Identification of Citronella Oil Fractions as Efficient Bio-Additive for Diesel Engine Fuel

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Abstract: Escalation fuel consumption occurs in various regions of the world. However, world oil reserves decline from year to year so that it becomes scarce and causes oil prices to surge up. This problem can be solved by saving fuel consumption. One method of saving fuel is adding bio-additives from citronella oil as a sustainable resource to diesel fuels. Citronellal, citronellol and geraniol are the main components of citronella oil which can be used as fuel additives. This study aimed to evaluate the effect of citronella oil fractions as bio-additives to the performance of diesel engine. The research stages include: extraction of citronella oil, vacuum fractionation of citronella oil, physical chemical characterization of citronella oil and its fractions, formulation of bio-additive -fuel blending, characterization of blending, and evaluation of fuel efficiency. The effect of concentration of the bio-additives was examined towards three diesel fuels; dexlite, pertamina-dex, and biosolar. The results showed two main fractions of citronella oil; citronellal dominant component (FA) and citronellol-geraniol dominant components (FB). The concentration variation of bio-additives was 0.1–0.5%. Fuel consumption efficiency was tested using diesel engine at an engine speed of 2000 rpm and a load increment of 1000, 2000 and 3000 psi with 7 min running time. The fractions represented the different tendencies to enhance the fuel efficiency up to 46%, influenced by the mixture’s concentration. Generally, citronella oil and the fractions showed the potency as bio-additive to diesel fuels.

Keywords: bio-additive; citronella oil; fuel additive; diesel fuel

1. Introduction

Since the beginning of the industrial revolution, fossil fuels have been primary energy sources and industrial chemicals. For decades, the benchmark for a country’s development has been linked to the level of fossil fuel consumption, which is increasingly elevated. For example, in Indonesia, fuel consumption for transportation is by 8.6% per year, higher than power plant and household demands with 4.6 and 3.7%, respectively [1]. The International Energy Agency (IEA) estimates that the world will reach maximum world oil production between 1996 and 2035. Along with increasing fuel consumption, diesel and biodiesel demand is also escalated. The limited nature of fuel, coupled with the challenges of skyrocketing costs of conventional oil, global warming issues, and other environmental pollution problems, has led to in-depth research on the use of renewable and sustainable alternative fuels [2].

Various researchers have offered several solutions, such as biodiesel production [3,4] and additives for diesel engine fuel [5,6]. The diesel fuel additive for compressing fuel consumption is interestingly developed because it is closely related to reducing emissions [2,7]. Several compounds consisting of glycerol-based compounds and furfural-based...
compounds were synthesized for those purposes. Miscibility, renewability of the resource, and energy-efficiency in production are the requirements for further industrial developments [8]. In addition, the use of natural product with simple processes highlighted the use of essential oil as a potential and renewable resource for diesel fuel additives. Previous studies revealed the enhanced ignition efficiency and combustion quality of diesel fuel by clove oil [9]. The improving brake thermal efficiency (BTE) and reduced brake-specific fuel consumption were expressed by combining some essential oils. In addition, a significant reduction in particulate matter (PM) emissions have been reported [9,10]. Other investigation also reported the role of essential oils as bio-additives, such as, pine wood oil [11], cinnamon oil [12], sweet orange oil [13], patchouli oil [14], lemongrass oil [15], and clove oil [9,16].

Based on the chemical composition and chemical structures, the chemical interaction between the additive and the fuel is the basic idea for the essential oil utilization in fuel. The characteristics consist of low vapor point, solubility, and stability in mixture with diesel fuel are of the consideration [15]. In addition, essential oils contain various kinds of chemical compounds containing oxygen atoms so that they are able to complete the combustion system in diesel engines [11]. This reduces harmful emissions such as hydrocarbons (HC), particulate matter, CO$_2$, and NOx emissions when added to fuel. In addition, it is used to increase the viscosity, anti-knock, octane, cetane, and cold flow properties of fuels as well as improve thermal stability, cleanliness and prevent corrosion of engines and engine parts [17]. Additionally, the metal-free feature of essential oils can better replace conventional additives such as tetra-methyl-lead (TML) and tetra-ethyl-lead (TEL). TML and TEL contain Pb, which produce toxic gases and are harmful to humans and the environment.

