ANALYSIS OF COMPOSITIONS AND FUEL SPECIFICATIONS OF THE AQUEOUS EMULSION FUELS OF GASOLINE (RON 90)-ETHANOL-WATER IN STABLE EMULSIONS AT LOW TEMPERATURES

Many countries worldwide encounter the greatest difficulties in improving people's life quality since fossil fuel reserves are decreasing, causing fuel prices to rise drastically. This problem has made many countries, including Indonesia, struggle to import them from producers in the Middle East. Adding a small part of ethanol to gasoline is one of the solutions that has been investigated and developed.

The previous works relating to blended fuels, gasoline and ethanol, generally employed absolute alcohol, which was expensive. A small surfactant was added to the mixture to stabilize the emulsion, and the blending was conducted in normal conditions (room temperature). If the composition of gasoline and aqueous ethanol is not precise, the components can be separated at a specific temperature.

The present study is aimed to report the analysis of compositions and fuel specifications of aqueous emulsions of gasoline (RON 90)-ethanol-water in a single phase without using a synthetic surfactant in the temperature range of 0–25 °C. The procedures were as follows: fermentation, ethanol distillation and purification, cooling, blending, and characterization of fuel specifications. Components of gasoline (RON 90)-ethanol-water formed a stable emulsion in the composition range of 28.00–99.79 %, 0.20–67.97 %, and 0.01–3.58 %. The observation found that continually increasing the amount of aqueous ethanol and temperature after one phase was attained would not lead to the separation of components. Therefore, gasoline and aqueous ethanol can form a single phase functioning as a surfactant binding water and fossil fuel. The decrease in temperature after the emulsion is stabilized can separate the components whereby it is caused by the faster density change of aqueous ethanol than gasoline

Keywords: gasoline, ethanol, water in one phase, fuel parameter, stable emulsion, gasoline and aqueous ethanol dissolve, conditions of gasoline and aqueous ethanol separation, single-phase, non-synthetic surfactant emulsion

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1. Introduction

People are facing the most significant problem ever since oil reserves are diminishing and the global temperature is rising [1]. The increase in air temperature, caused mainly by carbon-based gas emitted by the combustion of fossil fuels, negatively impacts global economic development. It also causes a longer dry season and more rainfall, influencing the decline in agricultural production.

Scientists strive to find new renewable energies to replace fossil fuels to overcome climate change [2–4]. Many investigations related to the study of new energy sources have been conducted for years. The new resources have the potential as primary energy in the coming years, such as biomass, wind, solar, wave, geothermal, nuclear, and emulsion fuel [5, 6]. Biomass is an optional raw material source for value-added materials, such as bioethanol, biogas, and solid fuel [7–9]. However, progress in scaling up the research of renewable energy seems slow in most countries, especially developing ones.

Even though ethanol is mainly derived from biomass, lignocellulosic and starchy materials are available abundantly, and it is challenging to move forward in an industrial stage. Lignocellulose consisting of cellulose, hemicellulose, lignin, and ash is treated before hydrolysis. Modifying the cellulose crystallinity using chemical or physical methods consumes much energy. The delignification of cellulose until it attains 100 % purity is almost impossible. The lignin content in the substrate decreases the rate of cellulose conversion to sugar. Another obstacle in the hydrolysis of cellulose to ethanol is the efficiency and price of the cellulase enzyme. Compared to amylase, cellulase's efficiency in converting cellulose to sugar is still low, and the price is high.

A descriptive explanation, as mentioned above, showed that bioethanol itself is not reliable for industrial-scale production unless mixed with conventional fuel. The production cost of bioethanol is higher compared to that of fossil ones. Ethanol is not yet feasible to be used as a fuel; it must be blended with fossil fuels, such as gasoline or diesel. Adding a small part of ethanol is just a supplement to fuels aimed at increasing the combustion rate assigned by the octane number, and it can be used in vehicles.

Many reports on blended fuels, ethanol, and fossil fuels have been published for years. Hydrous ethanol was mixed with gasoline, and their effect on combustion, including emissions, was studied. The results showed that hydrous gasohol (E10W) could run a conventional engine but NOx emissions increased [10]. Aqueous blended fuels containing 10 % and 20 % hydrous ethanol and gasoline were used and tested in the engine. The sound with hydrous ethanol and gasoline was found to be noisier than that with pure gasoline. But the measured current of aqueous fuels was comparable to pure fuel [11]. Pure 10 % ethanol blended with gasoline and diesel was successfully tested in conventional engines without modification. The experiment was conducted in normal conditions, and the observation found that the emulsion was separated into two phases since ethanol had a high affinity for absorbing water. The addition of surfactants, ETBE, and ethyl acetate aimed to resist the phase separation [12].

2. Literature review and problem statement

Bioethanol is employed to blend with gasoline forming an emulsion fuel called gasohol. Emulsion fuels, called blended fuels, have been of interest to researchers for years, as some are derived from bioresources [13]. An emulsion of 10 % ethanol and 85 % gasoline with 5 % water was applied to a single-cylinder machine. Fuel specifications, such as emission, power, and torque, were measured using computer software. Water, ethanol, and gasoline blends have been found to give promising results – low emissions and a slight increase in power and torque [14]. Testing of 60:40 gasoline-ethanol

10 %-water (E40) on the Otto engine found that NOx emissions were reduced, but fuel consumption increased compared to anhydrous blends [15]. Gasoline blended with 22 % pure ethanol (E22) and hydrous ethanol (H100) containing 4–4.9 % water was investigated, relating to HC (C2–C12) emissions in the exhaust system. The study revealed that ethanol emissions in the exhaust system using both fuels were insignificant after employing 6.0 L stainless steel canisters [16]. Although adding hydrous ethanol to gasoline could increase engine power and reduce carbon emissions, the ethanol concentrations used were not given, and the composition of components over a wide range was not presented.

A comparative study of the combustion and emission characteristics of an engine on diesel and ethanol/hydrous ethanol was conducted. It was found that less ethanol composition was feasible to apply in commercial combustion systems [17]. The study showed that the production of hydrous ethanol blended with fossil fuel, becoming emulsion substances, could be more efficient than that of absolute ethanol employing corn as a raw material. [18]. The first invention still used surfactants to strengthen the water, ethanol, and gasoline bond. 3, 6, 9, and 12 % (v/v) of ethanol 96 % were mixed with gasoline strengthened by solvent ethyl acetate forming a stable emulsion. The authors also investigated the effect of this surfactant on gasohol E5, E10, E15, and E20. The study found that the surfactant increased the phase stability of emulsions [19, 20]. The study, however, did not inform about the temperature range in the blending process and the ethanol concentrations employed were limited to 96 % and absolute ethanol.

