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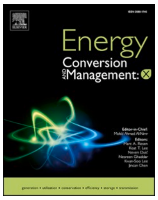

Investigation on yield, fuel properties, ageing and low temperature flow of fish oil esters

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ABSTRACT

Sustainable energy derived from waste resources helps to mitigate the greenhouse gas emissions generated from fossil fuels. In this study, a solid heterogeneous catalyst was synthesized by using eggshell and copper oxide [$CaCu(OCH_3)_2$]. Using this catalyst, biodiesel fuels were produced from waste sardine fish oil using either methanol, ethanol, or *iso*-propanol. To reduce the acid value of fish oil, esterification of the fish oil was performed before the transesterification process. Three biodiesel samples were produced, namely, fish oil methyl ester (FOME), fish oil ethyl ester (FOEE), and fish oil propyl ester (FOPE). Experimental analysis studies were carried out under various operating conditions such as alcohol-to-oil ratio (v/v), catalyst concentration, reaction time and reaction temperature. The results indicate that the optimal operating condition were a 16:1 alcohol: oil ratio, using 3% catalyst (w/w%), a 90 min reaction time; and reaction temperatures of 65 °C, 80 °C, 85 °C for methanol, ethanol, and isopropanol, respectively. The quality of prepared biodiesel samples revealed that both FOEE and FOPE have better physio-chemical properties than FOME. Ethanol and *iso*-propanol improved the low-temperature flow properties such as cloud point and pour points. In addition, stability studies performed over 10 months revealed that FOME is less stable than to FOEE and FOPE. These results will aid in strategies aimed at improving the use of polyunsaturated fish oils for biodiesel production.

Introduction

Due to the rapid growth in population and food style changes, food-processing industries are handling huge quantity of waste. Recycling and sustainable disposal of this waste is a big challenge for the industries and municipalities. The waste generated by the fish processing industry is disposed of indiscriminately often in landfills, which poses environmental, ecological and health risks [1]. In 2018, worldwide fish production was 179 million tonnes, with 156 million tonnes for food consumption and 22 million tonnes thrown away as waste (skin, tail, viscera, head, and fins) [2]. The fish wastes contain around 40–60% oil, which may be used to make value-added products and green fuels such as biodiesel [2]. Many developed and developing countries have been working hard to improve their bio-waste management and recycling technologies [3]. Turning bio-waste into sustainable fuel for energy generation is an attractive solution to combat both waste management and rising carbon emission issues [3]. Biodiesel, which has similar properties to fossil diesel, is produced by transesterifying animal oils, edible and non-edible plant oils [4]. Depending on the free fatty acid content, both esterification and transesterification processes might be required to turn fat/oils into biodiesel [4]. The cost of biofuels is an important factor, should be produced cost-effectively [5]. The cost of feedstock itself accounts for roughly 75–80% of the overall production cost [5]. Availability, affordability, and performance are the most important considerations in feedstock selection for the biodiesel production [6]. Globally, 95% of the biodiesel industry is reliant on edible oils, which raises the cost of both biodiesel and edible oils through competition and leads to the concept of the food vs. fuel dilemma [7]. As a result, non-edible oils, and waste resources (animal and waste cooking oil) are viable and prominent feedstock resources for biodiesel

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Abbreviations: ASTM, American Society for Testing and Materials; AV, Acid value; CFPP, Cold filter plugging point; CP, Cloud point; CN, Cetane number; CV, Calorific value; FOME, Fish Oil Methyl Ester; FOEE, Fish Oil Ethyl Ester; FOPE, Fish Oil Propyl Ester; FFA, Free Fatty Acids; FTIR, Fourier Transform Infrared; IV, Iodine value; KOH, Potassium Hydroxide; PP, Plugging point; SEM, Scanning Electron Microscopy; UFA, Unesterified fatty acids.

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production. To make methyl-ester or ethyl-ester; a catalyst, and an alcohol, (generally methanol or ethanol) are used [8]. These esters are non-toxic, biodegradable, renewable, and cleaner-burning fuels; making biodiesel a good choice for use in internal combustion engines [8].

The most widely used technique for producing biodiesel is transesterification. To accelerate the process, a homogeneous, heterogeneous, or enzymatic catalyst is used. The sole downside of using a heterogeneous catalyst is that it loses activity owing to leaching [9]. Heterogeneous catalysts can be recovered after the reaction and require fewer washing steps. Nano-catalysts have a huge surface area and better catalytic property [9]. They can overcome the disadvantages of other forms of catalysts. To manufacture large yields of biodiesel, researchers are focusing on the selection or creation of a highly selective and active heterogeneous catalyst. Alkaline earth oxides, such as CaO, MgO, and SrO, have been explored by scientists. Strong basic sites are present in these catalysts, which are favorable to the transesterification process [10]. Some of the most promising heterogeneous catalysts for biodiesel generation are CaO-based compounds. These catalysts are easily available and have high basicity that show high activity at mild reaction conditions. However, primary drawbacks of these catalysts is defusing during reused owing to Ca^{2+} leaching, which could contaminate the biodiesel [10]. The usage of combinations of CaO with other metal oxides, which can improve stability and activity of the catalyst, is one way to address this problem [10].

Kumar et al. [11], used eggshells as a heterogeneous catalyst to improve the transesterification of waste cooking oil for biodiesel production. The optimisation studies of time, temperature, oil: alcohol ratio, and catalyst quantity on biodiesel yield were conducted using Design Expert software. They found that the best biodiesel output was produced at 120 min, 50°Celsius, a 1:6 oil-to-alcohol ratio, and 5 g of eggshells. The findings were then confirmed under optimal conditions [11]. Mixed oxides ($CaO-Ca_3Al_2O_6$) were examined by Papargyriou et al. [12] as promising catalysts for biodiesel production from waste fish oil. In addition to pure CaO, other Ca/Al ratios in the range of 1.5–6 were investigated. The materials' catalytic activity was investigated in a transesterification process of cod liver oil with methanol at 65 °C, using a 1:12 oil to methanol molar ratio and 10% catalyst. After 2 h of reaction time, the Ca-Al catalyst converted triglycerides to methyl esters at a rate of over 97 percent [12].

