

Study of Aqueous Ethanol-Diesel-Biodiesel Prepared by Near-Isochoric Sub Critical Trans-Esterification

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Abstract: - This work aims at preparing the blended fuels in a stable emulsion in which the biodiesel was obtained from palm oil with applying the near isochoric subcritical trans-esterification. The work procedures are the following: the preparation chemicals needed; the synthesis of the biodiesel; POME (palm oil methyl ester) analysis; the blending process of the aqueous ethanol-biodiesel (Aq.Et-BD) and ethanol-diesel-biodiesel (Aq.Et-BD-D) whereby they formed in a stable emulsion. It was obtained that the compositions of water, ethanol, and biodiesel using ethanol 94-97% were ranged from 0.69-1.60, 10.74-38.40, and 69.57-88.57%. By employing ethanol with concentration 94-95%, the emulsion appeared many droplets distributed throughout the substance. It was observed by increasing biodiesel composition after a stable emulsion attained the phase did not change. After emulsions blended, the work was proceeded with the measurement of the fuel parameters such as density, SG, API, RPV, flash and pour points, cetane number, and distillation properties.

Keywords: Biodiesel, Blended Fuels, Emulsion, Ethanol, Stable Emulsion

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1 Introduction

The bio-resources materials have been attracting widely scientists aiming to overcome the deficiency of fossil-based fuels [1,2]. Some renewable materials had been successfully synthesized and utilized for energy purposes [3,4]. Lignocellulosic materials were also converted into more valuable chemicals, namely, sugars which would be prepared fuels [5,6]. The biofuels were successfully

manufactured, such as bioethanol, biogas hydrogen, methane, and solid fuel [7,8,9,10].

Furthermore, investigators around the world have been preparing the biodiesel by utilizing the full range of the edible- and non-edible- crude oils from plants such as palms, animals, *Calophyllum inophyllum* (nyamplung fruits), *Jatropha curcas*, *soybean*, *Pongamia pinnata*, tobacco seed (*Nicotiana tabacum* L.), rice bran, *Madhuca indica*, *Azadirachta*

indica, Hevea brasiliensis, castor, linseed, and microalgae as reviewed by the author [11].

The method employed on biodiesel production was still dominated by a conventional technique called trans-esterification. It can be carried out at atmospheric-, or high pressure and temperature conditions (sub- and supercritical fluids methods). Generally, the trans-esterification using subcritical fluids still employs base-based catalysts, namely KOH and NaOH [12]. Currently, the sub- and superfluids started to use a chemical reaction to produce biodiesel using less catalyst or even without catalyst [13].

Bioethanol is also being developed purposing to change a part of gasoline for heat engine fuel. The utilization of ethanol for fuel purposes is facing a challenge, for it is mainly derived from food, namely, corn and sugarcane. On the other hand, generation II ethanol, which is converted from lignocellulosic materials, is not feasible for scale-up. The most condition for employing lignocellulose is the pretreatment and enzymatic processes that are costly [7]. To overcome the problems must be increased to exceed human needs. The countries United States of America and Brazil are successful in developing ethanol, becoming a lucrative business thanks to a surplus of the starch and sugar from corn and sugarcane [14,15].

The works of blended fuels were reported by authors around the world of which the mixture consisted of ethanol-gasoline, ethanol-biodiesel, ethanol-diesel, and ethanol-diesel-biodiesel [16,17,18,19]. The other authors discovered that ethanol blends E85 of the gasohol fuel was a threshold blend whereby the fuel was not economical to produce since the caloric value started decreasing highly. Still, all ethanol blends showed less carbon emission [20]. The ethanol addition in large fraction into biodiesel-diesel blends could be applied to the high load diesel engine. The study found that the ignition delay increased by 38.5 %, but the burning duration decreased by 49 %. The negative impact of the ethanol blends the NO_x emission inclined significantly because of the oxygen existence [21]. When the ethanol was added to biodiesel, the combustion parameters were changed. The biodiesel-ethanol blends could improve fuel consumption and thermal efficiency compared to that of pure biodiesel. The parameters, heat release at any time, ignition delay, and smoke emission was higher if using biodiesel-ethanol blends [22].

As described previously, biodiesel can be produced by utilizing subcritical fluids with a pressurized gas such as CO₂, N₂, and H₂. This

investigation was to synthesize biodiesel from palm oil, applying the near isochoric subcritical. The application of the adjacent isochoric subcritical trans-esterification aims to avoid using the pressurized gas. Furthermore, the work does not use complicated instruments; neither were installed valves and regulators. The brief procedures are as follows: design and construction of the reactor, biodiesel preparation, characterization of POME employing GC/MS, the blending process of aqueous ethanol-biodiesel, and aqueous ethanol-biodiesel-diesel, and fuel parameters measurements.

