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Pork Lard Derived Biodiesel Production: Characterization, Engine Performance and Emission Analysis

Rohan Jeffry Robert* and C. R. Girish†*
*Department of Chemical Engineering, Manipal Institute of Technology, MAHE, Manipal-576104, India
†Corresponding author: C. R. Girish; girishcrtd@gmail.com

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ABSTRACT

The present work introduces a new methodology in the production of biodiesel from pork-lard waste having high cholesterol content and discusses its improved performance and emissions in a diesel engine. The traditional method of transesterification does not work with cholesterol due to the absence of triglycerides, therefore, the new improved method oxidizes cholesterol to fatty acids and then converts it to biodiesel ester. The procedure includes an acid reagent to break cholesterol and a renewable basic catalyst from seashells, for catalyzing the production. The acid-base system maintains the overall pH while yielding 95.6% conversion at the optimized conditions. The morphology of the produced catalyst was analyzed through FESEM and confirmed through XRD and EDX analyses. The physicochemical and ASTM properties were determined and the calorific value of the 20% biodiesel blend was found to be comparable with that of diesel. From the engine performance analysis, the thermal efficiency of the engine was observed to be higher and the exhaust emissions showed a maximum of 75% reduction in CO and 42.2% reduction in CO_2 emissions, proving it to be an environment-friendly fuel. Additionally, a 32.7% reduction in smoke opacity was also observed, thus decreasing the concentration of particulate matter in the atmosphere.

INTRODUCTION

The rate of urbanization and industrialization is growing more rapidly than ever, and so is energy consumption. Due to the same, the dependency on fossil fuels has increased and is seen to be exhausting over these years (Judith et al. 2015). Although a good source of energy, fossil fuel consumption results in extensive environmental problems such as global warming and greenhouse effects (Asri et al. 2018). This increased dependency and associated environmental concerns have raised global energy security issues and the urge for alternate fuels (Shahid & Jamal 2020). A few of the most promising and environmentally benign energy resources are solar, geothermal, wind, hydroelectric, and biomass energy (Cynamon & Bouwer 2015, Shahid & Jamal 2020).

Among these a potential option to replace or supplement the conventional petro-diesel is biodiesel. Unlike the latter, biodiesel does not contain any aromatic or sulfur compounds thus reducing the amount of CO, SO_2, and Hydrocarbon particulates (Karmakar et al. 2010). Additionally, it is a renewable source of energy, and it is relatively less toxic (Atadashi et al. 2011, Mofijur et al. 2016). Since the carbon emissions are equal to or lesser than the amount in the atmosphere, they can be considered carbon neutral (Pua et al. 2012). With these under consideration, biodiesel would be an ideal replacement or a possible supplement to conventional high-speed diesel (Sharma & Singh 2009. Rakopoulos et al. 2008).

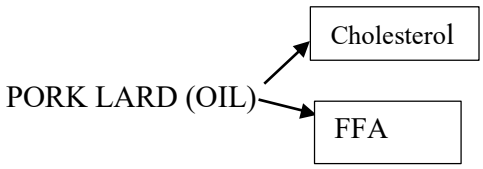
Biodiesel is usually produced from biomasses such as vegetable oils, edible/non-edible oils, and animal wastes (Mureed et al. 2018, Verma & Sharma 2016). Biodiesel production has become a topic of growing interest over the past few years, however, the consumption of edible or value-adding biomass as a source for these productions has questioned food security globally (Awolu & Layokun 2013, Živković et al. 2017, Choudhury 2014). Hence, non-edibles such as animal wastes from slaughter houses, for example, pork lard (Borugadda & Goud 2014, Baskar & Aiswarya 2016, Robert & Girish 2020, Živković et al. 2017) poultry waste (Adewale et al. 2015, Verma & Sharma 2016), beef tallow (Adewale et al. 2015, Andersen & Weinbach 2010, Verma & Sharma 2016), fish waste (Hong et al. 2013, Kara et al. 2018), etc. are considered.

Different methods of biodiesel production include transesterification and/or esterification, thermal cracking, pyrolysis, and micro-emulsions (Borugadda & Goud 2014). Transesterification among these is the most followed method. However, biodiesel can be produced through direct esterification as well (Zaher & Soliman 2015). Moreover, the nature and composition of the feed decide the method to be followed.

Transesterification is usually adapted when triglycerides are present in appreciable amounts. Triglycerides are branched ester compounds; transesterification converts one ester to a different ester (biodiesel) (Atadashi et al. 2013). If the feed oil under consideration contains more FFAs (free fatty acids), the production of biodiesel usually gets hindered by soap formation, if a basic catalyst is used (Atadashi et al. 2011, Shahzadi et al. 2018). The loss in yield is complimented by the complexity in biodiesel purification (Nakatani et al. 2009). An ideal method to overcome this drawback would be to employ an acidic catalyst. This would prevent soap formation.

Certain oils extracted from fats contain cholesterol. Regardless, the methods mentioned above do not account for converting cholesterol to biodiesel. The current work tries to develop a method to convert cholesterol along with the fatty acids into biodiesel esters. The method includes a single-stage reaction in two steps where an acidic catalyst would convert/oxidize cholesterol to fatty acids coupled with the conversion of fatty acids to biodiesel through an esterification reaction.

Nitric acid was carefully chosen as the oxidizing agent. The proposed conversion would follow the reaction shown in Eq. (2).



…(1)

$$CHOLESTEROL \xrightarrow{H(NO3)} LONG\ CHAIN\ FATTY\ ACID \quad \ldots(2)$$

$$LONG\ CHAIN\ FA + FFA \xrightarrow{propanol+Ca(OH)2} PROPYL\ ESTERS + H2O \quad \ldots(3)$$

Esterification in step 2 was carried out using isopropanol in the presence of a calcium hydroxide ($Ca(OH)_2$) catalyst as shown in Eq. (3). Since the first step involves a strong acid, the resultant would be highly acidic. Therefore, $Ca(OH)_2$ in the second would help maintain the overall pH as well while serving as a catalyst.

Biodiesel usually has a higher viscosity than conventional diesel (Monirul et al. 2017). Higher viscosities would lead to issues such as the clogging of fuel injection elements (Venkatesan & Nallusamy 2020). This could be overcome by blending biodiesel with conventional diesel (Babu et al. 2018). Recent developments in biodiesel have shown its potential by subjecting these blends to different combustion and emission analyses.

The biodiesel produced from pine oil and soap nut oil was blended in different proportions and it was studied that Brake thermal efficiency (BTE) improved while smoke, hydrocarbons, and carbon monoxide emissions decreased (Monirul et al. 2017). Pongamia pinnata biodiesel –diesel blends when used as fuel in engines up to 40% blending showed higher BSFC values and emissions of CO, CO_2, HC, NO_X in exhaust gas improved (Sureshkumar et al. 2008). A similar study on Pongamia pinnata biodiesel blend with Butanol and Diethyl ether (DEE) as additives was conducted by Yadav et. al. It was found that the BSFC could be decreased with addition of butanol and DEE in biodiesel-diesel blends (Yadav et al. 2018). Imdadul et al. (2017) from the experiments on biodiesel blends of candle nut oil of 10%, 20%, and 30% composition drew a conclusion that engine performance parameters such as BSFC increased to a value 1.5% and BTE decreased to 1.4% respectively. The emission parameters such as hydrocarbons and CO decreased reasonably and NO_X increased to 2.4% with respect to diesel (Imdadul et al. 2017). The potential of Glauca seed as feed stock for biodiesel blends was explored by Vijayaragavan et al. (2019), and blending was prepared with diesel and ethanol. It was reported that with biodiesel-diesel blends BTE and BSFC increased. But with ternary blending comprising of biodiesel-diesel-ethanol, the BSFC value decreased when compared to biodiesel-diesel blends (Vijayaragavan et al. 2019). The research conducted on canola oil biodiesel and its blends found that even with a 5% biodiesel blend showed that CO emission decreased to 14%. Thus the process proved to be environment friendly and reducing pollution (Roy et al. 2013).

Another study conducted by Alagu et al. used biodiesel- diesel blends with low concentrations of anti-oxidants additives such as butylated-hydroxytoluene (BHT) and butylated-hydroxyanisole (BHA). The experiments found that the BTE can be improved when additives are used in small proportions and it was effective in the blend (Alagu & Nagappan 2018). The efficacy of pentanol as an additive in cashew nut shell biodiesel blends were analysed by Devarajan et al. (2017) and reported that significant increase in BTE and reductions in CO, HC, NO_X, and smoke emissions. But BSFC values were compromised (Devarajan et al. 2017). Bragadewaran et al. (2018) also conducted experiments using additive Methyl tertiary butyl ether in Calophyllum inophyllum biodiesel blends to improve the engine performance. It was noticed that HC, CO and NOx decreased by 63.9%, 6.4% and 3.37% respectively. Therefore, the results proved that the addition of MTBE improved the fuel combustion and reduced HC, CO, and NO_X emissions (Bragadeshwaran et al. 2018). Waste cooking oil was utilized to produce biodiesel and blends of 10% and 15% were prepared with diesel. It was studied that the composition of CO, CO_2 and HC emis-

sions in exit gas reduced to appreciable levels. However, the NO_X emissions were reported higher when compared with diesel emission (Babu et al. 2018). Mahua oil and its various blends were prepared and the performance and emissions were investigated by Godignur et al. The study indicated that CO and HC emissions reduced as biodiesel in the blend increased (Godiganur et al. 2009). A study on orange oil biodiesel blends in engine at different compression ratios (CR) 17, 17.5 and 18:1 were conducted to check the engine performance. From the experimental findings, improved BTE and BSFC values were observed along with reduced CO and HC emissions (Karthickeyan et al. 2017). Thus, it can be concluded that limited literature is available on the study of engine performance and emission characteristics by using biodiesel obtained especially from animal waste as the feedstock. By doing this, it addresses two issues such as waste disposal management as well as finding a potential supplement to the existing fuel needs.