Ching-Velasquez et al. [13], investigated the use of an enzyme as a catalyst in the manufacture of biodiesel from waste fish oil. To improve biodiesel's maximum yield conditions, they employed *Thermomyces lanuginosus* immobilised lipase as a bio-enzyme catalyst. They observed a 75% yield with the following parameters: 35 °C, 10% (w/w%) catalyst and at 24 h stirring at 216 rpm with a continuous stirrer for 24 h. ASTM-D6751 standards are used to compile the fuel characteristics such as viscosity, density, calorific value, and cloud point [13]. Kumar et al. [14], used Indian sardine fish oil as a feedstock to explore the optimal transesterification process for effective biodiesel synthesis. Reaction temperature of 150 °C and KOH catalyzed transesterification process was used for biodiesel production. The impact of methanol volume percent, KOH weight percent, and reaction duration were investigated to determine the best yield conditions [14]. The biodiesel's physicochemical characteristics were determined using ASTM 6751 standard. The optimal process parameters reported for 97% biodiesel yield was 20% (vol.) methanol, 1.25% (w/w%) KOH, 25-minute reaction time [14]. Cardoso et al. [15], prepared ethyl esters (EE) from waste fish oil using an alkaline transesterification method. They evaluated ethanol concentrations, catalysts, and temperature required to obtain a high EE yield. The study resulted in 96.4% yield and a low acid value of 0.32 mg KOH/g with 0.7% NaOH catalyst, 54 °C reaction temperature, and an 11.7:1 ethanol-oil molar ratio [15].

While biodiesel has various advantages, its application is hampered by poor storage stability and cold flow qualities, such as cloud point (CP), plugging point (PP), and cold filter plugging point (CFPP) [16]. Long-term usage of vegetable oils or their alkyl esters in diesel engines causes injector coking, severe engine deposits, filter gumming, piston ring sticking, and lubrication oil thickening due to their poor cold flow properties. For achieving better fuel properties, both long-chain saturated fatty acid methyl esters (FAME) and polyunsaturated fatty acids should be present in modest amounts in biodiesel [17]. Lapuertaat et al. [18] investigated the effects of mixing ethanol and n-butanol on the cold flow characteristics of diesel and biodiesel fuels. Biodiesel fuels showed advantages in cold filter plugging point, cloud point, pour point, freezing point, and filterability from concentrations, according to the researchers. Blends with intermediate alcohol percentage resulted in higher cloud point and cold filter plugging point, but lower pour point [18].

From the literature summary, it is inferred that, a comparative study on methyl, ethyl and propyl esters produced from waste fish oil, as well as their long-term storage stability, has not been reported so far. In the present study, an attempt is made to prepare methyl, ethyl, and propyl esters of fish oil at optimised process conditions to compare the yield, fuel properties, ageing and low temperature flow characteristics. A newly modified heterogeneous catalyst $CaCu(OCH_3)_2$ is used at different operating conditions such as alcohol-to-oil molar ratio, catalyst concentration percentage, reaction time and reaction temperature to find the optimised process condition to produce biodiesel with improved low-temperature flow properties. All the prepared biodiesels samples were stored for 10 months in an airtight container and kept in a dark room at room temperature (15–20 °C) to study the variation in fuel properties with time (i.e., storage stability).

Materials and methods

Waste sardine fish oil was procured from a local market in Chennai (India). The presence of functional groups in the synthesis composite catalyst has been investigated using Perkin Elmer's Fourier transform infrared (FTIR) spectroscopy. Ziess microscopy (Model: EVO 18) combined with, scanning electron microscopy (SEM) have been used to investigate the surface morphology of the catalyst. The catalyst was separated from the glycerol using a chemical dilution and purification procedure to ensure reproducibility. Catalyst reproducibility was not investigated in this work.

Catalyst preparation

Eggshells were collected from the college canteen at Anna Univer-

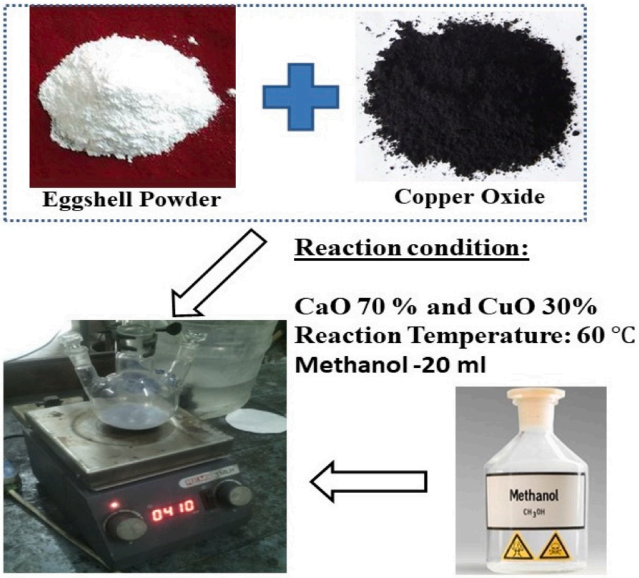


Fig. 1. Preparation of eggshell powder catalyst.

sity, Chennai, Tamil Nadu, India. Fig. 1 depicts the method for making eggshell powder. The eggshell was first washed in tap water before being cooked for 1 h in the distilled water to eliminate any contaminants [19]. It was sun-dried before being stored in an oven at 110 °C overnight. Initially, a basic grinder was used to create eggshell powder, but subsequently, a planetary ball mill machine was utilized to make fine calcium oxide (CaO) powder. As shown in Fig. 1, CaO powder was combined with copper oxide (CuO) to produce a composite methoxide powder. Equation (1) represents the chemical process [20]. Both catalysts on a weight basis of 70:30 (70 per cent CaO and 30 per cent CuO) were dissolved rapidly in 20 ml of methanol (99% pure) in a 200 ml three-neck round glass bottle reactor (Fig. 1) equipped with a glass reflux condenser with cool water circulation and a magnetic stirrer with the heater. The reaction was carried out at 65 °C and at atmospheric pressure for 10 h with continuous stirring at 600 rpm. The grey color slurry was generated after the reaction completed and was dried in an oven at 110 °C for 12 h. After drying, the composite powder was employed as a catalyst [20].

$$(\mathrm{CaCu})\mathrm{O} + 2\mathrm{CH_3OH} \xrightarrow{55^\circ \mathrm{C}} \mathrm{CaCu(OCH_3)_2} + \mathrm{H_2O} \qquad (1)$$

Experimental analysis procedure for transesterification

In this study, the conditions of transesterification were determined systematically by altering one parameter at a time and maintaining the others constant. For example, the temperature and catalyst were kept constant, and the methanol quantity increased. Similarly, reaction time, reaction temperature and catalyst were varied.

