



Biodiesel Production From Waste Cooking Oil using Homogeneous Catalyst

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Abstract

Due to the upsurge of awareness of the depletion of fossil fuel feedstock and environmental issues, biodiesel has become a more attractive choice. Biodiesel's productivity is deemed a fruitful and significant research field since its relevance obtains from the increased oil prices and environmental benefits. This paper presents a study of Alfa waste cooking oil used to produce biodiesel oil via the transesterification process. The investigation includes various variables such as transesterification time, catalyst ratio, temperature, and biodiesel yield. Two catalysts (NaOH and KOH) have been utilized in this study. The engine test was carried out at constant load with increasing speed to compare different fuels' performance relative to mineral diesel. The produced biodiesel was categorized according to ASTM D6751. The highest conversion and yield of biodiesel in the transesterification method were scrutinized using the KOH catalyst compared to the NaOH catalyst. The maximum conversion and yield of biodiesel are 97.76 and 94.4%, respectively, with optimum operating conditions of 60 °C reaction temperature, 3 hours reaction time, and KOH catalyst at 4% weight. Consequently, the engine test outcomes revealed similar **biodiesels trends** compared to diesel in terms of engine brake power and brake specific fuel consumption with increasing engine speed.

Keywords: Alfa waste cooking oil, Biodiesel fuel, Homogeneous catalyst, Sodium hydroxide, Potassium hydroxide.

1. Introduction

Vegetable oil is considered the main source of biodiesel. Its production depends chiefly on the plants like sesame oil produced locally and the other commercial oil produced from hazelnut, sunflower, and corn, but these crops' costs are inevitable [1]. It is difficult to avoid the catastrophic impact on biodiesel's environment, whether pure or mixed with other elements [2]. From a different perspective, the waste of such types of vegetarian oil can be a feasible choice to produce diesel oil. As the diesel is produced from vegetarian oil, various diesel types come from animal oil. For example, the chicken fried oil was utilized to produce diesel through single and two phases of transesterification called acid-based and base-catalyzed transesterification, respectively [3].

Renewable resources like waste cooking oil (WCO) can be utilized to produce biodiesel oil through base-catalyzed transesterification after separating the glycerol and purifying the crude methyl ester by employing activated carbon formed from spending tea waste [4].

The recent upsurge in the petroleum prices and serious impacts on the environment resulting from fossil fuel combustion as well as the increasing demands of petroleum products stemming from the increase in the population, expansion of various industries provoke the researchers' attention to find an alternate source for the conventional oil in many countries. Furthermore, petroleum fuel has been amassed in different parts of the world, especially in Middle East countries that become the pioneers

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compare with the other countries [5, 6]. Biodiesel (fatty oil, namely vegetarian and animal oil) can be obtained locally; therefore, it is an appropriate choice for different countries [7].

Despite its feasibility to be a substitute for conventional oil for automobiles, vegetarian oil has a clear, serious impact on the engines. It leads to clogging of the engine, damage of the engine as well as partial combustion [8]. The potential of gaining biodiesel can be dependent mainly on the structure of fatty acid of mono-alkyl ester, particularly when it is derived from animal fat and vegetable oils [9,10].

The biodiesel can be produced from edible and non-edible oil (animal and vegetable) [11]. The production of biodiesel is most frequently from vegetable and nonvegetable oil such as rapeseed, sunflower, palm, soybean, cottonseed, animal fat, and *Jatropha* seed. Regarding the decrease in the costs of biodiesel production, the less expensive feedstock comprising fatty acids such as non-edible oils, animal fats, and oils recycled or waste oil and byproducts of the refining vegetable oils and waste cooking oil (WCO) are utilized. These oils have prodigious significance for supplementing other conventional stuff. The non-edible plant oil can be chosen as low-price sources and from other sides like economic and waste management [12].

The remarkable issue that my country Iraq encountered in the last few decades is the fragile economic situation and the increase in the prices of fossil oil, which will be vanished one day [13, 14]. The biodiesel consists of high energy and carbon-based compound that can be prepared from numerous triglycerides (oil), alcohol, and an acid or base catalyst via a transesterification reaction. There is a preferable will in this reaction since the fatty acids are the most frequent source of decreased carbon chains. During this reaction, the oil goes through a trans-esterification directly from the alcohol, which results in a biodiesel molecule [15]. Furthermore, *Karanja* as a non-edible oil is feasible in terms of producing biodiesel through the transesterification of *Karanja* oil waste with methanol and NaOH. The obtained conversion of biodiesel was 92%, while; the conversion was 95% through employing of based catalyst. Nevertheless, the value of WCO for biodiesel production is inexpensive compare with edible vegetable oil [16]. The influence of diverse variables such as acid/oil, reaction temperature, methanol/oil ratios on the crude *Jatropha* oil pretreatment with acid-catalyzed [17]. Two phases