Thus, the present work attempts to produce biodiesel from pork lard waste which is a high cholesterol-containing fat using calcium hydroxide ($Ca(OH)_2$) as the catalyst, produced from sea shells. The work was carried out by oxidizing the cholesterol to fatty acid, and the resultant fatty acid was then esterified to propyl esters. The produced biodiesel was blended with commercial diesel in different proportions to check the calorific value. Based on the preliminary results obtained, the biodiesel blend having the better calorific value was used as fuel and the engine performance and emission characteristics were investigated.

In the previous work, ethyl biodiesel was produced while carrying out a direct esterification reaction (Robert & Girish 2020). The current study takes into account the chemistry that was concluded in the first research and worked towards a better fuel while using a prepared basic catalyst from a renewable source. While the first study was focused on developing a method to convert cholesterol-containing fats to biodiesel, the current work supplements the previous study by developing a better fuel with improved production yield. This study also tests the performance and emissions of the newly developed fuel in an engine, and compares the values with conventional diesel, hence proving the potential of the environmentally benign fuel. While most of the research focuses on using methyl or ethyl alcohol, the current study aims to show that isopropyl alcohol can also be used to produce biodiesel from waste animal fats. Additionally, the study also aims to show that $Ca(OH)_2$ can also be used as a basic catalyst for esterification instead of conventional KOH or NaOH. Furthermore, this research focuses on developing a fuel that would contribute lesser towards the emissions while producing a better energy output.

MATERIALS AND METHODS

Materials

The feedstock, pork lard fat was directly obtained from the local market in Hebri, Udupi, India. The semi-soft white solid fat was taken from the loin and the intestinal area. The solid fat was dry and heated in an open pan and the molten fat or liquid fat is collected and is used for the reaction as described elsewhere [18]. The molten pork lard rich in cholesterol was pale yellow, with a foul smell, and has a density of 0.790 g/cc. The catalyst, Seashells used for the synthesis of the catalyst was collected from the coastal area of Malpe, Udupi, India. Other reagents used in the experiments are Isopropyl alcohol (99%, Finar chemicals) and Nitric acid (Fisher chemicals) (assay 70%).

Catalyst Preparation

The seashells collected from the seashore were washed thoroughly with distilled water to remove any sand or salt present in the shells. After the thorough wash, the seashells were dried in a hot air oven at 90°C.

The shells were subjected to calcination at 900°C for 2.5 h. Before subjecting it to calcination inside the muffle furnace, the shells were crushed using a ball mill to increase the surface area for calcination. Calcination reaction converts the calcium carbonate [Ca(CO3)] to calcium oxide (CaO). The obtained CaO was then mixed with an excess of water to convert CaO to calcium hydroxide (Ca (OH)2). The slurry obtained was heated in the oven at 90^{O}C overnight to remove moisture. The calcium hydroxide obtained was directly used in the esterification process.

Characterization of Sea Shell Catalyst

The surface morphology of the catalyst prepared from seashells was studied using Scanning Electron Microscopy (SEM), Zeiss Company, Germany. The detection of calcium and carbon ions was carried out by Energy Dispersive X-ray (EDX) analysis.

The formation of calcium hydroxide in the catalyst was confirmed by the powder XRD technique (Rigaku X-ray diffractometer) with a high-intensity Cu Kα radiation ($\lambda = 1.54$ Å) at 40 kV and 20 mA. The measurement was conducted at a 2θ angle between 10° to 80° at a scanning rate of 2°C min^{-1} or with 0.0130° increasing step size.

Esterification

Before the esterification process, the feed which is initially a regular animal fat was heated in an open pan till the entire

caul fat melted. The remains of the fat were filtered out from the melted fat and this was used for the process.

The experimental setup consists of a 3-necked flask fitted with a reflux distillation column. One end of the three-neck is fitted with a thermometer and the other end was sealed using a glass cork. The experimental setup is shown in Fig. 1.

A given amount of pork caul fat (10 g) was taken in the 3-necked flask and was heated up to 60°C, and 1g of nitric acid was added to the fat. The reaction was allowed to carry out at 60°C for 15 min for the complete conversion of fat to long-chain fatty acids. The oxidized fat was then subjected to an esterification process with 6 g of isopropyl alcohol and 0.1 g of Ca(OH)2 as a catalyst.

The required amount of the catalyst was added to the oxidized fat taken in the flask. The alcohol was separately heated to 60°C and this was added to the fat-catalyst mixture once the catalyst had completely diffused into the fat. The reaction time was found to be 6 h for complete conversion to fatty acid propyl esters.

Purification

The propyl ester thus formed was impure with the presence of undesired products such as soap, water, and other possible side products or even excess catalyst. The reaction mixture was transferred to a decanter for gravity separation for over 6 h. This was followed by wet washing of biodiesel using warm distilled water (Atadashi et al. 2011). Washing was continued until the bottom layer produced a transparent layer. Any cloudiness in the bottom layer shows the presence of impurities in the biodiesel. The sample was allowed for gravity separation overnight as shown in Fig. 2, flash heated, and then immediately stored in airtight containers for further analysis.

Characterization of Biodiesel

The physiochemical properties of the pork lard biodiesel (propyl ester) were calculated according to standard testing procedures prescribed under ASTM (American Standard for Testing and Materials) and IS (Indian Standard). Density (IS 1448-P16), Viscosity (IS1448), Flashpoint (IS1448-P21), Water by distillation (IS1448[P:40]:2014, and Copper corrosion (IS1448 P-15) were measured following the IS 1448 standard procedures. ASTM standards were used for evaluating properties such as Acid number (ASTM D664), the elements (ASTM D7111-2016), and the Calorific value (ASTM D4809), and later all the values were compared with the standard values. Calorific value was found using Bomb Calorimeter (Rajdhani Scientific Instruments Co., New Delhi).

The feed oil composition, oxidation of cholesterol to long-chain fatty acids, and the conversion to fatty acid propyl esters were examined and confirmed by gas chromatography (Robert & Girish 2020). The gas chromatograph-mass spectroscopy instrument (Agilent GC model 7890A and MS model 5975C MSD) equipped with a column DB 5 MS having dimensions (30 mL x 0.25 mm ID x 0.25 um film thickness) was employed for the analysis. The mass spectrometer was operated in the electron impact ionization mode

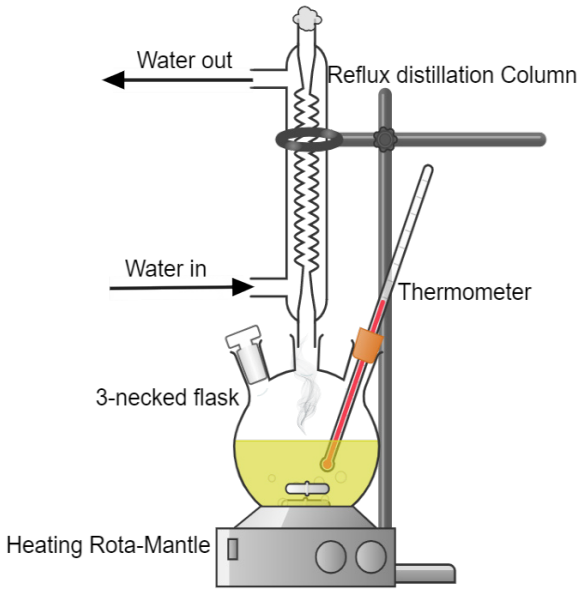


Fig. 1: Experimental setup for esterification.

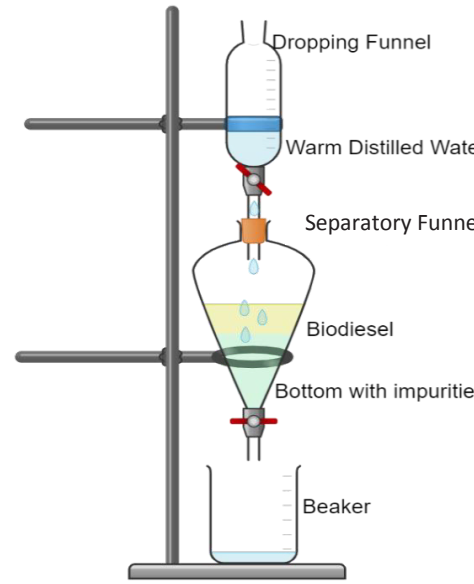


Fig. 2: Experimental setup for biodiesel purification.

at 70 eV in the scan range of 30–700 m/z. Helium was used as the carrier gas flowing at a rate of 1 mL/min. The sample was diluted with hexane and 1µL of the sample is injected into the instrument at an inlet temperature of 260°C. The column initial temperature was at 40°C and was later raised to 290°C at 6°C/min with a total run time of 47 min. The temperature of the transfer line and ion source was kept at a value of 300°C and 230°C respectively. Peaks obtained from the analysis were identified by comparing with standards of mass spectra from the NIST libraries 2011. The yield of biodiesel obtained after the reaction was calculated as in Eq. (4) (Nabora et al. 2019):

$$\%\ yield = \frac{weight\ of\ biodiesel\ obtained}{weight\ of\ feed\ oil\ taken} \times 100 \quad \ldots(4)$$

Blending of Biodiesel, Engine Performance, and Emission Analysis

Various blends were prepared by adding the required amount of biodiesel to commercial diesel. The experiments were done by preparing different blends such as B20, B50, and B80. For example, B20 blending was prepared by adding 20 g of biodiesel to 80 g of diesel in a 3-necked flask and subjected to stirring for 1 hour at 60°C. Then the calorific values of all the blends were measured using the standard method (ASTM D4809). Then depending on the preliminary studies obtained from the calorific values, the B20 blend was selected for measuring engine performance and emission characteristics. Under engine performance, parameters such as brake-specific fuel consumption (BSFC) and brake thermal efficiency (BTE) were calculated. The emission characteristics such as carbon monoxide (% vol), hydrocarbon (in ppm), carbon dioxide (% vol), NO_X (in ppm), and smoke (%) were measured. Moreover, the blends with a higher ratio of biodiesel will significantly increase BSFC and decrease BP and BTE (Nirmala et al. 2020), and have lower calorific values and higher densities which is not ideal for fuel (Raheman et al. 2013). The readings obtained from the engine performance and emission characteristics for the B20 blend were compared with high-speed commercial diesel (B0). These properties are measured to analyze the fuel performance when running a diesel engine in real-time.

