

**Automotive Experiences** 

Vol. 6 No. 1 (2023) pp. 80-93



p-ISSN: 2615-6202 e-ISSN: 2615-6636

## **Research** Paper

# Transesterification of Waste Cooking Oil using CaO Catalyst Derived from Madura Limestone for Biodiesel Production and Its Application in Diesel Engine

# Abdul Hamid<sup>1</sup>, Amin Jakfar<sup>1</sup>, Sirly Bifadilatur Romaniyah<sup>1</sup>, Ike Dayi Febriana<sup>1</sup>, Mohammad Abdullah<sup>2</sup>, Zeni Rahmawati<sup>3</sup>, Didik Prasetyoko<sup>3</sup>

<sup>1</sup>Department of Heavy Equipment Mechanical Engineering, Politeknik Negeri Madura, Sampang, 69281, Indonesia <sup>2</sup>Department of Ship Building Engineering, Politeknik Negeri Madura, Sampang, 69281, Indonesia <sup>3</sup>Department of Chemistry, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia

ahamchimie@poltera.ac.id

© https://doi.org/10.31603/ae.7879



Published by Automotive Laboratory of Universitas Muhammadiyah Magelang collaboration with Association of Indonesian Vocational Educators (AIVE)

#### Abstract

Article Info	In this study, we report biodiesel production from waste cooking oil using CaO catalyst			
Submitted:	derived from Madura limestone through a transesterification reaction. Many limestone			
13/09/2022	quarries in Madura can be used as heterogeneous catalysts because they are cheap, easy to			
Revised:	separate, and have high basicity. Conversion of limestone into CaO catalyst through			
29/01/2023	calcination at 900°C for 3 hours. The CaO catalyst formed was characterized using X-Ray			
Accepted:	Diffraction (XRD), Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscopy-			
30/01/2023	Energy Dispersive X-Ray (SEM-EDX) instruments. Biodiesel formed through the			
Online first:	transesterification reaction was analyzed using GC-MS. Furthermore, biodiesel blends from			
19/03/2023	waste cooking oil and pure diesel were prepared in volume percentages (B-10, B-20, B-30, B-			
	40, and B-100) for testing on diesel engine performance. The results of testing the highest			
	torque and brake horsepower (BHP) were obtained on pure diesel fuel (S-100) at 2.49 Nm and			
	381.12 watts, respectively. The lowest fuel consumption at 1500 rpm is produced on the B-20			
	at 0.186 kg/h. Overall, the emission characteristics of carbon monoxide (CO), nitrogen oxides			
	(NOx), and nitrogen monoxide (NO) with the lowest concentration resulted from biodiesel			
	blends rather than pure diesel.			
	Keywords: Biodiesel; Waste cooking oil; CaO; Limestone; Transesterification; Diesel engine			

## 1. Introduction

As is known, oil-based fuels are still the primary fuel for the industrial and transportation [1]. Due to the growth of the industrial and transportation sectors, the demand for oil-based fuels continues to increase and is predicted for the next few decades [2], [3]. As a consequence, oil reserves are rapidly decreasing which has the potential for an energy crisis [4]. In addition, environmental issues are also exacerbated by climate change, global warming, and exhaust emissions [5]. Therefore, an environmentally friendly alternative fuel is needed to reduce consumption of oil-based fuels [6], [7].

One of the alternative and popular fuels is biodiesel, both for the transportation and industrial sectors. The use of pure or mixed biodiesel is the most reasonable choice to replace diesel oil [8]–[10]. Biodiesel consists of a mixture of long chain fatty acid alkyl esters derived from vegetable oils or animal fats [11], [12]. Various plants that have been proven for biodiesel production include coconut [13], palm [14], soybean [15], [16], nyamplung [17], kemiri sunan [18], [19], and jatropha [20].

Triglycerides from vegetable oils or animal fats are converted into methyl esters through a transesterification reaction with alcohol and a catalyst [21], [22]. Ideally, a catalyst for

BY

transesterification should have characteristics such as being easily separated from its products, non-corrosive, regenerative or reusable, and more environmentally friendly because it does not require acid or water treatment at the separation stage [23], [24]. Istadi et al., [25] reported the reuse of a calcium oxide-based catalyst (K2O/CaO-ZnO) in the transesterification reaction of soybean oil. The catalyst used showed high catalytic activity with a yield of about 80% and could be reused after regeneration. Even after three cycles of use, the calcium oxide-based catalyst still shows stable catalytic activity. The heterogeneous reuse of catalysts from moringa oleifera leaf ash for biodiesel production has also been reported by Kolakoti et al., [26]. In their study, the catalyst was recovered after use and washed with methanol. The catalyst is then dried in an oven at 50 °C before reuse. The results showed that after using the catalyst five times in a row, the yield of biodiesel produced was still above 50%.

In many cases, heterogeneous catalysts are preferred over homogeneous catalysts because they are more environmentally friendly and easily separated from the product [27]. Calcium oxide (CaO) is one of the most studied heterogeneous catalysts due to its excellent activity in transesterification reactions, availability of waste, and low cost, and can be obtained from natural minerals. CaO catalysts are generally produced from the decomposition of calcium carbonate (CaCO<sub>3</sub>) at high temperatures between 600 and 1000 °C [28], [29]. CaCO<sub>3</sub> can be extracted from many natural substances or materials such as chicken eggshell [30], fish bone [31], and limestone [32]. Limestone is a mineral that wastes its availability in nature and consists of calcium and magnesium in the form of dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> [33]. In addition, the availability of limestone mines in Indonesia, especially on Madura Island is very abundant. So that it can be used as a heterogeneous catalyst for biodiesel production.

Apart from plant and animal fats, biodiesel is also produced from waste cooking oil obtained from restaurant or household waste [34], [35]. Abed et al [2] have examined the production of biodiesel from waste cooking oil. The results of their research show that the thermal efficiency of biodiesel blends is lower than pure diesel oil. The specific fuel consumption of biodiesel blends is higher than that of diesel fuel. The CO<sub>2</sub> emission content of the biodiesel blend is higher than diesel fuel. Meanwhile, the emission gas content of CO, smoke opacity, and HC for the biodiesel mixture is lower than diesel. Kataria et al [4] also conducted research on biodiesel from waste cooking oil which was tested on a CI engine at 1500 rpm. The thermal performance of diesel engines and emission parameters such as CO, HC, and NOx in the biodiesel-diesel mixture shows that biodiesel produced from waste cooking oil has lower emissions than conventional diesel.