Since the temperature on the planet's surface varies toward the location coordinate in a wide range, it is necessary to study the composition of aqueous ethanol and gasoline from 0 to 25 °C. However, as stated above, the previous reports need to mention the formation of gasoline (RON 90)-ethanol-water into a stable emulsion in a wide range of temperatures and fuel characteristics. The emulsion stability and phase separation of gasoline and ethanol at various temperatures were investigated. The increase and decrease in temperatures after a stable emulsion was formed were essential to observe.

Therefore, research on analyzing and developing aqueous ethanol and gasoline at low temperatures is relevant.

3. The aim and objectives of the study

The aim of the study is to analyze the composition and fuel specifications of gasoline (RON 90), ethanol, and water in a stable emulsion in the temperature range of 0–25 °C.

To achieve the aim, the following objectives are accomplished:

– to measure the volume of components (gasoline, pure ethanol, and water) contained in emulsions stabilized at low temperatures;

– to characterize the fuel parameters, density, specific gravity (SG), Reid vapor pressure (RVP), and research octane number (RON).

4. Materials and methods of research

4. 1. Chemical and reflux distillation used

The chemicals employed were aqueous ethanol, whose concentrations were 95–99 % and pure gasoline purchased

from the state oil company of Indonesia (PERTAMINA). The liquor with an ethanol concentration of 40 % and derived from a palm tree (*Arenga pinnata*) was purchased from a farmer. The liquor was poured in a boiler (200 L) connected to a reflux column (stainless steel model 6 in, sch 10, 304, and 3.40 mm) filled with pore packing materials with a density of 0.75–1.50 g/cm^3 and then heated until boiled. The vapor containing ethanol and water was directed to the packing materials whereby ethanol was separated with water backing to the boiler. The ethanol concentration obtained by this method was 95–96 %. Ethanol 97–99 % obtained was purified using a molecular sieve activated at high temperatures.

4. 2. Procedures

The chemicals and flasks were stored in a freezer until the temperature reached 0–25 °C. Then, all blending activities were conducted inside the freezer. Firstly, 20 mL of gasoline was poured into a flask, and aqueous 95 % ethanol was added gradually to the gasoline while stirring gently. When the mixture became bright and clear, the addition of ethanol was stopped, and similar steps were conducted for ethanol having concentrations of 97, 98, and 99 %. In this study, the volume of pure ethanol was obtained by multiplying the ethanol percentage by its volume, which was added, and the remnants were the volume of water. The composition of gasoline was obtained by dividing the gasoline volume by gasoline+aqueous ethanol volumes multiplied by 100 %. The composition of pure ethanol was determined by dividing the pure ethanol volume and gasoline+aqueous ethanol volumes multiplied by 100 %.

The use of a surfactant in emulsion fuel, as described previously, can increase the product price, which will not be competitive. The present product did not use a synthetic surfactant but rather hydrous ethanol, the price of which was much lower than that of an absolute one. Since blending was conducted over a wide range of temperatures, the fuel could be introduced into the engine in regions with high temperature alterations. The ethanol purity was assumed to be constant at any temperature, and volume reduction during mixing was ignored. Next, the two compositions, volume, and percentage (%v/v), were presented. The final step was the characterization of fuel specifications.

The characterization of fuel parameters followed the American Society for Testing and Materials (ASTM) and was carried out at the Oil and Gas Laboratory, Energy and Mineral Polytechnics, Cepu, Blora, Central Java, Indonesia. The fuel specifications measured are as follows: density, RON, RVP, and distillation assigned as RON/Research Octane Number (D2699, D2700, and D613; Kohler; New York USA), Reid vapor pressure (D323; Koehler; NY USA), and distillation (D86; Koehler; NY USA), respectively.

5. Results of analysis of compositions and fuel specifications of aqueous emulsion fuels of gasoline (RON 90)-ethanol-water in stable emulsions at low temperatures

5. 1. Compositions of gasoline, pure ethanol, and water at 0–25 °C

The study of aqueous ethanol forming a microemulsion with gasoline in a single phase was previously published [12, 21]. Table 1 shows the composition of gasoline (RON 90), pure ethanol, and water assigned as Gas, Et, and Wat in a stable emulsion vs. temperature in the range

of 0.00–25.00 °C using aqueous ethanol (Aq. Et) 95 %. The first composition is the ratio in volume, and the second is in percentage (%v/v). The gasoline volume was fixed at 20.00 mL in a flask, and aqueous ethanol was added gradually. When the mixture became clear and bright, the addition was stopped. The compositions shown in the table were an equilibrium condition in which aqueous ethanol was dissolved entirely into gasoline.

Table 1

Composition of gasoline (RON 90)-ethanol-water in a stable emulsion vs. temperature of 0.00–25.00 °C (Aq. Ethanol 95 %)

T (°C)	Volume (mL)				Composition (%v/v)		
	Gas	Aq. Et	Et	Wat	Gas	Et	Wat
0.00	20.00	50.29	47.77	2.51	28.45	67.97	3.58
2.00	20.00	47.18	44.82	2.36	29.77	66.72	3.51
2.50	20.00	46.40	44.08	2.32	30.12	66.39	3.49
3.00	20.00	45.63	43.35	2.28	30.48	66.05	3.48
5.00	20.00	42.52	40.39	2.13	31.99	64.61	3.40
8.00	20.00	37.86	35.96	1.89	34.57	62.16	3.27
10.00	20.00	34.75	33.01	1.74	36.53	60.30	3.17
12.00	20.00	31.64	30.06	1.58	38.73	58.21	3.06
15.00	20.00	26.98	25.63	1.35	42.57	54.55	2.87
18.00	20.00	22.31	21.20	1.12	47.27	50.10	2.64
20.00	20.00	19.21	18.25	0.96	51.01	46.54	2.45
23.00	20.00	14.54	13.82	0.73	57.90	40.00	2.11
25.00	20.00	11.43	10.86	0.57	63.62	34.56	1.82

50.29 mL of aqueous ethanol was dissolved with 20.00 mL of water, forming compositions of 28.45 gasoline, 67.97 ethanol, and 3.58 % water. When the temperature increased to 10 °C, the compositions of the three components changed significantly to 36.53, 60.30, and 3.17 %. The data showed that the gasoline content inclined and ethanol declined when the temperature was increased. When the temperature was increased to 25.00 °C, the gasoline, ethanol, and water compositions changed to 63.62, 34.56, and 1.82 %. The mentioned phenomenon relates to the interaction and collusion of molecules in the emulsion substance.