The engine used in this experimental setup was the Kirloskar TV1 vertical model IC diesel engine having the power of 3.5kW @1500 rpm equipped with a single-cylinder, four strokes, constant speed, and water cooled. It has other features such as a cylinder bore of 87.50 mm, a stroke length of 110.00 mm, connecting rod length of 234.00 mm, a dynamometer arm length of 185.0 mm, and the CR ranging from 12:1 to 18:1 was used to test the fuel. The samples were subjected to the fuel line to test the performance and emission characteristics of B0 and B20 blends. Engine loads were varied from 0-12Kg to perform the test on the fuel and its blend. The fuels were loaded into the engine's fuel line without any modifications and the engine was run at CR of 17.5 and 18 configurations. The engine was run for 3-5 min at each load to attain stability and then the readings such as engine speed, emission parameters, and fuel consumed were noted down. The exhaust gas analyzer (AVL DiGas 444) was used to measure the emission parameters such as HC, CO, CO_2, NO_X, and oxygen and the smoke meter (AVL 437C) was used for measuring the opacity of polluted air in diesel exhaust gases i.e. smoke of the fuels.

CALCULATIONS

The parameters BSFC and BTE were calculated using the formulae

$$Engine\ power\ (kW) = 2\pi NT \times 10^{-3} \quad \ldots(5)$$

N is engine speed (revolutions per second)

$$T = (load\ in\ Kg * 9.81 * r) \quad \ldots(6)$$

T is engine torque (N m), *r* is dynamometer arm length

$$Fuel\ mass\ flow\ rate\ \left(\frac{g}{h}\right) = 3600 \times fuel\ vol\ flow\ rate\ \left(\frac{ml}{s}\right) \times fuel\ density\ \left(\frac{g}{ml}\right) \quad \ldots(7)$$

$$BSFC = \frac{Fuel\ mass\ flow\ rate}{Engine\ power} \quad \ldots(8)$$

$$BTE = \frac{3600 \times C_v}{BSFC\left(\frac{g}{kWh}\right)} \quad \ldots(9)$$

C is the calorific value of the fuel (MJ/Kg)

RESULTS AND DISCUSSION

Characterization of Sea Shell Catalyst

The scanning electron microscopic image of the calcium hydroxide catalyst is shown in the figure. The pictures were taken at 1µm (40.0KX). Fig. 3A shows the images of calcium carbonate as observed similarly by (Tshizanga & Funmilayo 2017). Fig 3B shows the produced calcium hydroxide catalyst. The comparison between the two images shows the change in morphology between the raw material and prepared catalyst.

From EDX analysis, it was found that calcium is present as the main component of the catalyst. The higher percentage of oxygen shows the presence of calcium hydroxide, calcium oxide, and some traces of unconverted calcium carbonate which is shown in Fig. 4.

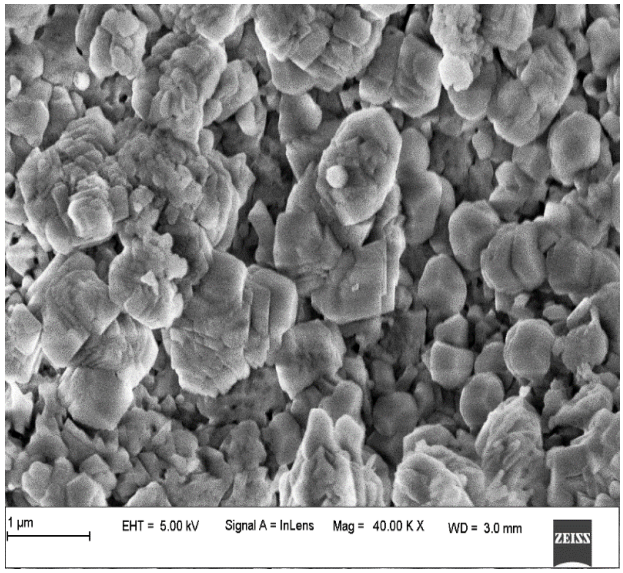


Fig. 3A: SEM image of seashell before calcination

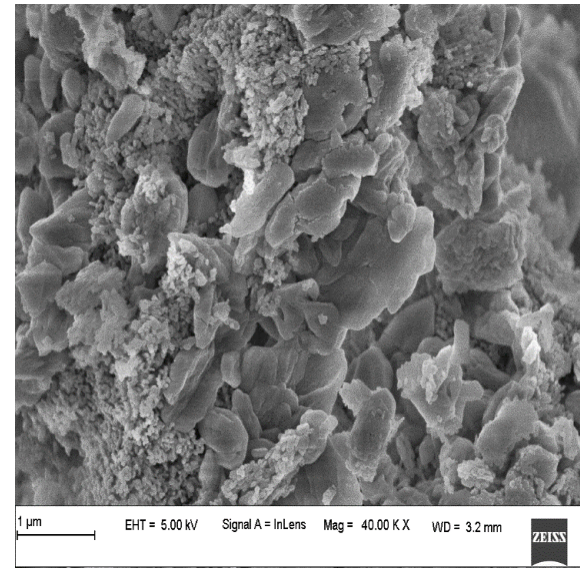


Fig. 3B: SEM image of the seashell catalyst

Fig. 5 shows the XRD patterns of the calcium hydroxide catalyst prepared from seashells. It can be seen that the peaks obtained from the XRD patterns are matching with those reported from the ICSD standard diffraction file. The distinct peaks were observed for the catalyst between 2θ=10–80°. The intensities of the major peaks for calcium hydroxide (ICSD Reference No:01-081-2041) namely [001], [100], [101], [102], [110], and [111] corresponds to the position at peaks 18.05°, 28.70°, 34.11°, 47.13°, 50.84° and 54.39° respectively with hexagonal structure. This confirmed the presence of calcium hydroxide in the prepared catalyst and similar kinds of results were reported in the work (Chingakham et al. 2019, Margaretha et al. 2012). The component calcium carbonate (ICSD Reference No:01-072-1907) was found at 39.37°, 43.12°, and 48.15° with trigonal configuration. Other minor components quartz low silica oxide (ICSD Reference No: 01-070-2538) at 59.70° with hexagonal structure and calcium oxide (ICSD Reference No:01-075-0264) at 32.38° with the cubic structure were observed.

Effect of Reaction Parameters

The yield of biodiesel produced depends upon the parameters such as the amount of catalyst, alcohol to oil ratio, the temperature of the reaction, and the time taken to complete the reaction. To produce a maximum yield, the reaction has to be optimized while consuming fewer reagents to keep

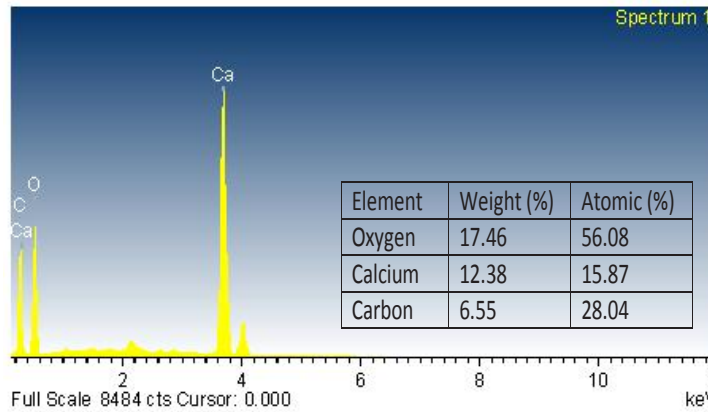


Fig. 4: EDX analysis of the sea shell catalyst.

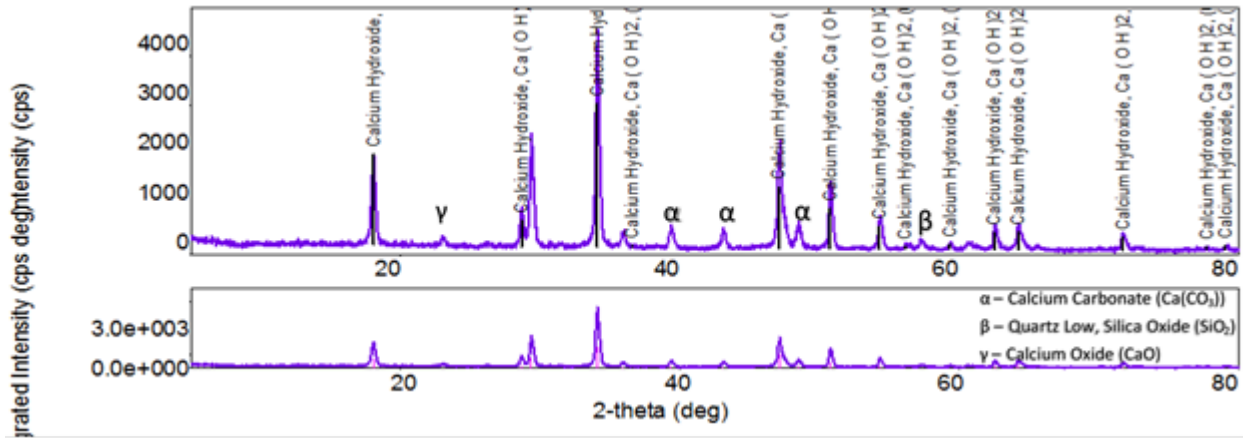


Fig. 5: XRD analysis of calcium hydroxide catalyst.

the cost and energy of production as low as possible. The range of the parameters for esterification has been selected from the preliminary experiments. It has to be considered that all the reagents for the reaction have been measured in terms of mass rather than volume. Since the experiments were carried out over a long period of time due to external weather conditions, the volume of the reagents could vary. Hence, the mass has been taken as the base of measurement, since it would be more reliable.

