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Review Paper

A Review of the Emission, Performance, Combustion, and Optimization Parameters in the Production of Biodiesel from Waste Cooking Oil

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Abstract

With the rising consumption of energy comes the challenge of the depletion of fossil fuels. Fossil fuels are non-renewable and finite energy sources with increasing energy demand as a result of the rise in human population and industrialization. This concern has led researchers to seek alternative energy sources that are both economically, technically viable, and environmentally beneficial. Biodiesel is considered an alternative source of energy supply. It is non-toxic, biodegradable, carbon-neutral, and ecologically friendly. However, the high cost of producing biodiesel from feedstocks impedes its commercialization. Hence, WCO used in the production of biodiesel helps to reduce the overall cost of production. The characteristics of the performance, emission, and combustion of the biodiesel produced from the transesterification of WCO are reviewed in this study. The molar ratio of methanol to oil, the concentration of the catalyst, reaction temperature, and time were used to investigate the optimization parameter required in the synthesis of biodiesel from WCO. The number of times the catalyst can be reused while maintaining a good catalytic activity in biodiesel production was also studied. The optimization models and techniques for the prediction of biodiesel yield were also studied.

Keywords: Waste cooking oil; Catalyst; Optimization parameter; Emission; Performance; Combustion characteristics

1. Introduction

The rapid rise of the human population, urbanization, industrialization, and transportation requirements have increased global energy demand. These energy demands and the rise in the global economy raise the concern of fossil fuel depletion [1]. The use of fossil fuels poses environmental risks such as greenhouse gas and pollution emissions [2]–[4]. These fossil fuels are finite, non-renewable, and with an increased cost have led researchers to an alternate energy source that is technically feasible, economically viable, and ecologically friendly. Biodiesel is a clean, safe, biodegradable, renewable, non-hazardous, carbon-neutral, and can be used as an alternative source of energy [5]. Biodiesel can be produced from either edible or non-edible feedstock. Examples of feedstock used in the production of biodiesel include karanja, palm, soybean, canola, sunflower, jatropha, rapeseed, etc [6]–[9]. Biodiesel can be produced via the transesterification process in which triglycerides from feedstocks react with alcohol in the presence of a catalyst [10]–[16]. Among the different types of alcohol used in the production of biodiesel, methanol is the most frequently used and it's specially selected because of the physical and chemical advantage it possesses. The scheme showing the transesterification of the triglycerides with methanol for the production of methyl esters is shown in **Figure 1** [17]. Biodiesel may also be used as a partial or complete replacement for diesel fuel in compression ignition engines for automotive locomotion or energy generation. The

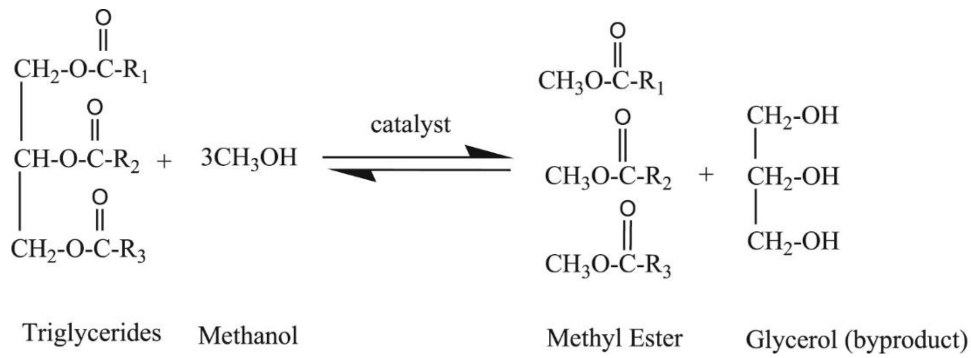

Figure 1. Schematic of the transesterification process [17]

diesel engine can be operated without any engine modification when using biodiesel either in its neat or blended form [18]–[21].

Biodiesel outperforms diesel fuel in terms of flashpoint, lubricity properties, and cetane number, with no discernible difference in heat of combustion. It also has kinematic viscosity and a specific gravity greater than diesel [13]–[14]. Biodiesel has also demonstrated a remarkable benefit in terms of reducing unburned hydrocarbon (UHC), smoke, carbon monoxide (CO), and particle matter (PM), but with the nitrogen oxide (NOx) emission slightly increasing [15]–[16].

Different types of catalyst have been used by many researchers and some of which has been discussed in this study. The transesterified catalysts can either be homogeneous or heterogeneous. The simplest approach is homogeneous transesterification; however, due to the homogeneity of the mixture and the existence of some difficulties in the product separation and purification steps involving the reactant, catalyst, and product; the heterogeneous transesterification process was preferred as it was cheaper with less difficult steps [26], [27]. A two-step trans-esterification process was used to remove the high FFA concentration and boost biodiesel production. Transition metal oxides, hydrotalcite, silica-based, and alkali-doped materials have all been used by different researchers in heterogeneous catalyst systems [27]–[29]. The most widely used alkali catalyst in the production of biodiesel is sodium hydroxide (NaOH) and potassium hydroxide (KOH); however, the alkali catalyst of KOH yielded better results [27], [30].

Several techniques such as central composite design (CCD) based on response surface methodology (RSM), Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscope (SEM), x-ray diffraction (XRD), x-ray absorption near-edge spectroscopy (NEXAFS), Brunauer, Emmett and Teller (BET), Fourier transform infrared spectroscopy (FTIR) among others have been used to perform the analysis [24]–[25]. The brake specific fuel consumptions (BSFC), brake thermal efficiency (BTE), heat release rate (HRR), ignition delay, and cylinder pressure were obtained to analyze the performance and combustion characteristics of the WCO biodiesel operated on a diesel engine. Similarly, the exhaust gas emissions of CO, CO_2, unburned HC, NOx, smoke, exhaust gas temperature (EGT), and particulate matter are also used to investigate the emission characteristics. The optimization parameters of molar ratio of methanol to oil, catalyst concentrations, reaction temperature and time as well as catalyst reusability in the production of biodiesel were also discussed in the study.

2. The WCO Cost Analysis

Abdallah El-Gharbawy [32] studied the cost analysis of producing biodiesel from WCO. A biodiesel power plant with a capacity of 100,000 tons per year was used in the study. The study showed that the production of biodiesel at optimum conditions achieved a maximum 99% biodiesel conversion rate. The study revealed that the cost of producing 1 liter of biodiesel from WCO is $0.515 where the current global price of 1-liter biodiesel and petro-diesel is at $1 and $0.678, respectively. Hence, the WCO biodiesel production has a reduced cost, good profit, and positive effect on the environment and subsequently reduces the dependence on petro-diesel [32]. The high cost of producing biodiesel from edible vegetable oil, which is attributed to the increase in demand for edible oil for human consumption, is a big impediment to its commercialization. More so, the price of raw material when using natural oils amounts to roughly 80% of the ultimate cost of the biodiesel generated [33]. Therefore, using a cheap oil like WCO would lower the overall cost of the final output. More so, WCO is a strong contender for the production of biodiesel since direct disposal of biodiesel can cause a variety of health and environmental issues [17], [18], [34], [35]. The WCOs used in most studies are collected from school cafeterias, household kitchens, and restaurants.