2 Methodology

2.1 Materials

The chemicals employed were a commercial palm oil ordered from the market in Minahasa Regency, North Sulawesi Indonesia. The aqueous ethanol was processed from a palm tree (*Arenga Pinnata*) sugar. The sap was fermented to be liquor and then distilled using a tool called reflux column filled with pores packing materials as used previously [23]. By using that technique yielded bioethanol with concentrations of 94-96%. The higher purity, 97%, was obtained employing an activated particle sieve (lime).

2.2 Instrumentation

A home-made reactor was designed and constructed with dimensions volume 600 mL and a tube 2 inches equipped by a thermometer (56-238; Sellery; Singapore) and fluid-filled pressure gauge (56-374; Sellery; Singapore). Instrument (GCMS-2010 QP; Shimadzu; Japan) based at Central Lab, Malang State University, East Java Indonesia, was used to identify the methyl esters formed whereby the operational conditions were 5 bar. The American Society for Testing and Materials (ASTM) procedures were followed to measure the fuel parameters in which the work was conducted at the Oil and Gas Engineering Laboratory, Polytechnic of Energy and Mineral Polytechnics, Cepu Blora Central Java, and at Samarinda State Polytechnic, East Kalimantan Indonesia. The fuel parameters measured included ASTM assignments, instrument specification, manufacturer, and the country as follows: density (15°C; D4052; Koehler; New York USA), viscosity (40°C; D445; KV1000; Kohler; New York USA), ASTM color (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

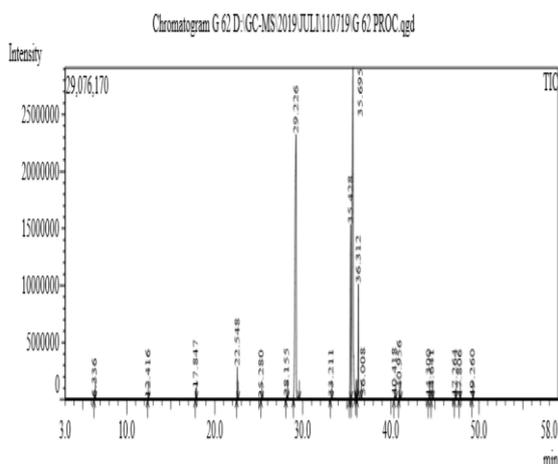
Manufacturing Company; Indianapolis USA), and distillation (D86; Koehler; New York USA).

2.3 Procedures

The technology used in the present work followed and modified the previous works as previously reported [24-25]. The proposed method considered a new process was a near isochoric subcritical transesterification.

The biodiesel was synthesis by reacting the palm- or coconut oil, methanol enhanced by catalyst KOH with a ratio of 10.75: 2.52: 0.01 (w/w), and the pressure was set at 1-15 bar and the temperature varied from 30-150°C for 1 h. The mixture was blended in a 1-liter flask and then was poured into the reactor. After the lid of the reactor was closed tightly, the gas stove was turned on. The gas was weighted in each experiment. All processes were carried out for 1 h, and during heating, the reactor was shaken each 5 min.

A



B

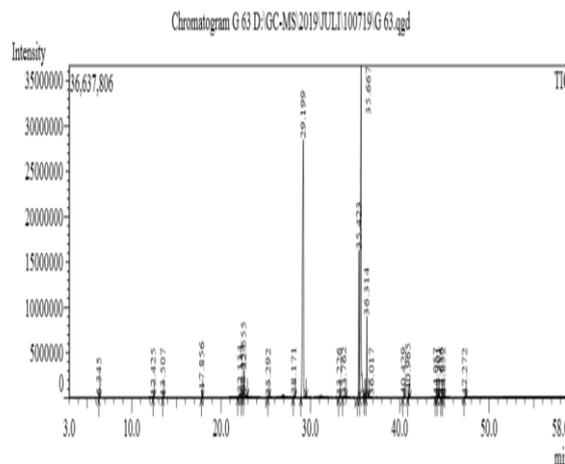


Fig. 1: The GC/MS spectra of the methyl esters and retention time (RT) by employing the near isochoric subcritical esterification mixture V 575 mL; P=1-15 bar (A) and V 550 mL; P=1-7 bar (B) for 1h; and T=30-150 oC

Table 1. The yield of biodiesel obtained assigned by yield1, yield2, yield3, and yield4 with two volumes of mixture 575 and 550 mL conducted at 15 and 7 bar for 1 h and maximum temperature 150°C.

