# STUDY OF THE COMPOSITIONS AND FUEL PARAMETERS OF THE EMULSION FUELS BIODIESEL-AQUEOUS ETHANOL AND BIODIESEL-AQUEOUS ETHANOL-DIESEL

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## Abstract

The present study investigates the compositions and fuel parameters of the aqueous ethanol-diesel-biodiesel emulsion fuel in a stable emulsion. The biodiesel obtained was characterized by employing gas chromatography-mass spectrometry measurement. The palm oil methyl esters were dominated by the *Hexadecanoic Acid* and *9-Octadecenoic Acid* (Z)-), while coconut oil methyl esters have mainly consisted of *Dodecanoic Acid* and *Tetradecanoic Acid.* The biodiesel was blended with aqueous ethanol and diesel until a stable solution was formed with specific compositions. The range compositions of water, ethanol, and palm oil biodiesel in the stable emulsion were 0.81-1.25, 12.70-40.42, and 58.33-86.49 %, while water, ethanol, and coconut oil biodiesel were 0.70-0.88, 13.71-22.63, and 76.67-85.42%. The sample prepared showed that the droplet appeared in the emulsion, which employed ethanol 94-95% but was distributed uniformly throughout the substance. The fuel parameters investigated were the density, viscosity, flash point, Reid vapor pressure, pour point, distillation properties, and the cetane number.

Keywords: Bioethanol, Biodiesel, Composition, Diesel, Emulsion, Water.

## 1. Introduction

The depletion of fossil-based fuels and global warming make scientists find alternative and renewable resources at developing fuels. The renewable energy which was employed should not be adding gas emission into the atmosphere. Biodiesel and ethanol are the fuels that can be potential and changing a part of petroleum. The carbon-dioxide gas emitted from combustion can be recycled by replanting the trees that produce the raw materials.

Biodiesel has been developed as alternative energy for years, whereby it was still mixed with diesel as a blended fuel [1, 2]. Techniques have been employed to increase the efficiency of the process to reduce the product's price [3]. Many feedstocks have been utilized for fuel production to find out the most possible to be employed as the raw material at the industrial scale [4, 5]. In a review, the bio-oils could be converted into biodiesel using many types of catalysts, including the NaOH and KOH and other bases, to improve the chemical reaction rate and the product's yield [6]. Scientists have also developed ethanol fuel for a hundred years as an alternative fuel utilizing many feedstocks (lignocellulosic and starchy materials) [7]. The development of ethanol as a fuel is the most challenging for scientists because of the price, and generally, the raw materials are mainly derived from starch or sugars [8]. For its price is still expensive, ethanol mixed with diesel is a good option to substitute a part of petroleum [9].

The blended fuels, binary (diesel-biodiesel) and ternary (diesel-biodiesel-ethanol) mixtures purposed to reduce the emission of the internal combustion engine [10]. For it contains oxygen, the addition of the ethanol into diesel could be increasing the NOx emission. Still, the burning duration declined significantly [11] while hydrated ethanol-diesel blends have been tested on the diesel engine. The work found that the ignition delay increased, but the NOx gas emission decreased [12].

The references survey, as described previously, showed that ethanol-diesel and ethanol-diesel-biodiesel could be employed as the fuel on the diesel engine. However, the ethanol-biodiesel-water and ethanol-diesel-water blends in stable emulsion biodiesel derived from palm- and coconut oils are not yet reported. The presence of water in the blended fuels forming a stable emulsion in a specific composition should be presented.

The present study was to investigate the wide-range compositions of biodiesel-ethanol-water, biodiesel-diesel-ethanol-water blends in a stable emulsion, and the fuel parameters of one mixed fuel using ethanol 94-97%. The biodiesel was prepared to utilize the palm- and coconut oils and characterized by a GC/MS technique. Two biodiesels obtained were assigned as palm oil methyl ester (POME) and coconut oil methyl ester (COME).

The compositions of blended fuels consisted of biodiesel-aqueous ethanol and biodiesel-aqueous ethanol-diesel are presented, and the fuel parameters of the optional blended fuel were measured. The compositions and fuel parameters of the two blended fuels biodiesel produced from palm- and coconut oils were compared. The fuel parameters measured were as follows density, specific gravity (SG), American petroleum institute gravity (API), flashpoint (FP-PMCC), flame colour, viscosity ($\sigma$), Reid vapor pressure (RPV), cetane number (CN), and pour point (PP).

## 2. Materials and Methods

### 2.1. Materials

The materials used were as follows: Palm oil was purchased from a commercial market, and coconut oil was obtained from a traditional industry producing the fried oil in Minahasa Regency, North Sulawesi, Indonesia. Ethanol was prepared from an *Arenga Pinnata* sap, in which steps were as follows: The sap tapped by a farmer from a tree was collected inside a plastic container and was kept for 4-5 days for yeasting. The fermentation was occurred naturally without adding a synthetical enzyme. The broth was poured into the boiler by a farmer and distilled traditionally using a bamboo column length of 50m. The liquor obtained by a farmer contained ethanol with concentration ranged from 30 to 45% (v/v). The alcohol then was purified by employing a reflux distillation whose column was filled by the thousands of packing materials as a previous report [13]. In this work, ethanol engaged had 94-96% concentrations, while 97% was obtained from an aqueous ethanol absorption process using lime particles.