Utilization of waste cooking oil into biodiesel has the advantage of increasing added value because of its availability [36]. Considering the availability of Madura limestone as a catalyst, our present study focuses on the production of biodiesel from waste cooking oil using the esterification-transesterification method with the addition of a CaO catalyst from Madura limestone. CaO was chosen because it consists of a cation having a Lewis acid site and an anion having a Bronsted base site. Among metal oxides, calcium oxide has attracted much attention for transesterification because it has several advantages such as high basicity and is more environmentally friendly due to its low solubility in methanol [37]. In addition, based on previous research from several references, it was shown that the CaO catalyst has excellent activity in the transesterification reaction biodiesel for production. Furthermore, the performance of biodiesel is verified in diesel engines, which includes torgue, brake horsepower (BHP) and fuel consumption (mb). Engine emissions were also checked, which included carbon monoxide (CO), nitrogen oxides (NOx) and nitrogen monoxide (NO).

#### 2. Methods

#### 2.1. Tools and Materials

The tools needed in biodiesel production are a hotplate, analytical balance, beaker glass, threeneck flask, condenser tube, water pump, hose, thermometer, stirrer, dropper, stative, separating funnel, hotplate, tachometer, stirrer, flow meter, diesel engines, and burettes. While the materials used in this study were waste cooking oil, methanol (Merck), H<sub>2</sub>SO<sub>4</sub> (Smart Lab), H<sub>3</sub>PO<sub>4</sub> (Merck), NaOH (Merck), and CaO catalyst from Pamekasan limestone, Madura island.

#### 2.2. Synthesis of CaO Catalyst from Limestone

To produce catalyst, limestone is crushed, sieved through a 150 mesh size, then dried in an oven at 110 °C for 2 hours. The dry limestone was then calcined at 900 °C for 3 hours to form CaO. Calcined solids were then characterized using X-Ray Diffraction (XRD), Fourier Transform Infra Red (FTIR) and Scanning Electron Microscopy-Dispersive X-Ray (SEM-EDX). Energy Characterization using XRD (Bruker D2 Phaser) was carried out by irradiating Cu K $\alpha$  at an angle of  $2\theta$  between 5°-80°, to determine the phase formed. FTIR (Nicolet Avatar 360 IR) characterization was carried out using KBr pellets at wave numbers between 4000 and 400 cm-1 to determine the functional groups of solid samples. Solids from the resulting calcination were also characterized by SEM-EDX (Phenom Desktop ProXL) to determine their morphology and elemental content.

# 2.3. Biodiesel Production

## 2.3.1. Degumming Process

Prior to the processing of waste cooking oil into biodiesel, it was filtered to separate the waste cooking oil from the residue. The degumming process was carried out by mixing waste cooking oil (500 ml) with 0.5% (2.5 ml) H<sub>3</sub>PO<sub>4</sub>. Then, it was heated at 80 °C and stirred at 400 rpm for 15 minutes.

#### 2.3.2. Esterification Process

In this process, waste cooking oil (160.26 grams) was reacted with methanol (164.6 grams),

with a ratio of 1:9 (mol/mol), then 2% (v/v) of H2SO4 (1.41 ml) catalyst was added from the waste cooking oil. The esterification reaction was carried out at 60 °C under stirring conditions at 900 rpm for one hour. The esterification result was then allowed to stand for 24 hours until two layers were formed. Then the bottom layer was taken and prepared for the transesterification step.

#### 2.3.3. Transesterification Process

Methanol (256 grams) was reacted with a CaO catalyst from Madura limestone as much as 2% (2.8 grams) by weight of oil (140.225 grams) while stirring until the solution was homogeneous. The resulting mixture is added to the waste cooking oil. The transesterification reaction was carried out at 60 °C under stirring conditions at 900 rpm for one hour. The ratio between methanol and waste cooking oil in transesterification is 1:12 (mol/mol). The results of the transesterification reaction were then allowed to stand for 24 hours to form two layers. The bottom layer which is biodiesel oil is then taken by decantation and then tested on a diesel engine. The biodiesel oil formed was also analyzed qualitatively using Gas Chromatography-Mass Spectroscopy (GC-MS) to determine the compounds present in biodiesel. The stages of biodiesel production from waste cooking oil are illustrated in Figure 1. Then, Yield biodiesel produced is calculated using Eq.(1) [26]:

$$Biodiesel \ yield = \frac{Weight \ of \ the \ biodiesel}{Weigt \ of \ the \ raw \ oil} \ x \ 100\% \ (1)$$

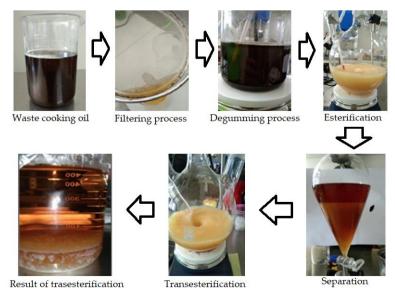


Figure 1. Scheme of biodiesel production from waste cooking oil

#### 2.4. Performance and Emission Characteristics

First, the fuel is put into the burette tube. The composition of the biodiesel fuel mixture is prepared by volume percentage, namely B-10, B-20, B-30, B-40, B-100, and pure diesel (S-100). The diesel engine is then started by turning the crank. After that, the speed of airflow required/inhaled is measured using a flowmeter. Diesel engine speed measured using (rpm) is а tachometer. Meanwhile, the emission content of the diesel engine is measured using a gas analyzer instrument. Based on this test, data on engine speed (rpm), time out of fuel, flow rate, and emission concentration of CO, NO, and NOx will be obtained. The schematic of the diesel engine setup can be seen in Figure 2. Specifications of the engine and instrument used for measuring the performance and emissions are presented in Table 1 and Table 2.