are used to produce the biodiesel with less acid value from a feedstock comprises high free fatty acid, initially an acid catalyst for esterification and for transesterification [18, 19]. The stuff used in biodiesel manufacture was from WCO and also can be employed as a feedstock in ultrasound cavitation, mechanical stirrers, alcohol, and numerous catalyst weight (0.5, 0.75, and 1 wt%). The use of biodiesel could reduce CO₂ and other harmful substances.

The comparison between conventional fuels and biodiesel fuel looks clear through the lower level of potentiality ozone formed in biodiesel compare with diesel fuel. From pure biodiesel, SO_x are fundamentally eradicated. The exhaust emissions of sulfur dioxide (SO₂) and sulfates in the combustion of biodiesel were lower than from diesel since the ratio of sulfur in the biodiesel is lower than the conventional oil. As a result, biodiesel is environmentally-friendly. No need to modify the diesel engine with the use of biodiesel, also considerable reductions of CO, particulate matter, and unburned hydrocarbons. NO_x emissions were marginally augmented [20]. The proportions of the emissions of CO from biodiesel are half of the emissions of CO from diesel. Therefore, the health impacts can be very serious, particularly on the human being's respiratory system. 35% of particulate matter is eradicated from biodiesel, while 65% are emitted from normal diesel. In the same line with the issue of emission, 91% of hydrocarbons are emitted from the automobile exhaust emissions when uses diesel fuel, while 9% only come from biodiesel. These indications reveal the significance of the utilization of biodiesel as an ideal alternative. From the purest biodiesel, the NO₂ emissions increased by 16 percent. However, as biodiesel fuel is free of sulfur, the technology of NO₂ control can be implemented efficiently to manage these emissions [21–23].

The capacity for degradation of biodiesel is fourfold more rapidly than conventional diesel. At a period of 28 days, pure biodiesel degraded 85 to 88 percent in water. The flashpoint of biodiesel is over 300 oF, above a diesel flash point of around 125 oF. The indices of tests unveiled that the flashpoint of biodiesel blends augmented with an increasing biodiesel proportion, which provides safe fuel handling [24]. The impacts of various parameters such as reaction temperature, reaction time, type, and concentration of catalyst utilized on the biodiesel yield have been scrutinized in this study.

2. Materials and methods

The effect of numerous parameters like reaction time, reaction temperature, type, and concentration of catalyst used on the biodiesel yield are inspected. The transesterification experiments were implemented in a flask three-necked (500 mL) (the 1st one for thermowell and the 2nd stopper used to feed the raw material and the 3rd for condenser) batch reactor. With a magnetic stirrer, a thermocouple is linked inside the sample and two necks.

For executing the trans-esterification reaction, for the manufacturing of biodiesel from nominated feeds (Afia waste cooking oil) alkali-based batch process was selected. The experimental (reactor) setup was made in the laboratory considering the quantity and types of chemicals and feedstock with a handling capacity of (300 mL + alcohol + catalyst) to be processed. The reaction flask setup was made such that it could be processed under different operating circumstances, i.e., the influence of catalyst loading, amount of alcohol, and operating temperature in the range 50-80 oC, and the transesterification process was performed at atmospheric pressure. The specification of the reactor is as presented in Table 1. Other equipment was used in this study, as shown in Table 2.

Table 1
Specification of the reactor.

Type of reactor	Simple batch reactor (3-Neck Round Bottom Reaction Flask (spherical))
Capacity (mL)	500
Diameter of reactor (D) cm	10
Diameter of opening (central neck) of reaction flask (d ₁) cm	2.4
Bar diameter (cm)	0.5
Material handling capacity	300 mL bio feed + Alcohol + catalyst

Table 2
Equipment's used in this study.

Equipment	Type
Magnetic stirrer	Heldolph Instruments GmbH & Co. KG, type: MR Hei-standard
Balance	Radwag Wagi Elektroniczne, model: as 220 /C/1.
Centrifuge	D-78532 Tuttingen, type werk Nr.
Thermometer	Electrical temperature scale (up to range 150 °C) was made.