3. Result and Discussions

3.1. Performance and Combustion Analysis of the Brake Specific Fuel Consumption and Brake Thermal Efficiency

The result in terms of the BSFC and BTE of the biodiesel blended with diesel was studied, and the result was compared to conventional diesel fuel. The performance characteristics of the methyl and ethyl ester biodiesels synthesis from WCO were investigated by Sanli et al. [18]. The test was performed with a direct injection (DI) diesel engine at a constant load of approximately 90% and varying engine speeds of 1100, 1400, and 1700 rpm, respectively. The test fuel used in the experiment is pure biodiesel of methyl ester (MEB) and ethyl ester (EEB), and a 20% blend of MEB and EEB with petroleum-based diesel fuel (PBDF) denoted as M20 and E20, respectively. The results revealed that ester fuels had greater BSFC than petrodiesel [18]. The BSFC and the thermal efficiency of both the methyl ester and ethyl ester biodiesel are shown in **Figure 2**.

Attia et al. [36] studied the performance characteristics of the blended fuel of WCO methyl esters and diesel at different ratios. Neat diesel (B0), neat biodiesel (B100), and B5, B20, B30, B50, and B70 was used as the test fuel. The result obtained from these blending ratios showed that the corresponding value of the engine performance for neat fuel had 10% high BSFC, a small difference in BTE of about 3% higher BSEC, and 2% lower exhaust gas temperature, T_{exh}. The study recommended a 30% to 50% WCO methyl ester biodiesel blending ratio for better performance characteristics [36]. The performance characteristics of biodiesel produced from WCO and its blend with diesel at various engine loads

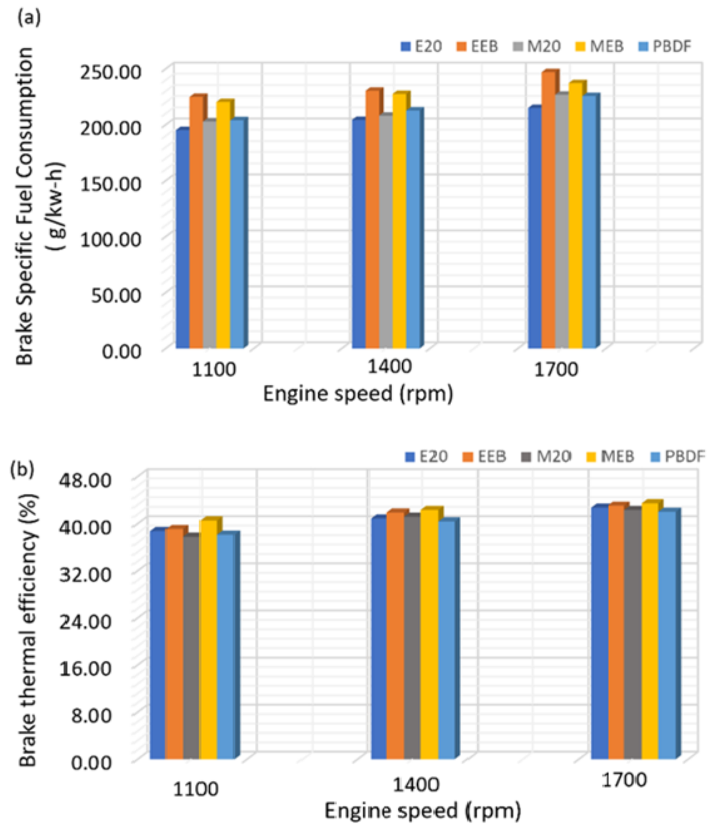

Figure 2. The BSFC (a) and BTE (b) of methyl ester and ethyl ester biodiesel [18]

and speeds were studied by Hui An et al. [20]. The engine speed was performed at different speeds of 800, 1200, 2400, and 3600 rpm representing the idle, low, medium, and high engine speeds, respectively. Three different engine loads of 100%, 50%, and 25%, corresponding to high, medium, and low loads were also used in the study. Three different blends ratio of 10% biodiesel and 90% diesel denoted by B10, 50% biodiesel and 50% diesel (B50), and pure biodiesel (B100) were studied. The performance characteristics of the result were compared with that of pure diesel. The study showed that the BSFC increases as the blending ratio increases. At 25% load, a large increase in BSFC was observed at 800 and 1200 rpm. The highest thermal efficiency of the biodiesel was obtained at 50% and 100% loads [20]. These investigations revealed that the ester fuel has better BSFC than petro-diesel. The BSFC increases as the blending ratio increases while the highest thermal efficiency of the biodiesel was obtained at 50% and 100% loads. A 30% to 50% WCO ester biodiesel blending ratio was recommended for better optimization.

3.2. Analysis of the Injection Timing, Injection Pressure, and Compression Ratio on Biodiesel Fuel Diesel Engine

The result in terms of the compression ratio (CR), injection timing (IT), injection pressure (IP) and heat release rate (HRR) of biodiesel blended with diesel was studied, and the result was compared to conventional diesel fuel. The effect of the performance on the addition of n-butanol and butylated hydroxytoluene (BHT) to WCO biodiesel on diesel engines was investigated by Prabu et al. [21]. The B20, B30, B40, and B100 fuel blends were used as the engine test fuel. The study showed that B30 + BHT had a BSFC of 7.3% greater than diesel and a 4.6% BTE less than diesel. The B20, BHT + B30, and B40 peak HRR was similar to that of diesel, but the HRR of Butanol + B30 was higher. The addition of antioxidants of BHT and B30 + 20% n-butanol improves the performance characteristics [21]. **Figure 3** shows the BSFC, BTE, and HRR of the WCO methyl ester biodiesel-diesel blends. Beyond CR of 18, there was a reduction in the trend of BTE. The EGT was observed to decrease with increased IT but increased with an increase in CR and IP. The study also revealed that increasing the IT-led to a reduced smoke emission. The engine performance was improved by carefully adjusting IT, IP, and CR [21]. The effect of different engine parameters and load factors on engine performance was investigated by Elnajjar et al. [37]. The engine was fueled with WCO biodiesel. The engine load and speed, IT, CR, and varied hydrogen mass flow rates were all studied. The study showed that the torque output and thermal efficiency of the engine improved once it was filled with hydrogen gas. Increasing the hydrogen percentage also resulted in improved engine performance. An improvement in thermal efficiency leads to a drop in specific fuel consumption (SFC). Except for the variance in pilot fuel injection time, the indicated mean effective pressure (IMEP) and maximum combustion pressure were rather consistent. When the IT was decreased, there was a significant drop in brake torque and thermal efficiency [37].