Name of sample	Yield1 (%w/w)	Yield2 (%w/w)	Yield3 (%v/v)	Yield4 (%v/v)
POME (575ml; 15 bar)	88.96	74.20	92.38	74.78
POME (550 mL; 7 bar)	88.35	73.94	89.84	72.72

After trans-esterification finished, the gas stove was turned off, and the reactor was cooled by using a wet cloth until the temperature was 30 °C. In this process, the pressurized gas was not employed, aiming at simplifying and declining the production cost. The mixture was poured into a flask and kept for hours until biodiesel and glycerol were separated into two phases.

The biodiesel was removed to another flask using a small tube where the tube edge touched just above the glycerol surface, and the flask heights are different from the ground. After the wash step, the samples were poured inside a bottle and stored in a rustic cabinet. The POME obtained was characterized, employing the GC/MS measurement, whereby it was to know the type of the methyl ester compounds. The compound analysis referred to literature reported by authors [26].

Table 2. The palm oil methyl ester compound (POME) and retention time (RT) by employing the near isochoric subcritical esterification (mixture V 575 mL; P=1-15 bar; t= 1h; T=30-150 °C ratio (in V) palm oil to methanol = 465.45:109.11; mass of KOH = 5g

RT	Compound	Formula	Area (%)
6.34	Octanoic acid	C ₉ H ₁₈ O ₂	0.04
12.42	Decanoic acid	C ₁₁ H ₂₂ O ₂	0.03
17.85	Dodecanoic acid	C ₁₃ H ₂₆ O ₂	0.37

22.55	Tetradecanoic acid	$C_{15}H_{30}O_2$	1.24
25.28	Pentadecanoic acid	$C_{16}H_{32}O_2$	0.02
28.15	9-Hexadecenoic acid	$C_{17}H_{32}O_2$	0.14
29.23	Hexadecanoic acid	$C_{17}H_{34}O_2$	37.42
33.21	Heptadecanoic acid	$C_{18}H_{36}O_2$	0.08
35.43	9,12-Octadecadienoic acid	$C_{19}H_{34}O_2$	12.58
35.69	9-Octadecenoic acid	$C_{19}H_{36}O_2$	40.95
36.31	Octadecanoic acid	$C_{19}H_{38}O_2$	6.24
40.42	11-Eicosenoic acid	$C_{21}H_{40}O_2$	0.13
40.96	Eicosanoic acid	$C_{21}H_{42}O_2$	0.49
44.30	Hexadecanoic acid	$C_{19}H_{38}O_4$	0.06
44.64	Heptadecanoic acid	$C_{19}H_{38}O_2$	0.08
47.26	9-Octadecenoic acid	$C_{21}H_{40}O_4$	0.06
47.81	Tetracosanoic acid	$C_{25}H_{50}O_2$	0.03
49.26	2,6,10,14,18-Pentamethyl	$C_{25}H_{42}O_2$	0.03

The simple steps were conducted at the blending of biodiesel-aqueous ethanol and biodiesel-aqueous ethanol-diesel. The procedures are the following: The 7 mL aqueous ethanol was poured into a flask 100 mL, and then biodiesel was mixed gradually while being shaken slowly. When the biodiesel was entirely dissolved with aqueous ethanol, the addition was stopped.

The blended fuel of aqueous ethanol-biodiesel (AqEB) in the stable emulsion was obtained with a composition (in V) VAq.Et.:VBD, or VEt:BD:W whereby VAq.Et., VBD, VEt., and W were assigned as the volumes of the aqueous ethanol, biodiesel, pure ethanol, and water, respectively.

The stable emulsions of aqueous ethanol-biodiesel-diesel (AqE-BD) were as follows: The aqueous ethanol was mixed firstly with diesel at a specific ratio. Biodiesel was poured gradually into the mixture while shaken gently until the three components were dissolved fully.

The composition of the aqueous ethanol, biodiesel, and diesel (AqE-BD-D), or the pure ethanol, biodiesel, diesel, and water (in V) whose assignments were VAq.Et.:VBD,:VD, or VEt.:VBD,:VD:W was established. The volume of pure ethanol was obtained from percentage times an amount of aqueous ethanol, and the rest was the volume of water.

The present work, the literature authored by [27], and the instrument instructions were a reference for fuel parameters discussion. Notably, the density, specific gravity (SG), API, Reid vapor pressure (RVP) followed the standard procedure of the American National Standard, as stated on the guidelines entitled Manual of Petroleum Measurement Standards/MPMS, Chapter. The

distillation property was modified the investigation published by authors [28].