### 2.2. Instrumentation

To characterize the type of a methyl ester and the carbon chain formed was employed a GS/MS instrument (GCMS-2010 QP; Shimadzu; Japan) operating at a pressure 5 bar and using a helium gas base at Central Lab Malang State University, East Java, Indonesia.

This study's fuel parameters followed as recommended *by the American Society for Testing and Materials (ASTM)*. They were conducted at Oil and Gas Laboratory, Energy and Mineral Polytechnics, Cepu, Blora, Central Java, and at Samarinda State Polytechnics, East Kalimantan, Indonesia.

The parameters characterized were as follow density (15°C; D4052; Koehler; New York USA), RON/*Research Octane Number* (D2699, D2700, and D613; ), viscosity (40°C; D445; KV1000; Kohler; New York USA), ASTM colour (D1599; K13200 Petroleum Colorimeter; Koehler; New York USA), flash point PMCC (D93; Electric Pensky - Martens; SDM Torino, Italy), Reid vapor pressure (D323; Koehler; New York USA), pour point (D97; Lawler Manufacturing Company; Indianapolis USA), and distillation (D86; Koehler; New York USA).

### 2.3. Procedures

### 2.3.1. Biodiesel preparation

The work was started preparing the biodiesel of which the feedstock was from palm- and coconut oil using a conventional technique (*trans-esterification*), which follows the previous reports [14]. The mixture of the palm/coconut oil, catalyst (KOH), and methanol ($CH_3OH$) with a mass ratio of 10.75: 2.52:0.01 was poured into a reactor equipped with a reflux column.

The reactor containing the mixture was put on the heater with magnetic stirring, and the temperature was set at 60-80°C. The electrical power supply, thermometer, and magnetic stirring were turned on, and rarely was the water flown into a reflux column. The process was taken for 1 hour and then continued to the carbon chain analysis. The samples were poured inside the isolated bottles and kept in the

temperature-control room. The biodiesel obtained was separated based on the raw material employed (palm- and coconut oils).

### 2.3.2. GC/MS measurement

The steps of GC/MS followed the instrument instructions: The helium valve opened, and the instrument connected to a computer was activated. The GC/MS real-time analysis was chosen, and then system configuration, vacuum control, auto startup was set up. After tuning and peak monitor view was selected, the water-air, m/z 69, and detector at 0.7 were activated. The PFTBA, filament, and acquisition were chosen for the initial parameters. The method, sample login by filling the sample identifications were opened until the colour turned to green.

The operation conditions were as follows: the column oven temperature was set at 100ºC, while the injection temperature was controlled at 250ºC. In measurement, the pressure in column 107.2 kPa with a column-, total-, and purge flow was 1.43 mL/min, 44.5 cm/s, and 3 mL/min, respectively. The present study referred to the previous investigations to analyse the biodiesel types formed in the transesterification process [15].

### 2.3.3. Blending process

The blending process of biodiesel and aqueous ethanol was carried out, just using a 100 mL flask. Initially, the blended fuels between ethanol and biodiesel were prepared. The seven milliliters of aqueous ethanol were poured into a container, and then the biodiesel was gradually mixed into ethanol until they formed a single phase at a total volume. The volume of pure ethanol was obtained by multiplication of ethanol volume added with its purity, and the residual volume was the water content (in v).

The blended fuels of biodiesel, diesel, and aqueous ethanol were prepared by conducting a similar way as described previously. In this step, firstly, aqueous ethanol and diesel with a specific ratio were poured into a flask, but they were separated into two phases. Biodiesel substance was added slowly to the mixture (ethanol and diesel) until components were dissolved completely. In this case, biodiesel and ethanol acted as a surfactant to bridge between the polar- and nonpolar substances.

### 2.3.4. Fuel parameters measurement

The method test of fuel parameters followed the previous report [16, 17] and was added with instructions stated in an instrument guideline. The trials were initiated by measuring the fuel density, SG, API, and Reid vapor pressure (RVP) parameters and adapted from the *American National Standard Method.*

Two manual guidelines entitled: (1). Standard test method for density, relative density (specific gravity), or API gravity of petroleum and liquid petroleum. (2). The standard test method for the vapor pressure of petroleum products (*Manual of Petroleum Measurement Standards/MPMS, Chapter*) was used as a reference for the experiment; meanwhile, the distillation properties have employed a procedure reported by authors [18]. In this study, the blended fuels used to measure their fuel parameters were just those employed in ethanol 96 %.

## 3. Results and Discussion

### 3.1. GC/MS analysis

The parameters and characteristics of the product, such as compositions, formula, and designation of biodiesel produced from two different feedstocks, palm- and coconut oils, were presented in Fig. 1 and Table 1.