To study the significance of each reaction parameter, experiments were carried out by varying one parameter while keeping the other parameters constant (Fadhil et al. 2017).

Effect of Propyl Alcohol

The influence of propyl alcohol on biodiesel yield was observed by varying the amount of alcohol to oil ratio in the range of 3:10 to 8:10. The temperature was maintained at 68-70°C for 6 h and 0.1 g of $Ca(OH)_2$ catalyst was used. It was observed that as the amount of alcohol increased the yield also increased up to 95% at an alcohol to oil ratio of 6:10. This is because the increase in alcohol continuously converts fat to propyl esters (Saravanan et al. 2019). It was found that increasing the amount of alcohol beyond 6g shows a small decrease in yield as the propyl esters are being formed as shown in Fig. 6.

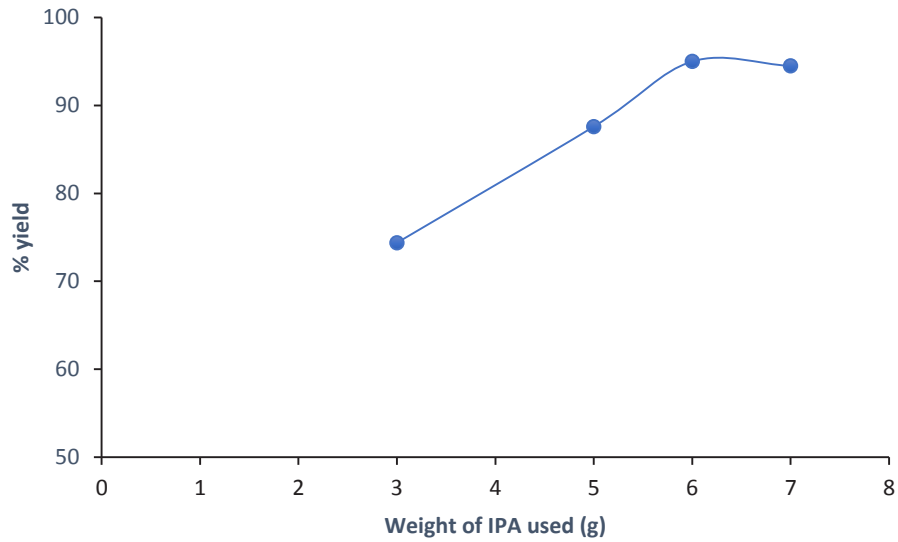


Fig. 6: Effect of propyl alcohol on esterification.

$$R1-COO-H \;+\; C_3H_7-OH \underset{68-70°C,\ 7\ hrs}{\overset{catalyst}{\rightleftarrows}} R1-COO-C_3H_7 \;+\; H2O$$

Long chain fatty acid Propyl alcohol Propyl ester

…(10)

This small decrease in yield may be because of the shift in reaction to attain an equilibrium (Maneerung et al. 2016). Another possible explanation for this decrease in yield is a potential interaction between excess isopropyl alcohol and the catalyst which would decrease the amount of catalyst available for the reaction (Asri et al. 2018).

Effect of Catalyst Loading

The optimum dosage of catalyst determines the maximum extent of biodiesel conversion. The effect of catalyst loading was observed by varying the amount of $Ca(OH)_2$ used from 0.1 to 0.5 g with respect to 10 g of oil under esterification at 68-70°C for 6 h. A maximum yield of 92% was observed at 0.1 g of catalyst as shown in Fig. 7. For every increase after 1 g, the yield decreased significantly to an extent where no yield was observed as thick viscous mass and emulsions were found. The decrease in yield could be due to poor diffusion of reagents (Viola et al. 2012). This poor diffusion is due to the increased viscosity of the mixture in the presence of an excess catalyst (Ezebor et al. 2014). Hence, there is a significant mass transfer resistance that affects the reactant system. Similar findings were observed by the authors on the effect of catalyst loading (Ashok et al. 2018). Since the reaction deals with fatty acids and not triglycerides, the formation of soap can be ruled out (Zhang & Jiang 2008).

Effect of Temperature

The effect of temperature on esterification was carried out with 10g of oil, 6g of IPA, and 0.1 g of $Ca(OH)_2$ for 6 hours. The temperature was varied between 30°C and 80°C and their corresponding yields were observed in the experiments. With an increase in temperature up to 65-70°C, there was a marginal increase in yield. It was observed that 65-70°C was optimum and the maximum yield of 95.6% was reported. It was also observed that beyond 70°C the yield decreased noticeably. The readings are reported in Fig. 8.

The initial increase in yield is because of the accelerated diffusion of the catalyst into the reactant system (Ning & Niu 2017). This is because the mass transfer rate is directly proportional to temperature (Stamenković et al. 2008). Further heating of the reaction system beyond 70°C causes the vaporization of IPA in the reaction system as its volatile even under room temperature. This causes a lowering of IPA concentration in the reaction system which leads to poorer conversion and hence a low yield was obtained. A similar trend of results was reported in the work (Maneerung et al. 2016, Ning & Niu 2017, Ashok et al. 2018).

Effect of Reaction Time

The effect of reaction time on biodiesel yield was investigated by varying the reaction time between 4hr to 10 h and by taking 10 g of oil, 6 g of IPA, and 0.1 g of $Ca(OH)_2$ catalyst. As the reaction time increased, the yield increased to give a maximum of 95.6% at 6 hours. Beyond 6 hrs, there was a

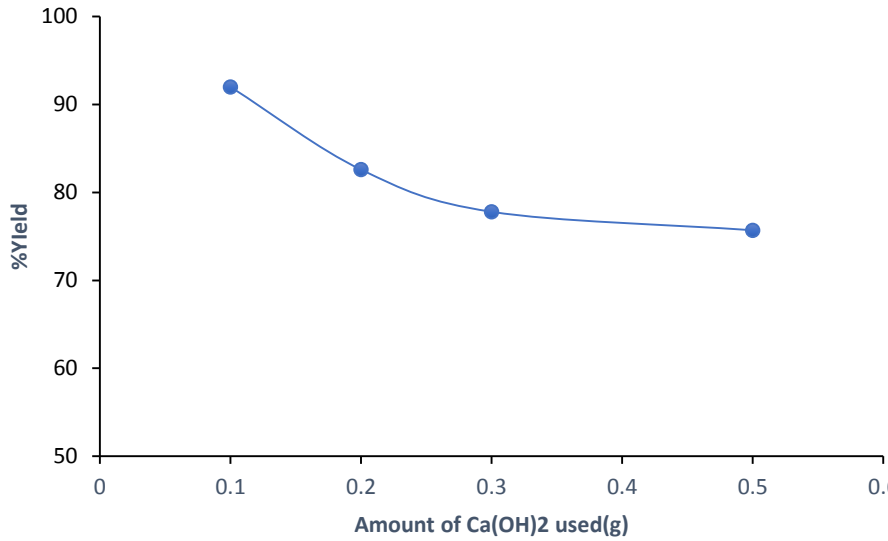


Fig. 7: Influence of catalyst loading on esterification.

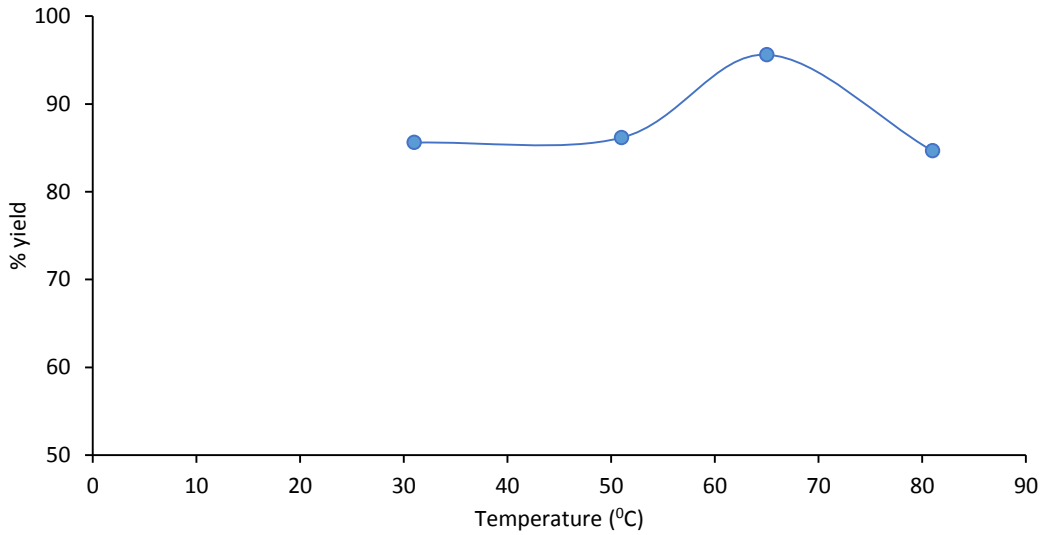


Fig. 8: Effect of temperature on transesterification.

small decrease in yield and thereafter it gave constant yield. The effect of reaction temperature on yield is represented in Fig. 9.