Due to the abundance source and ease of production, citronella oil is one of the important essential oils in several countries in Asia [18,19]. Besides enormous potential in pharmaceutical, food, and other chemical industries, the main compounds of citronella oil, citronellal, citronellol and geraniol, have properties to be potentially bound with interactions similar to reported essential oil for bio-additive applications. Practically, the composition of citronella oil depends on the fraction within the distillation process. Different compositions and combinations of citronellal, citronellol and geraniol as the main ingredient in the citronella oil reflected the different oxygen content that influenced diesel fuel combustion performance.

The novelty of this research is the utilization of fractions of citronella oil as the bio-additives. To our knowledge, there was no report on the utilization of citronella oil fractions to improve efficiency. Our hypothesis is that the more oxygenate content in the fraction, the more effective the combustion process in the engine, which means a more efficient the use of fuel. The distillation setting itself, which is related to energy consumption, needs to be optimized for investigating the optimum condition of citronella oil fractionation for bio-additives application. Based on these backgrounds, a study on citronella oil composition to the bio-additive performance toward diesel (DI) fuels was investigated. The study focused on the effect of fractions as the bio-additives. The significance of this research is related to the use of sustainable natural resource for minimizing energy, which is the main issue for sustainable energy in the future perspective.

2. Materials and Methods

The Flowchart of this research work is shown in Figure 1. The experimental section includes extraction of citronella oil, vacuum fractionation of citronella oil, physical chemical characterization of citronella oil and its fractions, formulation of bio-additive -fuel blending, characterization of blending, and evaluation of fuel efficiency.
2.1. Materials

The materials were citronella leaves, anhydrous sodium sulfate (Na$_2$SO$_4$), biodiesel, dexlite (light diesel), and pertamina-Dex (premium diesel). The equipment was laboratory glassware, refractometer, Oswald viscometer, steam distillation, vacuum fractional distillation equipment (B/R Instrument-Spinning Band Distillation System Model 36–100), Gas Chromatography-Mass Spectroscopy (GC-MS QP2010S Shimadzu, Tokyo, Japan), diesel engine (IN-DO R 180 iDi), dynotest hydraulic system, exhaust emission test equipment (StarGas 898).

2.2. Distillation of Citronella Oil

A total of 25 kg of citronella leaves were cut into small pieces, then put into a water-steamed distillation kettle. The chopped citronella leaves were distilled for 3–5 h with medium heat and turned on the cooling water circulation system for five repetitions. Every 30 min, the water-steam distillation system was checked. After that, the citronella oil was separated from hydrosol using a separator. Citronella oil was purified by adding anhydrous sodium sulfate (Na$_2$SO$_4$) until the water in the citronella oil separated. Finally, citronella oil was decanted and filtered to separate the Na$_2$SO$_4$ precipitate.

2.3. Vacuum Fractional Distillation

Citronella oil was further fractionated by fractional vacuum distillation equipment (B/R Instrument-Spinning Band Distillation System Model 36–100) at a pressure of 30 mmHg with a reflux ratio of 20:1 for 30 h. Two fractions containing citronellal (FA) and citronellol-geraniol (FB) were obtained by distilling citronella oil at the different conditions of fractional vacuum distillation, as shown in Table 1.
2.4. Physical and Chemical Characterization

The physical properties of distillates were performed using density (pycnometer method), refractive index (using Abbe refractometer), and color-odor that organoleptically refers to the Indonesian national standard method (SNI 06-3953-1995).

Chemical properties of the citronella oil were examined using gas chromatography-mass spectroscopy (GC-MS) using RTX-5MS column and helium gas as the mobile phase. We set injector temperatures of 80.0 and 300.0 °C, pressure of 42.3 kPa, and a total flow rate of 0.74 mL/minute. The Operational conditions of GC-MS shown in Table 2.