In this study, 20-25 liters of Afia waste cooking oil (AWCO) were collected from Farhad restaurant, Kirkuk (Iraq). Materials used in this work are NaOH, KOH, methanol (CH₃OH) (AR Grade). For all

experiments, the mixture was agitated and stirred at a constant speed (250 rpm). The transesterification reaction was performed into a 500 mL endowed rounded bottom flask with a magnetic stirrer used to heat the mixture into the flask. The transesterification reaction was carried out into a 500ml reaction flask. The transesterification process is conducted using catalyst percentage of (0.3 wt%, 0.4 wt%, 0.6 wt%, 0.7 wt%, 0.9 wt% and 1.0 wt% KOH or NaOH), at (1–3 h) reaction time, 50, 60, 70 and 80 ± 2 °C reaction temperature and at 1atm pressure. The feed of AWCO was free from water because that can cause slowing the transesterification reaction and further moisture or water consumes the catalyst. So, the feed of Afia waste cooking oil (AWCO) was preheated after collection at 110± 2 °C to ensure no water in the AWCO. AWCO sample was weighed carefully by the weighing machine. Figure 1 illustrates a flow diagram for the production of biodiesel.

For instance, the sample was 300 ml from AWCO, 100 ml CH₃OH and 0.7 wt% of KOH (same for other samples); this can be repeated the same for NaOH. The mixture was mixed and heated with temperature (60 oC ± 2) with continuous mixing for three hours; then, the mixture was turbid. The product was retained in

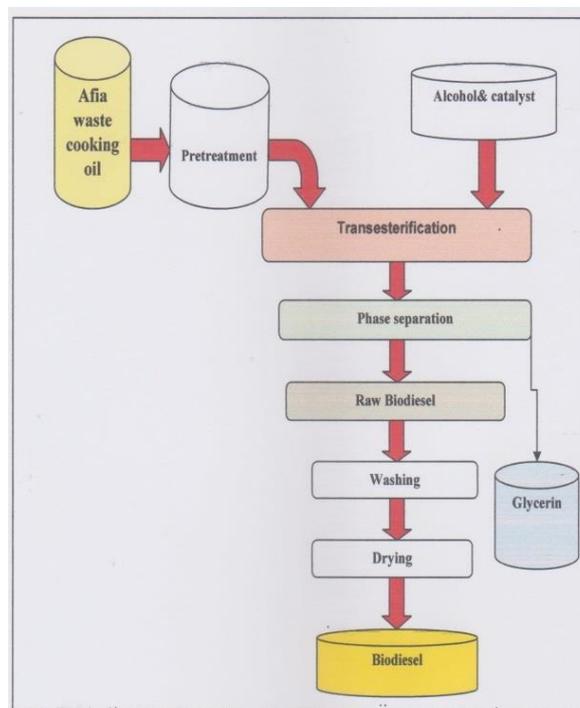


Fig. 1. A flow diagram for the production of biodiesel.

the separating funnel for a period of 12 hours. Two layers with different densities resulted from transesterification. The upper layer consists of biodiesel,

soap, and alcohol while, the down layer involves glycerin, impurities, excess alcohol, catalyst, and traces of unreacted oil. The two layers were separated and measured the separation of two phases. The upper layer was purified (alcohol was removed) via heating the mixtures to 80 °C, by heating mixtures at and washed three times by using warm distilled water.

The diverse properties of AWCO oil were measured before and after trans-esterification based on the ASTM standard test methods for each property. The tested properties comprise kinematic viscosity at 40 °C using (CP) Brookfield DVII + Pro. Viscometer, Specific gravity at 15 °C, Acid value (AV), flashpoint using Pensky Marten flash point apparatus, cloud and pour point using test jar method based on ASTM D2500 and ASTM D7683 test method respectively, and gross calorific value. Each test was reiterated in triplicate for highly accurate and reliable results. Diesel engine with the specifications shown in Table 3 has been used to conduct engine tests.

3. Results and Discussion

In this work, KOH or NaOH catalysts at different concentrations (0.4, 0.6, 0.8, and 1) as a weight percent were used. Figure 2 shows the effect of a base catalyst on the yield of biodiesel with an increasing ratio of KOH or NaOH concentrations. Based on the results obtained, the maximum yield was accomplished from AWCO at 0.4 wt% of KOH catalyst. An increase in base catalyst more than this limit, the transesterification reaction affected, and the yield reduced. This can be explained as further concentration means mass transfer becomes very important. However, an upsurge in the concentration of catalyst and reaction temperature resulted in a fluctuation in the yield of biodiesel production.