Biodiesel production process

Pretreatment of fish oil

Waste oils usually contain residues such as moisture, gum, and wax, which must be removed before biodiesel can be produced. The presence of crystals in fish oil at room temperature causes problems by clogging the filter paper, hence the oil was heated to 50 °C to eliminate this problem. Filtered fish oil was heated to 60 °C, 600 rpm stirrer speed with 1% phosphoric acid addition for an hour to remove the gum and wax. Phosphate compounds settled-out in the form of a precipitate [21].

Esterification of fish oil

Prior to transesterification, an acid catalyst process called esterification has been used to decrease the high acid value resulting from the presence of unesterified fatty acids [21]. Biodiesel production was carried out in Anna University's Biofuel Laboratory using a 5-litre capacity lab scale plant with a reflux condenser, stirrer, and heater as shown in Fig. 2. The amount of unesterified fatty acid (UFA) content in fish oil was calculated to be 5.12% using Eqs. (2) and (3) [22]. Before transesterification, this value should be reduced to below 2.5%. For esterification of oil, 2% sulphuric acid (v/v), and 6:1 methanol: oil molar ratio was employed in a 1-litre conical flask. Sulfuric acid and alcohol were mixed thoroughly to form a homogenous mixture, then poured into the hot oil which was stirred at 500 rpm and 60 °C reaction temperature for 180 min. The mixture was put into a separating funnel at the end of the reaction and allowed to settle for up to 10 h, where it separates into two layers. The top layer includes methanol and small amounts of glycerol, whereas the bottom layer contains esterified fish oil. The UFA content of the pretreated fish oil was determined to be 0.22%, and hence it is suitable for the next step, i.e., transesterification.

$$\text{Acid value (AV) in mgKOH/g} = \frac{\text{V*0.1N*Mw}}{\text{m}} \qquad (2)$$

$$\text{Unesterified fatty acid (UFA\%)} = \frac{\text{Acid value}}{2}\% \qquad (3)$$

Where, v-titration volume in ml, 0.1 N- normality of the titration solution, Mw- molecular weight of the catalyst used for titration (KOH) and m- oil sample weight in grams (g).

Transesterification reaction

Figure 3 depicts the transesterification reaction scheme using triolein as an example. The heterogeneous catalyst was used to produce fish methyl, ethyl, and propyl ester from fish oil (Fig. 4). The synthesis heterogeneous catalyst ($\mathrm{CaCu(OCH_3)_2}$) was calcinated at 800 °C for 6 h before use. The catalyst was added to the alcohol, and then the catalyst-alcohol mixture was added to hot oil. The mixture was then stirred at continuous stirrer speed of 600 rpm and simultaneously heated to a temperature to obtain maximum biodiesel yield. The reaction temperature would depend on the type of alcohol used. After that the mixture was transferred to a separating flask and allowed to settle overnight to separate the glycerol from the esters. Glycerol was used to settle the acid catalyst at the bottom. As illustrated in Fig. 4, the biodiesel was carefully separated, and the post-treatment procedure was carried out. The Biodiesel yield was calculated using Equation (4) [22].

$$\text{Biodiesel yield (\%)} = \frac{\text{Biodiesel weight}}{\text{Raw oil weight}} * 100 \qquad (4)$$

Post treatment process

Warm water was pumped through the ester, allowing soluble

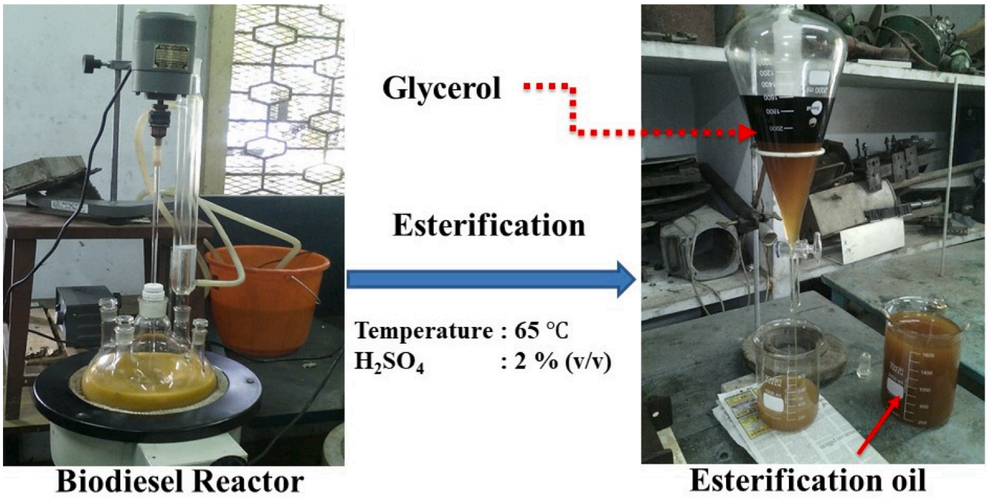


Fig. 2. Esterification of waste sardine fish oil.

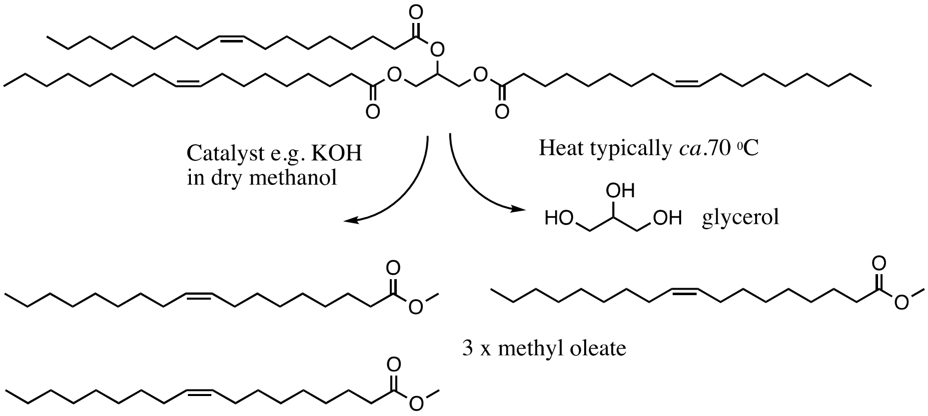


Fig. 3. Transesterification of triolein with methanolic KOH.