#### 3. Results and Discussion

#### 3.1. Characterization of CaO Catalyst

FTIR characterization results of limestone samples before and after calcination are presented in Figure 3. The peaks in the limestone before and after calcination have different intensities and wave numbers. The main absorption peak at 1472 cm<sup>-1</sup> and the minor absorption peak at 878 cm<sup>-1</sup> and 881 cm-1 from both samples indicated the presence of asymmetric stretching vibrations [38]. The peaks that widened at around 3437 cm<sup>-1</sup> and 3429 cm<sup>-1</sup> in both samples indicated the presence of OH group vibrations [39], [40]. The absorption band observed at 3698 cm-1 is the stretching vibration of the OH group. This vibration occurs due to the hydrolysis of CaO into Ca(OH)2 when exposed to air [41], [42]. These results are consistent with the characterization using XRD which showed that the CaO obtained contained a Ca(OH)<sub>2</sub> phase. Therefore, the role of calcination is very important to convert CaCO<sub>3</sub> to CaO [43].

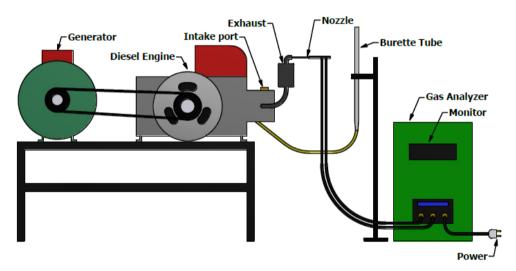


Figure 2. Set-up of performance and emission testing on diesel engine

Туре	: TF 70 LY-di		
Engine type	: Stroke horizontal diesel engine		
Number of cylinders	: 1 cylinder		
Diameter x step length	: 78 mm x 80 mm		
Cylinder volume	: 382 cc		
Maximum torque	: 2.58 kg.m/1600 rpm		
Instantaneous maximum power	: 7 hp/2400 rpm		

Table 1. Yanmar Diesel Engine Specifications
----------------------------------------------

Table 2. Gas analyzer instrument specifications				
Туре	: E8500-OCN-0-12			
Oxygen range	: 0-25%			
Carbon monoxide range	: 0 – 8000 ppm			
NO/NO <sub>x</sub> range	: 0 – 4000 ppm			

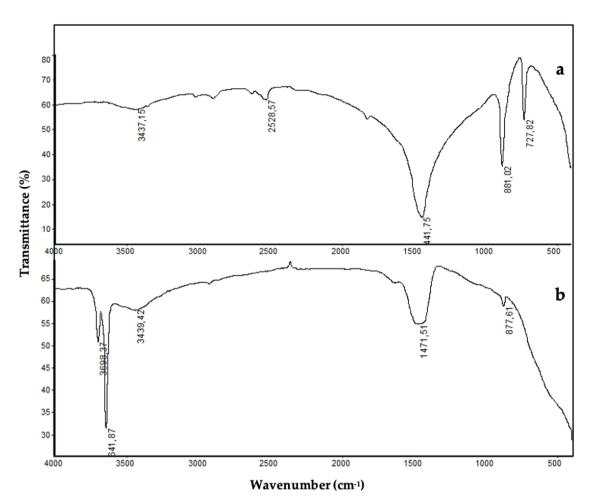


Figure 3. Infrared spectra of limestone samples: (a) before calcination and (b) after calcination

The results of the characterization using XRD of limestone samples before and after calcination are shown in Figure 4. Based on the diffractogram in Figure 4, it indicates that the limestone samples calcined at 900 °C for 3 hours underwent transformation from CaCO3 to CaO. This is supported by the characteristic peak of CaO which appears at  $2\theta = 36.95^\circ$ ;  $54.38^\circ$ ;  $64.28^\circ$  and 78.61° [33]. In addition, new peaks appeared in the limestone samples after calcination, namely at  $2\theta$ around 18.01°; 34.01° and 50.81° which is the Ca(OH)<sub>2</sub> phase and around 42.93° and 62.29° which is the MgO phase. Meanwhile, for limestone samples before calcination, the peak was seen at  $2\theta = 24.15^{\circ}$ ;  $31.03^{\circ}$ ;  $37.45^{\circ}$ ;  $41.21^{\circ}$ ; 45.02° and 51.47° where these peaks indicate the presence of a  $CaMg(CO_3)_2$  phase. So it can be concluded that the calcination process can decompose calcium carbonate (CaCO3) into calcium oxide (CaO) and carbon dioxide gas CO2 [44].

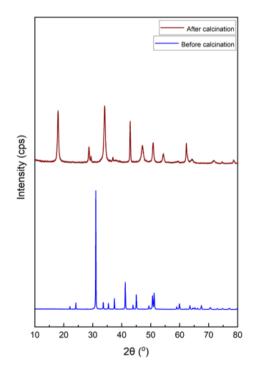


Figure 4. Diffractogram of limestone samples before and after the calcination process

Characterization using the SEM-EDX instrument in this study was used to determine the morphology and element composition of the CaO catalyst. Figure 5 shows that the morphology of the sample resembles the shape of a beam and prism with a particle size about 10 µm. In addition, small particles clustered together. The test results for the element content of the CaO catalyst showed that the element composition of the sample consisted of calcium, oxygen, magnesium, carbon and silica. The highest elemental content of the CaO catalyst consists of calcium and oxygen were 36.84% and 32.93%, respectively (Table 3).

Table 3.	The elements content of CaO catalyst
----------	--------------------------------------

Element	% Weight
Calsium (Ca)	36.84
Oxygen (O)	32.93
Magnesium (Mg)	19.03
Carbon (C)	11.01
Silicon (Si)	0.19

#### 3.2. Biodiesel Production Process

Free fatty acids (FFA) play a significant role in the biodiesel production process. The quality of waste cooking oil is determined by its free fatty acid (FFA) content by means of titration. A low FFA content is necessary to obtain a high biodiesel yield in the transesterification reaction, because the high FFA content causes a soap formation reaction (saponification reaction) and will ultimately lead to decrease in conversion and yield [45]. Therefore, waste cooking oil which has a high FFA content requires preparation beforehand. The FFA content for waste cooking oil in this study was obtained at 3.8%. The decrease in FFA levels can be done through esterification reactions. FFA can react with alcohol to form esters with an acid catalyst. The results show that the FFA content in the oil resulting from the esterification reaction using H2SO4 catalyst is 1.4%. The percentage of FFA in waste cooking oil decreases because FFA is converted to esters through esterification reactions. In addition, the catalyst will lower the activation energy of the reaction so that the reaction rate constant will increase. Biodiesel oil yield are illustrated in **Figure 6** and yield biodiesel produced in this study is equal to 72.41% (based on calculations using equation 1). Then, the chromatogram of the GC-MS analysis of biodiesel samples is shown in **Table 4** and **Figure 7**. The biodiesel sample consists of methyl ester compounds include myristic acid, palmitic acid, oleic acid, stearic acid and heneicosanoic acid.