Table 2. Operational conditions of GC-MS.

| Specification            | Value                  |
|--------------------------|------------------------|
| Model                    | GC-2010 Simadzu        |
| Engine type              | QP2010 SE              |
| Column temperature       | 80.0 °C                |
| Injector temperature     | 300.00 °C              |
| Injector mode            | Separated              |
| Flow control mode         | Pressure               |
| Pressure                 | 42.3 kPa               |
| Flow total               | 117.5 mL/min           |
| Column Flow              | 0.74 mL/min            |
| Linear velocity          | 31.8 cm/s              |
| Removal flow Rate        | 3.0 mL/min             |
| Temperature              | 80.0–320.0             |
| Source ion Temperature   | 25.00 °C               |
| Interface Temperature    | 300.00 °C              |
| Enhanced detector mode   | Relative               |
| Gain Detector            | 0.98 kV + 0.00 kV      |
| Scan Speed               | 1250                   |

2.5. Fuel Efficiency Test

The diesel bio-additive blending testing was performed onto three DI fuels: dexlite, pertamina-dex and biosolar. The tested bio-additive samples of citronella oil, FA and FB were at the varied concentration of 1.0; 1.5; 2.0; and 5.0%. For each test, the bio-additive:fuel volume ratio of 1:1 was utilized, and the stirring for fuel-citronella oil was conducted for 30 min before testing.

Determination of blending consumption and exhaust gas emissions was carried out. A total of 1000 mL blending analyzed for 7 min with variations in engine speed of 1500, 2000 and 4000 rpm, a load of 0, 25, 50, 25, 50, 75 and 100 W at constant torque using 125 cc diesel engine. The Diesel engine specification is shown in Table 3.
Table 3. Diesel engine specification.

| Specification       | Value                  |
|---------------------|------------------------|
| Model               | R 180 iDi              |
| Maximum power (kW)  | 5.7                    |
| Working power (kW)  | 5.0                    |
| Diameter (mm)       | 80 x 80                |
| Volume (L)          | 0.402                  |
| Weight (kg)         | 72                     |
| Fuel consumption    | 205                    |
| Type                | 4 stroke horizontal engine |
| Cylinder            | 1                      |
| Start system        | Crank                  |
| Cooling system      | hopper/radiator        |
| Lubricant system    | pressure combination system and distribution |
| Combustion system   | Antechamber            |

3. Results and Discussion
3.1. Characterization of Citronella Oil and the Fractions

Fractional distillation under vacuum conditions was performed to obtain the fractions of citronella oil, FA and FB, based on an immediate difference in boiling point in a vacuum at 30 mmHg pressure with a reflux ratio of 20:1. It referred to the optimum condition presented in previous work highlighting the pressure of 30 mmHg, which shows that the best reflux ratio for separating citronella oil is 20:1 [20]. A quick separation without any other chemicals required in the process is beneficial for fractionation [21]. In addition, the reduced pressure of the system to be less than 1 atm (760 mmHg) gives the reducing vapor point of the distillate without any excessive chemical change. Calculation of the vapor point of the solution in this condition can be completed through the Clausius–Clapeyron equation at a pressure of 30 mmHg. The enthalpy of vaporization of citronellal is 44.22 kJ/mol, citronellol 63.50 kJ/mol, and geraniol 54.61 kJ/mol. The results of calculations using the Clausius–Clapeyron equation obtained that the boiling points of citronellal, citronellol, and geraniol at a pressure of 30 mmHg were 97.86, 138.91, and 129.57 °C, respectively.

Physico-chemical characteristics of citronella oil and the fractionation results (FA and FB) were carried out based on SNI-06-3953-1995. Color is one of the parameters for beginning fractionation, and its measurement was carried out organoleptically or by direct eye observation at a distance of 30 cm. The results presented in Table 4 represent that the color of citronella oil and the fractions are pale yellow, which met the SNI standard stating the parameter of “no color difference”, namely pale yellow-brown. Another organoleptic parameter is odor. Odor testing was carried out with the sense of smell at a distance of 5 cm. The test results show that citronella oil has a fresh smell typical of lemongrass. FA fraction has a high citronellal content and smells of pungent lemon. FA fraction has a strong odor because it has more citronellal content compared to citronella oil. All odor test results follow SNI of citronella oil.