Figure 2 (a and b) presents the outcomes for the impact of reaction temperature on the biodiesel yield at constant pressure (1 atm) and different reaction temperatures of 50, 60, 70, and 80 °C. The figure presents the influence of base catalysts on the yield of biodiesel with an increasing ratio of KOH or NaOH concentrations. The indices of results showed that maximum yield was achieved from AWCO at 0.4 wt% of catalyst. An increase in base catalyst more than this limit, the transesterification reaction affected and the yield decreased due to the further increase leads to increasing the viscosity of the reaction medium under

the formation of dense slurry from the catalyst powder and the used oil which can result in difficulty in the homogeneous mixing of the reactants and consequently decreases in the interaction between the catalyst and reaction component. This can be clarified as further concentration means mass transfer becomes very significant. The yield of biodiesel production regularly increased with an increase in reaction temperature then tends to decrease after a certain maximum value. Alternatively, it presents a constant tendency to decrease with increasing catalyst concentration.

Table 3
Diesel engine specifications.

Type	Yanmar
Model	TF 120
Stroke	4-stroke
Colling system type	Water-cooled
Injection system	Direct injection
cylinder bore	92 mm
stroke length	96 mm
connecting road length	149.5 mm

As can be realized from Figure 3, the yield and conversion of biodiesel using KOH catalyst are greater than NaOH catalyst. Optimum operating variables gained are 60 °C, 3 h, and 0.4 wt% reaction temperature, reaction time, and KOH catalyst, respectively. The higher yield and conversion were at low temperature, but methyl ester conversion was good at increased temperature. It must be taking into consideration that the highest reaction temperature more than the boiling point for CH₃OH can affect chiefly the yield and conversion of biodiesel and also causing evaporation of alcohol (CH₃OH).

To ensure the produced biodiesel meets the standard limits of ASTM D6751, analysis for checking its properties were performed as presents in Table 3. Produced biodiesel meets the standard specifications. Figure 4 demonstrates the engine test results for brake specific fuel consumption (BSFC) and brake power (BP) at a constant half engine load. During the whole engine speed, the obtained engine BP with both biodiesels was found to be lower than that of diesel fuel. Engine BP with both biodiesels is found to be lower than that with diesel during the whole engine speed, and the maximum reduction is found to be about 19% at 2400 rpm engine speed, which can be attributed to the lower calorific value of biodiesel fuel compared to diesel fuel as shown in Table 4 [15]. Moreover, both biodiesels disclose higher BSFC during the whole engine speed, and the maximum

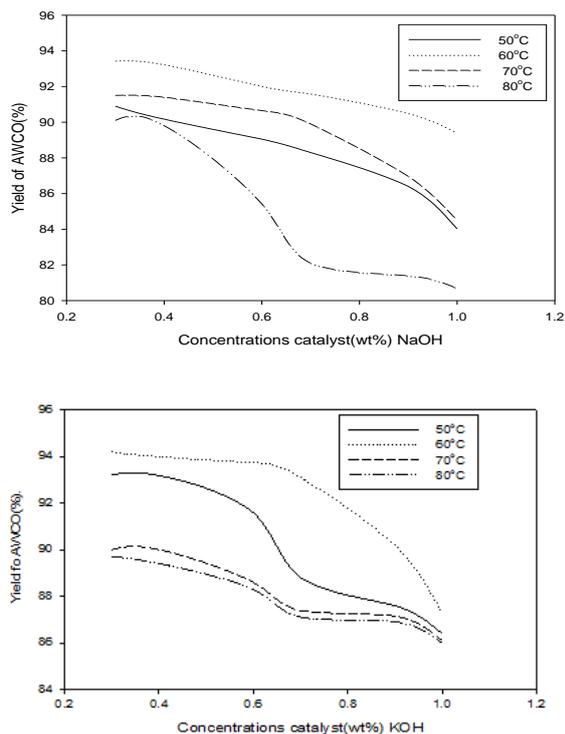


Fig. 2. Effect of temperature on biodiesel yield in case of KOH or NaOH.biodiesel at 60 °C

increase is found to be 17% at 1800 rpm engine speed, which can be attributed to the higher density of biodiesel fuel compared to diesel fuel, as shown in Table 4 [25]. Engine test results show similar trends for both biodiesels compared to diesel in terms of engine BP and BSFC with increasing engine speed.

