loading, process temperature, methanol to oil molar ratio, and reaction time. The parametric study conducted to optimise the process is presented in Fig. 6, which shows the effect of an independent variable on biodiesel yield. Catalyst loading significantly impacts biodiesel yield; based on this, it has been evaluated for a specified range, as shown in Table 1. Fig. 6a shows that initially, when catalyst loading was just one wt.%, the biodiesel yield was relatively less, which can be attributed to the fact that due to the less availability of active sites, the reactants might not have converted completely.

At low catalyst loading, biodiesel yield is low, and it starts increasing when catalyst loading increases and the trend remains the same in ascending order. Increasing biodiesel yield can be related to the fact reported earlier that the number of active sites is more in the reaction vessel for better biodiesel yield by increasing catalyst loading. Further on, the different behaviour in biodiesel yield was observed at higher catalyst loading (3.5 wt%) decreased. The decrement in biodiesel yield can be due to excess availability of heterogeneous catalysts in the reaction vessel, which can cause a hindrance in the mixing of reactants which may lead to less biodiesel yield [7,44]. Another factor regarding the low biodiesel yield at higher catalyst loading can be the mass transfer limitation of reactants and products at higher catalyst loadings. So, the optimum catalyst loading is 3 wt% for maximum biodiesel yield.

Fig. 6b shows the effect of reaction temperature on the product yield. It has been noticed that reaction temperature is the most influential parameter among biodiesel production reactions [45]. It can be seen that at lower reaction temperatures, the biodiesel yield is low. The low biodiesel yield can be related to several facts. A lower temperature reactant might not be adequately intermixed and interacted as both (oil and methanol) are immiscible, giving lower biodiesel yield.

Furthermore, the biodiesel yield increases when the temperature increases, proving the fact reported for lower biodiesel at a lower temperature. The reactants are excited enough to react appropriately to give a higher product yield at higher temperatures. However, this fact is only workable up to a specific temperature limit, such as for the current process, the maximum biodiesel yield is at 70°C. Thus, a higher temperature allows maximum reactants’ permeability to react and form product biodiesel. Despite this, it has been observed that if the temperature increases beyond 70°C, the biodiesel yield decreases. The decrease in biodiesel yield might be due to less availability of methanol in reaction media due to its low boiling point. Methanol is condensed continuously despite the biodiesel yield being less at 75°C. So, it can be concluded that temperature should be appropriately monitored to proceed with biodiesel products on a lab-scale or commercial scale.

Fig. 6c shows the effect of the reactants’ molar ratio (5–15) on biodiesel yield. Based on stoichiometric calculation molar ratio should be 3 of methanol to oil for complete conversion of triglycerides to methyl ester. However, due to the reversible nature of the reaction, methanol is supplied in excess amounts to keep the reaction progressing forward. Moreover, it has been reported that when the heterogeneous catalyst is used, the reaction dynamics change and the methanol to oil molar ratio should be optimised within a specific range [41,42]. It can be seen from Fig. 6c that initially, when the ratio of the reactants is 5, the biodiesel yield is not that good, which can be due to less availability of methanol.

Moreover, the ascending trend was observed by increasing the ratio of the reactants; it kept rising to the maximum till the ratio of the reactants reached 11. Due to the excess amount of methanol in reaction media, the process dynamics change, allowing more reactants to interact and transform into product biodiesel due to heterogeneous catalysts. Despite this fact, when the methanol to oil ratio was increased beyond 11, the biodiesel yield started decreasing, which can be related to the
fact that the downstream process became difficult at higher ratios. Due to the higher methanol to oil molar ratio and difficulty in the downstream process, separating the product from the by-product becomes difficult [37,41]. Thus, it can be concluded that the optimum methanol to oil molar ratio is 11, which gave the maximum biodiesel yield.