3 Results and Discussions

3.1 Facts Discovered

Before the experiment, the reactor designed and constructed was carried out a test purposing to know the property and safety. The application of the near isochoric subcritical method for biodiesel preparation found useful facts.

If the volume of the mixture was just similar to the reactor volume 600 mL, the pressure increased fast after the temperature reached 150 oC. Even though the temperature increased slowly, the pressure increased extremely from 15 until 50 bar just in few seconds. This situation was a danger and not safe for practical operation in Lab- and industrial scales. It was discovered that the reactants, palm oil, and methanol were difficult at reacting to be a biodiesel product whose the mixture volume was 0.99 of reactor volume. Sometimes the products obtained were only two-phase substances, palm oil, and methanol or one phase solution of which it was still under investigation.

In spite of a high pressure applied, sometimes the reactants could not react to the desired product, which might be caused by less collision between particles. Based on the previous description, the volume of the mixture was decreased to 575 and 550 mL to minimize the explosion of the reactor. When the amount of broth at 575 mL, the pressure could be attaining 15 bar and increase above it but slow, meanwhile 550 mL only achieved 7 bar.

Table 3. The palm oil methyl ester compound (POME) and retention time (RT) by employing the near isochoric subcritical esterification (mixture V 550 mL; P=1-7 bar; t= 1h; T=30-150 °C ratio (in V) palm oil to methanol = 445.45:109.11; mass of KOH = 4.5g

RT	Compound	Formula	Area (%)
6.34	Octanoic acid	C ₉ H ₁₈ O ₂	0.04
12.42	Decanoic acid	C ₁₁ H ₂₂ O ₂	0.04
13.51	Phenol, 2-methoxy-3-(2-propenyl)	C ₁₀ H ₁₂ O ₂	0.03
17.86	Dodecanoic acid	C ₁₃ H ₂₆ O ₂	0.35
22.13	9-Octadecenoic acid	C ₁₉ H ₃₆ O ₂	0.68
22.45	9-Octadecenoic acid	C ₁₉ H ₃₆ O ₂	0.63
22.55	Tetradecanoic acid	C ₁₅ H ₃₀ O ₂	2.00
25.29	Tetradecanoic acid	C ₁₅ H ₃₀ O ₂	0.04
28.17	9-Hexadecenoic acid	C ₁₇ H ₃₂ O ₂	0.17
29.20	Hexadecanoic acid	C ₁₇ H ₃₄ O ₂	36.23
33.23	Hexadecanoic acid	C ₁₈ H ₃₆ O ₂	0.07
33.76	9-Octadecenoic acid	C ₁₉ H ₃₆ O ₂	0.32
35.42	9,12-Octadecadienoic acid	C ₁₉ H ₃₄ O ₂	12.12
35.67	9-Octadecenoic acid	C ₁₉ H ₃₆ O ₂	40.88
36.31	Octadecanoic acid	C ₁₉ H ₃₈ O ₂	5.33
40.43	11-Eicosenoic acid	C ₂₁ H ₄₀ O ₂	0.16
40.96	Eicosanoic acid	C ₂₁ H ₄₂ O ₂	0.38
44.06	1,2-Benzenedicarboxylic acid	C ₂₄ H ₃₈ O ₄	0.12
44.85	1,2-Benzenedicarboxylic acid	C ₂₄ H ₃₈ O ₄	0.11
47.27	9-Octadecenoic acid	C ₂₁ H ₄₀ O ₄	0.09

3.2 Yield of Product

The yields obtained were influenced mainly by the temperature, amount of catalyst, time, and reaction time. The yields are defined as follows: yield1 and yield2 are defined as the mass of product/mass of palm oil and mass product/mass of palm oil + methanol. In contrast, yield 3 and yield4 are formulated as the volume of product/volume of palm oil and volume of product/volumes of palm oil + methanol, respectively, as shown in Table 3. Two volumes of the mixture were employed, namely, 575 mL (15 bar) and 550 mL (7 bar).

The data show that the yield1 and yield2 of POME, whereby the volume of the mixture was 575 (15 bar), were 88.96 and 74.20 % meanwhile, yield3 and yield4 were 92.38 and 74.78 %. Meanwhile, when the volume of the mixture was 550 mL and conducted at 7 bar, the yield1, yield2, yield3, and yield4 obtained 88.35, 73.94, 89.84, and 72.72 %. According to data shown that the yields obtained, which were conducted at 15 bar and 575 mL, were relatively more significant than those of 7 bar and 550 mL. The pressure could be influencing the yield of biodiesel obtained, which was comparable with previous work [29].