The initial RT, the *Octanoic Acid* ($C_9H_{18}O_2$), was formed firstly from both feedstocks with compositions 0.02 (POME) and 11.17 % (COME). The molecule *Dodecanoic Acid* ($C_{13}H_{26}O_2$) could be prepared from all feedstocks and yielded the most significant composition of 41.09% processed from coconut oil compared to that of 0.16 % from palm oil.

The 9-Octadecenoic Acid (Z)- ($C_{19}H_{36}O_2$) was converted from palm oil with the highest conversion observed at 43.35 % at 35.69 min, meanwhile COME was nothing. After RT 36.69 min, the values of conversion were not significant unless substance Octadecanoic Acid ($C_{19}H_{38}O_2$) yielded 5.71 (palm oil) and 2.77 % (coconut oil)- with RTs were 36.33 and 36.30 min, which were comparable to previous investigations [19-21].

The description shown above was suitable for investigators using many types of feedstocks as reviewed and published by the author [22-25]. The methyl ester compounds formed from coconut oil showed the similarity as conducted by investigators [26].
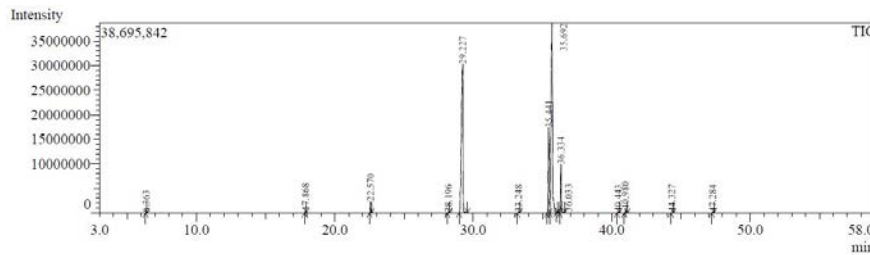


**(a)**
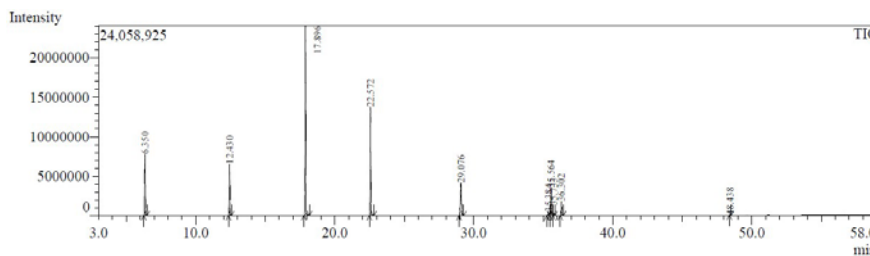


**(b)**

**Fig. 1. The GC/MS spectra of biodiesel prepared
from palm oil (a) and coconut oil (b) using atmospheric esterification
with temperature 60-80°C for 1 hour and the weight ratio of palm oil,
methanol, and catalyst KOH = 10.75: 2.52:0.01.**

**Table 1. The retention time (RT), composition,
formula, and biodiesel name derived from palm- and
coconut oils using a reference of Library: WILEY8.LIB.**

| No. | RT (min) | | Composition (%) | | Formula | Methyl Ester Assignment |
|---|---|---|---|---|---|---|
| | POME | COME | POME | COME | | |
| 1 | 6.36 | 6.33 | 0.02 | 11.17 | $C_9H_{18}O_2$ | **Octanoic Acid** |
| 2 | - | 12.43 | - | 8.50 | $C_{11}H_{22}O_2$ | **Decanoic Acid** |
| 3 | 17.87 | 17.89 | 0.16 | 41.09 | $C_{13}H_{26}O_2$ | **Dodecanoic Acid** |
| 4 | 22.57 | 22.57 | 0.97 | 19.27 | $C_{15}H_{30}O_2$ | **Tetradecanoic Acid** |
| 5 | 28.20 | - | 0.10 | - | $C_{17}H_{32}O_2$ | **9-Hexadecenoic Acid** |
| 6 | 29.23 | 29.08 | 37.14 | 9.68 | $C_{17}H_{34}O_2$ | **Hexadecanoic Acid** |
| 7 | 33.25 | - | 0.05 | | $C_{18}H_{36}O_2$ | **Heptadecanoic Acid** |
| 8 | - | 35.38 | - | 1.06 | $C_{19}H_{34}O_2$ | **8,11-Octadecadienoic Acid** |
| 8 | 35.44 | - | 11.94 | - | $C_{19}H_{34}O_2$ | **9,12-Octadecadienoic Acid (Z,Z)-** |
| 9 | - | 35.564 | - | 6.30 | $C_{19}H_{36}O_2$ | **9-Octadecenoic Acid** |
| 10 | 35.69 | - | 43.35 | - | $C_{19}H_{36}O_2$ | **9-Octadecenoic Acid (Z)-** |
| 11 | - | 35.733 | | 0.10 | $C_{19}H_{36}O_2$ | **9-Octadecenoic Acid (Z)-** |
| 12 | 36.03 | - | 0.01 | - | $C_{21}H_{36}O_4$ | **Nonanoic Acid** |
| 13 | 36.33 | 36.302 | 5.71 | 2.77 | $C_{19}H_{38}O_2$ | **Octadecanoic Acid** |
| 14 | 40.44 | - | 0.08 | - | $C_{21}H_{40}O_2$ | **11-Eicosenoic Acid** |
| 15 | 40.98 | - | 0.37 | - | $C_{21}H_{42}O_2$ | **Eicosanoic Acid** |
| 16 | 44.33 | - | 0.06 | - | $C_{19}H_{38}O_4$ | **Hexadecanoic Acid** |
| 17 | 47.28 | - | 0.05 | - | $C_{21}H_{40}O_4$ | **9-Octadecenoic Acid (Z)-** |
| 18 | - | 48.438 | 0.08 | 0.07 | Not available | |