Fig. 6d represents the effect of process time on biodiesel yield. The parabolic shape of the biodiesel yield trend within the specified process time range can be seen. This parabolic trend shows that initially, when process time was low, the biodiesel was low, and upon increasing reaction time, it increased. The increasing trend in biodiesel yield can be related to the fact that initially, due to a heterogeneous catalyst, the reaction might not be complete within a specified time. It has been reported that when a heterogeneous catalyst is used for biodiesel production reaction, the reaction rate changes and becomes low compared to a homogeneous catalyst [32]. So, heterogeneous catalysts required more reaction time to complete based on this fact.

Moreover, the peak of the parabolic trend in biodiesel yield concerning time is achieved when it reaches 100 min which means that reactants are converted to produce biodiesel by the maximum allowable limit. Further on, when reaction time is exceeded by 100 min, the decrease starts in a parabolic trend. This trend can be attributed to reversible reactions that may start tending to decrease the biodiesel yield [12]. Moreover, excess reaction time can cause difficulty separating product products from by-products, leading to lower biodiesel yield. Thus, the optimum reaction time for the current process in the presence of a novel synthesised catalyst is 100 min.

A parametric study is essential for reporting any feasibility of a specific process. Moreover, based on the parametric study, optimum conditions can be predicted. So, based on the parametric study for the current process, the optimum set of parameters is catalyst loading 3 wt% with a process temperature of 70°C and methanol to oil molar ratio of 11 when the reaction time was 100 min, giving optimum biodiesel yield of 95.29 wt%.

3.8. Fuel properties analysis of biodiesel

The biodiesel produced from animal fat in the presence of a synthesised novel catalyst is analysed by several techniques, as shown in Table 3, to report its feasibility as fuel. The results for produced biodiesel are compared with ASTM6751 and EN14214 standards to prove its feasibility as an efficient fuel. First, biodiesel comprises methyl esters with less or no fatty acids. If the fatty acids are more than the eligible limit defined by ASTM6751 and EN14214, then the acid value of biodiesel calculated based on the titration is high. Biodiesel produced from animal fat has a 0.17 mg KOH/g acid value within the allowable limit; this biodiesel will be suitable for use as fuel. It is essential to measure the acid value as it also helps report its feasibility for defining its storage duration and transportation. Biodiesel with a higher acid value might be corrosive and causes a problem in storage and transportation containers [34,46].

Further on, the density of produced biodiesel is 876 kg.m⁻³, which is within the limit defined by the EN standard. Higher density biodiesel might cause more mass transfer, leading to atomisation problems [23]. The viscosity of producing biodiesel is within the defined limits of standards ASTM6751 and EN14214, which is 3.97 mm².s⁻¹. It has been observed that appropriate viscosity indicates that biodiesel composition is allowable for saturated and unsaturated methyl esters [47]. The biodiesel with higher viscosity can be attributed to the fact that low saturated fats are in excess amount, which will cause problems with fuel atomisation and storage in colder regions [48].

The flashpoint of produced biodiesel in current research work is 162°C which is higher than the minimum limit defined by ASTM6751 and EN14214 standards. The flashpoint must be determined as it can

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Biodiesel</th>
<th>EN 14214</th>
<th>ASTM 6751</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Value (mg KOH/g)</td>
<td>0.17</td>
<td>0.50 max</td>
<td>0.80 max</td>
</tr>
<tr>
<td>Density (kg.m⁻³) at 25 °C</td>
<td>876</td>
<td>860-900</td>
<td>–</td>
</tr>
<tr>
<td>Viscosity (mm².s⁻¹) at 40 °C</td>
<td>3.97</td>
<td>3.5-5.0</td>
<td>1.9-6.0</td>
</tr>
<tr>
<td>Flashpoint (°C)</td>
<td>162</td>
<td>120 min</td>
<td>93 min</td>
</tr>
<tr>
<td>Cetane number</td>
<td>64.28</td>
<td>51 min</td>
<td>47 min</td>
</tr>
<tr>
<td>Cloud point (°C)</td>
<td>0.87</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>–4.3</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cold Filter Plugging Point (°C)</td>
<td>–2.17</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Free Glycerin (%)</td>
<td>0.012</td>
<td>0.020 max</td>
<td>0.020 max</td>
</tr>
<tr>
<td>Total Glycerin (%)</td>
<td>0.119</td>
<td>0.250 max</td>
<td>0.240 max</td>
</tr>
</tbody>
</table>

*Not specified. EN 14,214 uses time- and location-dependent values for the cold filter plugging point (CFPP) instead.