Fig. 1 shows a triangular graph of gasoline (RON 90)-pure ethanol-water in a stable emulsion relative to the temperatures of 0.00–25.00 °C introducing ethanol 95 %. The solid circles represent the compositions of gasoline, pure ethanol, and water in which emulsions formed in one phase. The emulsion stability was influenced significantly by both the composition and room temperature.

The trapezoidal area was where gasoline, ethanol, and water emulsions were stable. Even though the area was tiny, the number of composition combinations was infinite. Adding ethanol after a stable emulsion was formed did not change the stability. The ethanol molecules strongly bind gasoline and water, functioning as surfactants. The less ethanol was added to the mixture, the less gasoline was dissolved, forming a stable emulsion.

Table 2 presents the data on gasoline (RON 90)-pure ethanol-water compositions in a stable emulsion in the temperature range of 0.00–25.00 °C using ethanol with a purity of 97 %. The data presented in Tables 1, 2 showed that the compositions of gasoline, ethanol, and water were sensitive to temperature. Furthermore, the data revealed that the composition was influenced by the amount of water in the emulsion substance.
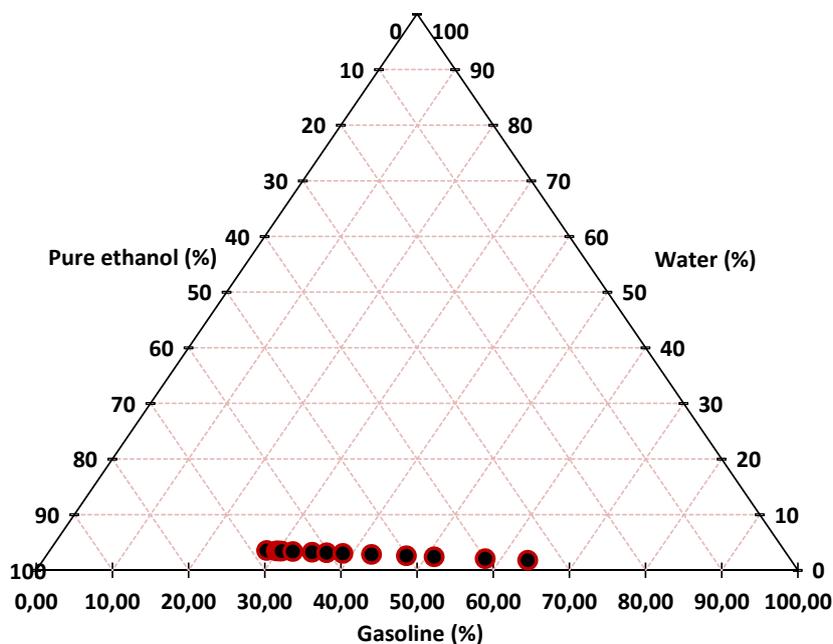
Fig. 1. Triangular graph of gasoline (RON 90)-pure ethanol-water in a stable emulsion vs. temperature of 0.00–25.00 °C (Aq. Ethanol 95 %)

Table 2

Compositions of gasoline (RON 90)-pure ethanol-water in a stable emulsion vs. temperatures of 0.00–25.00 °C (Aq. Ethanol 97 %)

T (°C)	Volume (mL)				Composition (%v/v)		
	Gas	Aq. Et	Pure et	Wat	Gas	Pure Et	Wat
0.00	20.00	16.00	15.52	0.48	55.56	43.11	1.33
2.00	20.00	15.00	14.55	0.45	57.14	41.57	1.29
4.00	20.00	13.00	12.61	0.39	60.61	38.21	1.18
4.50	20.00	12.00	11.64	0.36	62.50	36.38	1.13
5.00	20.00	11.00	10.67	0.33	64.52	34.42	1.06
6.00	20.00	10.00	9.70	0.30	66.67	32.33	1.00
7.00	20.00	9.75	9.46	0.29	67.23	31.79	0.98
6.00	20.00	9.50	9.22	0.29	67.80	31.24	0.97
8.00	20.00	9.00	8.73	0.27	68.97	30.10	0.93
16.00	20.00	8.00	7.76	0.24	71.43	27.71	0.86
18.00	20.00	5.00	4.85	0.15	80.00	19.40	0.60
20.00	20.00	4.00	3.88	0.12	83.33	16.17	0.50
22.00	20.00	2.91	2.82	0.09	87.30	12.32	0.38
24.00	20.00	1.87	1.81	0.06	91.46	8.28	0.26
25.00	20.00	0.82	0.80	0.02	96.04	3.84	0.12

When the ethanol purity increased to 97 %, which means the amount of water was decreased, the compositions of gasoline, ethanol, and water changed highly. The gasoline composition inclined significantly to 55.56 % using the ethanol purity of 97 %, in which the water content was 1.33 % at 0.00 °C. Compared to previous data, the gasoline composition was just 28.45 % using ethanol 95 %, much less than present data; meanwhile, the ethanol composition declined significantly to 43.11 %. Fig. 2 shows a triangular graph of gasoline-pure ethanol-water in a stable emulsion relative to temperatures of 0.00–25.00 °C using ethanol 97 %. Since the amount of water decreased, the trapezoidal area in which gasoline, ethanol, and water were dissolved became minor compared to that of ethanol 95 %. The area where the three components

were stable also contained an infinite number of composition combinations resulting from a single phase. The temperature change strongly altered the compositions of gasoline and ethanol, as shown in the data. The gasoline composition, for example, at 0.00 °C was 55.56 % and increased highly to 66.67 % at 6.00 °C.