### 3.2. Compositions of POME, Aqueous Ethanol, and Diesel

The composition of bioethanol, which was dissolved entirely with biodiesel, was depending on the ethanol concentration. The ethanol 94-96 % (v/v) was obtained directly from the separation process of yeasted *Arenga Pinnata sap*, while ethanol 97-98 % was purified employing the lime particles. The compositions of water, pure ethanol, and biodiesel (POME) in stable emulsion using 5 mL of aqueous ethanol initially are in Table 2. The first discusses the compositions of biodiesel and aqueous ethanol in which biodiesel was derived from palm oil. It was found that a minimum ethanol concentration, which could be dissolved with biodiesel and diesel, was 94 %.

**Table 2. Compositions of water (Wat), pure ethanol (Et),
and biodiesel (BD) in stable emulsion employing the aqueous
ethanol (Aq.Et) with concentration 94-97% and volume 5 mL.**

| Aq.Et %v/v | Volume (mL) | | | | Compositions (%v/v) | | |
|---|---|---|---|---|---|---|---|
| | BD | Aq.Et | Wat | Et. | Wat. | Et | BD |
| **97** | 7 | 5 | 0.15 | 4.85 | 1.25 | 40.42 | 58.33 |
| **96** | 9 | 5 | 0.20 | 4.80 | 1.43 | 34.29 | 64.29 |
| **95** | 25 | 5 | 0.25 | 4.75 | 0.83 | 15.83 | 83.33 |
| **94** | 32 | 5 | 0.30 | 4.70 | 0.81 | 12.70 | 86.49 |

When ethanol volumes for concentrations 97, 96, 95, and 94 % were set 5 mL, biodiesel volumes needed to be mixed with ethanol until they formed stable emulsion

were 7, 9, 25, and 32 mL. The data showed that the higher the ethanol concentration added is, the lower of biodiesel content needed. The compositions of water, pure ethanol, and biodiesel for ethanol 94 % were 0.81, 12.70, and 86.49 %(v/v), and the compositions changed to 1.43, 34.29, and 64.29 % if using ethanol 96%.

The original diesel cannot be entirely dissolved with aqueous ethanol unless added with a surfactant substance. In this work was discovered that biodiesel could be having a surfactant property, which could be a connection between aqueous ethanol and diesel to four components, pure ethanol, biodiesel, diesel, and water were mixed with exact compositions as displayed in Fig. 2. However, the mixture showed a droplet that appeared in solutions, especially the low ethanol concentrations. When 96 %was employed, the compositions of four components varied depending on the ratio of aqueous ethanol and diesel. Composition of pure ethanol, biodiesel, diesel, and water in the stable emulsion for the proportion of diesel and aqueous ethanol 10:7 was 8.96, 77.33, 13.33, 0.37 % and altered to 24.00, 62.50, 12.50, and 1.00 % with ratio 5:10.

When aqueous ethanol with concentration decreased to 94, and 95% and diesel's ratio to aqueous ethanol were varied, the four components' compositions changed compared to previous data, as shown in the table. When the diesel ratio to aqueous ethanol (95%) was at 5:15 9 (v/v), biodiesel needed to be dissolved was 5 mL. The composition of pure ethanol, biodiesel, diesel, and water was recorded at 18.27, 74.36, 6.41, and 0.96 %. The more biodiesel mixed was increased, the more biodiesel must be added to form a single phase. In this investigation, the ethanol 94 % was critical for blending aqueous ethanol, biodiesel, and diesel. Though the four components were dissolved, the droplets started to appear in the solution. This phenomenon was a surfactant property to connect between polar and nonpolar substances. The presence of biodiesel and ethanol could be absorbed more air into a solution, for its surface was more open than a single component. When diesel's ratio to aqueous ethanol changed from 7:7 to 10:7, the composition was 5.72, 85.22, 8.70, and 0.37 %.
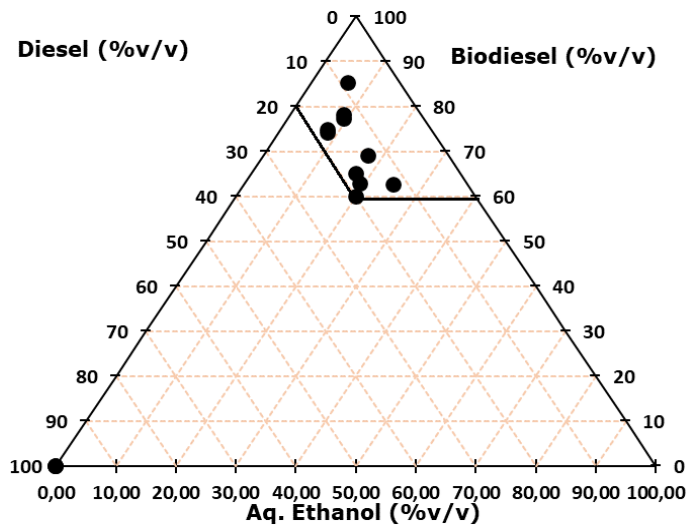