Table 4. Physical Characteristics of Citronella Oil and Its Fractions.

| Parameter       | Unit      | Citronella Oil | FA         | FB         | SNI-06-3953-1995       |
|-----------------|-----------|----------------|------------|------------|------------------------|
| Color           | -         | Pale yellow    | Pale yellow| Pale yellow| Pale yellow–brown      |
| Smell           | -         | Fresh typical  | Strong typical | medium typical | citronella oil         |
| Density         | g/mL      | 0.882          | 0.867      | 0.878      | 0.880–0.922            |
| Refractive Index| nD        | 1.475          | 1.449      | 1.467      | 1.466–1.475            |

Density characteristics were carried out using a pycnometer. The results showed that the densities of citronella oil, FA, and FB, respectively, were 0.882; 0.867; 0.878 g/mL. In its pure state, citronellal (C_{10}H_{18}O BM 154.25 g/mol) has a density of 0.855 g/mL, citronellol
(C_{10}H_{20}O BM 156.27 g/mol) is 0.855 g/mL, and geraniol (C_{10}H_{18}O BM 154.25 g/mol) is 0.889 g/mL. Compared to the SNI standard, the results are valued as good results within the range of 0.880 to 0.922 g/mL. Refractive index measurement was conducted on a refractometer, giving the values of 1.475; 1.449; 1.467 for citronella oil, FA, and FB, respectively. They are represented to be qualified within the acceptable range of refractive index of 1.466–1.375. Conclusively, citronella oil and its fractions are met following SNI standard from the four parameters.

The chemical components of citronella oil and their fractions were determined by GC-MS, and the compared chromatograms are presented in Figure 2. The data in Table 5 represent the identification results of citronellal, citronellol and geraniol. Citronellal is identified at 6.38 min of retention time with the percentage of peak area of 19.01%, citronellol is identified at 7.46 min and a peak area of 20.48%, and at 7.86 min geraniol was identified at 18.81%. Other minor components were identified at a percentage below 5%. It can be concluded that in terpenoid groups (monoterpenoid C_{10}) are found many essential oils, and they are composed as secondary metabolites and are characteristic of each essential oil [22,23]. The percentage is acceptable as it is similar to what was reported by [24], reporting the component of citronellal (36.11%), geraniol (20.07%) and citronellol (20.82%).

Meanwhile, regarding citronella oil (Javanese type), ISO 3848:2016 states the range of citronellal content (31.00–40.00%), citronellol content (8.00–14.00%) and geraniol content (20.00–25.00%).

Table 6. Density of Fractions of Citronella Oil.

| Sample                      | Result (kg/m³) | Standard (SNI) (kg/m³) |
|-----------------------------|----------------|------------------------|
| Citronella Oil              | 882.6          | 880–922                |
| Citronellal fraction (F2)   | 867.1          | 850–860                |
| Citronellol-geraniol fraction (F3) | 878.4 | 870–899               |

Table 7. The refractive index of Fractions of Citronella Oil.

| Sample                      | Result       | SNI Standard           |
|-----------------------------|--------------|------------------------|
| Citronella Oil              | 1.4751       | 1.4660–1.4750          |
| Citronellal fraction (FA)   | 1.4486       | 1.4440–1.4540          |
| Citronellol-geraniol fraction (FB) | 1.4668 | 1.4660–1.4770         |

Referencing [9], a good bioadditive must contain oxygenate (O atoms), which can increase the oxygen content in the fuel so that efficient combustion occurs in diesel engines. FA and FB have potential to be diesel fuel bioadditives. Both citronellol and geraniol have similar physicochemical properties, such as boiling points of 225 °C and 226 °C.
Table 5. Main Compounds of Citronella Oil.

| Retention Time (minute) | Content (%)  | Compound                  |
|-------------------------|--------------|---------------------------|
| 4.670                   | 3.840        | Limonene                  |
| 6.380                   | 19.010       | Citronellal               |
| 7.460                   | 20.480       | Citronellol               |
| 7.860                   | 18.810       | Geraniol                  |
| 9.210                   | 3.720        | Citronelyl acetate        |
| 9.620                   | 3.850        | Linalyl acetate           |
| 10.300                  | 5.030        | Trans-caryophyllene       |

Citronellal, citronellol and geraniol compounds tend to be semipolar compounds. In separation, the interaction of the three compounds with the GC column (nonpolar) is only affected by the boiling point of the compound. The three main compounds have similar polarity and interact weakly with the GC column so that the three compounds have relatively short retention times. Citronellal has a lower boiling point than citronellol and geraniol. The -OH group (alcohol) in citronellol and geraniol can form strong hydrogen bonds so that the boiling point becomes higher. Citronellal is a type of monoterpenoid aldehyde (-CHO). Therefore, citronellal has a faster retention time than citronellol and geraniol.