3.3. Emission Characteristics of Biodiesel Produced from WCO

The result in terms of the CO, CO_2, HC, NOx, smoke, particulate matter, and EGT of the biodiesel-diesel blended fuel were studied by researchers using different diesel engines at varying engine load and speed; the result was then made in comparison to that of diesel. The influence of the WCO biodiesel-diesel blend investigated using a four-cylinder natural-aspirated DI diesel engine was studied by Cheung et al. [38]. The gas emission, the mass concentration of the particle, and the particle's size distribution were investigated. The different biodiesel-diesel blends of B10, B20, B30, and pure biodiesel test fuels were used in the study. From the study, the addition of biodiesel led to a decrease in particulate mass concentrations, CO, and HC while the emission of NOx increased. The result showed that the volatile mass fraction of the particulate matter increases, and the ignition temperature of the soot decreases when the percentage of biodiesel present in the fuel increases, or the engine load decreases [38]. The emission characteristics obtained by Sanli et al. [18] showed that the biodiesel generated a reduced CO and total hydrocarbon (THC) than PBDF, but produced higher NOx. The comparison of the exhaust gas emission with petroleum-based diesel engines is shown in **Figure 4**.

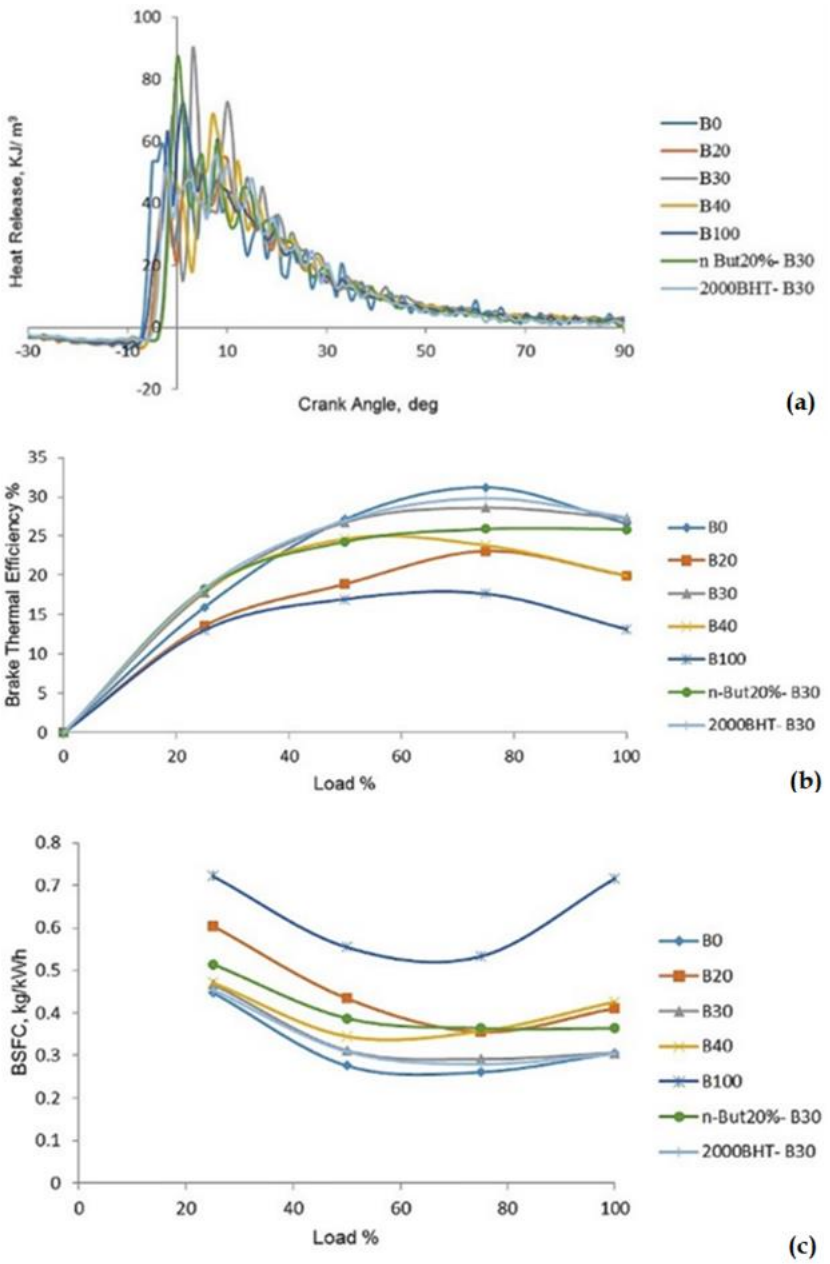

Figure 3. The HRR (a) , BTE (b) and BSFC (c) of WCO methyl ester biodiesel-diesel blends [21]

Attia et al. [36] investigated the engine emission characteristics of different biodiesel-diesel blends obtained from WCO methyl ester and conventional diesel fuel. The test was carried out on a 5.775 kW power, single-cylinder and1500 rpm constant speed. The pure diesel (B0), pure biodiesel (B100), and biodiesel-diesel blends of B5, B10, B20, B30, B50, and B70 were used in the study. The engine emissions resulted in a 25% reduction in CO, a 20% reduction in UHC, a 6% reduction in NOx, and a 20% increase in smoke opacity. A 30% to 50% WCOME biodiesel blending ratio was recommended for better emission performance [36]. The regulated and unregulated emissions characteristics of the diesel engine were investigated by Man et al. [39]. The neat diesel, neat biodiesel (B100), and biodiesel-diesel blends of B10, B20, and B30 were used as the test fuel. The unregulated emissions of 1,3-butadiene, ethene, formaldehyde, propene, acetaldehyde and benzene, toluene, and xylene (BTX) were studied. Similarly, the unburned HC, CO, particulate mass concentrations emissions, and NOx was also investigated. The result obtained from the regula-

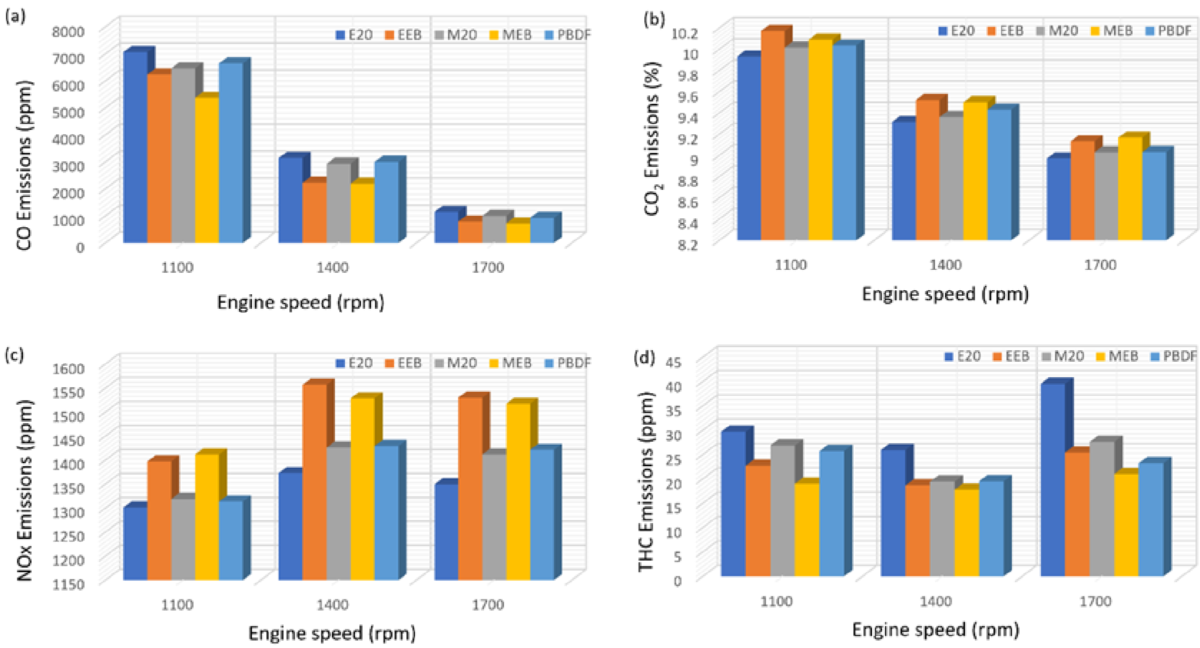

Figure 4. The CO (a), CO_2 (b), NOx (c), and THC (d) of biodiesel fueled diesel engine campared with PBDF [18]