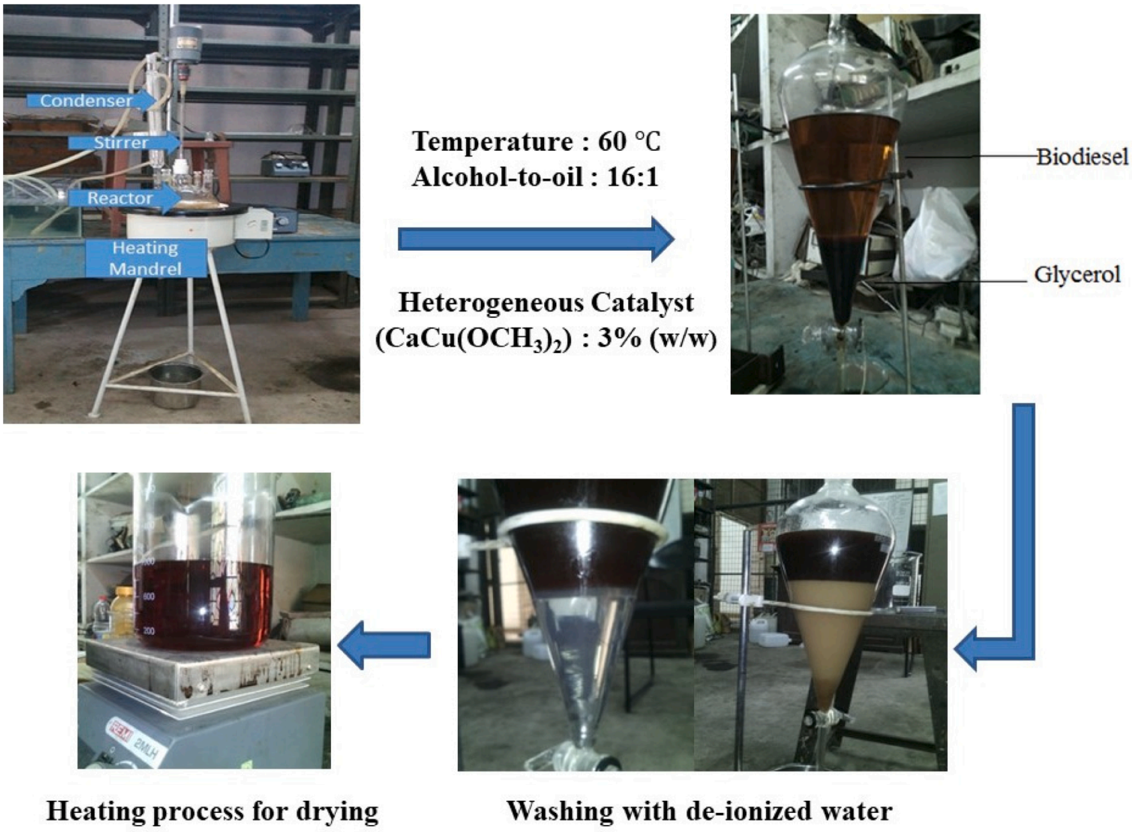


Fig.4. Fish oil biodiesel production process.

materials, excess catalyst, and other contaminants to wash out and partition into a lower layer. The water was taken from the vessel regularly until it was completely emptied and left for 10 h (Fig. 4). Drying was accomplished by gradually raising the temperature to 110 °C until all moisture in the oil evaporated and the pop sound was no longer audible [23].

Results and discussions

Catalyst characterization - SEM and FTIR analysis

The FTIR spectrum of the synthesis [CaCu(OCH$_3$)$_2$] catalyst is given in Fig. 5 and identifies key functional groups - OH stretching vibration (3640.972 cm^{-1}), C - H stretching alkane (3051–2905 cm^{-1}), the C = O stretching vibration (1256 cm^{-1}), C - C bond stretching (8630 cm^{-1}), and C - O (1300–1000 cm^{-1}) [23]. The morphology of the [CaCu(OCH$_3$)$_2$] catalyst is shown in Fig. 6. The particle had an uneven stone-like form (Fig. 6(a)). As demonstrated in Fig. 6 (b), the particle size was not smaller than 100 nm, thus it could not be classified as a nanoparticle. Since the catalyst was heated at a high temperature for a long period, it had taken on the appearance of a cluster [23].

Experimental analysis

Alcohol-to-oil molar ratio

Biodiesel yield was investigated with respect to the type of alcohol, molar ratio, reaction temperature, reaction time and catalyst percentage. Methanol, ethanol, and propanol were selected in a different molar