Meanwhile, the ethanol composition declined significantly from 43.11 % to 32.33 % in a similar temperature change. When the temperature inclined to 20 °C, the gasoline composition continued bending to 83.33 %, while ethanol was 16.17 %. The temperature was set at 25.00 °C, which is called the common condition; the composition of gasoline changed to 96.04 % compared to that of ethanol varying to 3.84 %, which was the lowest content observed. The significant change was caused by the variation in the density of both ethanol and gasoline. The increase in temperature caused the volume of substances to be expanded, and their density decreased. Both parameters, temperature and ethanol concentration, as mentioned, influenced the formation of a stable emulsion.

The composition comparisons of gasoline, pure ethanol, and water using ethanol 95 and 97 % were different, which means that the presence of water affected the rate of stable emulsions. Previous investigators reported a similar analysis using a triangular graph employing technical ethanol [22].

Table 3 presents the compositions of gasoline (RON 90)-pure ethanol-water in a stable emulsion at a temperature of 0.00–22.00 °C and using ethanol 98 %. The water content decreased in the emulsion substance. The table shows that the composition trend of gasoline, ethanol, and water using ethanol 98 % was comparable with employing ethanol 95 (Table 1) and 97 % (Table 2). Increasing ethanol purity would improve the gasoline composition and reduce the ethanol content in a stable emulsion. Mixing three components at 0.00 °C yielded the gasoline, ethanol, and water composition at 66.67, 32.67, and 0.67 %. Compared to the previous data with an ethanol concentration of 97 %, gasoline, and pure ethanol were formed at 55.56 and 43.11 %, meaning that the gasoline composition was increased and ethanol declined.
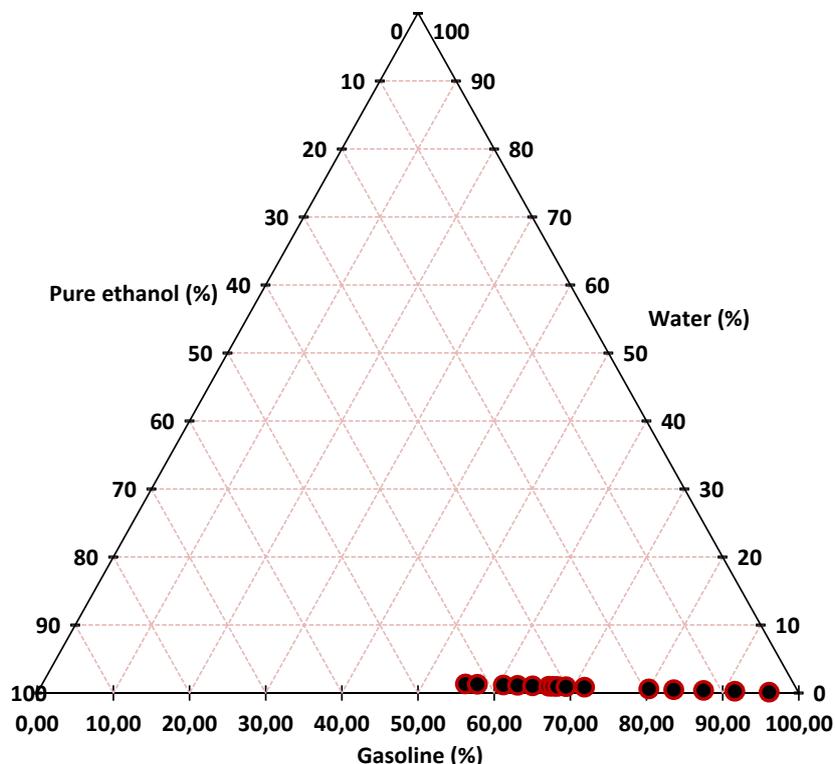
Fig. 2. Triangular graph of gasoline (RON 90)-pure ethanol-water in a stable emulsion vs. temperature of 0.00–25.00 ˚C
(Aq. Ethanol 97 %)

Table 3

Compositions of gasoline (RON 90)-pure ethanol-water in a stable emulsion vs. temperature of 0–22 ˚C (Aq. Ethanol 98 %)

T (˚C)	Volume (mL)				Composition (%v/v)		
	Gas	Aq. Et	Pure et	Wat	Gas	Et	Wat
0.00	20.00	10.00	9.80	0.20	66.67	32.67	0.67
10.00	20.00	8.00	7.84	0.16	71.43	28.00	0.57
12.50	20.00	5.00	4.90	0.10	80.00	19.60	0.40
14.70	20.00	4.00	3.92	0.08	83.33	16.33	0.33
15.00	20.00	3.00	2.94	0.06	86.96	12.78	0.26
16.50	20.00	2.75	2.70	0.06	87.91	11.85	0.24
17.00	20.00	2.50	2.45	0.05	88.89	10.89	0.22
17.00	20.00	2.45	2.40	0.05	89.09	10.69	0.22
20.00	20.00	2.00	1.96	0.04	90.91	8.91	0.18
22.00	20.00	0.59	0.58	0.01	97.12	2.82	0.06

The blending conducted at 10.00 ˚C changed the composition of gasoline and ethanol. The portion of gasoline was observed at a 71.43 % increase compared to the previous temperature. The ethanol content showed the opposite trend, recorded at 28.00 ˚C. The temperature was added two times to 20.00 ˚C, and the percentages altered to 90.91 % gasoline and 8.91 % pure ethanol, respectively. With mixing at 22.00 ˚C, the water content was recorded at 0.06 %. Meanwhile, gasoline and ethanol were dissolved completely at 97.12 and 2.82 %, the last observation.

Fig. 3 shows a linear graph of gasoline, pure ethanol, and water in a stable emulsion at a temperature of 0.00–22.00 ˚C employing ethanol 98 %. The linear graph needed to be prepared since the triangular graph analysis formed a minimal area whereby the three components were dissolved completely. The linear line represents the equilibrium state where gasoline and aqueous ethanol are mixed uniformly. The coordinates are shown: gasoline is on the horizontal line, and aqueous ethanol compositions are on the vertical line. The line describes the composition of gasoline and aqueous ethanol in a stable emulsion. It is easy to predict the mathematical relation that relates the gasoline and aqueous ethanol compositions in a large temperature range. In the triangular graph analysis, there is an area where the components mixed are in a stable emulsion. In the linear graph analysis, as long as the line shown in the figure is in a stable emulsion in which aqueous ethanol is dissolved entirely with gasoline. Compositions of gasoline, pure ethanol, and water in a stable emulsion blended at 0–20.00 ˚C employing ethanol 99 % are shown in Table 4. Since the ethanol concentration was very high, the water content was nearly zero. For the technical constraints, the blending process occurred until the temperature was 18.00 ˚C and the ethanol composition, mixed with 98.89 % gasoline, was 1.10 %. Then, the blending was conducted at 15 ˚C, the composition of gasoline was reduced to 95.24 %, and pure ethanol went up to 4.71 % in a single phase. Pure ethanol blended with 88.89 % gasoline was 11.00 % at 10.00 ˚C. The compositions of gasoline, pure ethanol, and water blended at 0.00 ˚C were 80.00, 19.80, and 0.20 %, respectively, which is observed at the lowest temperatures.