**Fig. 2. Triangular graph of compositions of aqueous ethanol, biodiesel (POME), and diesel in stable emulsion using ethanol 94-96%.**

The stable emulsion using ethanol with a concentration below 94% was possible to prepare, but I needed more biodiesel mixed. The blending required more POME, and the number of the droplet would be increasing if compared to that of the higher concentration. The emulsion fuel usage for combustion inside the engine, whereby ethanol purity was below 96 %, was challenging to scientists. Moreover, the higher content of biodiesel of the fuel should also be addressed. Currently, the unmodified conventional engine of transportation- and industrial sectors had been employed biodiesel with a portion of 20 % and expected to be increased to 30 % in 2025 in Indonesia. In this research, applying the ethanol 96% for the blended fuels was feasible since it was easy to obtain by utilizing a surplus of starchy material.

By unifying the data shown in Table 2 and Fig. 2, the trapezoidal region bordered by lines is where the emulsions are stable. The addition of biodiesel after stable emulsion attained does not occur a separation. The solid circles describe that the components contained in the emulsion substance are in equilibrium condition.

### 3.3. Compositions of COME, Aqueous Ethanol, and Diesel

This session aims to analyse the composition of pure ethanol, biodiesel, and water, and aqueous ethanol, biodiesel, and diesel, just formed in a stable emulsion. Generally, the composition of components using *COME* was similar to *POME*, as described previously. Compared to POME employment, the amount of ethanol needed to be mixed with biodiesel derived from coconut oil was smaller but relatively similar when using 94 and 95 %, as shown in Table 3. The data show that the composition of biodiesel for both methyl esters was somewhat similar to each other.

The amount of COME needed inclined when the aqueous ethanol purity decreased, which was comparable with using POME maintaining the ethanol volume at 7 mL. The 7 mL ethanol 97 % and 96% could be forming a stable emulsion with 23 and 30 mL biodiesel, and when concentration decreased to 95 and 94%, the amounts of COME were 36 and 41 mL.

**Table 3. Composition of pure ethanol, biodiesel,**
**and Water in stable emulsion using aqueous ethanol 94-97%.**

| Aq.Et %v/v | Volume (mL) | | | | Compositions (%v/v) | | |
|---|---|---|---|---|---|---|---|
| | BD | Aq.Et | Wat | Et. | Et. | BD | Wat |
| 97 | 23 | 7 | 0.21 | 6.79 | 22.63 | 76.67 | 0.70 |
| 96 | 30 | 7 | 0.28 | 6.72 | 18.16 | 81.08 | 0.76 |
| 95 | 36 | 7 | 0.35 | 6.65 | 15.47 | 83.72 | 0.81 |
| 94 | 41 | 7 | 0.42 | 6.58 | 13.71 | 85.42 | 0.88 |

The previous description was the compositions of the components without the presence of diesel. The diesel substance was the pure nonpolar component which had a different property compared to biodiesel. The first diesel was mixed with aqueous ethanol, whose concentrations were 94-97%. The solutions were separated, similar to the blending of the mixture between diesel, biodiesel (POME), and aqueous ethanol.

The compositions of aqueous ethanol, biodiesel, and diesel in the stable emulsion, which ratio of diesel to aqueous ethanol was altered 7:7, 10:7, 15:7, and 20:7 (v/v) for ethanol concentrations were 96, 95, and 94 % displayed in Fig. 3. By employing ethanol 96, 95, and 94 % for the first ratio, compositions of aqueous

ethanol, biodiesel, and ethanol were 15.91, 68.18, and 15.91 %, 14.00, 72.00, and 14.00 %, and 10.77, 78.46, and 10.77 %. The addition of diesel volume could be increasing in the biodiesel volume needed to form a stable emulsion. At the biggest ratio (20:7) the compositions changed to 9.09, 64.94, and 25.97 % (ethanol 96 %), 7.87, 69.66, and 22.47 % (ethanol 95 %). As displayed in the figure, the trapezoidal area is the zone where three components, aqueous ethanol, diesel, and biodiesel, are stable emulsions. With the increase of biodiesel after the equilibrium condition was formed, the emulsion was not changing, comparable with the previous POME-based emulsion.