Test results for biodiesel from waste cooking oil related to fuel properties such as kinematic viscosity at 40 °C, density at 15 °C, acid number and flash point are presented in Table 5. The properties of biodiesel obtained were compared with international biodiesel standards, namely ASTM D6751. Based on the results of kinematic viscosity analysis, the biodiesel synthesized from waste cooking oil was higher than the standard according to ASTM D6751. Therefore, the presence of high viscosity can lead to the formation of excess exhaust smoke during combustion due to poor fuel atomization in the combustion chamber [46]. However, the viscosity can be adjusted by mixing using pure diesel when testing on diesel engines.

Based on **Table 5** it can be concluded that the properties of biodiesel based on density slightly exceed the limits of the standard. As for flash point and acid number according to ASTM D6751 standard. The properties of biodiesel fuel can also be affected by the composition of the methyl ester [47]. The content of methyl esters is presented in **Table 4**. Based on the table, it shows that the unsaturated methyl esters are more in the biodiesel produced from waste cooking oil, which is around 52.13% and the saturated methyl esters are around 46.32%. The highest methyl ester content was observed as oleic acid which was around 51.24%.

	F -	8	
No	Compound	Yield (%)	
1	Myristic acid	0.89	
2	Palmitic acid	38.87	
3	Oleic Acid	51.24	
4	Stearic Acid	7.45	
5	Heneicosanoic acid	0.46	

Table 4. Methyl ester composition using GC-MS

Total Saturated : 46.32%; Total Unsaturated: 52.13%

	1	1		0
Properties	Method	Unit	ASTM D6751 (Standard)	Biodiesel produced from waste cooking oil
Kinematic viscosity at 40 °C	ASTM D-445	cSt	3.5-5.0	15.41
Density at 15 °C	ASTM D-1298	kg/m <sup>3</sup>	860-900	902
Acid number	SNI 7182.2015	mg-KOH/g	max 0.5	0.00024
Flash point	ASTM D-92	°C	min 101	186

Table 5. Properties of biodiesel produced from waste cooking oil

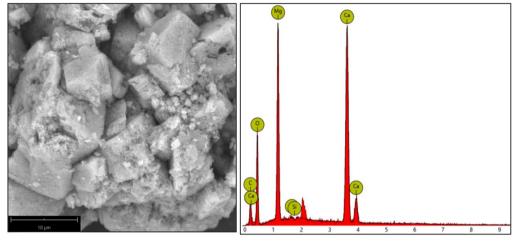


Figure 5. Morphology and element composition of CaO catalyst

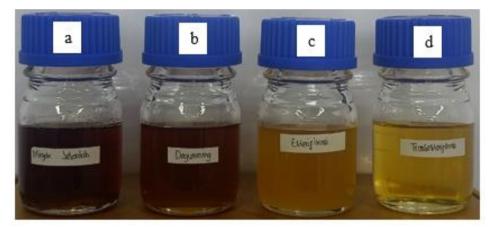
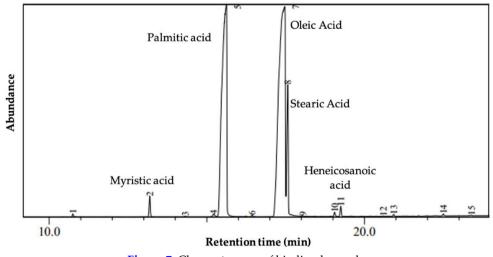
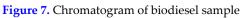


Figure 6. (a) Waste cooking oil; (b) Degumming product; (c) Esterification product; (d) Transesterification product





## 3.3. Performance and Emission Testing on Diesel Engine

Based on Figure 8, it shows that the torque value decreases along with the increase in the biodiesel blends into diesel fuel. This decrease in torque value occurs because the average effective pressure value decreases with the addition of biodiesel fuel. The highest torque value is produced by pure diesel fuel (S-100) at 2.49 Nm. While the lowest torque value is B-100 at 2.4 Nm.

The results of Brake Horse Power (BHP) test from the composition of the fuel blends between biodiesel and diesel can be seen in Figure 9. Based on the figure, it shows that the BHP value increases with increasing engine speed. This is because with the increase in engine speed, the temperature in the combustion chamber will increase. So that the power generated also increases. The magnitude of BHP value is also influenced by the torque, the higher of torque, the higher of BHP value. BHP will decrease when the torque reaches the lowest point and the engine speed passes the maximum point. Based on Figure 9, the fuel that has the highest BHP value is pure diesel (S-100) at 1500 rpm, which is 391.12 watts. While the lowest BHP value is obtained at B-100 of 251.35 watts at 1000 rpm.

The results of fuel consumption (Mb) between variations in fuel blends and diesel engine speed are shown in **Figure 10**. Fuel consumption for biodiesel blends from waste cooking oil is lower than pure diesel. The value of fuel consumption increases with increasing engine speed. This is because with the increase in engine speed, the

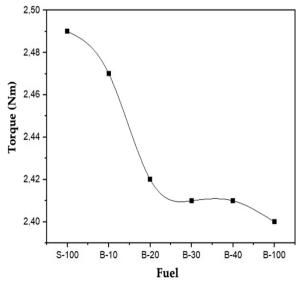


Figure 8. Output torque on various fuel

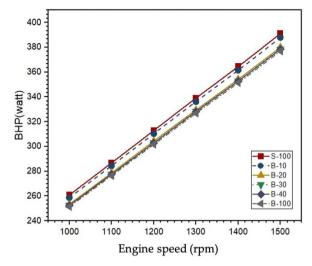


Figure 9. Eengine speed v.s. Brake Horse Power (BHP)

need for fuel in the combustion process also increases. The value of Mb is inversely proportional to the time it runs out of fuel. The longer the time it runs out of fuel, the smaller the Mb value. Biodiesel blends (B10, B20, B30, B40 and B100) showed a reduction in fuel consumption at the same engine speed when compared to pure diesel. Based on **Figure 10**, it is found that at 1500 rpm, the fuel that has the highest fuel consumption value is pure diesel (S-100) at 0.218 kg/h. While the lowest fuel consumption value is in the B-20 at 0.186 kg/h.