ted emission for all test conditions showed that the HC emission, CO emission, and particulate mass concentrations reduced while the NOx emission increased when made in comparison to diesel [39]. Furthermore, the unregulated emissions of acetaldehyde, formaldehyde, propene, 1,3-butadiene, and ethene, increase as the proportion
of biodiesel in the diesel fuel increases. The increase in benzene emissions was offset by those of xylene and toluene and hence, no notable change in BTX emissions. The study showed that the engine load had a considerable effect on both regulated and unregulated emissions [39].

The emission characteristics of the WCO biodiesel and biodiesel-diesel blends operated in a diesel engine were studied by H. An et al. [20]. The study was performed at different engine loads and speed. The engine speed was varied from 800, 1200, 2400, and 3600 rpm representing idle, low, medium, and high engine speed, respectively. The study employed engine loads of 25%, 50%, and 100%, which correspond to low, intermediate, and full loads, respectively. Biodiesel derived from WCO with three different blends ratio of 10 % in volume of biodiesel denoted by B10, 50% biodiesel blend (B50), and pure biodiesel (B100) was studied and was made in comparison to those of pure diesel [20]. The CO, NOx, HC, and CO_2 exhaust emissions were also measured and analyzed. At a 25% load, the WCO biodiesel resulted in an increase in CO emissions but a decrease in CO_2 and HC emissions. The NOx emitted at all operating condition showed that the B100 was lesser than those produced by diesel. However, at low engine speed and high load, the reverse trend was observed revealing that low engine speed has a substantial influence on the emission process [20]. Prabu et al. [21] investigated how exhaust emissions affected the addition of n-butanol and butylated hydroxytoluene (BHT) to WCO biodiesel in a diesel engine. The different blending ratio of B20, B30, B40, and neat biodiesel was used as the test fuel in the diesel engine. Methanol, NaOH, and sulphuric acid catalyst were used in the transesterification reaction. The result showed that B30 + n-butanol emitted 37.5% less CO emission, 9% more NOx emission, and 2.3% more EGT than diesel. The B100 biodiesel emitted 51% lesser EGT than that of diesel [21]. Chiatti et al. [40] investigated how the blending ratio of WCO biodiesel and ultra-low sulfur diesel (ULSD) influences particle size distributions in small-scaled diesel engines. An 8.5 kW four-stroke DI diesel engine was used in the experiment. Three different test fuel of pure ULSD, B20, and B40 was used in the study. Engine loads of 50%, 60%, 70%, and 80% were tested at engine speeds ranging from 2400-3600 rpm at 300 rpm intervals was used to perform the tests. The study showed that the overall number of particles emitted by the engine was reduced in the WCO biodiesel than that of diesel fuel. The reduction was more noticeable as the amount of biodiesel in the blend increased [40]. The study also showed that B20 and B40 have smaller mean particle diameters than ULSD virtually in the entire engine operating field. The engine operating parameters influenced the particle size distribution: higher load lowered the proportion of smaller diameters while higher engine speed reduced the particle diameters. Yildiz et al. [41] investigated the production of renewable biofuel from WCO from the standpoint of waste to fuel per energy. Biofuel produced from WCO has higher viscosity and density than diesel since it contains fatty acids. This means that biofuel has a denser and higher viscosity fuel than diesel. In terms of CO and HC emissions, the biofuel emitted into the environment has a lesser effect than that diesel fuels; and this helps in the betterment of the environment. Furthermore, when CO_2 and NOx emissions are considered, biofuel was at a disadvantage since it emits more CO_2 and NOx than diesel. Aside from the emission outcomes, biofuel has a lower "soot concentration" value than diesel fuel. In relation to total particle concentration, biofuel has a substantial advantage over diesel fuel for a healthier and more sustainable environment [41]. Balasubramanian et al. [42] analyzed the engine emission characteristics of WCO and its blend with biodiesel. The B100, B60, B40, and B20 of the WCO biodiesel-diesel blends were used as test fuels. The NOx emission in the blends was decreased by introducing an EGR into the intake at varied ratios of 5%, 10%, and 15%. The results showed that B20 blend fuel was the best fuel for improving the engine's emission, characteristics (excluding NOx) [42].

The emission characteristics of biodiesel obtained from WCO operated in a diesel engine were also studied by Mahesh et al. [24]. Pure diesel, neat diesel (B100), and biodiesel-diesel blends (B10, B20, and B50) were used to drive the engine. The EGT increased significantly as the biodiesel blend ratio increased as a result of the increased temperature of combustion in the engine. As the amount of biodiesel in the blend increase, the smoke density decreases. The emission characteristics showed that unburned HC, CO, and particulate matter emissions were lower than that of biodiesel. The NOx emissions and EGT, on the other hand, were found to be higher [24]. The BMEP of the different emissions is shown in **Figure 5**.

3.4. Effect of Catalyst on the Optimization Conditions in Biodiesel Production

Kannan et al. [43] determined the optimum conditions for obtaining the highest biodiesel generated from WCO through the transesterification process. The result showed that methanol to oil molar ratio of 0.4:1, 0.5 wt.% concentration of KOH, 45 °C reaction temperature, 3.5 hr reaction time, and 200 rpm stirring rate gave methyl ester yield of 97%. Mahesh et al. [24] investigated the production of a heterogeneous catalyst of CaO and KBr using the wet impregnation method. The influence of process parameters such as catalyst loading, methanol to oil ratio, and reaction time were investigated. The optimum conditions were obtained at 3 wt.% catalyst loading, 12:1 methanol to oil molar ratio, and a 1.8 hr reaction time. The optimal conditions for esterification in the production of biodiesel from WCO were studied by Meng et al. [44]. The reaction conditions of catalyst concentrations, methanol to oil molar ratio, reaction time, and reaction temperature were investigated in the study. As the quantity of sodium hydroxide was increased, the WCO conversion efficiency improved proportionately. Good quality biodiesel was produced at 1.0 wt.% NaOH catalyst concentration, 9:1 methanol to oil molar ratio, 90-minute time, and 50 ^{0}C temperature [44].