The small decrease in yield may be due to the equilibrium of the system. This may cause the reaction to shift towards the reactant side (Nabora et al. 2019) and in turn, decrease the number of propyl esters to maintain equilibrium. The yield values remained consistent beyond 6 hrs showing that the system has reached equilibrium and all possible conversions had taken place (Asri et al. 2018). Similar results were discussed in the work (Niju et al. 2015).

Characterization of Biodiesel

Gas chromatography analysis of biodiesel (propyl esters): GC results provide peaks that help to identify different compounds present along the x-axis, the retention time. This qualitative analysis provides a technique to test the purity of the produced biodiesel and most importantly, a method to track the reaction conversion at each step of the production methodology (Gupta et al. 2018). The presence of cholesterol in the feed and the oxidation of cholesterols to fatty acids are reported as well with relevant GC-MS support. The GC profile for the fat has been presented in table 1. Similarly,

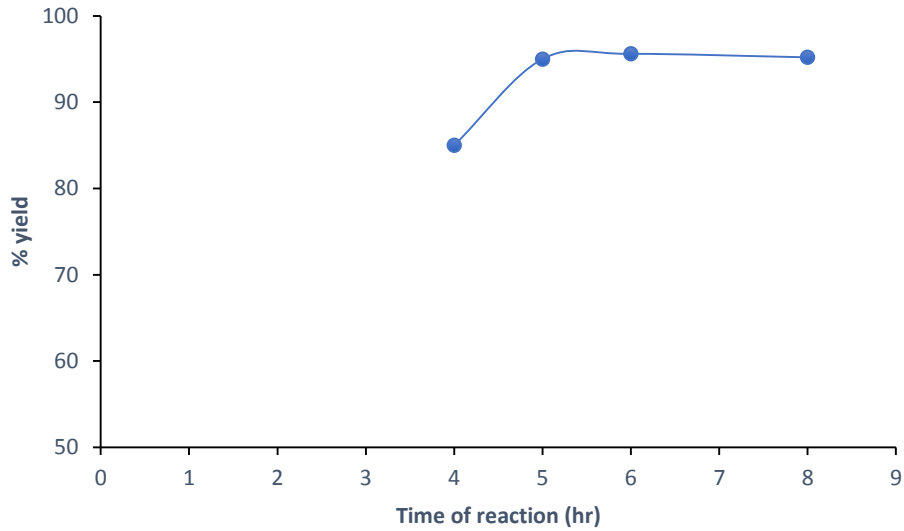


Fig. 9: Influence of reaction time on esterification.

Table 1: Feed oil composition obtained using a gas chromatograph.

Sl.No.	Feed oil composition	Molecular formula	Molecular weight	Content [%]	Retention time, min
1	Hydroperoxide, 1-methylhexyl	$C_7H_{16}O_2$	132.2	5.704	4.166
2	2-Heptenal, (E)-	$C_7H_{12}O$	112.16	4.510	7.618
3	Nonanal	$C_9H_{18}O$	142.2	2.250	11.408
4	2-Decenal, (E)-	$C_{10}H_{18}O$	154.24	6.686	15.304
5	2,4-Decadienal	$C_{10}H_{16}O$	152.23	8.366	16.629
6	Heptadecane, 2,6,10,14-tetramethyl-	$C_{21}H_{44}$	296.57	1.394	20.581
7	E-14-Hexadecenal	$C_{16}H_{30}O$	238.40	1.565	24.102
8	3-Trifluoroacetoxydodecane	$C_{14}H_{25}F_3O_2$	282.34	2.122	31.856
9	Butanamide	C_4H_9NO	87.12	2.302	32.460
10	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester	$C_{19}H_{38}O_4$	330.50	5.577	34.227
11	Unknown			1.973	36.608
12	E,E-1,9,17-Docasatriene	$C_{22}H_{40}$	304.6	7.498	36.690
13	RT Cholesterol	$C_{27}H_{46}O$	386.65	50.053	44.521

the peaks from the ester GC profile were analyzed and the presence of Isopropyl Palmitate, i-Propyl 9-octadecenoate, and Isopropyl stearate in major proportions were confirmed in Fig. 10. This finding was in accordance with the expected chemical reaction presented in Eq. (10). The conversion of cholesterol to fatty acids and further conversion to corresponding propyl esters are reported in Tables 2 and 3 respectively. The average molecular weight of the biodiesel was estimated to be 316.54 $g.mol^{-1}$.

Determination of physicochemical properties of biodiesel: The different properties of the produced biodiesel were determined as per standard procedures and are shown in Table 4. The properties such as density, viscosity, water content, acid number, flash point, presence of sodium, potassium, and calorific value were evaluated.

Flashpoint is very significant from the safety aspects when storage and transportation of fuel are under considera-

Table 2: The composition of nitric acid-treated feed oil using gas chromatography

Sl.No.	Feed oil composition	Molecular formula	Molecular weight	Content [%]	Retention time, min
1	Pyridine	C_5H_5N	79.10	6.03	4.268
2	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256.4	17.28	19.898
3	2-octyl-Cyclohexane	$C_{14}H_{28}$	196.3	3.39	21.575
4	9-Octadecenoic acid, (E)-	$C_{18}H_{34}O_2$	282.4	46.65	21.63
5	Octadecanoic acid	$C_{18}H_{36}O_2$	284.4	16.58	21.77
6	Allyl octadecyl ester	$C_{23}H_{42}$	382.5	5.93	22.34
7	9-Octadecenal, (Z)-	$C_{18}H_{34}O$	266.4	4.15	23.89

Table 3: Fatty acid propyl ester composition from GC-MS analysis

Sl.No.	Fatty acid propyl ester composition	Molecular formula	Molecular Weight [$g.mol^{-1}$]	Fatty acid ester [%]	Retention Time, min
1	Isopropyl Palmitate	$C_{19}H_{38}O_2$	298.5	27.638	21.086
2	i-Propyl 9-Octadecenoate	$C_{21}H_{40}O_2$	324.5	51.338	22.692
3	Isopropyl stearate	$C_{21}H_{42}O_2$	326.6	21.024	22.923

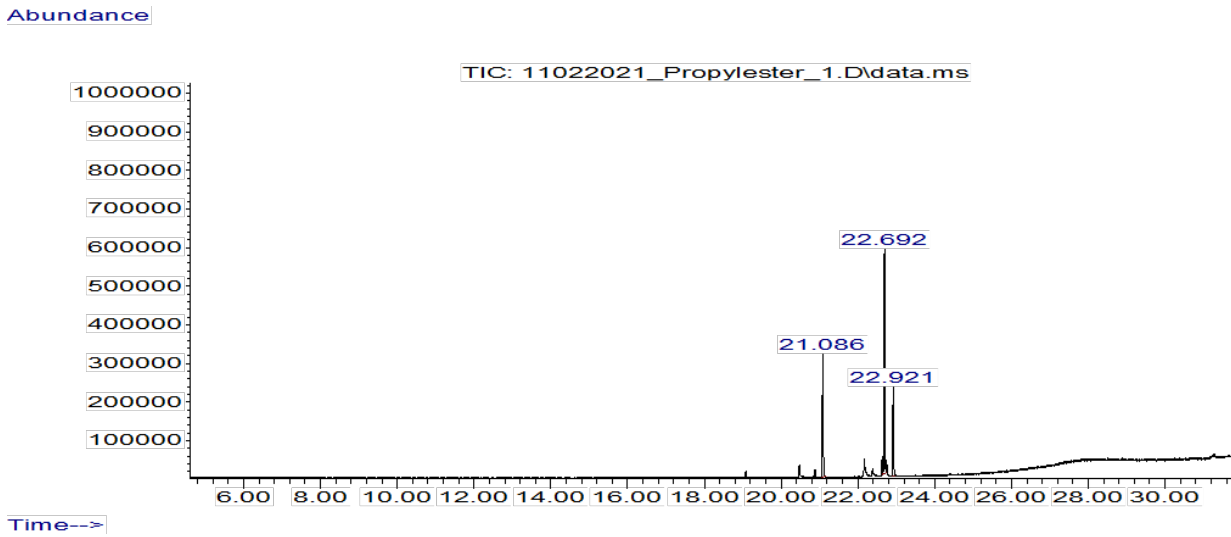


Fig. 10: GC-MS profile of propyl esters.

tion. The higher flashpoint for a fuel shows that the fuel has a larger storage capacity and less risk of fire accidents (Chavan et al. 2017, Sánchez-Arreola et al. 2019). The acid value shows the corrosiveness of the fuel because the engine and storage tanks having fuels with high acid values corrode fast (Al-Muhtaseb et al. 2018). The increase in viscosity affects fuel injection into the engine chamber and this affects the quality of combustion (Mazaheri et al. 2018, Sánchez-Arreola et al. 2019). The moisture content is to be maintained as low as possible to enhance the combustion (Chavan et al. 2017). All the physicochemical properties evaluated were within the range specified by the Standard procedures and have satisfied ASTM standards.

Determination of calorific value of biodiesel and its blends: Calorific value is a measure of the fuel's ability to generate energy on combustion. Therefore, for a given amount of fuel, the power output will be high for fuel with a high calorific value (Kakati et al. 2017). The calorific value of fuel affects the BSFC and BTE of the diesel engine (Jena et al. 2010).