3.3 Compound Analysis

According to GC/MS measurement (Fig. 1), the methyl esters synthesized from palm oil were diverse that were recorded from C₉H₁₈O₂

(Octanoic acid) until C₂₅H₄₂O₂ (2,6,10,14,18-Pentamethyl) and the compositions were varied depending on RT as presented in Table 2. Two peaks appear on the spectra and represent the compounds dominated by the POME. The most significant component of the POME (575ml; 15 bar) was observed at 40.95 %, whose compound name was 9-Octadecenoic acid (C₁₉H₃₆O₂). The second and third places were followed by Hexadecanoic acid, and 9,12-Octadecadienoic acid recorded their compositions 37.42% and 12.58%, which were proportional to the investigations done by authors [30].

The variation of the volume of the mixture and the operational pressure was carried out, aiming to analyze the methyl ester compounds released from triglycerides after being reacted with methanol as displayed in Table 3. If compared with the data shown in Table 2, there are slightly different from the compositions of each compound obtained. The change of operational parameters, especially the volume of mixture and pressure, could influence the symmetry of the GC/MS spectra slightly since compounds obtained in the second step were more diverse.

Compositions of Pure Ethanol-Biodiesel-Water (Et-BD-W)

Table 4 describes the composition (%v/v) of the Pure Ethanol, biodiesel, and water in one phase (stable emulsion) whereby the ethanol volumes are

varied 8, 7, 7, and 9 mL and conducted at 1-15 bar, 30-150°C for 1 h. To determine the stable emulsion using a vision method by eyes was easy but resulted in a high error since measuring the exact volume could be different in each observation. As shown in

the data in a table that the composition measured was altered in the specific initial volume of aqueous ethanol. To minimize the error was conducted four times by changing the initial volume of aqueous ethanol.

Table 4. Composition (% v/v) of the Pure Ethanol-Biodiesel-Water in a stable emulsion with an initial volume of the aqueous ethanol 7 – 9 mL (P = 1-15 bar; T 30-150oC for 1 h)

Et (%)	Volume (mL)			Composition (%)			
	BD	Aq.Et	W	Et	Et	BD	W
97	22	8	0.24	7.76	25.87	73.33	0.80
96	25	7	0.28	6.72	21.00	78.13	0.88
95	30	7	0.35	6.65	17.97	81.08	0.95
94	41	9	0.54	8.46	16.92	82.00	1.08
96	12	8	0.32	7.68	38.40	60.00	1.60
95	26	7	0.35	6.65	20.15	78.79	1.06
94	62	8	0.48	7.52	10.74	88.57	0.69
97	16	7	0.21	6.79	29.52	69.57	0.91
96	27	7	0.28	6.72	19.76	79.41	0.82
95	43	7	0.35	6.65	13.30	86.00	0.70
94	50	7	0.42	6.58	11.54	87.72	0.74
97	16	7.33	0.22	7.11	30.49	68.57	0.94
96	27	7.33	0.29	7.04	20.50	78.64	0.85
95	43	7.00	0.35	6.65	13.30	86.00	0.70
94	50	8.00	0.48	7.52	12.97	86.21	0.83

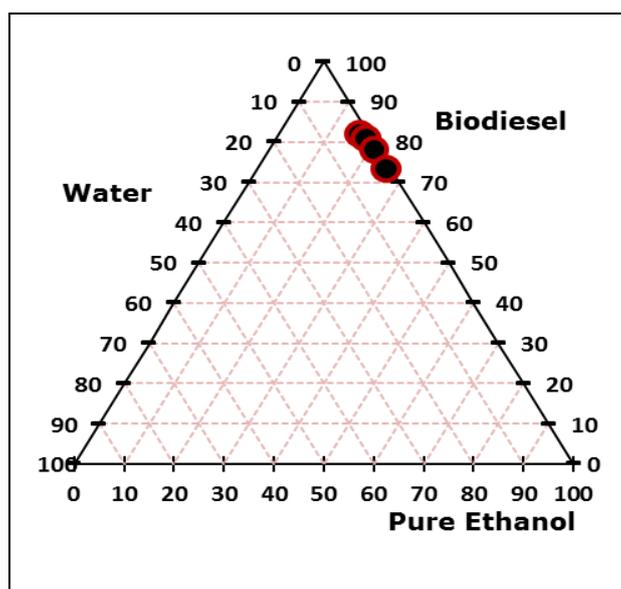


Fig. 2: The ternary system of pure ethanol-biodiesel-water in a stable emulsion whereby POME was synthesis by employing the near isochoric subcritical esterification mixture V 575 mL; P=1-15 bar for 1h; and T=30-150 °C

In the first trial, 8 mL aqueous ethanol, 97% could be dissolved with 22 mL biodiesel in a stable emulsion. At the same time, volume decreased to 7 and 7.33 mL; the biodiesel needed mixed ideally was reduced highly to around 16 mL. When aqueous ethanol concentration declined to 96 %, the amount of biodiesel mixed increased. By using two 7 mL and 7.33 mL, ethanol 96 %, biodiesel dissolved were 25, 27, and 27 mL, while 8 mL ethanol 96 % decreased biodiesel volume to 12 mL. It was indicative that ethanol and biodiesel acted as a surfactant.