Sahar et al. [4] also studied the utilization of WCO in the synthesis of biodiesel. The WCO was pretreated with mineral acids before being transesterified in the presence of a KOH base as a catalyst to lower the FFA concentration. Mineral acids of HCl, H_2SO_4, and H_3PO_4 were used for the pretreatment. Although all three acids functioned well in the lowering of FFAs, the catalyzed reaction H_2SO_4 yielded the highest conversion of 70.7%. The highest fatty acid methyl ester (FAME) was obtained at a 1:3 methanol to oil molar ratio and 50-minute time. The influence of temperature on FAME was investigated from 30 to 60 °C, with the maximum FAME production of 94% achieved at 60 ^{0}C. The study showed that acid pretreatment followed by a base-catalyzed WCO reaction was a reliable biodiesel production process [4]. Inexpen-

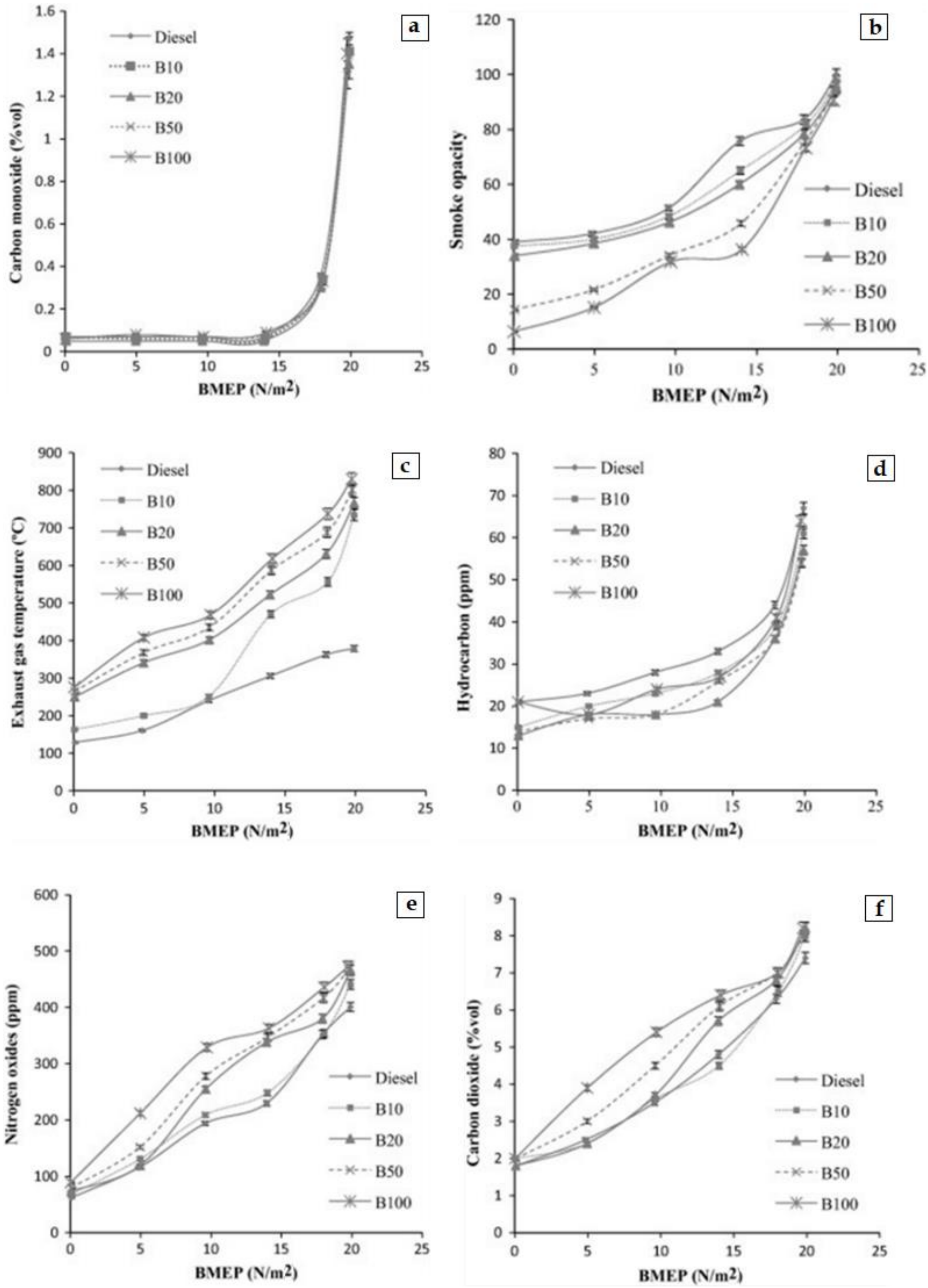

Figure 5. The effect of biodiesel, diesel, and biodiesel-diesel blend on BMEP: (a) carbon monoxide, (b) smoke opacity, (c) exhaust gas temperature, (d) hydrocarbon, (e) nitrogen oxides, and (f) carbon dioxide [24]

sive heterogeneous catalyst of CaO/SiO_2 made from eggshell and peat clay wastes was used in the production of biodiesel from WCO developed by Putra et al. [3]. The study found that the CaO catalyst was capable of producing 78 % biodiesel. The influence of optimum parameters of reaction temperature and time was also studied. The use of silica as a support, which was obtained from peat clay waste, increased bio-diesel production to 91%. The optimum reaction time was obtained at 60 minutes and the biodiesel yield was found to increase as the temperature increased. The characterization analysis was used to suggest a reaction mechanism. According to the mechanism, CaO assisted in the generation of biodiesel via the transesterification process, whereas silica aided the esterification reaction [3].

Cai et al. [2] developed a cost-effective and feasible method for producing biodiesel from high-FFA feedstocks like WCO. The soap formed from the FFA and NaOH served as a catalyst in the esterification of crude glycerol with the FFAs in WCO. Two experimental procedures were used to test the esterification of recycled crude glycerol in biodiesel synthesis. The initial experiments and the recycling experiments. The study showed that esterification of FFA from WCO could be efficiently catalyzed by alkali (soap). The crude glycerol and the soap used as a catalyst could both be recycled. The energy consumption of methanol recovery was lowered by substituting methanolysis with glycerol in the pretreatment. Over 99% of the FFA in the WCO was converted to acylglycerols under optimal conditions. The study revealed that the biodiesel from WCO with high acid value was achievable at a low- cost and the FAME yield was about 98.6 % [2]. Fereidooni et al. [45] investigated the optimum condition for generating a high yield of biodiesel from WCO by utilizing KOH as a homogeneous catalyst with an electrolysis technique. The reaction was carried out at an ambient temperature and environmental conditions. A 96% biodiesel yield was obtained from WCO in the presence of a 0.5 wt.% KOH catalyst, 1:6 methanol to oil molar ratio, 50 voltage, 10 wt.% solvent of acetone, and 2 wt.% water for two hours. The study showed difficulty in the formation of FAME in the absence of a catalyst affirming the fact that electrolysis alone did not promote transesterification [45]. Patil et al. [46] investigated the production of quality biodiesel fuel from low-cost high FFA WCO using a microwave-assisted process and sulfuric acid. A two-step acid esterification followed by alkali transesterification was employed using methanol, sulfuric acid, and KOH catalyst to convert the high FFA oil to its ester. A modified domestic microwave oven with an output power of 80 W was used for the microwave-aided transesterification. The sulfuric acid catalyst amount varied in the range of 0.3 to 2%. The study showed that the maximum yield for WCO was achieved at 0.5% acid catalyst concentration [46]. When a 2% alkaline catalyst of KOH was used at a 9:1 molar ratio, the highest biodiesel yield of 92% was obtained. A 40 °C to 100 °C temperature range was used to study the reaction temperature. From the study, the highest production of WCO was found at a temperature 80 °C. More so, it was also observed that for microwave aided heating, a 6 minute time was adequate, however for conventional heating, a 105 minute time was necessary to get a comparable biodiesel yield. The microwave method of heating required energy of about 11 times less than that which the conventional method would require in achieving the same biodiesel yield from [46]. A heterogeneous catalyst of $Na\text{-}SiO_2@TiO_2$ used in the transesterification process for the production of biodiesel from WCO was studied by Naeem et al. [47]. The reaction dependent parameters was varied to determine the maximum biodiesel yield. The economic feasibility of using these catalysts under optimum reaction conditions showed that the activity of $Na/SiO_2@TiO_2$ catalyst was active throughout a five run period and produce a biodiesel yield of 98% at reaction temperature of 65 ^{0}C and reaction time of 120 minute [47].