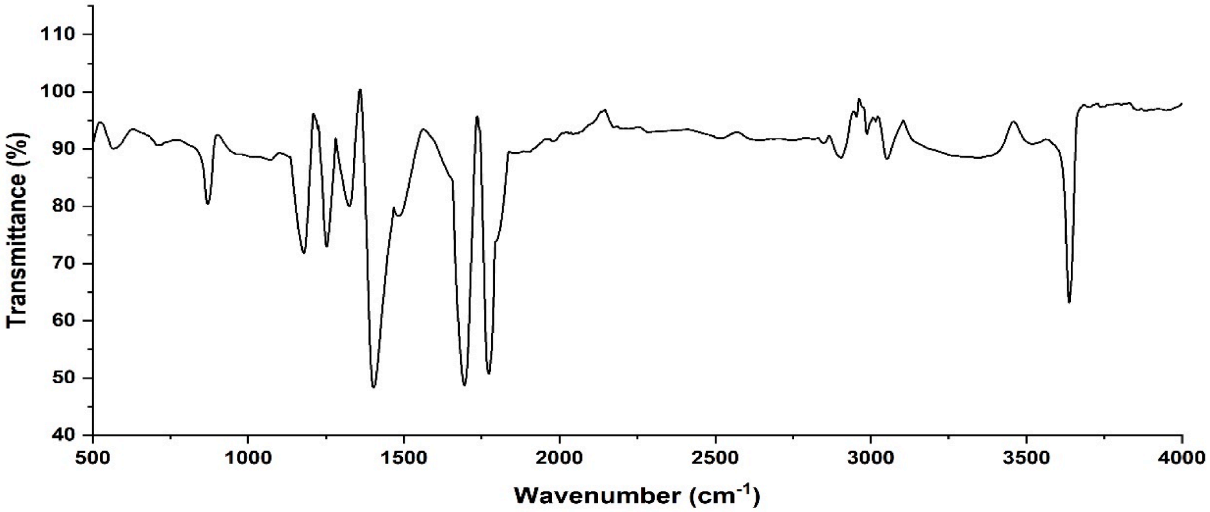


Fig. 5. FTIR spectrum of synthesis catalyst [$CaCu(OCH_3)_2$] [23].

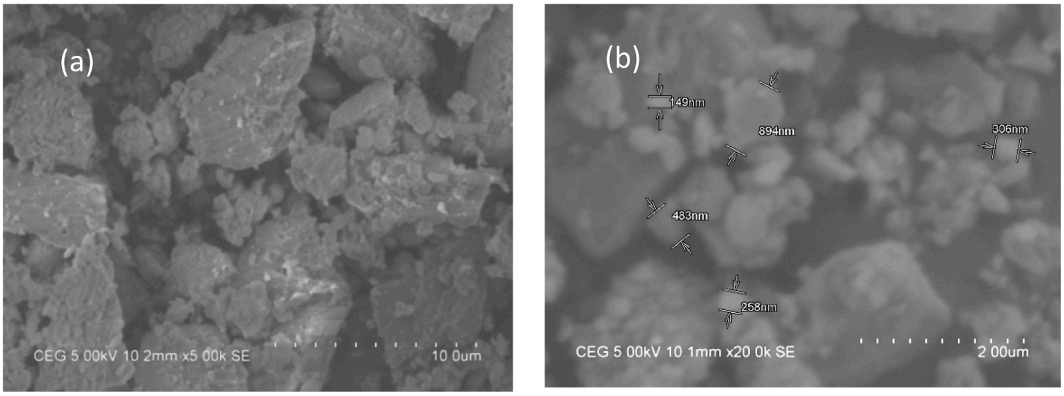


Fig. 6. Morphology of the [$CaCu(OCH_3)_2$] catalyst [23].

ratio ranging from 4:1 to 22:1 for biodiesel production and the optimum molar ratio is shown in Fig. 7 (a). It was observed that at a ratio of 16:1, methanol, ethanol, and isopropanol gave the highest yield percentage, with higher ratios reducing the yield. (Fig. 7(a)). Increasing the alcohol percentage increased biodiesel yield due to the role of the –OH group during transesterification reaction [23]. Using an alcohol: oil ratio ranging from 4:1 to 16:1, ester yield increased by up to 94%; but beyond 16:1, the ester yield reduced. The biodiesel output was reduced because the dissolving of glycerol in the extra methanol slowed the chemical process. The decrease in ester content is likely due to mixture dilution which reduces the solid catalyst concentration and slows down the hydroxide (–OH) ion-exchange process during reaction [24,25].

Catalyst concentration

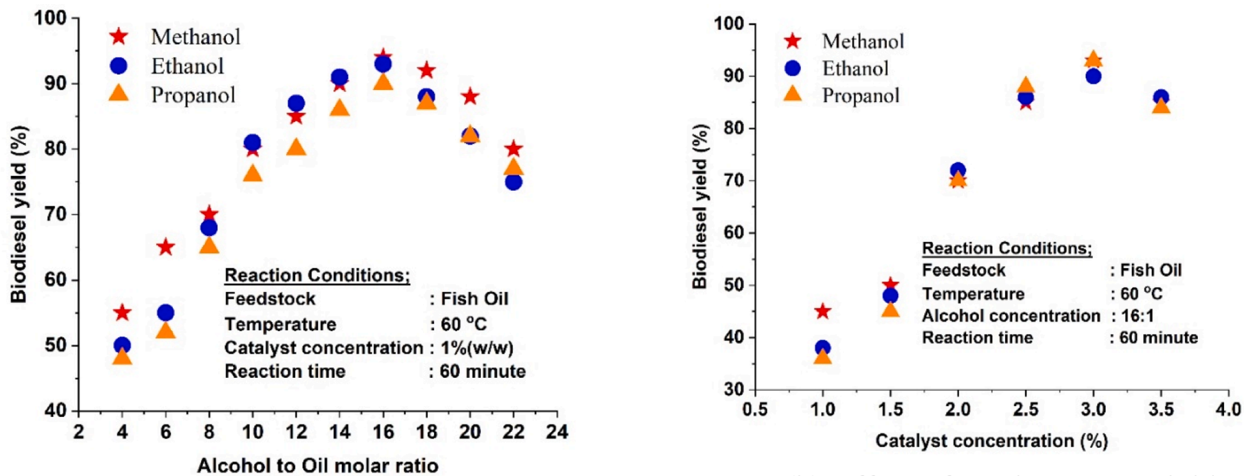
The solid catalyst percentage required for transesterification was measured from 1% to 3.5% by weight basis (w/w%) (Fig. 7(b)). It was observed that the ester content increased with increased catalyst from 1% to 3% (w/w%). At lower concentration (1–2), biodiesel yield was lower due to incomplete chemical reaction. The highest yield of ester obtained was 93% using 3% (w/w%) of the catalyst. Further increases in the catalyst proportions decreased the biodiesel yield. The catalyst is crucial in shortening the methanolysis reaction time. Increased catalyst concentration speeds up the chemical reaction, but it also raises the viscosity of the reaction mixture [22]. The rate of mixing efficiency is reduced when the reaction mixture has a high viscosity [22]. Another reason for the decrease in the yield for using higher catalysts levels could be explained on the basis of perceptible degradation following a more rapid rate of product generation [22].