The data present that the composition trends of blended fuels using *COME* were relatively comparable to that of *POME*. But the composition of ethanol needed to be blended with diesel and biodiesel (*COME*) was less than that of POME. GC/MS data show that the COME was mainly dominated by methyl esters, which have carbon chain $C_9$, $C_{11}$, and $C_{13}$ compared to those of POME were $C_{17}$ and $C_{19}$. The facts showed the length of the carbon chains on the methyl ester influenced by the compositions of the ethanol, biodiesel, and water of the blended fuels.

The findings disclosed that biodiesel (*POME and COME*) acted as the surfactant, which more dominant compared to ethanol. The addition of biodiesel continually in the mixture after stable emulsion formed, the separation did not occur

A comparative study has shown that aqueous ethanol could be dissolved entirely with gasoline without using a synthetic surfactant. After the stable emulsion formed, the stable emulsion kept existing though the ethanol was added continually.
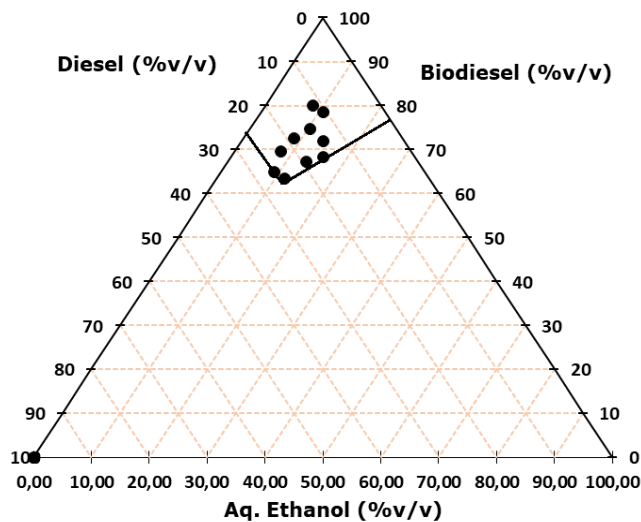


**Fig. 3. Triangular graph of compositions of aqueous ethanol, biodiesel (COME), and diesel in stable emulsion using ethanol 94-96%.**

Even though the stable emulsions were formed, the solutions were not clean and clear compared to that of gasohol (aqueous ethanol and gasoline). The observations were carried out for weeks, and found the facts presenting the droplets were distributed uniformly in solution.

The presence of the droplets appeared clear, especially using a lower concentration of ethanol. The absorption of air and interface interaction (surface tension) could be contributing to the presence of droplets. Since the ethanol's boiling point is less than biodiesel and diesel, the change of compositions is possible because of evaporation, which is not investigated.

As described in the introduction section, the blended fuels involving absolute ethanol have been studied intensively, including their heat engine application. Because the study of compositions of the biodiesel, diesel, and aqueous ethanol and biodiesel and aqueous ethanol in the stable emulsion was the new work, this discussion was not compared with the other reverences published previously.

### 3.4. Fuel Parameters Analysis

There are six samples investigated: Two pure biodiesels, POME and COME, COME-diesel-aqueous ethanol, POME-diesel-aqueous ethanol, COME-aqueous ethanol, and POME-aqueous ethanol, as displayed in the food note below the table. The blended fuels finished to prepare, the fuel parameters, which were density, Specific gravity (SG), API, and cetane No (Cet.No), were analysed as shown in Table 4.

The highest density of the samples was 0.89 g/cm$^3$ belongs to biodiesel derived from coconut oil. The most significant value of the density related to the length of the carbon chain of COME which was less than POME. When ethanol, whose density was less than biodiesel, was blended, the density decreased slightly to 0.85 and 0.87 g/cm$^3$. The data showed that the SG quantities (specific gravity) were relatively close to the density. The density of biodiesel, as published previously, was 0.87 - 0.88 g/cm$^3$ depending on the feedstocks employed, and the pure diesel was around 0.83 - 0.84 g/cm$^3$ [27]. Meanwhile, the density of blended fuels of diesel, ethanol, and biodiesel was recorded at 0.82 - 0.87 g/cm$^3$ depending on each component's composition.

**Table 4. The fuel parameters density, API, and cetane No of the biodiesel (POME and COME) and their blends (biodiesel-diesel-aqueous ethanol) which an ethanol concentration of 96%.**

| Sample- | ρ/15˚C g/cm$^3$ | SG/15 ˚C g/cm$^3$ | API, (15 ˚C) | CN |
|---|---|---|---|---|
| 1 | 0.88 | 0.88 | 26.90 | - |
| 2 | 0.89 | 0.89 | 25.20 | 86.40 |
| 3 | 0.87 | 0.87 | 29.20 | - |
| 4 | 0.85 | 0.86 | 32.10 | 66.10 |
| 5 | 0.87 | 0.87 | 28.60 | 78.90 |
| 6 | 0.85 | 0.85 | 33.30 | - |

1) POME; 2) COME; 3) COME-D-Aq.Et=35:10:7; 4); POME-D-Aq.Et=58:10:7; 5) COME-Aq.Et=30:7; 6) POME-Aq.Et=9:5. *API: American Petroleum Institute gravity;* Cetane number (CN).