Gouran et al. [48] studied the production of biodiesel from WCO using refined wheat bran ash, CaO, and methanol as catalysts. The catalyst concentration, methanol to oil volume ratio, reaction temperature, and reaction time were used to determine the FAME purity and process optimization. The reusability of the catalyst was tested for a period of five runs and showed no notable decrease in catalytic activity throughout the five-run period. The result from the study revealed that biodiesel purity was 93.6% when the methanol to oil volume ratio, catalyst concentration, reaction temperature, and time was 1.46:1, 11.66 wt.%, 54.6 °C, and 114.21 minutes, respectively [48]. Wheat bran ash, being a byproduct of wheat processing, was thus suggested to be a viable choice for biodiesel purification. Jamil et al. [31] investigated the use of metal-organic frameworks (MOFs) built on calcium (Ca) and copper (Cu) as catalysts in the esterification and transesterification processes for biodiesel synthesis from WCO. The interaction of the various process factors and optimal conditions for biodiesel production was investigated using the RSM. Cu-MOF produced a 78.3% biodiesel yield when used in the synthesis of WCO biodiesel while a 78% yield was obtained from Ca-MOF. When the heterogeneous catalyst of Cu-MOF + Ca-MOF was used compared to the individual catalyst, the result showed that the heterogeneous catalyst has an 85% biodiesel yield, indicating its suitability for use as a catalyst. The RSM study revealed that catalyst loading, and reaction temperature are the two most important parameters affecting biodiesel yield, whereas the alcohol to oil molar ratio affects the quality of the biodiesel produced [27]. The production of an anthill-zinc oxide catalyst and its use in the production of biodiesel from WCO was investigated by Yusuff et al. [49]. The influence of blending on biodiesel characteristics was also addressed. The maximum biodiesel production of 83.16% was produced when the catalyst concentration, the molar ratio of methanol to oil, and reaction temperature of 0.5 wt.%, 17.99:1, and 66.54 °C, respectively were used. The optimization result showed that all of the tested optimization parameters had a considerable influence on biodiesel production. The ZnMA composite was observed to be relatively stable after many reuses in the study [49]. The production of biodiesel from WCO using the heterogeneous catalyst of KOH supported on a calcined cow bone in the transesterification process was investigated by Aghel et al. [50]. Using the box-behnken design (BBD), the maximum purity was obtained by varying the optimization parameters. The study showed that a 99.56% maximum biodiesel purity was obtained when the volume ratio of oil to methanol, toluene-to-oil concentration, reaction temperature, reaction time, and the ratio of cow bone to KOH of 2:1, 10 wt.%, 63.53 °C, 85 secs and 4.07:1 g/g, respectively were used. The catalyst was reusable seven times with a good catalytic activity while a small decrease in FAME of about 8.2% was observed after seven experimental runs [50].

Helmi et al. [51] used the electrolysis method to convert WCO to biodiesel using phosphomolybdic acid ($H_3PMo_{12}O_{40}$, PMA) supported by clinoptilolite as a possible green acid catalyst. The effect of independent parameters of catalyst weight, reaction time, voltage, and the molar ratio of methanol-to-oil for the optimization of the biodiesel was studied and evaluated using the RSM-CCD. From the study, the maximum biodiesel yield was observed to be 96.73% when the catalyst weight, reaction time, voltage, and molar ratio of methanol-to-oil was 3.02 wt.%, 4.1 hours, 20.34 V, and 8.86:1, respectively. Moreso, a sufficient mean yield of 83.4% was produced when the catalyst was reused five times [51]. The production of biodiesel from WCO using CuO/ZnO as a photocatalyst in the transesterification process was studied by Guo et al. [52]. The study showed that the optimum conditions for the reaction are 5 % catalyst dose, 9:1 ethanol to oil molar ratio, 65 °C temperature, and 2 hours reaction time with a biodiesel yield of 93.5%. In the sixth cycle experiment, the percentage of biodiesel generated was more than 80% indicating high catalytic activity and sustainable functionality. Cholapandian et al. [53] studied the production of biodiesel from WCO using calcium oxide (CaO) nanocatalyst obtained from Acalypha indica. The study showed that the highest yield of 94.74% was achieved under optimal conditions of 11.8:1 methanol to oil molar ratio, 2.4 wt.% catalyst concentration, 63.7 °C temperature, and 70 minutes. The CaO nanocatalyst showed a 92.82 % catalytic efficiency in the conversion of the biodiesel up to the third cycle [53]. The reusability of the catalyst in the production of biodiesel is shown in **Figure 6**, while the effect of the various optimization parameters

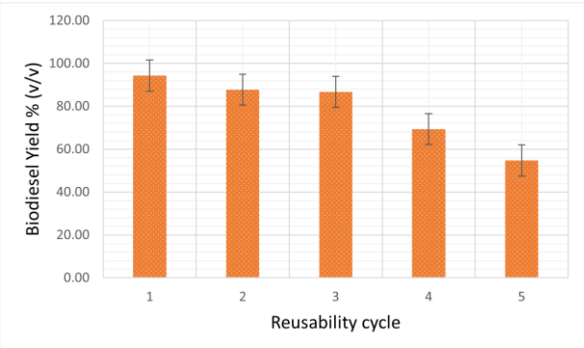

Figure 6. Catalyst reusability cycle in the production of biodiesel [53]