From the experiments, it could be seen that the calorific value of B100 was 35.7 $MJ.kg^{-1}$ when compared to diesel which was 43.6$MJ.kg^{-1}$ Fig. 11. The calorific value was in accordance with the standard EN 14213 range which is 35$MJ.kg^{-1}$ (Shankar et al. 2017). As the ratio of biodiesel in the blend increases, the calorific value

Table 4: Physico-chemical properties of biodiesel.

Sl.No.	Property	Units	Method	Result	Std Range
1	Density at 15.0°C	$g.mL^{-1}$	IS 1448-P16	0.863	0.86 - 0.88
2	Kinematic viscosity at -40°C	cSt	IS 1448	11.93	8to12
3	Flash point	°C	IS 1448 – P21	52	35to65
4	Calorific Value	MJ/Kg	ASTM D4809	35.7	>35
5	Water by distillation	%	IS 1448 [P:40]:2014	1.1	1.1
6	Copper corrosion (3h at 50°C)		IS 1448 P-15	1a	Not worse than class 1.
7	Acid number (Inflection end –point)	mg $KOH.g^{-1}$	ASTM D664 (Method A)-2017a	9.3	5 to 20
8	Elements by ICP		ASTM D7111-2016		1
	Sodium	$mg.kg^{-1}$		<1	
	Potassium	$mg.kg^{-1}$		<1	

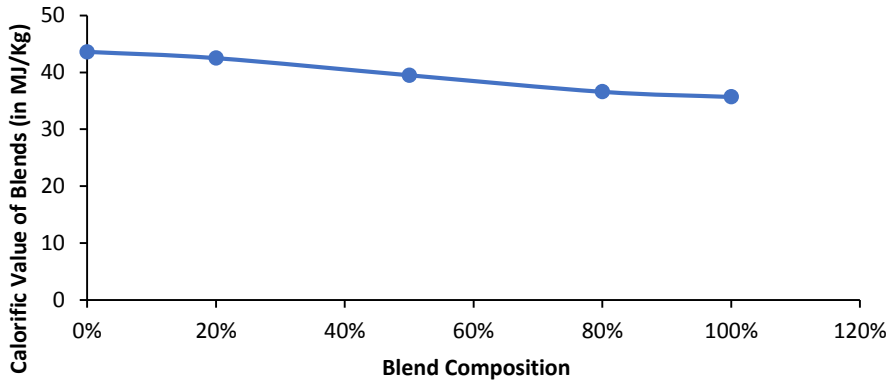


Fig. 11: Calorific values of biodiesel blends.

decreases. Similar conclusions were drawn by researchers (Mofijur et al. 2015). Although the calorific value decreased with blend ratio, the B20 blend had a closer and comparable value when compared to diesel. Hence B20 was selected for engine performance and emission analyses. The decrease in calorific value is because of the increase in oxygen content (Patel & Sankhavara 2020) and frictional losses due to the increased density of the fuel mixture (Dash et al. 2010.).

Engine Performance Analysis

Brake-specific fuel consumption (BSFC) and brake thermal efficiency (BTE) are the parameters used to quantify the significance of the fuel performance in the engine.

BSFC: An ideal engine should produce high brake power while consuming less fuel (Zaher & Soliman 2015). Generally, as the load on the engine increases, the BSFC value decreases. This is because BSFC is the ratio of total fuel consumption to brake power and as the load increases brake power increases more generously than the total fuel consumed and thus bringing down the overall ratio of BSFC (Nirmala et al. 2020, Sureshkumar et al. 2008). From the results, it could be seen from Fig. 12A, that at a CR of 17.5, BFSC for all loads was higher than or nearly equal to that of commercial diesel B0. A similar trend of results was reported by the authors in previous works (Sureshkumar et al. 2008, Teoh et al. 2019). It could be observed that at a load of 12 kg, the readings for B20 and B0 were almost coinciding with an increase of just 16g.KWh^{-1}. Although the BSFC at CR17.5 were high for B20, the difference between the readings was not more than an average of 3.7%.

However, at CR 18 the B20 blend produced better BSFC when compared to B0 as shown in Fig. 12B. There was an average decrease of 5.1% BSFC over the range of loads. A similar trend of results with lower BSFC readings was reported by the authors (Asri et al. 2018). Lower BSFC describes the fuel to be more efficient during burning with improved combustion characteristics (Rosha et al. 2019). At CRs biodiesel blends perform better than commercial diesel as combustion characteristics increases due to improved mixing of the fuel and air (Rosha et al. 2019).

Another possible reason for the lower BSFC may be the synergistic effect of biodiesel with diesel. It was justified that, the oxygen present in the biodiesel must have helped the overall blend achieve better combustion (Raheman et al. 2013). On the other hand, few researchers explained that the BSFC increases as a result of leaner combustion due to the presence of increased oxygen content in the blend. When the combustion becomes extra lean, more fuel may be required to achieve a given power output (Kadir et al. 2020). The present work produced biodiesel which consists of esters in the range C16-C20 when compared to other works, the amount of oxygen does not increase enormously when the blend ratio increases. Therefore, it can be concluded that the increase in oxygen in B20 blend is ideal enough to improve the combustion characteristics at higher CR and also not contribute to extra lean combustion.

BTE: It is the ratio of total brake power to the chemical energy from the fuel (Mishra et al. 2020). It evaluates the potential of a given fuel in transforming its chemical energy into useful work (Sivaramakrishnan 2018). It was observed that BTEs were at an average of 1.1% less for B20 when compared to B0. The small difference in BTE is due to the lower calorific value and higher density of the B20 blend. However, as the load increases, the BTE of B20 was coinciding with B0 and at the highest load of 12 kg, the value was higher for B20 (BTE(B20)- 26.79%, BTE(B0)- 26.62%) (Fig. 13A). This is because of the reason that at higher loads, BTE increases because of increased brake power (Sundar & Udayakumar 2020).

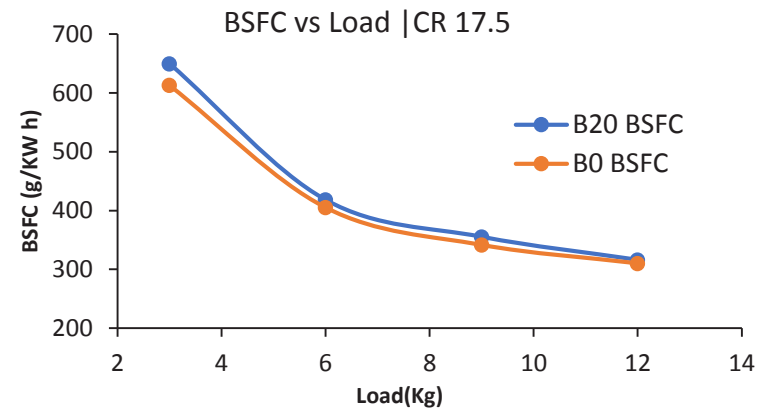


Fig. 12A: BSFC of B20 and B0 for varying Loads at CR 17.5.

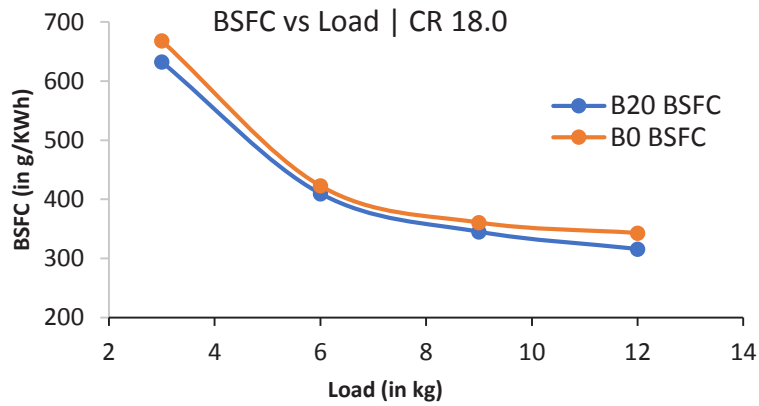


Fig. 12B: BSFC of B20 and B0 for varying Loads at CR 18.

For CR of 18, BTE was observed to be higher for B20 than commercial diesel B0 for all the loads. There was an average increase of 8.2% on all loads and as discussed with respect to CR of 17.5, at a maximum load of 12 Kg highest increase in BTE was observed (BTE(B20)- 26.80%, BTE(B0)- 24.06 %) as shown in Fig. 13B. This increase in thermal efficiency at higher CR is because of the improved combustion due to the increase in cylinder temperature and expansion work (Dash et al. 2020).

Exhaust Emission and Combustion Analysis

The exhaust gas from the engine during the B20 and B0 run was analyzed for its emission characteristics ranging from the composition of the gaseous mixture and smoke opacity. The significance of these analyses is aimed to prove that the current fuel understudy contributes lesser towards the emission of greenhouse gases and air pollution. Researchers have shown that even low blends of biodiesel can bring down the emission to a significant level (Mofijur et al. 2016). Anderson &Weinbach (2010) had shown that although there was a slight increase in fuel consumption for the biodiesel blend, there could be a potential decrease in CO_2 emissions and it was an appreciable finding. Moreover, the B20 blend had comparable calorific value with commercial diesel it was subjected to emission analyses as well.

CO and CO_2 emissions: Fig. 14A and Fig. 14B show the combined CO and CO_2 percentage emissions over varying loads at CR 17.5 and 18 respectively. CO emission corresponds to incomplete combustion i.e., partial-oxidation of the fuel. Over the ranges of load for both CRs, the CO emission for the blend B20 was very much less than that of pure diesel B0. At CR 18, the analyzer recorded an average of 75% reduction in CO emission when compared to CR 17.5, which was 46%. The reduced CO emission is because the increased biodiesel ester composition enriches the fuel with more oxygen. Since these extra oxygen molecules promote further oxidation, there will be an improvement in combustion characteristics with the increase in blend ratio (Tüccar et al. 2014).