Fig. 4 presents the linear graph of gasoline, pure ethanol, and water in a stable emulsion, with temperatures varying in the range of 0.00–22.00 ˚C applying aqueous ethanol 99 %. The graph describes the compositions of gasoline, pure ethanol, and water in which those components are mixed uniformly. The straight line consists of points representing the three-component compositions whereby the sum of contents is 100 %. The number of points on the line was infinite, which meant that the compositions of gasoline, pure ethanol, and water were endless in a single-phase mixture.

Table 4

Compositions of gasoline (RON 90)-pure ethanol-water in a stable emulsion vs. temperature of 0–18 °C (Aq. Ethanol 99 %)

| T (°C)	Volume (mL)				Composition (%v/v)		
	Gas	Aq. Et	Et	Wat	Gas	Et	Wat
0.00	20.00	5.00	4.95	0.05	80.00	19.80	0.20
4.00	20.00	4.00	3.96	0.04	83.33	16.50	0.17
4.00	20.00	4.00	3.96	0.04	83.33	16.50	0.17
6.00	20.00	3.00	2.97	0.03	86.96	12.91	0.13
6.60	20.00	3.00	2.97	0.03	86.96	12.91	0.13
10.00	20.00	2.50	2.48	0.03	88.89	11.00	0.11
11.00	20.00	2.00	1.98	0.02	90.91	9.00	0.09
12.00	20.00	1.90	1.88	0.02	91.32	8.59	0.09
15.00	20.00	1.00	0.99	0.01	95.24	4,71	0,05
17.00	20.00	0.49	0.48	0.00	97.63	2.35	0.02
18.00	20.00	0.23	0.22	0.00	98.89	1.10	0.01
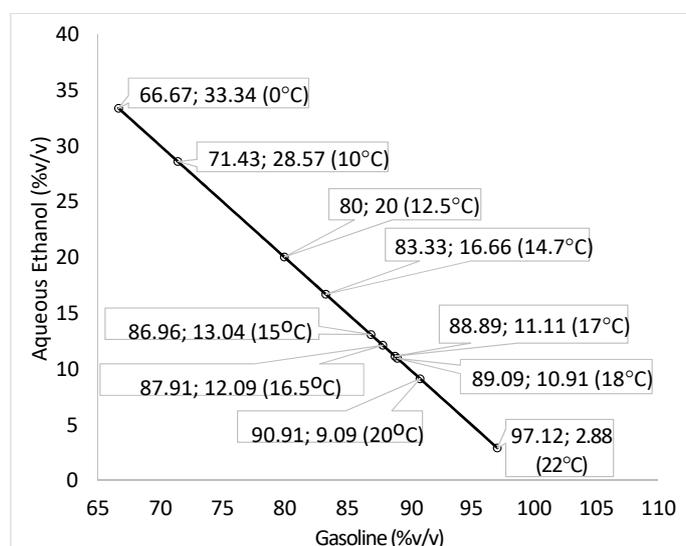
Fig. 3. Linear graph of aqueous ethanol-gasoline (RON 90) in a stable emulsion vs. temperature of 0.00–22.00 °C (Ethanol 98 %)
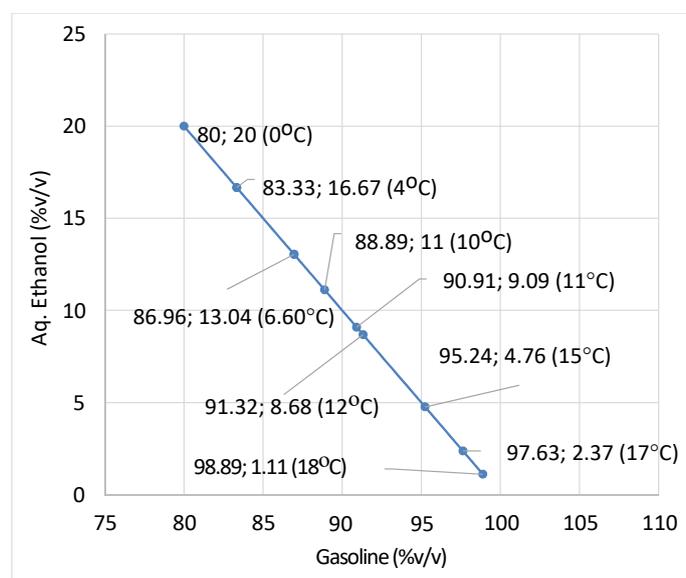

Fig. 4. Linear graph of aqueous ethanol-gasoline (RON 90) in a stable emulsion vs. temperature of 0.00–18.00 °C (Ethanol 99 %)

The critical fact found in this investigation was that adding aqueous ethanol continuously did not change the emulsion stability when a single phase was attained. The opposite is shown by the addition of gasoline (reducing ethanol); the emulsion phase occurred as aqueous ethanol and gasoline separated. The present findings were compared with the previous work published by the authors [10, 23].

5. 2. Fuel specifications

Measurements of fuel specifications were conducted at the Energy and Minerals Laboratory in Cepu City, Central Java, Indonesia, thousands of kilometers from Manado. Since the conditions were slightly different compared to those in Manado, gasoline, pure ethanol, and water compositions were calibrated. Ethanol employed was a commercial one purchased from a chemical store in Surabaya city. A slight change in temperatures and compositions compared to those obtained in Manado city was found. The blending temperatures were 13.00, 15.00, and 16.00 °C, and the ethanol purity used was 95, 97, 98, and 99 %. Meanwhile, samples E and F compositions were similar to those measured in Manado. Table 5 presents the compositions of gasoline, pure ethanol, and water employing aqueous ethanol 95, 97, 98, and 99 % for fuel specifications measurement conducted at temperatures of 13.00, 15.00, and 16.00 °C and measured in another laboratory, as mentioned previously.