The value of the *API* parameters was inversely proportional to the density and SG quantities. The highest density was the smallest value of the APIs, which was defined as the water's weight compared to a particular fuel. The APIs of the COME and POME were 25.20 and 26.90, respectively. The most significant API value recorded at 33.30 belonged to the sixth sample, whose ethanol composition was more significant than the rest of the blended fuels.

The CN of the COME was 86.40, but the CN of the POME, sample 3, and sample 6 could not be verified since its values were much less than reasonable. The sample measured by their CNs showed the addition of ethanol to biodiesel, and diesel generally declined the values. The CNs of the POME-diesel-aqueous ethanol and COME-aqueous ethanol were 66.10 and 78.90, respectively. If referring to previous works showed that the CNs were varying at a range of 25.46 - 67.47 depending on the FAME composition and the feedstocks used [28]. The CNs for all samples were more prominent than that of pure biodiesel. It was an indication the combination of ethanol, biodiesel or ethanol, biodiesel, and diesel improved the engine performance, including CN quantity [29]. The additional parameters essential in combustion inside an engine were viscosity, flash point, Reid vapor pressure (RVP), pour point, and ASTM colour, as presented in Table 5. In this measurement, however, the RVP parameter values were not detected by the instruments employed. The viscosities recorded successfully were ranged from 3.54 mm$^2$/s, which belonged to the POME-aqueous ethanol assigned by 1a, until 5.77 mm$^2$/s of COME-aqueous ethanol sample (sample 2a). If compared to pure ethanol and biodiesel, their viscosities were around 1.10 and 2.78 mm$^2$/s, which were less than the present work as reviewed previously [30]. The previous report showed that the addition of diesel in the blended fuel could be increasing the viscosity up to 3.00 mm$^2$/s [31].

As seen, the COME-based emulsion's viscosity was higher than that of POME, in which the variation was proportional with flashpoints. The flashpoints (FP-PMCC) of samples 1a and 2b were 55 and 65 °C than those of 66 and 72 °C of the samples 1b and 2a. It could be concluded that the fewer carbon chains that belonged to the biodiesel, the less of the temperature of the fuel to be burn. Compared to previous research reviewed by other authors, pure biodiesel was in the range of 100-170 °C [32]. It means that the ethanol present in the fuels can be reducing the flashpoint highly.

**Table 5. Viscosity, ASTM Colour, flash point, and pour point of the blended fuels POME-aqueous ethanol, COME-diesel-aqueous ethanol, COME-aqueous ethanol, and POME-diesel-aqueous ethanol using ethanol 96%.**

| Sample | Vis. ($\sigma$) 40 °C, mm$^2$/s | ASTM Color | Flash Point PMCC, °C | Pour Point, °C |
|---|---|---|---|---|
| 1a | 3.54 | D 0.50 | 55 | 2 |
| 1b | 5.18 | D 2.00 | 66 | 6 |
| 2a | 5.77 | D 0.50 | 72 | 11 |
| 2b | 4.27 | D 2.0 | 65 | 3 |

Sample 1a: POME-Aq.Et; 1b: COME-D-Aq.Et; 2a: COME-Aq.Et; 2b: POME-D-Aq.Et

As shown in the table, the fuel colour was much better than diesel and ranged from D 0.50-2.00. The combination of biodiesel (POME or COME) and ethanol resulted in the least colour scale recorded at 0.50, but diesel's addition changed the light colour highly to D 2.00. Sometimes the fuel industry operates in different conditions- it can be working in the summer in which temperature reaches 40-50°C and the winter in which temperature drops below 0 °C. The least temperature of the fuel whereby it can be flowing in the pipe must be investigated. The pour point (PP) of COME-aqueous ethanol gave the highest value observed at 6 °C, in which the fuel, especially biodiesel, was occurring a phase transition. The pure biodiesel in

low temperature (below 15 ºC) formed a gel, which increased the friction. The COME-based blended fuels had higher pour points (6 and 11 ºC) than those of POME recorded at 2 and 3 ºC. The previous investigation showed that the POME pours cloud points were around 14 and 15, which were indicative that the addition of ethanol reduced the pour point [33].

Generally, the engine's fuels consist of many fractions whose melting, boiling, and pour temperatures are different. Since the boiling point is other, the amount of the substance vaporizing at a specific temperature is also additional, as shown in Table 6. The initial boiling point of all samples occurred at a similar temperature recorded at 76 ºC. The amounts of substance evaporating in the temperature range 76 - 78 ºC were obtained 5 - 10 % (v/v) of all blended fuels. The initial boiling points displayed at 78 ºC were mostly related to the ethanol presence. When the fuels evaporated at 20 %, the boiling temperatures started to be profoundly different, whereby the first and third samples were still 78 and 80 ºC, while the second and fourth fuels were boiled at 235 and 255 ºC. The wide temperature gap was caused by ethanol's amount, whose boiling point was 78 ºC existing in fuels. When the ethanol was finished, the boiling point would increase remarkably to the initial boiling point of a certain biodiesel fraction.