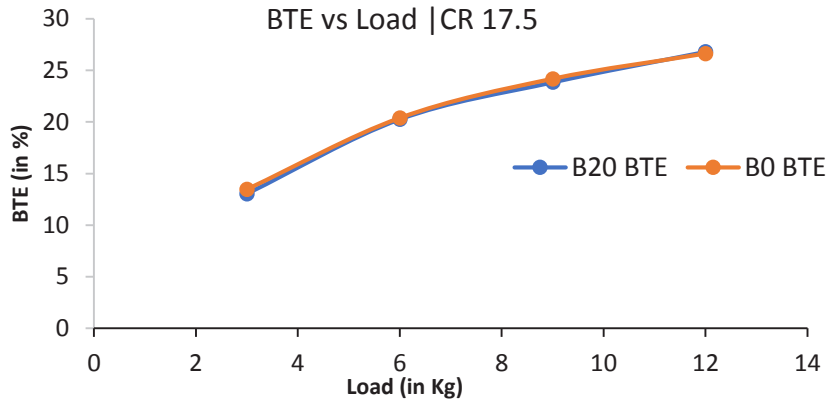


Fig. 13A: Variation of BTE with increasing loads at CR 17.5.

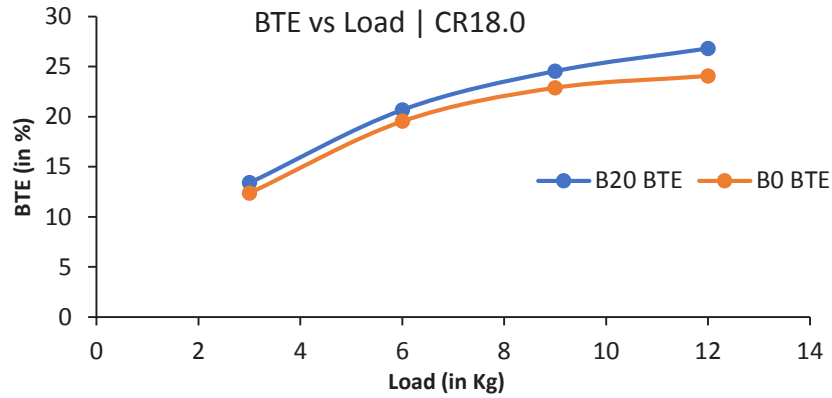


Fig. 13B: Variation of BTE with increasing loads at CR 18.

Furthermore, in comparison of these emissions over CRs, it could be concluded that at a higher CR of 18.0, both CO and CO_2 emissions were appreciably lesser than the emissions at a CR of 17.5. At higher CRs as discussed earlier, the pressure, as well as the temperature in the cylinder, is relatively high.

Hence, combustion characteristics are enhanced due to this elevation in temperature (Kaisan et al. 2017). With respect to CO_2 emissions, at CR 17.5 an average reduction of 42.2% was observed whereas, at CR18, it was recorded as 41.2 %. From the above results obtained from CR 17.5 and CR 18, it could be proved that blending has decreased the overall CO_2 and CO emissions. The reduced CO_2 emissions are because of the decrease in carbon atoms present in the fuel blend compared to diesel (Babu et al. 2018).

NO_X: NO_X corresponds to different oxides of Nitrogen. It was reported by the researcher that most biodiesel and its blends produce NO_X emissions which are more than that produced by commercial diesel (Nirmala et al. 2020). Biodiesel contains more oxygen and this sums up to a better and improved combustion. Hence, more NOx emissions are recorded due to this increased combustion (Imdadul et al. 2017). Similar observations were recorded in the present study as given in Fig. 15.

At higher CRs, as concluded earlier with respect to CO emissions, there is an increase in temperature and therefore, combustion advances, and more NO_X gases are released (Rahman et al. 2014). Similar findings were observed in the present work as well. As a general trend for all CRs, with an increase in load, NOx emissions increase due to increased fuel consumption at higher loads (Nguyen et al. 2020).

Although NO_X emissions are recorded to be higher for B20 at both CRs, the magnitude of the increase may not be accounted is considering the emissions are in ppm levels. For CR 17.5 and 18.0, the average increase in NO_X emissions is 0.25% and 3.35% respectively signifying that NO_X emissions for B20 and B0 are comparable.

HCs: The emission of lesser hydrocarbon (HC) corresponds to better and cleaner combustion (Imdadul et al. 2017, Godiganur et al. 2009). HC at all loads and CRs are lower for the B20 blend than for B0, and the reason for this decrease

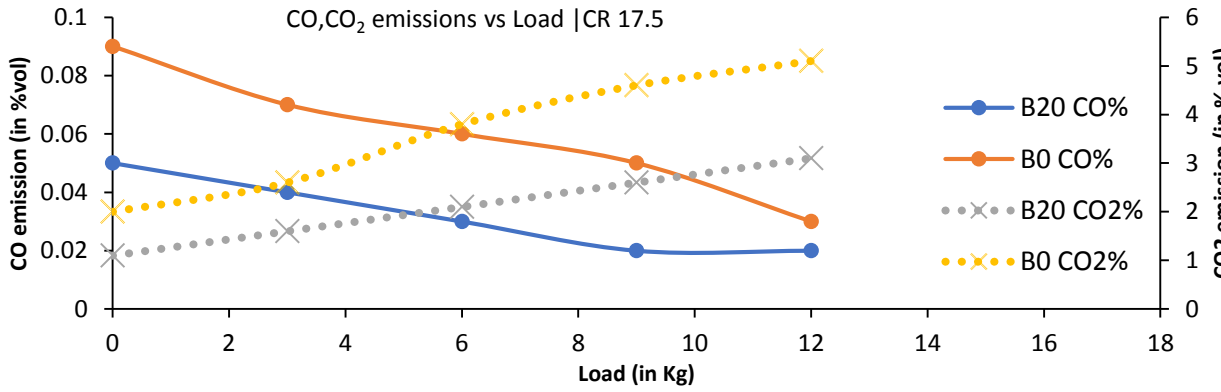


Fig. 14A: CO and CO_2 emissions with increasing load at CR17.5.

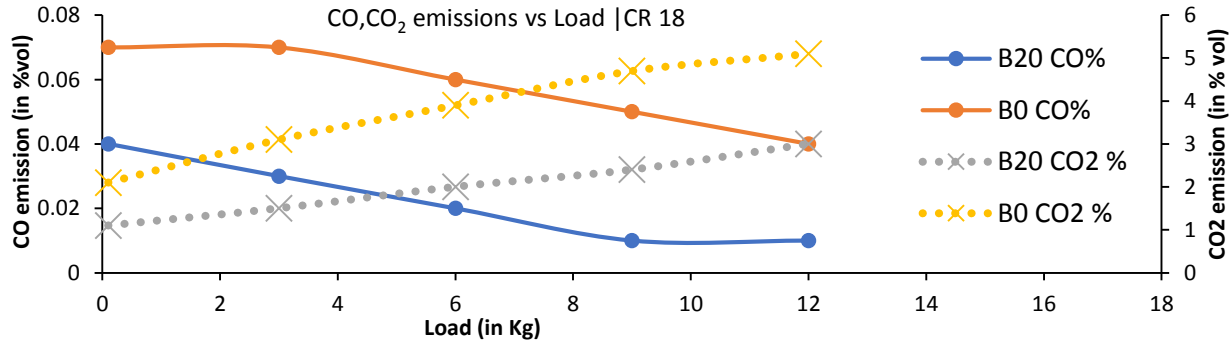


Fig. 14B: CO and CO_2 emissions with increasing load at CR 18.

attributes to the complete or enhanced combustion of the fuel mixture (Rahman et al. 2013). With the increasing amount of biodiesel in the blend, the concentration of oxygen increases. Therefore, enhanced combustion is observed due to the better oxidation of hydrocarbons (Sivaramakrishnan 2018). As load increases, for all CRs, the HC emission increases

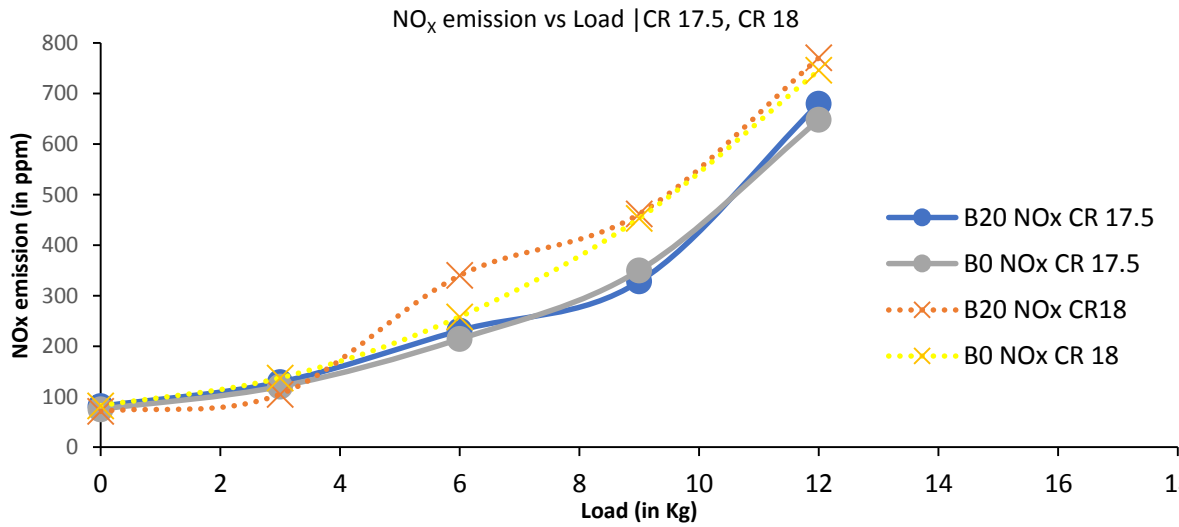


Fig. 15: NO_X emissions with varying loads at CR 17.5 and CR18.