Table 5

Compositions of gasoline, pure ethanol, and water employing aqueous ethanol 95, 97, 98, and 99 % and 99 % mixed at 13.00, 15.00, and 16.00 °C for fuel specifications measurement

Aq. Et (%)	T (°C)	Composition (%v/v)		
		Gas	Et	Wat
95/A	13.00	41.03	56.03	2.95
97/B	15.00	71.43	27.71	0.86
98/C	16.00	86.96	12.78	0.26
99/D	13.00	95.47	4.49	0.05
95/E	25.00	63.62	34.56	1.82
99/F	18.00	98.89	1.10	0.01

All data are very close to those obtained in the Renewable Energy lab located in Manado city. Blending ethanol 95 % at 13.00 °C, the compositions: 41.03 % gasoline, 56.03 % pure ethanol, and 2.95 % water are close to previous data. By employing ethanol 99 % at a similar temperature, the compositions of the three components were recorded at 95.47, 4.49, and 0.05 %, respectively. After conducting the composition calibration, the work analyzed the fuel specifications, such as RON value, RVP, and density, as shown in Table 6. The samples are A, B, C, and D for those employed in ethanol 95, 97, 98, and 99 %, conducted at 13.00.00, 15.00, 16.00, and 13.00 °C, respectively.

The sample assigned with A using ethanol 95 % was observed to have a density of 0.77790 g/cm³. Meanwhile, those employed 97 and 98 % blended at 15.00, and 16.00 °C had a density of 0.74928 and 0.73860 g/cm³. For ethanol 99 % mixed at 13.00 °C, the density went down to 0.73541 g/cm³, which was the most negligible value recorded in the present measurement.

Table 6

Fuel specifications of the blended fuels of gasoline, pure ethanol, and water employing aqueous ethanol 95, 97, 98, and 99 % mixed at 13.00, 15.00, 16.00, and 25.00 °C

Sample	Specifications		
	ρ (g/cm^3)	RVP (psi)	RON
A	0.77790	8.40	89.20
B	0.74928	6.50	95.00
C	0.73860	–	92.40
D	0.73541	8.00	91.10
E	0.77300	7.10	–
F	0.71600	–	–

Compared to the previous study reported, another author showed that the density of gasohol containing 90 % gasoline and 10 % ethanol was 0.75000 g/cm^3 [24]. As a result, the densities of samples E and F blended at 25.00 and 18.00 °C slightly shifted to 0.77300 and 0.71600 g/cm^3.

The previous value was comparable with the present value belonging to the samples assigned by B, C, and D, in which ethanol contents were 27.71, 12.78, and 4.49 %, respectively. While sample A had the highest value of fuels since it contained ethanol at 56.03 %, which was the most extensive alcohol composition employed in the characterization of fuel specifications. The measured densities corresponded to what was required as a specification fuel.

The Reid vapor pressure parameter, abbreviated RVP and having a pressure unit (psi), was also measured carefully, aiming to know the volatility level of the gasohol components in the burning chamber. The RPV of sample A using ethanol 95 % at 13.00 °C was 8.40 psi. When the ethanol purity was increased to 97, 98, and 99 %, the RVP changed to 6.50, 11.40, and 8.00 psi, respectively, and blending temperatures were 15.00, 16.00, and 13.00 °C.

The RVP value of sample E using ethanol 95 % and blended with gasoline at 25 °C was observed at 7.10 psi, less than for sample A employing a similar ethanol purity. It was shown that the blending temperature and composition significantly influenced the RVP value. A comparative study with the previous work published by the authors [25] presented that RVP for gasohol E10, E20, and E25 were 0.59, 0.63, and 0.65 kg/cm^2, or 8.40, 8.96, and 9.24 psi, which were close to the present study.

Another fuel specification is the Research Octane Number, abbreviated RON, defined as the fuel reference to resist during combustion in the engine without a bias knocking. The RON values obtained from the measurement were comparable with most previous works in the present investigation. The RON values of samples A to B were noted at 89.20, 95.00, 92.40, and 91.10 employing aqueous ethanol at 95, 97, 98, and 99 %, respectively. The sample assigned A, whose ethanol composition was 27.71 %, had an RON value similar to the previous report [26]. Gasohol E30, whose pure ethanol and gasoline compositions were 30 and 70 %, reported RON of 95.00.

Table 7 shows the distillation property of blended fuels of gasoline, pure ethanol, and water assigned by E and F samples employing aqueous ethanol 95 and 99 % mixed at 25 and 18 °C. The parameter describes the rate of fuel that vaporizes as the temperature increases. Three parameters are attached to the measurement of the distillation parameters, namely IBP (initial boiling point), FBP (final boiling point), and an amount of residue measured in ml.

Table 7

Distillation property of blended fuels of gasoline, pure ethanol, and water assigned by E and F samples employing aqueous ethanol 95 and 99 % mixed at 25.00 and 18.00 °C

Sample E		Sample F	
%	T (°C)	%	T (°C)
IBP	50.00	IBP	53.00
10 %	55.00	10 %	55.00
20 %	63.00	20 %	59.00
30 %	64.00	30 %	66.00
40 %	66.00	40 %	74.00
50 %	67.00	50 %	89.00
60 %	68.00	60 %	102.00
70 %	69.00	70 %	119.00
80 %	70.00	80 %	148.00
90 %	72.00	90 %	189.00
FBP (91 %)	92.00	FBP (96 %)	195.00
Residue (ml)	3.60	–	2.00

The IBP of sample E was recorded at 50.00 °C, less than that of sample F detected at 53.00 °C, whereby the difference was mainly influenced by the gasoline composition. The temperatures were constant at 55.00 °C when both fuels were vaporized and were recorded at 10 %. The sample E and F temperatures were noted at 63.00, and 59.00 °C as 20 % of fuels escaped from the mixture. Temperatures changed to 67.00, and 89.00 °C for samples E and F at 50 % of fuels disappeared from the blends and increased to 68.00 and 102.00 °C as the fuel remnant was 60 %. When temperatures of sample E were set at 69.00, 70.00, and 72.00 °C, fuels vaporized in amounts of 70, 80, and 90 %, while sample F was heated at 119.00, 148.00, and 189.00 °C. The FBP in both samples was measured at 92 and 195 °C, and the amount of fuels evaporated was observed at 91 % and 96 %.