used in the study is shown in **Figure 7**. Rezania et al. [54] investigated the possibility of $LaPO_4$ foam as a heterogeneous catalyst for biodiesel production from highly acidic WCO. The unique $LaPO_4$ nanoparticles doped nickel foam as a heterogeneous nanocatalyst were produced and analyzed. The study showed that a $LaPO_4$ foam nanocatalyst was employed successfully to trans esterify WCO in the presence of methanol. A 91 % biodiesel yield was obtained when a 1:5 molar ratio of oil to methanol and a reaction temperature of 120 minutes was used. The study shows that $LaPO_4$ foam can be used as a potential catalyst in the production of biodiesel and maintain its catalytic activities for up to six cycles [54]. Sipayung et al. [55] designed and optimized a CaO catalyst supported by zinc acetate dihydrate and n-hexane as a solvent to produce biodiesel from WCO. Four independent variables of methanol ratio, hexane ratio, reaction temperature, and reaction time were used as independent variables in the study. The optimum condition for maximum biodiesel yield was determined using the RSM-based BBD. A maximum yield of 97.30% was obtained when the 12:1 methanol molar ratio, 0.75:1 n-hexane volume ratio, 60 °C reaction temperature and 3.5-hour reaction time were used. These independent variables all exhibited high significance according to the significance test [55]. The MgO/CaO composite catalysts based on industrial waste materials were prepared as a heterogeneous catalyst in the production of biodiesel from WCO by Aghel et al. [56]. The optimum conditions required for maximum biodiesel yield was investigated. The result showed a 9 wt.% catalyst concentration, 63 °C reaction temperature, and 2:1 methanol to oil molar ratio produced the maximum activity with the FAME percent greater than 93.32%. The catalytic activity of the catalysts increased progressively when the calcination temperature was increased [56]. Helmi et al. [57] studied a novel reusable heterogeneous catalyst based on the immobilization of phosphomolybdic acid (HPMo) on graphene oxide substrate (HPMo-GO) and also investigated the optimum conditions for obtaining the highest biodiesel yield. The result showed that the maximum FAME yield of 91% was obtained at 0.85 wt.% catalyst concentration, 15 hours, 60 V voltage, and 6:1 methanol to oil molar ratio. The HPMo-GO catalyst has a large specific surface area, making it active and reusable as a green catalyst, and was used four times, yielding an average of 83.35% FAME [57]. Guo et al. [33] investigated a highly

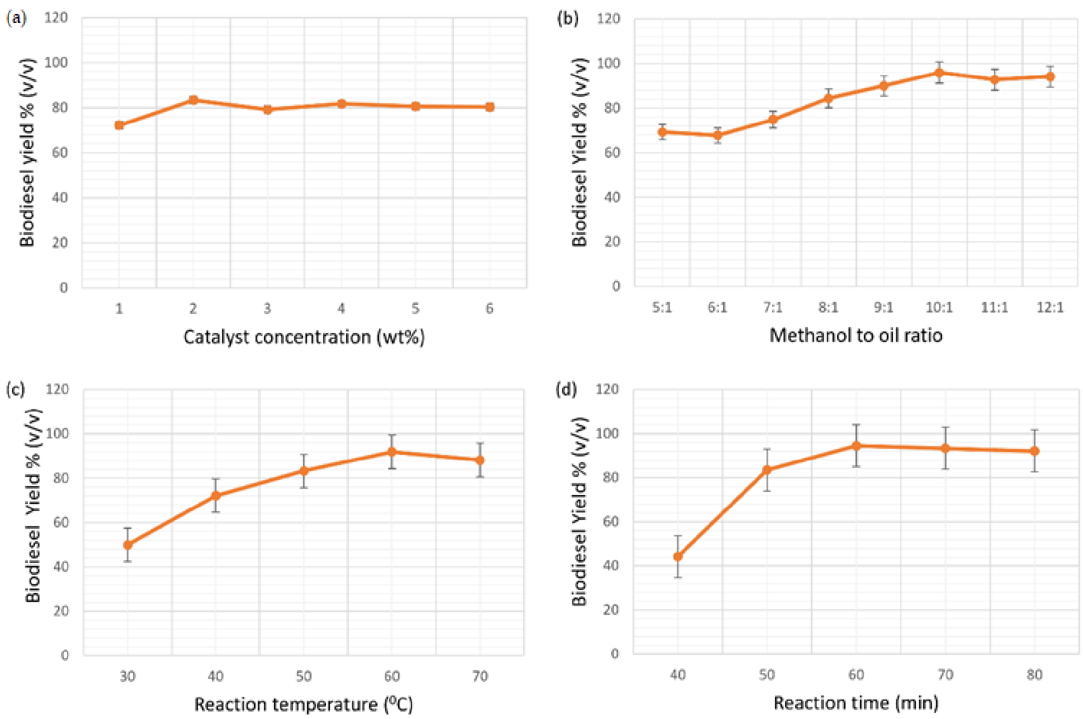

Figure 7. The effect of catalyst concentration (a), methanol to oil ratio (b), reaction temperature (c), and reaction time (d) in the production of biodiesel [53]

active and reusable photocatalyst of La^{3+}/ZnO-TiO_2 for the esterification of FFA with ethanol. The La^{3+}/ZnO-TiO_2 was prepared using the sol-gel method. The NaOH catalyst was used in the transesterification of triglycerides with ethanol. The result showed that after recycling the catalyst five times, the conversion of FFA remains over 87%, making it extremely advantageous for producing biodiesel via transesterification [33]. The synthesis of the heterogeneous magnetic acid catalyst of MoO_3/$SrFe_2O_4$ used in the transesterification of WCO was studied by Gonçalves et al. [58]. The interactions between the optimized parameters and catalyst reusability were studied. The optimum reaction conditions were obtained at a 10% catalyst dose, 40:1 alcohol-to-oil molar ratio, 164 °C reaction temperature, and a 4-hour time. For this optimized condition, the maximum ester conversion value was 95.4%. Furthermore, after eight reaction cycles, the catalyst still displayed catalytic and magnetic activity, indicating that it has a promising future for research and application [58]. The production of biodiesel from WCO using clay/calcium oxide as a catalyst was studied by Mohadesi et al. [59]. The influence of the five parameters which include the catalyst concentration, concentration of toluene, oil-to-methanol volume ratio, reaction temperature, and reaction time on the purity of the biodiesel was investigated using the RSM. The study revealed that the optimum conditions for achieving a 97.16% purity are obtained when the catalyst concentration, toluene concentration, reaction temperature, reaction time, and volume ratio of oil-to-methanol were 9.6 wt.%, 16.13 wt.%, 54.97 °C, 74.32 min, and 1.94 vol: vol, respectively [59]. Aghel et al. [60] used clinoptilolite/CaO catalyst to investigate heterogeneous catalysis during transesterification. The study showed that the transesterification process of methanol and WCO in the presence of a CaO catalyst based on clinoptilolite produce biodiesel of about 85% FAME purity [60].