**Table 6. The distillation properties of Biodiesel (POME/COME)-
aqueous ethanol and biodiesel (POME/COME)-diesel-aqueous
ethanol blends in stable emulsion using ethanol 96%.**

| Test | Sample- | | | |
|---|---|---|---|---|
| | 1a | 1b | 2a | 2b |
| | ºC | ºC | ºC | ºC |
| **IBP** | 76 | 76 | 76 | 76 |
| **5%** | 77 | 77 | 76 | 77 |
| **10%** | 78 | 78 | 77 | 78 |
| **20%** | 78 | 235 | 80 | 255 |
| **30%** | 78 | 253 | 247 | 295 |
| **40%** | 318 | 280 | 268 | 315 |
| **50%** | 325 | 296 | 282 | 323 |
| **60%** | 326 | 314 | 308 | 328 |
| **70%** | 328 | 330 | 324 | 332 |
| **80%** | 337 | 334 | 334 | 336 |
| **90%** | 350 | 336 | 340 | 346 |
| **FBP** | 355 | 340 | 348 | 350 |
| **Dist. %** | 99.00 | 98.00 | 99.00 | 94.00 |
| **Residu, ml** | 0.2 | 0.2 | 0.10 | 0.40 |

IBP: Initial boiling point; FBP: Final boiling point; 5%: 5% of fuel evaporated.

The 30 % ethanol in the first fuel evaporated, which was still occurred at 78 ºC, the rest of the fuels boiled at 253, 247, and 295 ºC. After 40 % of fuels were evaporated, the boiling points are shown only belonged to biodiesel (POME and COME), for the ethanol was empty inside a flask. The data showed that the boiling points of the COME-based fuels were always higher than those of the POME, of which carbon chains influenced them. When fuels evaporated 80 %, the temperature was already observed at 337 (sample 1a), 334 (sample 1b), 268 (sample 2a), and 336 ºC. The FBPs were attained whereby the fuels disappeared (sample 1b

- 2b) of the flask at 99 %, 98 %, 99 %, and 94 %, and temperatures were 355, 340, 348, and 350 °C. The residual substances obtained were 0.2, 0.10, and 0.40 mL, mainly of the diesel fraction whose boiling temperatures were above the FBP.

## 4. Conclusions

The stable emulsions of the biodiesels-aqueous ethanol and biodiesel-diesel-aqueous ethanol have been successfully prepared, whose the feedstocks employed the palm- and coconut oils. The data showed that the aqueous ethanol, whose concentrations were 94-97 %, could be dissolved with biodiesel and diesel. It was found by adding biodiesel continually into the mixture whereby the stable emulsion was formed would not separate the components. It was observed the emulsion substances created foam and bubble distributed throughout the solution. The numbers and volumes of the foams and bubbles increased concerning time, especially the blended fuels using ethanol in less concentration. The interface tensions between components and the air dissolved into the substance could be influencing the existence of the foams and bubbles. The compositions of aqueous ethanol and biodiesel and aqueous ethanol, diesel, and biodiesel (POME) were different from employing COME. The difference of the methyl ester obtained shown by GC/MS spectra was contributing to the composition of each component in the emulsified substance. It was discovered that aqueous ethanol, diesel, and pure ethanol could be forming stable emulsion, but in ethanol concentration, 94-95% of the emulsion appeared the droplets. In the ethanol purity of 94-96%, the compositions range of water, biodiesel, diesel, and pure ethanol occurred at 0.37-1.00, 62.50-85.22, 8.70-20.00, and 5.72-24.00%.

### Nomenclatures

| | |
|---|---|
| *FBP* | Final boiling point, °C |
| *FP-PMCC* | Flashpoint- Pensky-martens closed cup, °C |
| *IBP* | Initial boiling point, °C |
| *P* | Pressure, Pa |
| *PP* | Pour point, °C |
| *RVP* | Reid vapor pressure, Pa |
| *SG* | Specific gravity, g/cm$^3$ |
| *T* | Temperature, °C |
| *t* | Time, s |
| *V* | Volume, mL |
| *%v/v* | Percent volume per volume, mL/mLx100% |

***Greek Symbols***

| | |
|---|---|
| $\rho$ | Density, $g/cm^3$ |
| $\sigma$ | Viscosity, $mm^2/s$ |

**Abbreviations**

| | |
|---|---|
| ASTM | American society for testing and materials |
| API | American petroleum institute |
| Aq.Et | Aqueous ethanol |
| BD | Biodiesel |
| CN | Cetane number |
| COME | Coconut oil methyl ester |
| D | Diesel |
| FAME | Fatty acid methyl ester |
| Et | Ethanol |
| MPMS | Manual of petroleum measurement standard |
| POME | Palm oil methyl ester |
| RON | Research octane number |
| GC/MS | Gas chromatography-mass spectrometry |
| Wat | Water |

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