*Not specified.
help predict its safe storage and transportation for hot regions and atmosphere. A Flashpoint is a maximum temperature that fuel can withstand without self-ignition; thus, the flashpoint improves fuel quality in terms of storage and transportation [12]. Cetane’s number of product biodiesel was determined to be 64.28, higher than the allowable limit defined by ASTM6751 and EN14214 standards. It is referred to as the anti-knocking property of biodiesel; thus, efficient biodiesel should have a higher cetane number to run the engine properly [31]. Cold flow properties, including cloud point, pour point, and cold filter plugging point, were measured for biodiesel. It has been observed that the cloud point is 0.87 °C, the cold filter plugging point is −2.17 °C, and the pourpoint is −4.3 °C for producing biodiesel. One of the drawbacks of biodiesel being used as a fuel is its poor low-temperature properties as it causes hindrance in its usage in colder regions [32]. Thus, biodiesel with better low-temperature properties is preferred, and the product biodiesel produced in the current research work has better cold flow properties. Glycerin is a by-product that should be removed entirely from biodiesel. The glycerin in biodiesel is 0.012 % free glycerin and 0.119 % total glycerin, less than the maximum allowable limit defined by ASTM6751 and EN14214 standards. Higher glycerin content can cause the poor fuel properties of biodiesel [46]. Thus, it can be concluded from all determined properties that the product biodiesel is the potential that it can be used as potential fuel for diesel engines.

3.9. Catalyst reusability

Catalyst evaluation and the parametric study showed that synthesised novel catalyst is high in biodiesel production. Thus, experimental work carried out was on a lab-scale, which confirmed the catalyst’s efficiency, which can be one of the solutions to fulfil the dire need for an efficient heterogeneous catalyst for commercial-scale biodiesel production. One of the basic concerns while using a homogeneous catalyst for biodiesel production was its lack of reusability, which can be overcome by using a heterogeneous catalyst [10]. Moreover, due to its reusability factor, the process will become more economical using heterogeneous catalysts. The reusability study for the synthesised novel catalyst is shown in Fig. 7, in which two trends are seen; one shows the reusability of catalyst without its treatment before every experimental run, while in other cases, the catalyst after each run is collected and washed thoroughly with alcohol and dried before use. It can be seen that when the catalyst was treated before usage, the biodiesel yield was quite good without any appreciable loss. However, when the catalyst is used without any pretreatment. In that case, biodiesel yield starts decreasing quite rapidly, which might be because some deposited reaction media may hinder the active sites tending to give higher biodiesel yield. The catalyst used after treatment showed very virtuous results with an almost minor decrement in biodiesel yield. This indicates that the catalyst’s active sites are intact, and less or no activity loss can be reported. So, it can be concluded that catalyst must be pretreated before being used in the reaction vessel.

3.10. Conclusions

In the current research work, a unique approach has been adopted to synthesise the novel catalyst successfully. The catalyst precursor (CaO-SiO2) was derived from waste lab glass (SiO2), and lime (CaO) was derived from waste eggshells which were further modified by active material cerium oxide to produce a novel catalyst (Ce-CaO-SiO2). Based on the detailed characterisation, it was revealed that the synthesised catalyst possesses all features suitable for biodiesel production. A detailed parametric study was conducted, which showed the effectiveness of the catalyst. The optimum set of independent variables is; process temperature (70 °C), time (100 min.), methanol to oil molar ratio (11) and catalyst loading (3 wt%), which produced biodiesel yield of 95.29 wt%. In addition, a study on the reusability of the catalyst revealed that it could be reused up to five times without significant activity loss, proving its commercial viability. Thus, it can be concluded that the synthesised catalyst is highly effective and can be used to produce biodiesel.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

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References