If using ethanol 97% and transformed into the composition (%v/v), the composition of pure ethanol, biodiesel, and water in the first trial was 25.87%, 73.33%, and 0.80% and changed to 17.97%, 81.08%, and 0.95% for ethanol 95%. The compositions of the third trial for similar ethanol concentrations were observed at 29.52%, 69.57%, 0.91% and 13.30%, 86.00%, and 0.70 %, which were comparable to each other. The range of pure ethanol, biodiesel, and water in all ethanol concentrations and volumes could be summarized 10.74%-38.40%, 60.00%-88.57%, and 0.69%-1.60 %, respectively. The data disclosed that the water variations were relatively small. Generally, the less aqueous ethanol concentration was blended, the more the amount of biodiesel was added to be a stable emulsion.

To know and analyze the substances formed in non- and stable emulsions of the pure ethanol-biodiesel-water, it was necessary to describe them in the ternary graph as presented in Fig. 2. The areas where the aqueous ethanol and biodiesel mixed entirely becoming stable emulsion were very narrow. Two ternary diagrams, as shown relatively, gave a similar trend whereby the equilibrium lines were located just on the right side of triangles (before reader). The areas where aqueous ethanol and biodiesel in the stable emulsion were situated between the equilibrium line and the right side- and stretched up to the left side of triangles just below the corner. Even though the areas are limited for all ternary systems, the number of composition combinations of aqueous ethanol and biodiesel was infinite.

The work invented the addition of biodiesel continually after Aq.Et-BD substance was formed a stable emulsion, would not occur a separation of components. It was different in creating a stable emulsion of the aqueous gasohol in which it would not be separated by adding aqueous ethanol continually, as reported by authors [23].

Compositions of Aqueous Ethanol-Biodiesel-Diesel (Aq.Et-BD-D)

The presence of diesel on the mixture gave a composition that was different from previous fuels whereby four components, pure ethanol-biodiesel-diesel-water, could be a stable emulsion (Table 5). In this presentation, the four components were reduced to be three substances, aqueous ethanol, biodiesel, and diesel which could be presented in ternary graphs. In preparation for blended fuels, biodiesel acted as an important substance to set a stable emulsion.

In the first step, aqueous ethanol and diesel were mixed with a specific ratio (v/v), and then biodiesel was added gradually until a stable emulsion was formed. At one ethanol concentration, the proportion of aqueous ethanol to diesel was altered, as shown in the table. The seven mL of aqueous ethanol 96 % and diesel could be dissolved entirely with 23 mL biodiesel in which composition of Aq.Et, BD, and D were 18.92%, 62.16%, and 18.92 %. The ratio changed to 7:5; the composition was recorded at 12.73%, 78.18%, and 9.09% that the biodiesel percentage increased. The volumes of aqueous ethanol and diesel at 7 and 15 mL mixed with 63 mL biodiesel resulted in compositions 8.24, 74.12, and 17.65 %.

When ethanol 95 % were employed whose water content inclined, the composition trends relatively changed since biodiesel needed to form a stable emulsion increased. The seven mL of aqueous ethanol and diesel needed 26 mL biodiesel increasing from 23 mL (ethanol 96 %). The increase of biodiesel was to balance the addition of water content in the mixture and the similar trend shown by ethanol 94%. Identical as described previously that in all ethanol concentrations, were found that the addition of biodiesel continually after a stable emulsion was formed would not separate the components.

Figure 3 displays the angular graph of Aq.Et-BD-D in a stable emulsion whereby ethanol mixed was 96 % (A) and 95 % (B). If compared with the ternary diagram of pure ethanol-biodiesel-water, the equilibrium lines of aqueous ethanol-biodiesel-diesel were very different since the presence of diesel. To know the area where the aqueous ethanol, biodiesel, and diesel in the stable emulsion were by drawing the straight lines from equilibrium points to the right (before reader) until the triangular side. The area of which the lines were passing through was that the three components formed one phase substance. The straight lines drawn to the right were the biodiesel composition increased; bioethanol was constant, but diesel decreased in which the components were kept in a stable emulsion. The equilibrium lines, as shown in the triangular graph,

could be having similar trends if using ethanol with a concentration of 94 %.