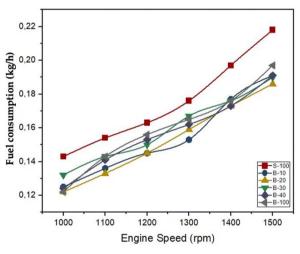
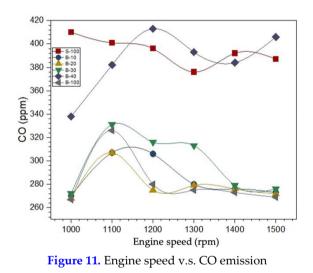


Figure 10. Engine speed v.s. fuel consumption

The graph of the CO gas emission concentration from fuel variations to engine speed is shown in Figure 11. Carbon monoxide (CO) is one of the compounds formed during the combustion stage between hydrocarbon fuels [4]. The formation of CO emission depends on the equivalence type fuel-air ratio, of fuel,

atomization rate, injection start time, injection pressure and engine speed [48]. Overall, based on Figure 11 shows that the content of CO gas emissions increased at 1000 rpm-1100 rpm and decreased at 1200-1500 rpm. This happens because of the reduced time required for fuel evaporation in the combustion chamber. The CO concentration of biodiesel blends fuel is lower than pure diesel. This is because the biodiesel blends has more oxygen molecules and a lower carbon content, resulting in better combustion [2]. The higher oxygen concentration will cause more complete combustion. Complete combustion will result in lower exhaust emissions, where CO will be oxidized to carbon dioxide (CO2) [49]. Based on Figure 9, it can be concluded that fuel with the highest CO concentration was pure diesel (S-100) at 410 ppm on 1000 rpm. While the lowest CO concentration was obtained at B-100 with a value of 269 ppm at 1500 rpm.



The graph of the relationship between nitrogen oxides (NO<sub>x</sub>) emission concentration and engine speed of the fuel blends is shown in Figure 12. The results of the overall NOx emission concentration decreased with increasing engine speed. NOx gas can be formed from a combination of nitrogen oxides (NO) and nitrogen dioxide (NO2) from the reaction between nitrogen gas and oxygen in the air during combustion [4]. The amount of NO<sub>x</sub> is affected by the amount of oxygen contained in the combustion chamber. NOx is formed due to excess oxygen at high temperatures, so the higher the oxygen, the higher of NO<sub>x</sub> level [2]. Based on the results of testing the NOx emission concentration, the highest NOx concentration was obtained the pure diesel at 150 ppm on 1000 rpm. While the lowest NO<sub>x</sub> concentration was obtained at B-10 with a value of 82 ppm at 1400 rpm. The exhaust emissions from biodiesel-fired engines also depend on variations in the fatty acid content. The increase in the concentration of NO<sub>x</sub> emission gas is influenced by the presence of unsaturated fatty acids such as oleic acid in biodiesel [50].

NO compounds are part of the formation of the emission NOx compounds. Therefore, concentration of NOx gas is always higher than that of NO. This can be seen in the graph between Figure 12 and Figure 13. Based on Figure 13, the gas emission concentration decreases with increasing engine speed. The decrease in NO emission levels is caused by the decrease in oxygen levels in the combustion chamber. The highest NO concentration was obtained in pure diesel (S-100) with a value of 143 ppm at 1000 rpm. While the lowest NO concentration was obtained at B-10 with a value of 79 ppm at 1400 rpm.

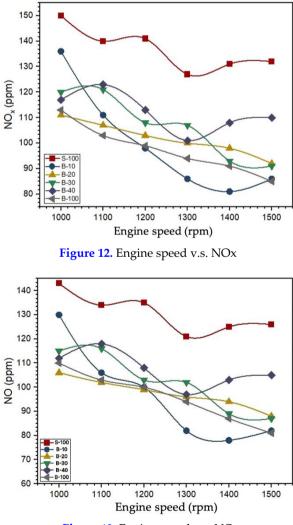


Figure 13. Engine speed v.s. NO

Overall, biodiesel fuel provides better results on the emission concentration of diesel engine when compared to pure diesel fuel. The best blends composition is produced on the B-100 because it produces a relatively significantly reduced emission concentration. The more biodiesel mixture causes the more oxygen atoms so that the fuel can burn completely. High carbon monoxide (CO) is formed due to lack of oxygen in the reaction with fuel during the combustion process [51]. In addition, the increase in CO emission gas can be caused by the high temperature where there is a reaction between carbon dioxide (CO2) and carbon (C) which produces CO gases. At high temperatures CO2 can decompose back into CO and oxygen. The reaction for the formation of CO is faster than the formation of CO<sub>2</sub>, so that the final product of combustion may still contain CO gases. For testing the performance of diesel engines, the best fuel composition is produced by pure diesel fuel. The torque and BHP values of pure diesel fuel are relatively higher when compared to biodiesel. The difference in torque generated by the engine is due to the increasing percentage of biodiesel added to diesel engine fuel which causes the viscosity of the fuel to increase. The decrease in torque from the biodiesel blends is due to the increasing percentage of the fuel mixture so that the resulting calorific value is lower, causing the torque value to decrease. As for the BHP value of the biodiesel fuel blends, it is almost close to the BHP value produced by pure diesel fuel. The decrease in power in the biodiesel fuel blends is probably due to the ignition delay in the diesel engine, resulting in a rougher engine sound and a loss of generated power.

Uncertainty calculations are divided into two types, namely types A and B. Type A is calculated based on test repetition data, while type B uncertainty can be calculated based on reliable data other than test results, such as instrument certificates/equipment used. In this study, the estimation of uncertainty is based on the resolution value of the tool specifications. Determination of type B uncertainty is divided into 3 based on the type of data distribution, namely a normal distribution if the certificate data shows a level of confidence (usually written a confidence level of 95% or 99%), rectangular distribution if the data range has the same level of probability or the shape of the probability is unknown, and finally the triangular distribution if the data distribution shows one value that has the highest probability of appearing. The certificate for the E8500 Emission gas analyzer does not have confidence interval data and the shape of the data distribution, so the uncertainty calculation is based on the assumption of a rectangular distribution [52]. The formula used is (2):

$$\mu_x = \frac{x}{\sqrt{3}} \tag{2}$$

Where  $\mu x$  is the uncertainty value, x is the resolution value on the tool certificate.