Physically, each fraction has a different color; FA is pale yellow, and FB 4 is yellow-brown. The increasing citronellal content was achieved in FA, as it is about 89.37% compared to citronella oil which is 19.01%. Likewise, FB contains more citronellol and geraniol—in the range of 27.36–31.71%—compared to citronella oil (18–20%). According to previous work [24], isolation of citronella oil by vacuum fractionation distillation was able to increase the levels of citronellal up to 90%, citronellol up to 30% and geraniol up to 45%.

The density of citronella oil and its fraction is shown in Table 6 and the refractive index in Table 7.

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| Citronella Oil          | 882.6          | 880–922                |
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Table 7. The refractive index of Fractions of Citronella Oil.

| Sample                          | Result      | SNI Standard          |
|---------------------------------|-------------|-----------------------|
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| Citronellal fraction (FA)       | 1.4486      | 1.4440–1.4540         |
| Citronellol-geraniol fraction (FB)| 1.4668   | 1.4660–1.4770         |

Referring to [9], a good bio-additive must contain oxygenate (O atoms), which can increase the oxygen content in the fuel so that efficient combustion occurs in diesel engines. FA and FB have potential to be diesel fuel bio-additives. Both citronellol and geraniol have similar physicochemical properties, such as boiling points of 225 °C and 226 °C, respectively. It was not easy to separate them through fractional vacuum distillation (physics) which relies on differences in the boiling points of the compounds. In addition, citronellol is a functional group isomer of geraniol.

3.2. Utilization of Citronella Oil Fractions as Bio-Additives

The use of citronella oil fractions as bio-additives was tested based on previous research, which mentioned that the optimum percentage of at 0.1–1.0% can save fuel up to 50% [15,25]. There were 36 formulas used, with three different types of diesel fuel, two types of bio-additives, and four variations of concentration of bio-additives.
The physical characteristics of blending were determined to see the changes in physical properties after the addition of bio-additives. Density characteristics were carried out using a pycnometer and kinematic viscosity was carried out using an Oswald viscometer according to SNI 8220:2017. Viscosity indicates the ability of a fluid to flow through an area per unit of time. This is important related to the mechanism of fuel atomization shortly after leaving the nozzle into the combustion chamber [15].

The Effect of adding citronella oil and the fractions to density and viscosity of fuel is represented by the data in Tables 8 and 9. Based on the Indonesian standard (SNI 8220:2017) regarding the specifications for type 48 diesel fuel, the density of at least 815 kg/m$^3$ is a maximum of 860 kg/m$^3$ and the viscosity is a minimum of 2.0 m$^2$/s, a maximum of 4.5 m$^2$/s. This shows that after the addition of bio-additives, there is no significant change in the physical properties of diesel fuel. The maintaining viscosity values in the addition of the bio-additives are related to the similar response of the volume restricting the movement of the lon- chain hydrocarbon molecules. The viscosity of DI fuel is also related to temperature and pressure dependency, which are important for fuel performance [20].

Table 8. Density of fuel-bio additive blending.

| Tested Bio-Additive | Concentration | Biosolar (kg/m$^3$) | Dexlite (kg/m$^3$) | Pertamina-Dex (kg/m$^3$) |
|---------------------|---------------|----------------------|--------------------|----------------------------|
| Without additive    |               | 853.133              | 839.873            | 808.819                    |
| FA                  | 0.1           | 851.239              | 832.702            | 812.741                    |
|                     | 0.15          | 854.030              | 836.888            | 809.214                    |
|                     | 0.2           | 851.139              | 837.444            | 809.713                    |
|                     | 0.5           | 853.432              | 835.985            | 811.708                    |
| FB                  | 0.1           | 850.640              | 831.713            | 813.136                    |
|                     | 0.15          | 851.538              | 841.851            | 808.801                    |
|                     | 0.2           | 851.937              | 835.455            | 809.524                    |
|                     | 0.5           | 853.432              | 833.166            | 810.092                    |
| Citronella oil      | 0.1           | 851.239              | 832.327            | 809.111                    |
|                     | 0.15          | 853.332              | 837.319            | 808.457                    |
|                     | 0.2           | 851.637              | 837.083            | 808.767                    |
|                     | 0.5           | 851.837              | 834.160            | 809.696                    |

Table 9. Viscosity of fuel-bio additive blending.