Table 4

Analysis of original Afia waste cooking oil compared to its biodiesel produced at 60 °C, 3 h, and 0.4 wt% KOH catalyst

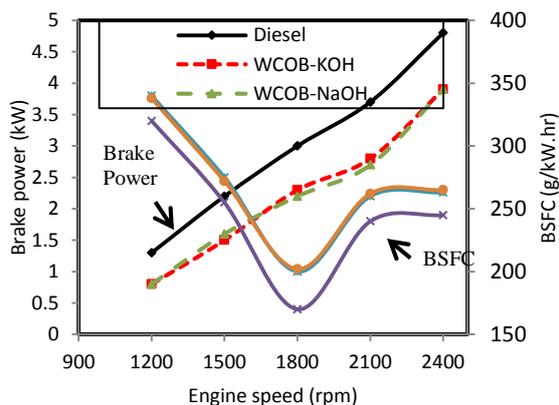


Fig. 4. Variation of Engine BP and BSFC with increasing engine speed.

4. Conclusions

In this experiment, the biodiesel fuel has been manufactured from Afia waste cooking oil (AWCO) by utilizing potassium hydroxide (KOH) and sodium hydroxide (NaOH) as homogenous catalysts. According to the obtained results in this study, the biodiesel yield and conversion obtained by using KOH catalyst were greater than NaOH catalyst. Moreover, using KOH catalyst, less soap formed during the reaction as compared with NaOH catalyst. The maximum conversion and yield of biodiesel are 97.54 and 94.935%, respectively achieved at optimum operating variables are 60 °C reaction temperature, 3 hours reaction time, and 0.4 catalyst concentration of KOH. The indices of obtained results discovered that the influence of reaction time was significant and affected the characteristics of biodiesel, such as specific gravity and viscosity as presented slightly unreacted raw materials (AWCO). A decline in yield and conversion of biodiesel has been seen, and the saponification in the reaction when further increasing in catalyst concentration more than the optimum. The tested features of biodiesel (viscosity, flash point, cloud point, pour point, specific gravity, gross calorific value) and elemental analysis were based on ASTM D6751 fuel standard specifications. Engine test outcomes indicate similar inclinations for both biodiesels compared to conventional diesel regarding engine BP and BSFC with rising engine speed.

5. Conflicts of interest

Properties	Original Afia waste cooking oil	Afia waste cooking oil biodiesel
Kinematic viscosity at 40 °C (CP) Brookfield DVII + Pro Viscometer	28 mm ² /s	6.39 mm ² /s
Specific gravity at 15 °C	0.91 gm/ml	0.883 gm/ml
Acid value (AV)	8.4177	0.702
Flashpoint Pinsky Marten flashpoint apparatus	164 °C	140 °C
Cloud point ASTM D2500 test jar method	-1 °C	10 °C
Pour point ASTM D7683 test jar method	-12 °C	-4 °C
Calorific value	---	38.6 MJ/kg

There are no conflicts to declare.

References

[1] Rajendran N, Gurunathan B. Process optimization, green chemistry balance and technoeconomic analysis of biodiesel