Meanwhile, the amount of residues scaled was 3.60 and 2.00 ml, which was dominated by water and a long C-chain. On average, the temperature of sample F was higher than that of sample A for a similar amount vaporized. The gasoline composition of sample F was much higher than that of sample E. Gasoline with RON 90 contained some ingredients with a different C-chain. Sample E had an almost comparable composition of gasoline and ethanol, which highly influenced distillation properties.

6. Discussion of experimental results of the study of compositions and fuel specifications of the aqueous emulsion fuels of gasoline (RON 90)-ethanol-water in stable emulsions at low temperatures

Table 1 shows the composition of gasoline (RON 90)-ethanol-water in a stable emulsion vs. temperature of 0.00–25.00 °C applying aqueous ethanol 95 %. The data show that the compositions of gasoline, pure ethanol, and water in a single phase strongly depend on the substance temperature. The volume of aqueous ethanol added to gasoline was highly significant when the temperature decreased. The addition aimed to stabilize the emulsion after it was separated into two phases because of the temperature decrease.

The separation of components was due to the change in the physical properties of each component of the substance. The density of water and ethanol decreased as the emulsion

temperature declined and the phase separation occurred. In addition, the weight of aqueous ethanol increased, causing the bonds between nonpolar parts of ethanol and gasoline to be broken at a lower temperature.

The change in the water amount was much less than that of pure ethanol. Therefore, when the emulsion was unstable, a small amount of ethanol must be added gradually and stirred gently until the solution was mixed uniformly. The addition could be recovered from the weak interaction of gasoline and ethanol.

The areas of gasoline, pure ethanol, and water in a stable emulsion concerning the temperature at 0.00–25.00 °C are presented in the triangular graph as shown in Fig. 2, described as presented in Table 1. The figure showed that the solid circles represented gasoline, pure ethanol, and water compositions in the stable emulsion. The region where the three components were dissolved uniformly was bordered and located just below the line, which was a trapezoidal shape. Even though the area representing the stability of the substance was small, the combination of the compositions of gasoline, pure ethanol, and water was infinite.

It was discovered that adding aqueous ethanol after the emulsion was stabilized at each temperature did not change the substance stability. Furthermore, the stability of the solution did not alter though the emulsion temperature increased. The phenomena were critical in applying the blended fuels into the engine. Generally, Indonesia has temperature variations at 15.00–35.00 °C, which is rather small compared to Europe and North America. Therefore, the blending of gasoline and ethanol at 95 % should be carried out at least at the country's temperature. If mixing is conducted at average temperatures (25−30 °C), the emulsion would be separated into gasoline and aqueous ethanol at lower temperatures.

The second experiment blended gasoline, pure ethanol, and water in a stable emulsion in the temperature range of 0.00−25.00 °C, employing ethanol with a purity of 97 %, as shown in Table 2 and Fig. 3. The mechanism of blending was similar to the previous work. The data showed a significant change in the volume of aqueous ethanol added and its composition if employing ethanol 97 %.

Generally, the amount of aqueous ethanol 97 % added with gasoline forming a stable emulsion was smaller than that of 95 %. It was influenced by the water content of the emulsion and the interactive force between components of the polar parts. The higher the purity of ethanol mixed, the less the ethanol volume was added to gasoline, which affected its composition.

The main fact was that the lower the temperature set, the more aqueous ethanol was added to the mixture forming a stable emulsion. The findings gave valuable information on how to maintain the stability of emulsion fuels in a wide range of temperatures. The analysis of the emulsion stability employing ethanol at 97 % was relatively similar, concerning 95 %.

The gasoline composition changed from 96.04 % at 25.00 °C to 55.56 % at 0.00 °C using ethanol 97 %. It was higher than ethanol at 95 %, recorded at 63.62–28.45 %. Meanwhile, the composition of pure ethanol assigned by Et ranged from 3.84–43.11 % using ethanol 97 %, less than that of employing ethanol 95 % noted at 34.56–67.97 %. The data presented that the compositions of gasoline and ethanol changed significantly when the alcohol purity was altered.

The use of 95 % and 97 % ethanol could need a modification of the engine, especially the combustion system. To keep the emulsion stable, blending should be held at 0.00 °C for Indonesia. As observed from the data, the ethanol compositions were more than 50 %, which could not be used on a conventional engine. On the other hand, the composition of ethanol, blended with gasoline at 25.00 °C, could be applied on a traditional engine, as it was just 3.84 %.

The area is a triangular graph where the three components were dissolved uniformly and were narrowed by applying ethanol 97 %. The trapezoidal area was close to the line, which was the component of gasoline, as presented in Fig. 3. It was caused by the ethanol composition mixed entirely into gasoline getting small, especially at room temperature compared to that of ethanol 95 %. The point at the left side before the reader was the position describing the compositions of the three components blended at 0.00 °C, while the right side was which was mixed at 25.00 °C. Though the area was narrower, the composition combinations forming stable substances were infinite, similar to the previous ones. The facts found that the addition of ethanol and the temperature increase after the stability is met did not result in a phase separation compared to that of ethanol 95 %.

The triangular graph could not be presented since the coordinates describing the compositions almost meet with the line of gasoline compositions; instead, 2D was used to plot the composition of aqueous ethanol concerning gasoline for ethanol 98 and 99 %, as shown in Fig. 4, 5. The use of ethanol 98 and 99 % highly decreased the minimum composition of ethanol added with gasoline forming the emulsion fuel as presented in Tables 3, 4.

The high purity of alcohol (98 and 99 %) needed a tiny amount of ethanol to be mixed with gasoline forming a single-phase solution. On the other hand, the amount of gasoline added increased significantly. The water content is influenced mainly by the minimum amount of ethanol dissolved entirely in gasoline. Ethanol mixed, however, at lower temperatures inclined in which the trend was relatively similar to that of employing low-purity ethanol.

Compared to previous data, the ethanol composition at 25.00 °C using 98 and 99 % was low enough and could be applied in a conventional engine. The problem was the phase separation at lower temperatures unless the blending process was conducted at a lower temperature. As mentioned, phase separation could be avoided by mixing fuels at the least temperature in the region. However, the ethanol amount must be higher than that of blended at 25.00 °C so that the engine is modified.