| Tested Bio-Additive | Concentration (%) | Viscosity (m$^2$/s) |
|---------------------|-------------------|---------------------|
|                     |                   | Biosolar            | Dexlite            | Pertamina-Dex               |
| Without additive    |                   | 4.58                | 4.19               | 2.47                        |
|                     | 0.1               | 4.53                | 4.02               | 2.42                        |
| FA                  | 0.1               | 4.54                | 3.83               | 2.48                        |
|                     | 0.15              | 4.37                | 3.63               | 2.53                        |
|                     | 0.2               | 4.42                | 3.86               | 2.59                        |
|                     | 0.5               | 4.59                | 3.63               | 2.62                        |
| FB                  | 0.1               | 4.34                | 3.70               | 2.47                        |
|                     | 0.15              | 4.52                | 3.72               | 2.59                        |
|                     | 0.2               | 4.39                | 3.68               | 2.52                        |
|                     | 0.5               | 4.49                | 3.78               | 2.60                        |
| Citronella Oil      | 0.1               | 4.60                | 3.81               | 2.43                        |
|                     | 0.15              | 4.51                | 3.96               | 2.50                        |
|                     | 0.2               | 4.41                | 3.60               | 2.54                        |
|                     | 0.5               |                     |                    |                             |
3.3. Characterization of Citronella Oil and the Fractions

The effect of bio-additive on fuel consumption is the most crucial parameter in this research. Fuel consumption occurs in the combustion process due to air compression in the engine combustion chamber. The amount of fuel consumed is measured in weight units per unit of time. Mathematically, the fuel consumption is shown in the following equation (Equation (1)):

\[ f_c = \frac{b}{t} \times \gamma f \times \frac{3600}{1,000,000} \]  

where \( f_c \) is fuel consumption expressed in kg/h, \( b \) is the volume of fuel consumption expressed in milliliters (mL), \( t \) is the time used, which is expressed in seconds (s), and \( f \) is the density of fuel expressed in kg/m³.

The efficiency of diesel fuel consumption is carried out volumetrically, namely by calculating the fuel economy consumption when the engine produces power within a certain time frame. The purpose of determining consumption efficiency is to determine the optimum formula to improve fuel quality. The diesel engine used is a one-cylinder compression ignition (CI) type with a maximum speed of 2500 rpm for 7 min. Measurements were made by comparing the consumption volume of blending with the control. The calculation of fuel consumption results shows a decrease in fuel consumption when bio-additives are added. The decrease in fuel consumption is due to the compounds in bio-additives acting as oxygen providers, also called oxygenate compounds. The more oxygen content is contained in fuel; the easier and more completely the combustion will occur [26,27].

The results of experiments are presented in Figure 3. It is seen that at all varied concentrations, citronella oil and the fractions significantly affect the efficiencies towards tested fuels; dexlite, pertamina-dex, and biosolar. In more detail, the increasing efficiency of biosolar is most intensive compared to pertamina-dex and dexlite. In addition, the effect of concentration is not linear with the efficiency for all tested fuels, particularly for biosolar; the trends are increasing efficiency at increasing concentration. A specific pattern was expressed by the use of FA and FB in the diesel fuel which showed the optimum concentration of 0.2%. Still, the efficiency decreased at the increasing concentration, representing the possible chemical or oxidative effect of the bio-additives.

Generally, by comparing FA, FB and citronella oil, it was found that FA had the most influence. This phenomenon is closely related to the greater abundance of oxygen in the fraction. This is also associated with more oxygen in biosolar, which presented better efficiency. The alcohol (-OH) and aldehyde (-CHO) groups (containing oxygen) in blending will react with CO gas and charcoal (C) to form CO₂, which causes fewer CO and green emissions [28]. In the combustion chamber, there are three main reactions: initiation, propagation, and termination. The availability of oxygen is important to produce an efficient, constant chemical reaction in the combustion chamber.

\[ 4 \, \text{H}_2\text{C}_{12}(l) + 74 \, \text{O}_{2}(g) \rightarrow 48 \, \text{CO}_2(g) + 52 \, \text{H}_2\text{O}_{(aq)} \]  

(2)

\[ 2 \, \text{H}_2\text{C}_{12}(l) + 31 \, \text{O}_{2}(g) \rightarrow 12 \, \text{CO}(g) + 12 \, \text{CO}_2(s) + 26 \, \text{H}_2\text{O}_{(aq)} \]  

(3)