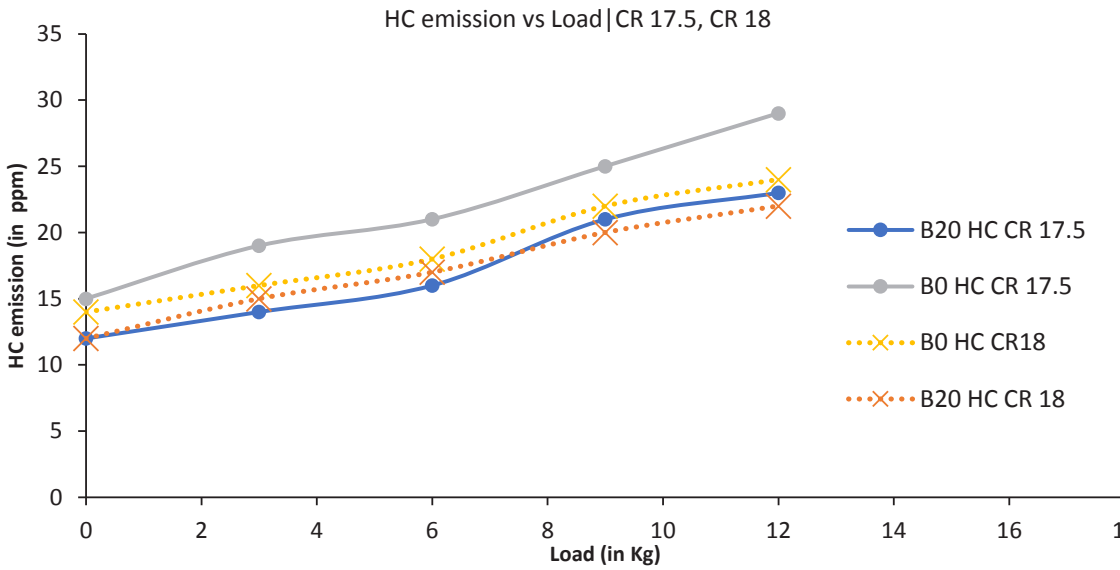


Fig. 16: Hydrocarbon emission with increasing load at CR 17.5 and CR18.

significantly. To maintain the engine speed at higher loads, more fuel is consumed. Hence more combustion takes place resulting in the release of more hydrocarbons irrespective of fuel blend. From the data reported in Fig. 16, it could be concluded that at CR 17.5 and CR 18, there were an average decrease of 21% and 9% HC emissions respectively. It is also very important to observe that at CR 18, the HC emissions were lower than that at CR 17.5. The reason behind this observation is common to those reported earlier under other emission parameters as elevated temperature and pressure contribute towards better combustion.

Smoke Opacity: The lack of air or oxygen in the combustion chamber causes smoke during combustion. In addition to this, an increased C/H ratio in fuel and accumulation of fuel can also cause increased smoke in the chamber (Jeevanantham et al. 2019). The variation in Smoke Opacity with increasing loads is presented in Fig 17. It could be observed that with an increase in load, the smoke opacity also increases. It was also observed that the smoke opacity for B20 was lesser compared to B0 for all CRs. An average decrease of 19.3% and 32.7% in smoke opacity was found between B0 and B20 at CR 17.5 and CR 18 respectively. This decrease

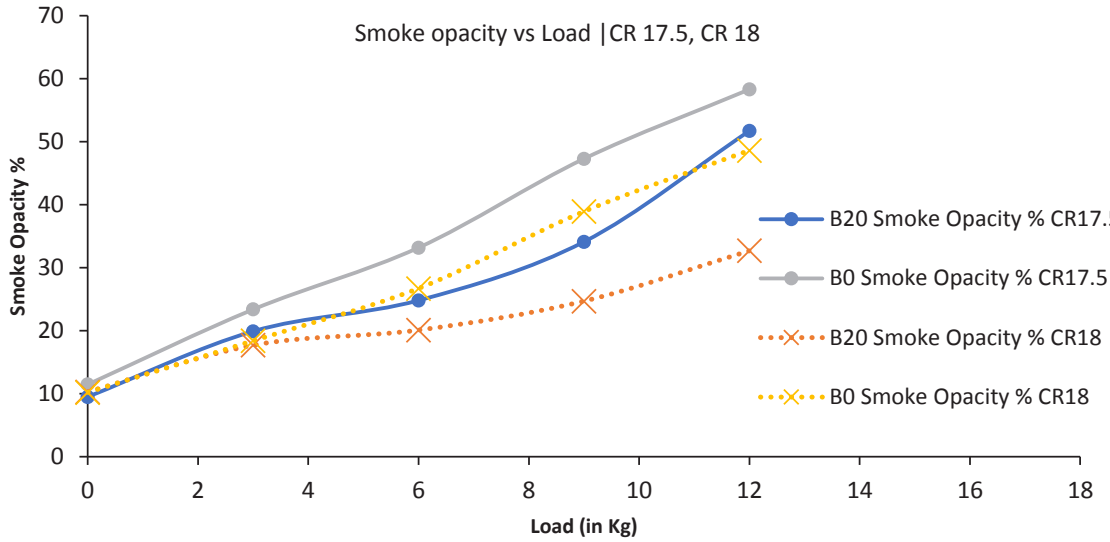


Fig. 17: Smoke opacity with varying loads at CR 17.5 and CR18.

between B0 and B20 is because of the oxygenated fuel mixture as discussed earlier as well as in the work (Kakati & Gogoi 2016). The enrichment of oxygen in fuel facilitates combustion and the presence of more oxygen oxidizes further soot in the combustion chamber (Can 2020, Rosha et al. 2019). As far as CRs are concerned, smoke opacity decreased with increased CR from 17.5 to 18.

CONCLUSION

Waste pork fat from the slaughterhouse was used as the feedstock for producing biodiesel. Due to the presence of high cholesterol content, the traditional method of producing biodiesel could not be carried out because of the absence of triglycerides. Hence, an economical way of producing biodiesel using seashells as a potential renewable catalyst was explored. The presence of calcium hydroxide in the produced catalyst was confirmed through XRD and FESEM-EDX analysis. The idea behind $Ca(OH)_2$ as the catalyst proves the chemistry that any basic compound with available OH^- ions can act as the catalyst. This significantly means that any potential source with the ability to produce a basic compound can be used as the catalyst. The influence of operating parameters such as alcohol to oil ratio, temperature, amount of catalyst, and reaction time on the biodiesel yield was investigated. From the esterification reaction, the maximum yield of 95.6% was obtained and the optimum conditions were found to be alcohol to oil ratio of 6:10, 0.1 g $Ca(OH)_2$ catalyst, temperature 65-70°C, and reaction time of 6 h. The presence of propyl esters in the produced biodiesel after esterification was confirmed through the peaks obtained from GC-MS analysis. Since the biodiesel produced had promising and satisfactory parameters in accordance with ASTM standards, further investigations were required to check the potential of biodiesel blending. Hence the produced B20 blend showed a similar calorific value to that of commercial diesel (B0). The promising B20 blend was further subjected to engine tests to analyze its performance and emission characteristics.

During the investigation, different operating conditions such as variable loads and CR of the engine were tested with the B20 blend as the fuel and compared with B0. The experimental findings portray the B20 blend as a promising fuel and the results are reported as follows.

The BSFC at CR 18 was lower by 5% for the B20 blend when compared to B0. However, at CR 17.5 the BSFC rating was higher for the B20 blend. BSFC of the engine decreases with increased compression, as higher CRs favor efficient combustion.

- The Brake Thermal efficiency (BTE) of the engine, was recorded higher at CR18. Nonetheless, at CR17.5, the BTE values were almost the same for B20 and B0. At full load conditions, maximum efficiency was observed.
- A gas analyzer recorded the emissions from the engine exhaust and significant improvements in the emissions were projected. This is a result of the advanced combustion of the better-oxygenated fuel.
- At both, the CRs, CO, and CO_2 emissions were very much lower for B20 than for B0. The average reductions in CO_2 emissions were 41.2% and 42.2% at CR 17.5 and CR18 respectively. Similarly, the average decrement in CO emissions was found to be 46% and 75% at CR17.5 and CR18 respectively.
- The hydrocarbon emissions also followed the above trend producing emissions which are 21% and 9% lesser for B20 at CR 17.5 and CR18 respectively. The NO_X emissions were higher at both the CRs and the increase was only 0.25% and 3.35% at CR 17.5 and CR18 respectively. The smoke emissions were also recorded at appreciable low levels at B20 loading compared with B0. An average reduction of 19.3% and 32.7% in smoke opacity was obtained at CR 17.5 and CR 18 respectively.

With the above findings, it could be easily concluded that B20 served as a better fuel. At both the engine configurations, especially at CR 18, B20 was found to be more efficient while consuming lesser fuel. This projects the potential scope of supplementing the future energy requirements. Complementing this, B20 also addresses an important concern regarding greenhouse gases, global warming, and air pollution since the fuel stands out remarkably as the emission levels are appreciably low. By commercializing the pork lard biodiesel, problems related to waste disposal from slaughterhouses can be resolved. Also, the biodiesel produced is less toxic and non-hazardous, thus the approach can be considered an environmentally benign process.

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