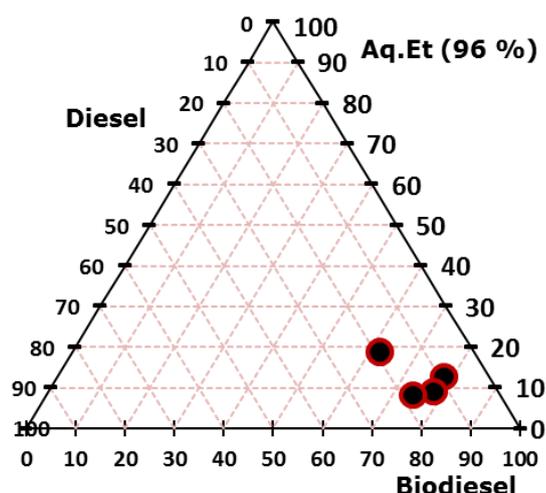


Fig. 3: The ternary system of aqueous ethanol-biodiesel-diesel in a stable emulsion whereby POME was synthesis by employing the near isochoric subcritical esterification mixture V 575 mL; P=1-15 bar for 1h; and T=30-150 °C (ethanol 96 %)

Table 5. Compositions of Aqueous ethanol (Aq.Et.), biodiesel (BD), and diesel (D) in stable emulsion using ethanol 96%

Et (%)	Volume (mL)			Composition (%)		
	Aq.Et	BD	D	Aq.Et	BD	D
96	7	23	7	18.92	62.16	18.92
96	7	43	5	12.73	78.18	9.09
96	7	60	10	9.09	77.92	12.99
96	7	63	15	8.24	74.12	17.65
95	7	26	7	17.51	65.00	17.50
95	7	44	10	11.47	72.13	16.39
95	7	62	15	8.34	73.81	17.86
95	7	67	20	7.44	71.28	21.28
94	7	30	7	15.9	68.18	15.91
94	7	49	10	10.61	74.24	15.15
94	7	71	15	7.53	76.34	16.13

3.4 Fuel Parameters

The fuel parameters such as density (ρ), specific gravity (SG), API, and cetane number (CN) were measured and analyzed, as displayed in Table 6. The density and specific gravity of the first sample (Aq.Et-BD), whereby biodiesel preparation was conducted at 7 bar, were similar at 0.84 g/cm³ (15 oC) while the rest parameters were not measurable. The density and specific gravity of the pure biodiesel were recorded at a similar figure of 0.87 g/cm³.

Meanwhile, API and CN were 29.40 and 62.50. All parameters could be measured for the mixture of aqueous fuel ethanol, biodiesel, and diesel (Aq.Et-

BD-D). When the pressure increased to 15 bar, the specific fuel parameter relatively changed. The pure biodiesel gave density 0.87, SG 0.87 g/cm³, and API 29.80, which slightly increased compared to that of 7 bar.

Similar parameters, as previously described, had been investigated by authors [31]. They found that the parameters density, SG, and API of the biodiesel and emulsion of ethanol, biodiesel, and diesel gave a comparable result with a present study. At the same time, the cetane numbers were different, which could be caused by the various standard employed [32].

Table 6. The fuel parameters density, API, and CN of the biodiesel and its blending, Aq.Et-BD (7 bar), Aq.Et-BD (15 bar), and Aq.Et-BD-D (7 bar) with ethanol concentration 96%

Sample	ρ (g/cm ³)	SG (15°C)	API (15°C)	CN
Aq.Et-BD 7 bar	0.84	0.84	-	-
BD 7 bar	0.87	0.87	29.40	62.50
Aq.Et-BD (15 bar)	0.84	0.84	35.40	-
BD (15 bar)	0.87	0.87	29.80	85.00
Aq.Et-BD-D (7 bar)	0.85	0.85	33.50	71.40

API: American Petroleum Institute gravity

Table 7. Viscosity, ASTM Color, flash point, and pour point of the blended fuels aqueous ethanol-biodiesel and aqueous ethanol-biodiesel-diesel using ethanol 96% (15 bar)

Fuels	Viscosity 40°C (mm ² /s),	ASTM Color	Flash Point (°C)	Pour Point, °C
Aq.Et-BD	3.64	D 1.0	65	2
Aq.Et-BD-D	4.29	D 3.0	56	3