The formations of a single phase of gasoline, pure ethanol, and water were interesting to be investigated. The blending of those components did not involve other solvents or synthetic surfactants. Generally, the surfactant material is needed to bind the polar- and nonpolar substances, whereby both are dissolved entirely. We focused on the presence of ethanol and its characteristics. The ethanol molecule with the chemical formula C_2H_5OH consists of nonpolar (-C-C-) and polar sections (-OH). It is well known that ethanol binds strongly with water due to electrical interactions of the polar parts. When gasoline, whose chemical formula is dominated by C_8H_{18}, was mixed with aqueous ethanol, the exchange was fragile, as it had no polar branch. As a polar substance, gasoline interacts with -C-C- parts of ethanol to be dissolved uniformly. Aqueous ethanol, whose water is bound electrically, leads to the blending of gasoline, pure ethanol, and water in the exact composition, forming a stable emulsion. The works reported previously, which had a comparable re-

sult, explained that hydrous ethanol could be dissolved into gasoline for many compositions [23].

The present study offers a new technology to blend mixed fuels, aqueous ethanol, and gasoline without employing a synthetic surfactant in a wide range of temperatures. As a result, the stability of emulsions can be set by the component's composition and temperature. Compared to the existing technology in blending emulsion fuels, it generally employs many synthetic surfactants and absolute ethanol, and mixing is carried out at room temperature.

The proposed technology has limitations in terms of emulsion stability. In emulsions, phase separation would occur if the temperature is decreased. To restore the stability of the emulsion, it is necessary to raise the temperature to the initial one or add some aqueous ethanol. Therefore, installing an electronic device connected to the fuel tank to control the temperature and eliminate the disadvantages is necessary.

The characterization of fuel parameters used in the sample is presented in Table 5. The slight shifts of fuel compositions were calibrated in a laboratory held in other areas where the conditions differed. The fuel parameters measured are as follows: density (ρ), Reid vapor pressure (RVP), research octane number (RON), and distillation properties, as shown in Tables 6, 7.

Density is the crucial parameter of fuels describing the product density or weight per volume. The higher the fuel density, the higher the product's inside volume. On average, the density of conventional fossil fuels, diesel and gasoline is 0.755 and 0.800 g/cc, respectively. The density of emulsion fuel containing ethanol 95 % blended at 13.00 °C was 0.77790 g/cc, which was higher than at 25.00 °C. It is shown that the density of the emulsion mixed at lower temperatures was more significant than at higher temperatures. The density of emulsions blended at two temperatures employing ethanol 95 % (samples A and E) was significantly higher than that of conventional fuels. The water content and temperature strongly influenced the increase in emulsion density.

In the emulsion blended at 15.00 °C and containing ethanol 97 % (sample B), the density declined to 0.74928 g/cc, almost similar to pure gasoline but less than in previous samples. The decrease in water content or increase in ethanol purity caused a decline in emulsion density. The trend was comparable to samples C, D, and F, with 98 and 99 % ethanol purity.

The RVP was the important parameter of fuel describing its volatility level at a temperature of 37.80 °C. It means that the higher the RVP of the emulsion, the more volatile the fuel is. For example, the emulsion containing ethanol 95 % blended with gasoline at 13.00 °C is more extensive than at 25.00 °C. This is caused by the ethanol composition mixed at a lower temperature. However, for ethanol 98 % blended with gasoline at a temperature of 16.00 °C, the volatility level could not be detected. Generally, the RVP of pure ethanol was observed at 9.00–9.50 psi, depending on fuel type. The data showed that adding a small part of ethanol decreased the volatility of the emulsion, as shown in the table.

The other parameter indicating the fuel quality is Research Octane Number assigned by RON. The fossil fuel employed in the present study was gasoline, whose RON value was 90, locally called *pertalite*. The addition of ethanol generally inclined the RON value of emulsion fuels recorded as 91.10, 92.40, and 95.00. However, the RON value of gasoline added with ethanol 95 % at 13.00 °C declined to 89.20, which could be caused by either the high ethanol composition or a measurement error.

The fractions containing the fuel are measured by a distillation method, which results in a parameter called the distillation property, as presented in Table 7. The distillation properties of samples E and F were investigated, whereby they had remarkable differences in the compositions of the components. Sample F was dominated by gasoline since the emulsion consisted of ethanol 99 %, while sample E had high ethanol but below 50 %.

Generally, the boiling points of sample F are higher compared to that of sample E, but in the initial boiling points, the amount of the fuels evaporated was 10 and 20 %. After those temperatures, sample F boiling points increased more rapidly, which meant that the fractions of gasoline had a higher boiling point than ethanol. This is because the components contained in gasoline, whose RON value is 90, are substances with higher boiling points than ethanol.

The present study explains that aqueous ethanol, with 95–99 % concentrations, can be dissolved in gasoline in an exact composition in a wide range of temperatures, which is yet investigated previously. The application of this fuel is challenging, as it has high ethanol content, especially at low temperatures. The engine is needed to be modified to use this new fuel and blending should be conducted at the least temperature of the country for phase separation to occur. The study conducted by the authors showed that ethanol 80–90 % could be blended forming a stable emulsion at room temperatures (25.00–30.00 °C). The next work would investigate the stability of ethanol mixed with gasoline at low temperatures. The advantage of the proposed fuels is that the preparation of aqueous ethanol is not complicated compared to that of absolute ethanol. The production of low-purity ethanol can be carried out by the home industry being run by a farmer and the price is much lower than for absolute alcohol.

7. Conclusions

1. It was found that the compositions of gasoline (RON 90)-ethanol-water formed a stable emulsion in the range of 28.00–99.79 %, 0.20–67.97 %, and 0.01–3.58 % at low temperatures.

2. The fuel parameters measured were different from that of pure gasoline. The presence of aqueous ethanol in the emulsion strongly influenced the fuel parameters. The densities and RVP of the emulsion blended at low temperatures ranged from 0.71600–0.77790 g/cm^3 and 6.50–8.40 psi. The IBP of gasoline blended with ethanol 95 and 99 % was 50.00 and 53.00 °C, while the FBP was recorded at 92.00 and 195.00 °C, respectively.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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