- production from castor oil using heterogeneous nanocatalyst. *Bioresour Technol* 2020;320:124347.
- [2] Talebian-kiakalaieh A, Aishah N, Amin S, Mazaheri H. A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy* 2013;104:683–710.
- [3] Hagos FY, Ali OM, Mamat R, Abdullah AA. Effect of emulsification and blending on the oxygenation and substitution of diesel fuel for compression ignition engine. *Renewable and Sustainable Energy Reviews* 2017;75.
- [4] Adekunle AS, Oyekunle JAO, Oduwale AI, Owotomo Y, Obisesan OR, Elugoke SE, et al. Biodiesel potential of used vegetable oils transesterified with biological catalysts. *Energy Reports* 2020;6:2861–71.
- [5] Ali OM, Mamat R, Abdullah NR, Abdullah AA. Characteristic of blended fuel properties and engine cycle-to-cycle variations with butanol additive. *AIP Conf. Proc.* 2015; 1660, 070006-1–070006-11; doi: 10.1063/1.4915724., 2015.
- [6] Ali OM, Mamat R, Abdullah NR, Abdullah AA. Effects of Blending Ethanol with Palm Oil Methyl Esters on low Temperature Flow Properties and Fuel Characteristics. *International Journal of Advanced Science and Technology* 2013;59:85–96.
- [7] Permpool N, Bonnet S, Gheewala SH. Greenhouse gas emissions from land use change due to oil palm expansion in Thailand for biodiesel production. *Journal of Cleaner Production* 2015;134:1–7.
- [8] Binhayeeding N, Klomklao S, Prasertsan P, Sangkharak K. Improvement of biodiesel production using waste cooking oil and applying single and mixed immobilised lipases on polyhydroxyalkanoate. *Renew Energy* 2020;162:1819–27.
- [9] Ali OM, Mamat R, Masjuki HH, Abdullah AA. Analysis of blended fuel properties and cycle-to-cycle variation in a diesel engine with a diethyl ether additive. *Energy Conversion and Management* 2016;108:511–9.
- [10] Ali OM, Mamat R. Improving Engine Performance and Low Temperature Properties Of Blended Palm Biodiesel Using Additives . A review. *Applied Mechanics and Materials* 2013;315:68–72.
- [11] Ali OM. Evaluation of diesel engine performance with high blended diesel-biodiesel fuel from waste cooking oil. *IOP Conference Series: Materials Science and Engineering*. 2019;518(3):1-6
- [12] Athar M, Zaidi S. A review of the feedstocks, catalysts, and intensification techniques for sustainable biodiesel production. *J Environ Chem Eng* 2020;8:104523. <https://doi.org/10.1016/j.jece.2020.104523>.
- [13] Ali OM, Mamat R, Faizal CKM, Yusop AF. Influence of oxygenated additive on blended biodiesel-diesel fuel properties. *Applied Mechanics and Materials* 2013;393:487–92.
- [14] Ali OM, Mamat R, Faizal CKM. Improvement of Blended Biodiesel Fuel Properties with Ethanol Additive. *International Journal of Advanced Science and Technology* 2013;55:21–32.
- [15] Ali O, Mamat R, Najafi G, Yusaf T, Safieddin Ardebili S. Optimization of Biodiesel-Diesel Blended Fuel Properties and Engine Performance with Ether Additive Using Statistical Analysis and Response Surface Methods. *Energies* 2015;8:14136–50.
- [16] Munir M, Ahmad M, Rehan M, Saeed M, Lam SS, Nizami AS, et al. Production of high quality biodiesel from novel non-edible *Raphanus raphanistrum* L. seed oil using copper modified montmorillonite clay catalyst. *Environ Res* 2020;110398.
- [17] Xue B, Luo J, Zhang F, Fang Z. Biodiesel production from soybean and *Jatropha* oils by magnetic $\text{CaFe}_2\text{O}_4\text{-Ca}_2\text{Fe}_2\text{O}_5$ -based catalyst. *Energy* 2014;68:584–91.
- [18] Ali OM, Mamat R, Faizal CKM. Effects of Diethyl Ether Additives on Palm Biodiesel Fuel Characteristics and Low Temperature Flow Properties. *International Journal of Advanced Science and Technology* 2013;52:111–20.
- [19] Ali OM, Mamat R, Faizal CKM. Review of the effects of additives on biodiesel properties, performance, and emission features. *Journal of Renewable and Sustainable Energy* 2013;5:012701.
- [20] Wan Ghazali WNM, Mamat R, Masjuki HH, Najafi G. Effects of biodiesel from different feedstocks on engine performance and emissions: A review. *Renewable and Sustainable Energy Reviews* 2015;51:585–602.
- [21] Ali OM, Mamat R, Abdullah NR, Abdullah A. Analysis of Blended Fuel Properties and Engine Cyclic Variations with Ethanol Additive. *Journal of Biobased Materials and Bioenergy* 2015;9:108–41.
- [22] Ali OM, Mamat R, Abdullah NR, Abdullah AA. Investigation Of Blended Palm Biodiesel-Diesel Fuel Properties With Oxygenated Additive. *ARPN Journal of Engineering and Applied Sciences* 2016;11:5289–93.
- [23] Ali OM, Mamat R, Abdullah NR, Abdullah AA. Commercial And Synthesized Additives For Biodiesel Fuel : A Review. *ARPN Journal of Engineering and Applied Sciences* 2016;11:3650–4.
- [24] Moraes PS, Engelmann JI, Igansi AV, Sant'Anna Cadaval Jr TR, Antonio de Almeida Pinto L. Nile tilapia industrialization waste: Evaluation of the yield, quality and cost of the biodiesel production process. *J Clean Prod* 2020;125041.
- [25] Omar I. Awada, R. Mamat, Obed M. Ali, N.A.C. Sidik, T. Yusaf KK, Kettner M. Alcohol and ether as alternative fuels in spark ignition engine: A review. *Renewable and Sustainable Energy Reviews* 2018;82:2586–605.