Reaction time

Reaction time was another major component that influenced biodiesel output. By maintaining the catalyst loading constant, the interaction impact of reaction duration and molar ratio was investigated. Reaction times were explored from 20 to 120 min (Fig. 7(c)). The biodiesel yield was lower at the shortest response time. Because there is a solid catalyst present, the rate of mass transfer is slower at first, by reducing diffusion in the reaction mixture [22]. It is observed that the ester content increased with increased reaction time from 20 to 90 min and then reached equilibrium [25,26]. The decrease in yield value is due to subsequent degradation of the product with time [25,26].

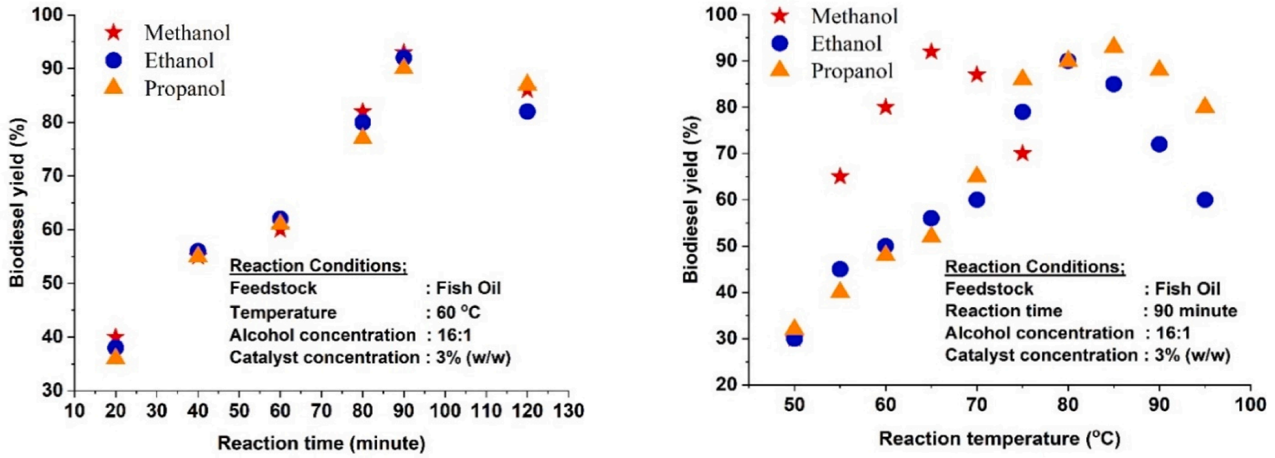
Reaction temperature

The reaction temperature was investigated over the range from 50 °C to 90 °C as shown in Fig. 7(d). Transesterification always occurs below the boiling point of alcohol. It was observed that 65 °C, 80 °C and 85 °C temperatures were suitable for methanol, ethanol, and isopropanol to obtain higher yields and beyond these, alcohol starts to vaporise which lowers the alcohol concentration resulting in a decrease in ester content. The difference between reaction temperatures in methanol, ethanol, and propanol is due to the different boiling point of the alcohols [15,26]. The boiling point of methanol, ethanol and propanol are 65 °C, 78.5 °C and 97 °C respectively [27].



(a) Effect of Alcohol ratio on yield

(b) Effect of catalyst % on yield



(c) Effect of reaction time on yield

(d) Effect of reaction temperature on yield

Fig. 7. Experimentally analyzed transesterification reaction parameters.

Above experimental investigations concludes that 16:1 alcohol-to-oil molar ratio, 3% (w/w) catalyst, reaction time of 90 min, and reaction temperatures of 65 °C, 80 °C, and 85 °C for methanol, ethanol, and propanol respectively; were best operating conditions to carry out the transesterification reaction for biodiesel production.

Characterization of fuel properties

Table 1 lists the fuel characterization equipment and standards utilized. While Table 2, lists the fuel characteristics compared to the biodiesel standards. The fatty acid profile of the waste sardine fish oil used in this study was obtained from previously published work [22] and is given in Table 3. The major component (36%) is the polyunsaturated fatty acid, eicosapentaenoic acid (20:5), with three monounsaturated fatty acids, namely palmitoleic acid, oleic acid and gadoleic acid also being present at significant levels (combined value of 47%).

Table 1
List of the instruments used for characterization.

Fuel Properties	Name of the Instrument	Standards
Density	Pycnometer	ASTM D4892-14
Kinematic viscosity	Ubbelohde viscometer	ASTM D4603-18
Calorific Value	Bomb Calorimeter	ASTM D240-19
Oxidation stability	Rancimat Method (AOCS Cd 12b-92)	EN 14112
Iodine value	Titration method	EN 14111
Flash Point	Closed cup	EN 3679

Effect of alcohol chain length on fuel properties

It was observed that fuel density and viscosity increased with an increase in the chain length. FOPE showing the highest viscosity (4.6 mm^2/s) (Table 2), which is about 4.3% and 2.1% higher as compared to FOME and FOEE. Higher viscosity in turn affects fuel spray penetration, atomization and fuel droplet size which influence the combustion and emission characteristics [30]. Whereas density of FOPE was observed to be 0.45% and 0.11% higher than FOME and FOEE (Table 2). Fuel density has a direct impact on fuel performance since the fuel injection pump injects fuel by volume rather than mass, therefore the air–fuel ratio and energy content are regulated by fuel density for improved combustion [30]. The heat of combustion of the fuel is referred to as the calorific value (CV) of the fuel. Biodiesel has a lower CV than diesel due to the availability of oxygen [31]. It is observed that CV for FOPE was found to be higher about 0.72% and 0.12% as compared to FOME and FOEE (Table 2). Increasing the number of carbons in acyl chains of fatty acids, decreases the relative proportion of oxygen in the molecule leading to an increased heating value. [27]. Fuel flash points (FP) provide important information on storage safety issues and in this regard FOPE shows a 1.5% higher FP as compared to FOME and FOEE. The flash point temperatures of all biodiesels are close to each other and also close to the international standard (Table 2). They are much higher than fossil diesel value (Table 2).

The cetane number (CN) increases with carbon chain length. CN for

Table 2
Comparison of physicochemical properties of fish oil biodiesel.