When burning in a diesel engine, two possible combustion reactions will occur, a complete combustion reaction (Equation (2)) or an incomplete combustion (Equation (3)). Complete combustion occurs when there is sufficient oxygen in the engine combustion chamber. Incomplete combustion occurs when there are insufficient oxygen molecules to burn one complex hydrocarbon molecule in diesel fuels completely. In this study, diesel fuel, pertamina-dex, dexlite, and biosolar were mixed with bio-additives from fractions FA and FB of citronella oil. The diesel fuels-bio-additive mixture is expected to reduce emissions from CO gas and charcoal (soot). This is because the FA and FB fractions contain citronellal and citronellol-geraniol, which have oxygenated aldehyde (-CHO) and alcohol (-OH) functional groups to contribute to the availability of oxygen in the combustion chamber when the diesel engine is running. According to previous research, it was found
that a mixture of citronella-diesel oil was able to reduce CO gas emissions by 23–30%, NOx 31–36%, SOx 12–22%, and particulates 30–33% compared to that without the addition of bio-additives [11,12].

![Figure 3](image-url)

**Figure 3.** Effect of bio-additive concentration on fuel consumption efficiency for. (a) Pertamina-dex (b) Dexlite (c) Biosolar.

The bulk structure of the compounds contained in essential oils can reduce the strength of the van der Waals bonds of the compounds that make up the fuel. The bond between the fuel molecules is a fragile dispersion force [9,14]. Meanwhile, citronellal, citronellol, and geraniol compounds have dipole–dipole interactions between their molecules. Dipole–dipole interactions, which are stronger than dispersion forces, can facilitate the breaking of intermolecular bonds. Therefore, this causes the fuel molecules to break up easily to achieve more efficient combustion process. The interactions of compounds in diesel fuel after adding bio-additives are shown in Figures 4–6. The interactions that occur are induced dipole forces, namely interactions between compounds with permanent dipole moments that influence non-polar compounds. The presence of oxygen and the volatility of the citronellal, citronellol and geraniol supplied easier oxidation for faster compression in DI fuel. Oxidation reactivity of DI fuel is supplied by the combination of chemical interactions including the van der Waals and hydrogen bonding in the fuel mixture with additive. Similar results were reported by the influence of additive and oxygen-rich fuel [29,30].

Based on the volume of fuel consumption obtained, the fuel consumption efficiency can be calculated. Consumption efficiency shows an increase in fuel quality after adding bio-additives. Based on the fuel consumption test, FA with citronellal as the main component has a higher consumption efficiency compared to FB (citronellol and geraniol as the main components) and citronella oil. The lessened flash point is probably the main reason for this as citronellal, citronellol, and geraniol have flash points of 86 °C, 99 °C, and 108 °C, respectively. The lessened flash point represents the ease of being burnt and oxidized.
Another factor is the viscosity, which affects liquid fuel properties. Viscosity is related to the flow rate and characteristics of the spray or mist of fuel into the combustion.
chamber [20]. The higher the viscosity, the more difficult the fuel is to move and spray or atomize into the combustion chamber, so the combustion process is not optimal. Low viscosity helps in atomization, evaporation, and diffusion, and increases the interaction of fuel with air. Based on the viscosity test of fuel that has been mixed with bio-additives, the fuel that has been mixed with the citronellal fraction (FA) gives the lowest viscosity value compared to the citronellol-geraniol (FB) fraction and citronella oil.

Generally speaking, the results from this work show the potential of the use of essential oil as a sustainable bio-additive in minimizing energy consumption, especially DI fuel. More exploration for other fuel as well as techno-economic studies are required.

4. Conclusions

This study initiated the examination of fractionation to citronella oil and its use as bio-additive to diesel fuel. The results showed two main fractions of citronella: dominant containing fraction (FA) and citronellol-geraniol dominant containing fraction (FB) obtained at different vacuum fractionation conditions. The fractions and citronella oil exhibited the capability to be bio-additives to diesel fuel as shown by the acceptable density and viscosity in tested varied concentrations (0.1–0.5%). In addition, the fuel consumption examination represented the significant ability of the tested sample to reduce fuel consumption to 46% depending on the concentration of the bio-additive. Generally, at the tested concentration range, the increasing concentration affects the reduction of fuel consumption. The next work to be carried out is emission testing to investigate whether the emission quality is improved using bio-additives.

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