The resolution value on the tool is 1 ppm. So that the results of calculating the estimation of uncertainty from testing CO, NO and  $NO_x$  emissions from all samples were obtained at 0.5774 ppm.

## 4. Conclusion

The conversion of waste cooking oil into biodiesel using CaO catalyst from Madura limestone has been successfully made through an esterification-transesterification reaction. Characterization using XRD shows that limestone undergoes a transformation from CaCO3 to CaO where the characteristic peak of CaO is seen at  $2\theta$ around 36.95°; 54.38°; 64.28° and 78.61°. The results of characterization using SEM-EDX showed that the highest element content was calcium with a beam-like morphology. The prospect of converting waste cooking oil into fuel and its significant effect on fuel performance has been a concern especially the emission content produced. The concentration of CO, NOx and NO emissions from the combustion of a diesel engine using a biodiesel blend is relatively lower than using pure diesel. In addition, the consumption of biodiesel blends is less than using pure diesel. Diesel engine performance such as torque and power parameters produced from pure diesel is higher than biodiesel blends.

#### Acknowledgements

The author would like to thank all parties, both colleagues who have helped in this research and students of Politeknik Negeri Madura who have also assisted in setting up the equipment.

# 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

## Funding

No funding information from the authors.

#### 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.

## References

- [1] F. Nadeem et al., "Eco-benign biodiesel production from waste cooking oil using eggshell derived MM-CaO catalyst and condition optimization using **RSM** approach," Arabian Journal of Chemistry, vol. 14. no. 8, p. 103263, 2021. doi: 10.1016/j.arabjc.2021.103263.
- [2] K. A. Abed, A. K. El Morsi, M. M. Sayed, A. A. E. Shaib, and M. S. Gad, "Effect of waste cooking-oil biodiesel on performance and exhaust emissions of a diesel engine," *Egyptian Journal of Petroleum*, vol. 27, no. 4, pp. 985–989, 2018, doi: 10.1016/j.ejpe.2018.02.008.
- [3] T. Kivevele, T. Raja, V. Pirouzfar, B. Waluyo, and M. Setiyo, "LPG-Fueled Vehicles: An Overview of Technology and Market Trend," *Automotive Experiences*, vol. 3, no. 1, pp. 6–19, 2020, doi: 10.31603/ae.v3i1.3334.
- [4] J. Kataria, S. K. Mohapatra, and K. Kundu, "Biodiesel production from waste cooking oil using heterogeneous catalysts and its operational characteristics on variable compression ratio CI engine," *Journal of the Energy Institute*, vol. 92, no. 2, pp. 275–287, 2019, doi: 10.1016/j.joei.2018.01.008.
- [5] M. Kuniyil *et al.*, "Production of biodiesel from waste cooking oil using ZnCuO/Ndoped graphene nanocomposite as an efficient heterogeneous catalyst," *Arabian Journal of Chemistry*, vol. 14, no. 3, p. 102982, 2021, doi: 10.1016/j.arabjc.2020.102982.
- [6] S. K. Bhatia *et al.,* "Conversion of waste cooking oil into biodiesel using heterogenous

catalyst derived from cork biochar," *Bioresource Technology*, vol. 302, no. December 2019, p. 122872, 2020, doi: 10.1016/j.biortech.2020.122872.

- [7] S. O. Gultom, "Mikroalga: Sumber Energi Terbarukan Masa Depan," Jurnal Kelautan: Indonesian Journal of Marine Science and Technology, vol. 11, no. 1, p. 95, 2018, doi: 10.21107/jk.v11i1.3802.
- [8] M. Setiyo, D. Yuvenda, and O. D. Samuel, "The Concise Latest Report on the Advantages and Disadvantages of Pure Biodiesel (B100) on Engine Performance: Literature Review and Bibliometric Analysis," *Indonesian Journal of Science and Technology*, vol. 6, no. 3, pp. 469–490, 2021, doi: 10.17509/ijost.v6i3.38430.
- [9] A. Sule, Z. A. Latiff, M. A. Abbas, I. Veza, and A. C. Opia, "Recent Advances in Diesel-Biodiesel Blended with Nano-Additive as Fuel in Diesel Engines: A Detailed Review," *Automotive Experiences*, vol. 5, no. 2, pp. 182– 216, 2022, doi: 10.31603/ae.6352.
- [10] A. C. Arifin, A. Aminudin, and R. M. Putra, "Diesel-Biodiesel Blend on Engine Performance: An Experimental Study," *Automotive Experiences*, vol. 2, no. 3, pp. 91– 96, 2019, doi: 10.31603/ae.v2i3.2995.
- [11] W. Roschat *et al.*, "Catalytic performance enhancement of CaO by hydrationdehydration process for biodiesel production at room temperature," *Energy Conversion and Management*, vol. 165, no. January, pp. 1–7, 2018, doi: 10.1016/j.enconman.2018.03.047.
- [12] D. M. Marinković *et al.*, "Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives," *Renewable and Sustainable Energy Reviews*, vol. 56, pp. 1387–1408, 2016, doi: 10.1016/j.rser.2015.12.007.
- [13] Y. Rathore, D. Ramchandani, and R. K. Pandey, "Experimental investigation of performance characteristics of compressionignition engine with biodiesel blends of Jatropha oil & coconut oil at fixed compression ratio," *Heliyon*, vol. 5, no. 11, p. e02717, 2019, doi: 10.1016/j.heliyon.2019.e02717.
- [14] M. Vergel-Ortega, G. Valencia-Ochoa, and J. Duarte-Forero, "Experimental study of emissions in single-cylinder diesel engine

operating with diesel-biodiesel blends of palm oil-sunflower oil and ethanol," *Case Studies in Thermal Engineering*, vol. 26, no. December 2019, p. 101190, 2021, doi: 10.1016/j.csite.2021.101190.