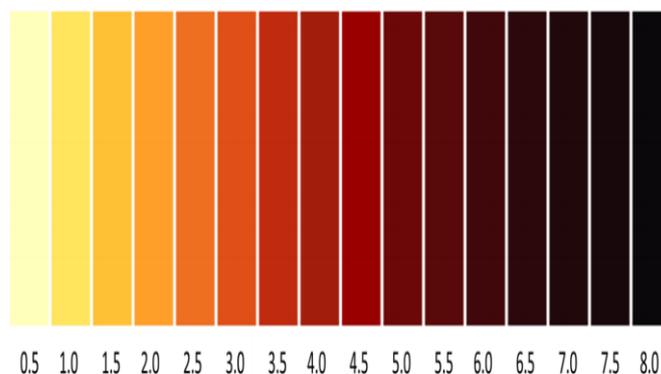


Fig. 4: The scale of the demonstrative light color of the flame appearing of the fuel-burning issued by ASTM D1500 standard

The color quantity called ASTM color of the flame of both fuels was different depending on the component contained in the fuel. The flame color of the aqueous ethanol-biodiesel was quantized at D1.0, which was dominated by yellowish. When diesel was added into the mixture to be aqueous ethanol-biodiesel-diesel, the flame color changed profoundly to D3.0, which started to change, becoming red. The quantity of flame color of the fuel was regulated by a standard issued by ASTM D1500, as shown in Fig. 4. The flashpoint of Aq.Et

was 65 oC and declined to 56 oC for Aq.Et-BD-D blends meanwhile, the pour points were recorded at 5 and 6 oC that were higher from previous reports employing diesel-ethanol blends recorded at -36 until -9oC [33]. The pure diesel and biodiesel had viscosity values around 3.11 and 4.51 mm2/s, as investigated by authors [34], which were relatively similar to the present work. If compared to that study, the flashpoints of the current work were less, which might be caused by the ethanol presence.

Table 8. The amount of fuels (aqueous ethanol-biodiesel and aqueous ethanol-biodiesel-diesel) evaporated as temperature increases (Ethanol 96%)

Sample		Test
Aq.Et-BD-D (°C)	Aq.Et-BD (°C)	
76	76	IBP
77	76	5 %
78	77	10 %

93	78	20 %
289	78	30 %
310	79	40 %
320	323	50 %
325	325	60 %
329	328	70 %
334	330	80 %
345	348	90 %
353	353	FBP
98.00	98.50	Dist. %
0.30	0.30	Res mL

FBP: Final boiling point; 10%: 10% of fuel evaporated

It is essential to measure and analyze the distillation property of the fuel, which is to know the amount of fuel evaporated concerning the temperature increase, as shown in Table 8. Two fuels boiled at a similar point 76°C of which was called the initial boiling point (IBP). The points could be belonged by the fraction of diesel fuel, which had the least boiling point. When 5 % of those fractions were evaporated, ethanol started to boil at 78 oC. The amount of ethanol for other fuel (Aq.Et-BD-D) finished evaporating first compared to the first fuel (Aq.Et-BD), which had more alcohol.

The first sample of which ethanol evaporated entirely at temperature 79°C had disappeared 40 % while the second sample evaporated a similar amount at 310°C. When the fuels had evaporated 50 %, the boiling temperatures were relatively close recorded at 432 and 322°C. The temperatures were close until the number of fuels transformed into vapor at 90 %. The final (FBP) boiling points and residues showed the same figures observed at 353°C and 0.30 mL. The results of the present study are comparable with works that used raw material coconut oil and palm oil employed the sub-critical and conventional trans-esterification [35, 36].

4 Conclusion

The palm oil methyl ester (POME) was processed successfully by employing the new technique called the near isochoric trans-esterification. The methyl ester compounds obtained were dominated by 9-Octadecenoic acid (C₁₉H₃₆O₂) and Hexadecanoic acid (C₁₇H₃₄O₂), whose composition was 40.95 and 37.42 % conducted at 15 bar for 1h which were relatively similar for 7 bar. The POME was blended with aqueous ethanol and diesel, forming stable emulsions, aqueous ethanol-biodiesel, and aqueous ethanol-diesel-biodiesel. The higher ethanol concentration employed > 96 %; the

blended fuels were clear and less of droplets. In ethanol 94-95 %, the droplets appearing in the solution increased rapidly but distributed uniformly throughout the solution. The results showed that the compositions of aqueous ethanol, diesel, and biodiesel in stable emulsions were in the range of 7.44-18.92, 9.09-21.28, and 62.16-78.18%. The fuel parameters of biodiesel and emulsions such as density, SG, API, viscosity showed a similarity with the previous works and standards.

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