3.5. *Optimization Models and Techniques in the Improvement of Biodiesel Produced from WCO*

A. Kolakoti et al. [61] studied the production of biodiesel using the heterogeneous catalyst of waste chicken eggshell (WCES). Artificial Neural Network (ANN) modeling and RSM optimization was performed to obtain the maximum biodiesel that will be produced. The result showed that the optimized condition of 1.5 wt. % of catalyst concentration, 10:1 of molar ratio, 120 minute time, and 50 °C temperature produced a 91.42% yield in biodiesel. The catalyst was reusable up to 5 times. The result showed that the ANN model achieved the highest coefficient of correlation values R (99.24), R2 (98.48), and the lowest mean square error (MSE) of 0.08 in comparison to the RSM model. The result revealed that the ANN model is highly superior and more effective than the RSM [61]. The study of biodiesel production from WCO using the optimization techniques of Taguchi and the ANN model was further performed by A. Kolakoti et al. [62]. The study at a catalyst concentration of 15%, 12:1 molar ratio, 55 °C reaction temperature, and 1 hr reaction time gave a maximum biodiesel yield of 92.17%. The coefficient of determination was used to determine the accuracy of the models. The result showed that the ANN (0.9955) and the Taguchi (0.9959) values were similar. The study showed that both model predictions are highly precise and accurate [62].

Y. Rajesh et al. [63] investigated the use of a definitive screening design (DSD) to predict the maximum biodiesel yield from waste frying palm oil (WFPO). The optimization parameters of 1 wt.% catalyst concentration, 6:1 molar ratio, and 55 °C reaction temperature gave a corresponding biodiesel yield of 96.23%. Experimental analysis was also carried out with an average biodiesel yield of 95 %. The result showed that the predicted yield using the DSD techniques agreed with the experimental value [63]. Ceyla Özgür [64] investigated the optimization of biodiesel produced from WCO using the RSM model. A catalyst concentration of 0.77wt.%, the molar ratio of 6.05:1, reaction temperature of 62.75 ^{0}C, and reaction time of 72.63min gave a predicted maximum biodiesel yield of 93.124%. The optimum biodiesel yield obtained experimentally was 92.8%. The study showed that both the experimental result and the RSM predicted value is in good agreement with each other [64]. Y. H. Tan et al. [65] studied the application of Taguchi and RSM technique in the optimization of biodiesel produced from WCO. The catalyst of chicken and ostrich eggshell derived from CaO was used in the transesterification process. The optimum parameter of ~1.5 %w/v catalyst concentration, ~10:1 molar ratio, 65 ^{0}C reaction temperature, and ~2 hr reaction time in the Taguchi and RSM technique gave a maximum biodiesel yield of ~96% (chicken eggshell) and ~98% (ostrich eggshell). In terms of the optimized parameter used, the result showed that both techniques accurately predicted the optimum biodiesel yield [64]. R. Selvaraj et al. [66] studied microwave-assisted biodiesel production from WCO and process optimization using the RSM and ANN model to predict the maximum biodiesel yield. A 1% catalyst concentration, 6:1 alcohol to oil molar ratio, 75 °C reaction temperature, and 1 min reaction time produced a maximum biodiesel yield of 95%. The ANN gave a higher R2 value of 0.99 than that of RSM (0.98). The result showed that simulation using ANN was better when compared to that of RSM [66]. A. Avinash et al. [67] studied and compared the amount of biodiesel produced from WCO using the prediction made by the RSM and ANN models. A three-level design of experiment performed on WCO in biodiesel production for the two model prediction was carried out by varying the reaction condition of catalyst concentration, reaction time, molar ratio, and stirrer speed. The study obtained a catalyst concentration of 0.75% wt./wt., a reaction time of 1 hr, a 9:1 molar ratio, and a stirrer speed of 500 rpm as the optimum reaction condition. A maximum biodiesel yield of 95.05% was obtained from the experiment which was also in agreement with the prediction of both models. When the two models were compared, the result showed a high R2 and lower RSM of 0.99 and 1.97, respectively for RSM while that of the ANN model were R2 = 0.95 and RMSE (root mean square error) = 2.71. The result revealed that the ANN is much better in the predicting the content of biodiesel than that of the RSM model [67].

4. Conclusion

A study on the performance, emission, combustion characteristics, optimization parameters used in the production of biodiesel from WCO and its blends with diesel was considered. The conclusion drawn based on several investigations shows that the engine performance can be improved by controlling the compression ratio and injection parameters. The engine load and speed have a substantial influence on the emission and combustion characteristics of the diesel engine. The WCO used in the production of biodiesel led to an increase in NOx emission but a decrease in particulate mass concentration, CO_2, CO, and HC emissions. The WCO biodiesel blend in diesel of up to 30% improved the performance of the engine and reduced exhaust emissions compared to higher blends. The free fatty acid content reduced significantly as the amount of methanol increased. The independent process parameters of catalyst concentration, methanol to oil molar/volume ratio, reaction temperature, and reaction time all exhibited high significance in the amount of biodiesel yield. The catalyst concentration, methanol to oil molar ratio, reaction temperature and time optimum values ranges from 0.5 - 10 wt.%, 1.94:1 – 40:1, 50 °C - 164 °C, and 40 min - 4 hrs., respectively. The catalytic activity is found reusable for a period of 3-8 runs/cycles at an optimum condition in the synthesis of biodiesel. The maximum yield of biodiesel obtained from WCO range between 70.7 – 98.62% which makes it a less expensive alternative source of energy used in the operation of a diesel engine. The WCO also helps to reduce the overall cost of producing biodiesel. The optimization techniques showed that ANN model is much better than the RSM model in the prediction of biodiesel content. Both Taguchi and ANN models predicted a precise and accurate value of biodiesel yield. The DSD predicted yield also agrees with the experimental value.

Author’s Declaration

Authors’ contributions and responsibilities

The authors made substantial contributions to the conception and design of the study. The authors took responsibility for data analysis, interpretation and discussion of results. The authors read and approved the final manuscript.

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Availability of data and materials

All data are available from the authors.

Competing interests

The authors declare no competing interest.

Additional information

No additional information from the authors.

Abbreviations

CO	Carbon Monoxide
CO_2	Carbon Dioxide
UHC	Unburned Hydrocarbon
NO_x	Oxides of Nitrogen
NO	Nitrogen Oxide
BTE	Brake Thermal Efficiency
DI	Direct Injection
BSFC	Brake Specific Fuel Consumption
CR	Compression Ratio
IT	Injection Timing
IP	Injection Pressure
CI	Compression Injection
SFC	Specific Fuel Consumption
IMEP	Indicated Mean Effective Pressure
BMEP	Brake Mean Effective Pressure
BSEC	Brake Specific Energy Consumption
FFA	Free Fatty Acid
EGT	Exhaust Gas Temperature
EGR	Exhaust Gas Recirculation
PM	Particle Matter
WCO	Waste Cooking Oil
WCOME	Waste Cooking Oil Methyl Ester
CCD	Central Composite Design
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction
NEXAFS	X-Ray Absorption Near-Edge Spectroscopy
BET	Brunauer, Emmett and Teller
FTIR	Fourier Transform Infrared Spectroscopy
BHT	Butylated Hydroxytoluene
CRDI	Common-Rail Direct Injection
aTDC	After Top Dead Center
ISFC	Indicated Specific Fuel Consumption
HRR	Heat Release Rate,
Pmax	Peak Pressure
ULSD	Ultra-Low Sulfur Diesel
FAME	Fatty Acid Methyl Ester
XPS	X-Ray Photoelectron Spectroscopy
BJH	Barrett-Joyner-Halenda
BBD	Box-Behnken Design
RSM	Response Surface Methodology
ANN	Artificial Neutral Network
DSD	Definitive Screening Design

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