- [15] Z. Zhu *et al.*, "Soybean biodiesel production using synergistic CaO/Ag nano catalyst: Process optimization, kinetic study, and economic evaluation," *Industrial Crops and Products*, vol. 166, no. 666, p. 113479, 2021, doi: 10.1016/j.indcrop.2021.113479.
- [16] A. Bhikuning, "The simulation of performance and emissions from rapeseed and soybean methyl ester in different injection pressures," *Automotive Experiences*, vol. 4, no. 3, pp. 112–118, 2021, doi: 10.31603/ae.4682.
- [17] M. Fadhlullah, S. N. B. Widiyanto, and E. Restiawaty, "The potential of nyamplung (Calophyllum inophyllum L.) seed oil as biodiesel feedstock: Effect of seed moisture content and particle size on oil yield," *Energy Procedia*, vol. 68, no. 2015, pp. 177–185, 2015.
- [18] Z. Rahmawati, H. Holilah, S. W. Purnami, H. Bahruji, T. P. Oetami, and D. Prasetyoko, "Statistical Optimisation using Taguchi Method for transesterification of Reutealis Trisperma Oil to Biodiesel on CaO-ZnO Catalysts," *Bulletin of Chemical Reaction Engineering & Catalysis*, vol. 16, no. 3, pp. 686– 695, 2021, doi: 10.9767/BCREC.16.3.10648.686-695.
- [19] S. Supriyadi, P. Purwanto, D. D. Anggoro, and H. Hermawan, "The Effects of Sodium Hydroxide (NaOH) Concentration and Reaction Temperature on The Properties of Biodiesel from Philippine Tung (Reutealis Trisperma) Seeds," *Automotive Experiences*, vol. 5, no. 1, pp. 57–67, 2022, doi: 10.31603/ae.5986.
- [20] L. Díaz, D. Escalante, K. E. Rodríguez, Y. Kuzmina, and L. A. González, "Response surface methodology for continuous biodiesel production from Jatropha curcas oil using Li/pumice as catalyst in a packed-bed reactor assisted with diethyl ether as cosolvent," *Chemical Engineering and Processing Process Intensification*, vol. 179, no. May, 2022, doi: 10.1016/j.cep.2022.109065.
- [21] M. J. Borah, A. Das, V. Das, N. Bhuyan, and D. Deka, "Transesterification of waste

cooking oil for biodiesel production catalyzed by Zn substituted waste egg shell derived CaO nanocatalyst," *Fuel*, vol. 242, no. May 2018, pp. 345–354, 2019, doi: 10.1016/j.fuel.2019.01.060.

- [22] W. Xie and H. Wang, "Synthesis of heterogenized polyoxometalate-based ionic liquids with Brönsted-Lewis acid sites: A magnetically recyclable catalyst for biodiesel production from low-quality oils," *Journal of Industrial and Engineering Chemistry*, vol. 87, pp. 162–172, 2020, doi: 10.1016/j.jiec.2020.03.033.
- [23] X. F. Li, Y. Zuo, Y. Zhang, Y. Fu, and Q. X. Guo, "In situ preparation of K2CO3 supported Kraft lignin activated carbon as solid base catalyst for biodiesel production," *Fuel*, vol. 113, pp. 435–442, 2013, doi: 10.1016/j.fuel.2013.06.008.
- [24] T. F. Dossin, M. F. Reyniers, R. J. Berger, and G. B. Marin, "Simulation of heterogeneously MgO-catalyzed transesterification for finechemical and biodiesel industrial production," *Applied Catalysis B: Environmental*, vol. 67, no. 1–2, pp. 136–148, 2006, doi: 10.1016/j.apcatb.2006.04.008.
- [25] I. Istadi, U. Mabruro, B. A. Kalimantini, L. Buchori, and D. D. Anggoro, "Reusability and stability tests of calcium oxide based catalyst (K2O/CaO-ZnO) for transesterification of soybean oil to biodiesel," *Bulletin of Chemical Reaction Engineering & Catalysis*, vol. 11, no. 1, pp. 34– 39, 2016, doi: 10.9767/bcrec.11.1.413.34-39.
- [26] A. Kolakoti, M. Setiyo, and M. L. Rochman, "A Green Heterogeneous Catalyst Production and Characterization for Biodiesel Production using RSM and ANN Approach," International Journal of Renewable Energy Development, vol. 11, no. 3, pp. 703– 712, 2022, doi: 10.14710/ijred.2022.43627.
- [27] A. P. Purnamasari, M. E. F. Sari, D. T. Kusumaningtyas, S. Suprapto, A. Hamid, "The and D. Prasetyoko, effect of mesoporous H-ZSM-5 crystallinity as a CaO support on the transesterification of waste cooking oil," Bulletin of Chemical Reaction Engineering & amp; amp; Catalysis, vol. 12, no. 329-336, 2017, doi: 3, pp. 10.9767/bcrec.12.3.802.329-336.
- [28] I. Dayi Febriana et al., "Pemanfaatan Batu

Kapur Madura sebagai Katalis dalam Pembuatan Bioedesel dari Minyak Nyamplung," *IJCA (Indonesian Journal of Chemical Analysis)*, vol. 5, no. 1, pp. 09–17, 2022, doi: 10.20885/ijca.vol5.iss1.art2.

- [29] A. Ketcong *et al.*, "Production of fatty acid methyl esters over a limestone-derived heterogeneous catalyst in a fixed-bed reactor," *Journal of Industrial and Engineering Chemistry*, vol. 20, no. 4, pp. 1665–1671, 2014, doi: 10.1016/j.jiec.2013.08.014.
- [30] K. Ngaosuwan, W. Chaiyariyakul, O. Inthong, W. Kiatkittipong, D. Wongsawaeng, and S. Assabumrungrat, "La2O3/CaO catalyst derived from eggshells: Effects of preparation method and La content on textural properties and catalytic activity for transesterification," *Catalysis Communications*, vol. 149, p. 106247, 2021, doi: 10.1016/j.catcom.2020.106247.
- [31] A. Lesbani, S. O. Ceria Sitompul, R. Mohadi, and N. Hidayati, "Characterization and Utilization of Calcium Oxide (CaO) Thermally Decomposed from Fish Bones as a Catalyst in the Production of Biodiesel from Waste Cooking Oil," Makara Journal of Technology, vol. 20, no. 3, p. 121, 2016, doi: 10.7454/mst.v20i3.3066.
- [32] J. Cai, S. Wang, and C. Kuang, "A Modified Random Pore Model for Carbonation Reaction of CaO-based Limestone with CO2 in Different Calcination-carbonation Cycles," *Energy Procedia*, vol. 105, pp. 1924–1931, 2017, doi: 10.1016/j.egypro.2017.03.561.
- [33] N. Widiarti *et al.*, "Upgrading catalytic activity of NiO/CaO/MgO from natural limestone as catalysts for transesterification of coconut oil to biodiesel," *Biomass Conversion and Biorefinery*, 2021, doi: 10.1007/s13399-021-01373-5.
- [34] D. Ayu, R. Aulyana, E. W. Astuti, K. Kusmiyati, and N. Hidayati, "Catalytic Transesterification of Waste cooking Oil to Biodiesel: Effect of Oil-Methanol Molar Ratio and Reaction Time," *Automotive Experiences*, vol. 2, no. 3, pp. 73–77, 2019, doi: 10.31603/ae.v2i3.2991.
- [35] A. Kolakoti, M. Setiyo, and B. Waluyo, "Biodiesel Production from Waste Cooking Oil: Characterization, Modeling and Optimization," *Mechanical Engineering for*