Properties	Unit	Diesel [28]	Biodiesel [28]	Diesel [29]	Methanol [27]	Ethanol [27]	Propanol [27]	FOME	FOEE	FOPE
Standard No.	–	ASTM D975	ASTM D6751	–	–	–	–	–	–	–
Density (40 °C)	g/m^3	0.820–0.860	0.88 (at 15 °C)	0.830	0.791	0.789	0.809	0.877	0.88	0.881
Viscosity (40 °C)	mm^2/s	2–4.5	1.90–6.00	2.27	0.58	1.13	1.74	4.4	4.5	4.6
Calorific Value	MJ/kg	–		44	19.58	26.83	30.63	39.96	40.20	40.25
Boiling point	°C	–	–	180–360	65	78.5	97	–	–	–
Flash Point	°C	60–80	min 130	56	–	–	–	124	124	126
Pour Point	°C	−15 to −35	−15 to −16	–	–	–	–	2.3	−2.2	−9
Cloud Point	°C	−15 to 5	−3 to −12					5	2.0	−3.2
Cetane Number		46	min 47	49	5	8	12	52	55	58
Oxidation Stability	h	–	min. 3 h^a-	–	–	–	–	8	10	12
Iodine Number	Iodine g/100 g	–	120^a	–	–	–	–	132	132	130
Acid Number	$mKOH/g$	–	max 0.50	–	–	–	–	0.2	0.3	0.35
FFA	%	–		–	–	–	–	0.1	0.15	0.17

a – EN14214.

Table 3
Fatty acids composition of waste sardine fish oil [22].

Fatty acids	Notation	Composition (mol%)
Lauric acid	C12:0	0.26
Myristic acid	C14:0	8.44
Pentadecanoic acid	C15:0	2.29
Palmitoleic acid	C16:1	24.31
Oleic acid	C18:1	13.24
Linoleic acid	C18:2	4.16
Gadoleic Acid	C20:1	9.48
Eicosapentaenoic acid	C20:5	36.17
Behenic acid	C22:0	1.01
Nervonic acid	C24:1	0.64
Saturated fatty acids (SFA)		12.00
Monounsaturated fatty acids		47.67
Polyunsaturated fatty acids		40.33

FOPE was observed to be *ca.*10% and 5% higher as compared to FOME and FOEE (Table 2). The CN indicates the fuel's ignition quality; a greater CN indicates better combustion, especially when starting from a cold start. Lower CN fuels have a longer ignition delay (ID), resulting in increased fuel buildup and burning in the pre-mixed combustion phase, which boosts thermal NOx production [32]. The cetane number (CN) of the fuel is calculated using Equations (6) and (7) [33]. The oxidation stability (OS) of biodiesel fuel is a significant fuel quality in terms of storage stability and performance. Increased viscosity and acidity, as well as the production of gum or silt, are all symptoms of an unstable fuel. The OS of all biodiesels meet the biodiesel standard (Table 2). The unsaturation degree of FAME has a considerable impact on OS; in general, the higher the unsaturation, the lower the OS [27]. Longer chain alcohols result in decreasing moisture content and improving oxidative stability (OS). The OS increases with a lower number of double bods (C = C) since the methylene carbon between double bonds is prone to oxidation [23]. FOPE shows a relatively slow rate of oxidation (*ca.*12 h) which is about 33% and 16% lower when compared to FOME and FOEE and correlates with the carbon content of each alcohol. The iodine value (IV) of biodiesel is determined by the degree of unsaturation of the acyl chains and so will not be affected by the alcohol used as these are all saturated alcohols and also same fish oil was used for transesterification. It was found that the IV of all biodiesels are close to each other and also close to the biodiesel standard (Table 2).

$$\text{Cetane Index (CI)} = \frac{(\text{Aniline Point }(^{\circ}\text{F}) \times \text{Degree of API }(60^{\circ}\text{F}))}{100} \tag{6}$$

$$\text{Cetane Number} = 0.72 \times \text{CI} + 10 \tag{7}$$

Low temperature properties

Cloud point and pour point refer to the cold flow or low-temperature properties of the fuel. Nucleation and crystal development are the two fundamental connected phases in crystallization [16,17]. When the temperature of biodiesel is lower than melting point in the first stage, the liquid molecules form a high intermolecular interaction, creating adequate thermodynamic force in the liquid. The liquid molecules eventually coalesce to create solid structures known as crystal lattices or crystallites [16,17]. This crystallization in the gasoline happens quickly, causing agglomeration and clogging of the fuel line and filters. It wreaks havoc on engine performance and fuel distribution. In comparison to saturated organic molecules, the unsaturated fatty acid component in biodiesel fuels have a lower melting point. Most northern European, US and colder countries experience this problem [34]. This problem can be eliminated by using different alcohol such as ethanol and propanol [34]. We observed that the cold flow properties were improved by using ethanol and isopropanol (Fig. 8). FOPE shows the lowest pour point (−9 °C) and cloud point (−3.2 °C) as compared to FOME and FOEE as shown in Table 2. Increasing the alcohol carbon, also improved the freezing point of the fuel [34,35]. However, the pour point of all biodiesels does not meet the ASTM D6751 biodiesel standard (Table 2). Only the cloud point temperature of the FOPE meets the biodiesel standard. Interestingly, the cloud point temperatures of all biodiesels meet the ASTM D975 fossil diesel standard. This current investigation suggests that changing the carbon content in the alcohols could help in achieving the lower pour point temperatures.

Effect of storage on long-term stability

In the present work, three different biodiesel samples that are FOME, FOEE and FOPE were stored for a duration of 10 months, and its effects on their fuel properties were studied. The samples were stored in airtight containers in the dark at room temperature (15–20 °C). The variation in the properties of fuel samples with storage time is shown in Fig. 9. It is observed that with an increase in the storage time; density, viscosity and the acid value increased whereas the calorific value, oxidation stability, and iodine value decreased for all fuel samples [35]. The degradation of stored samples starts with hydrogen abstraction from the alkaline group next to or between the double bond (-C = C-) in the unsaturated alkyl esters which lead to the formation of free radicals resulting in the production of hydroperoxides on reacting with atmospheric oxygen [35]. The hydroperoxides are capable of crosslinking into larger aggregates resulting in increased density and viscosity as shown in Fig. 9. Increasing the number of -C = C- in the molecule also increases its reactivity with oxygen, so C20:5 is more reactive than less unsaturated acyl components.