*Society and Industry*, vol. 1, no. 1, pp. 22–30, 2021, doi: 10.31603/mesi.5320.

- [36] E. Permana and M. Naswir, "Kualitas Biodiesel Dari Minyak Jelantah Berdasarkan Saponifikasi Proses Dan Tanpa Saponifikasi," JTT (Jurnal Teknologi Terapan), 26, 2020, doi: vol. 6, no. 1, p. 10.31884/jtt.v6i1.244.
- [37] C. Sronsri, W. Sittipol, and K. U-yen, "Performance of CaO catalyst prepared from magnetic-derived CaCO3 for biodiesel production," *Fuel*, vol. 304, no. July, p. 121419, 2021, doi: 10.1016/j.fuel.2021.121419.
- [38] T. Maneerung, S. Kawi, Y. Dai, and C. H. Wang, "Sustainable biodiesel production via transesterification of waste cooking oil by using CaO catalysts prepared from chicken manure," *Energy Conversion and Management*, vol. 123, pp. 487–497, 2016, doi: 10.1016/j.enconman.2016.06.071.
- [39] A. R. Gupta and V. K. Rathod, "Waste cooking oil and waste chicken eggshells derived solid base catalyst for the biodiesel production: Optimization and kinetics," *Waste Management*, vol. 79, pp. 169–178, 2018, doi: 10.1016/j.wasman.2018.07.022.
- [40] O. N. Syazwani, S. H. Teo, A. Islam, and Y. H. Taufiq-Yap, *Transesterification activity and characterization of natural CaO derived from waste venus clam (Tapes belcheri S.) material for enhancement of biodiesel production,* vol. 105. 2017.
- [41] J. Boro, L. J. Konwar, and D. Deka, "Transesterification of non edible feedstock with lithium incorporated egg shell derived CaO for biodiesel production," *Fuel Processing Technology*, vol. 122, pp. 72–78, 2014, doi: 10.1016/j.fuproc.2014.01.022.
- [42] F. J. S. Barros *et al.*, "Glycerol oligomers production by etherification using calcined eggshell as catalyst," *Molecular Catalysis*, vol. 433, pp. 282–290, 2017, doi: 10.1016/j.mcat.2017.02.030.
- [43] M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, and J. Hidaka, "Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production," *Fuel*, vol. 87, no. 12, pp. 2798– 2806, 2008, doi: 10.1016/j.fuel.2007.10.019.
- [44] Rakhmad, N. Hindryawati, and Daniel, "Pembuatan Katalis Basa Heterogen Dari

Batu Gamping ( Limestone )," *Prosiding Seminar Nasional*, pp. 101–105, 2017.

- [45] N. U. Soriano, R. Venditti, and D. S. Argyropoulos, "Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification," *Fuel*, vol. 88, no. 3, pp. 560–565, 2009, doi: 10.1016/j.fuel.2008.10.013.
- [46] A. Kolakoti, P. R. Mosa, T. G. Kotaru, and M. Mahapatro, "Optimization of biodiesel production from waste cooking sunflower oil by taguchi and ann techniques," *Journal of Thermal Engineering*, vol. 6, no. 5, pp. 712–723, 2020, doi: 10.18186/THERMAL.796761.
- [47] A. Kolakoti and B. V. A. Rao, "Effect of fatty acid composition on the performance and emission characteristics of an IDI supercharged engine using neat palm biodiesel and coconut biodiesel as an additive," *Biofuels*, vol. 10, no. 5, pp. 591–605, 2019, doi: 10.1080/17597269.2017.1332293.
- [48] C. Sayin and M. Gumus, "Impact of compression ratio and injection parameters on the performance and emissions of a di diesel engine fueled with biodiesel-blended diesel fuel," *Applied Thermal Engineering*, vol. 31, no. 16, pp. 3182–3188, 2011, doi: 10.1016/j.applthermaleng.2011.05.044.

- [49] W. Saputro, J. Sentanuhady, A. I. Majid, W. Prasidha, N. P. Gunawan, and T. Y. Raditya, "Karakteristik Unjuk Kerja Mesin Diesel Menggunakan Bahan Bakar B100 dan B20 Dalam Jangka Panjang," *Journal of Mechanical Design and Testing*, vol. 2, no. 2, p. 125, 2020, doi: 10.22146/jmdt.55523.
- [50] A. Kolakoti, A. V. Kumar, R. Metta, M. Setiyo, and M. L. Rochman, "Experimental studies on in-cylinder combustion, exergy performance, and exhaust emission in a Compression Ignition engine fuelled with neat biodiesels," *Indonesian Journal of Science and Technology*, vol. 7, no. 2, pp. 219–236, 2022.
- [51] A. Hamid *et al.*, "An Improvement of Catalytic Converter Activity Using Copper Coated Activated Carbon Derived from Banana Peel," *International Journal of Renewable Energy Development*, vol. 12, no. 1, pp. 144–154, 2023, doi: 10.14710/ijred.2023.48739.
- [52] S. Rasul, A. M. Kajal, and A. Khan, "Quantifying Uncertainty in Analytical Measurements," *Journal of Bangladesh Academy of Sciences*, vol. 41, no. 2, pp. 145–163, 2018, doi: 10.3329/jbas.v41i2.35494.