The increase in oxygenation of the acyl chain decreases its calorific value (Fig. 9). Hydrolysis of the fuel esters leads to the formation of unesterified fatty acids and an increase in the acid value (Fig. 9). The products generated from acyl chain oxidation are complex and include the formation of aldehydes, ketones and volatile hydrocarbon gases [36,37]. Oxidation stability (OS) were found to be decreased with time due to increase the moisture% and pigments with time (Fig. 9). As the

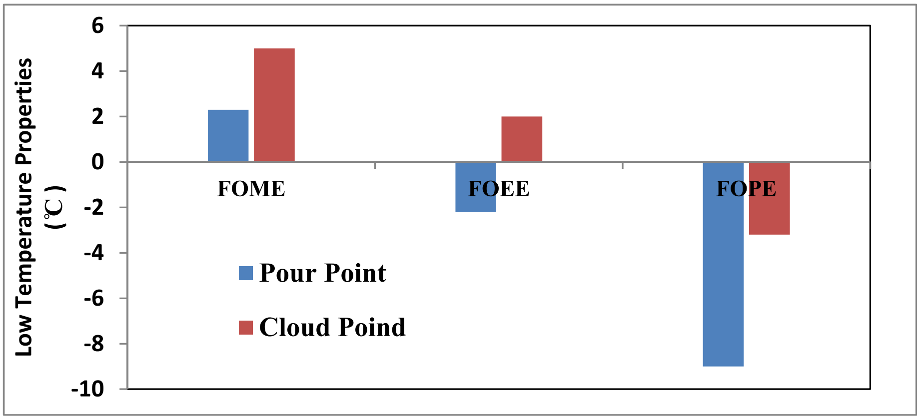


Fig. 8. Low-temperature properties.

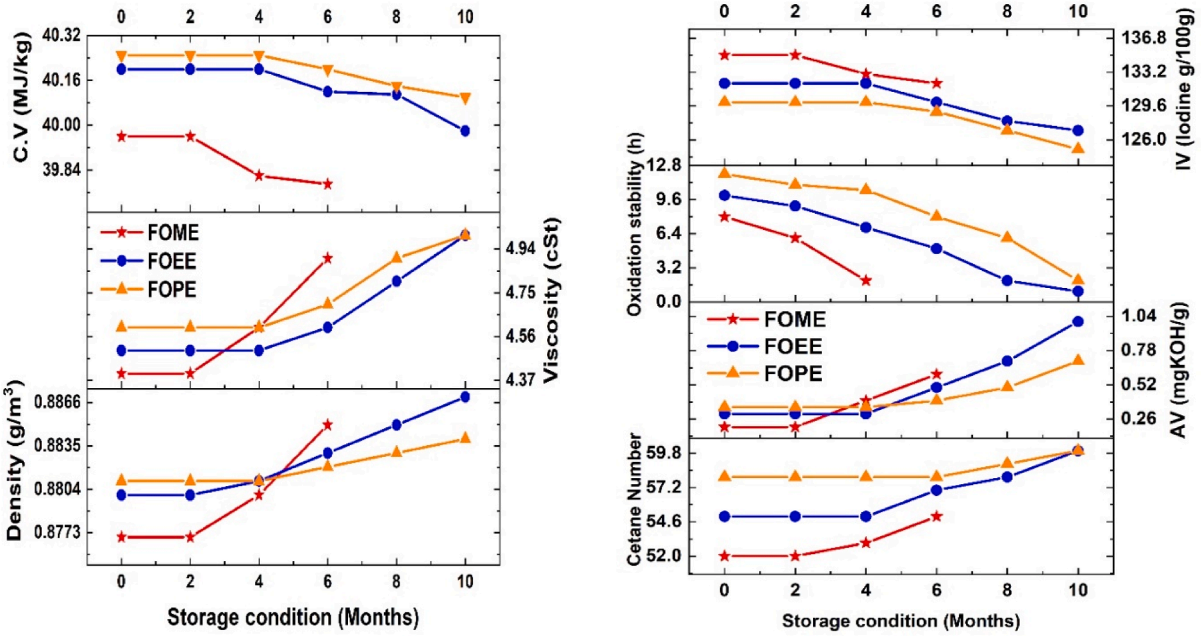


Fig. 9. Effect of storage period on fuel properties.

double bonds are consumed in this process, the iodine values decrease (Fig. 9). It was observed that FOME degraded within 6 months and formed gums (Fig. 10) whereas for both FOEE and FOPE this was not observed, even after 10 months. This study shows that the rate of autoxidation reaction and degradation is faster for FOME samples.

Fig. 10. Gum formation in FOME.

Conclusion

A solid heterogeneous catalyst was synthesized by using eggshell and copper oxide to form $[CaCu(OCH_3)_2]$ and used for biodiesel production using waste sardine fish oil as a feedstock. Fish biodiesel was produced from the waste fish oil using different alcohols [methanol (FOME), ethanol (FOEE), and isopropanol (FOPE)]. The process was optimized for alcohols-to-oil molar ratio, catalyst concentration, reaction time and reaction temperature to find the best condition for higher yields. Low-temperature flow properties were improved when either ethanol or isopropanol was used. Increasing the carbon number of the alcohols increased the freezing point. FOPE showed better cold flow properties and increased freezing point. During storage over a 10-month period the density, viscosity and acid values increased, whereas the calorific values and iodine values decreased with the methyl ester being the least stable over time. Overall, Isopropanol is the best option for producing biodiesel with great storage stability. Future work will focus on the performance and emissions of these three fuels in the internal combustion engines. Recycling and reuse of the heterogenous catalyst is another area to future work.

CRediT authorship contribution statement

Vikas Sharma: Conceptualization, Methodology, Investigation, Formal analysis, Resources, Data curation, Writing – original draft, Visualization. **Abul K. Hossain:** Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition, Visualization, Data curation. **Gareth Griffiths:** Methodology, Supervision, Funding acquisition, Writing – review & editing, Data curation. **Ganesh Duraisamy:** Conceptualization, Supervision, Resources, Project administration, Funding acquisition, Writing – review & editing, Visualization. **Justin Jacob Thomas:** Conceptualization, Methodology, Investigation, Formal analysis.

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.

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