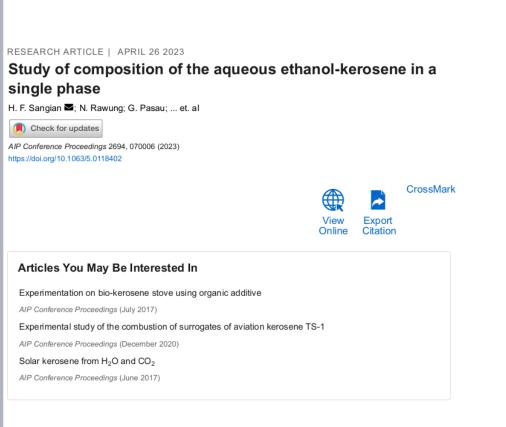
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Study of Composition of The Aqueous Ethanol-Kerosene in A Single Phase

H F Sangian^{1,a)}, N Rawung¹, G Pasau¹, Gerald Tamuntuan¹, S H Tongkukut¹, A
As'ari¹, M D Bobanto¹, D P Pandara¹, A Tanauma¹, F Ferdy, H S Kolibu¹, V A
Suoth¹, F S Sagai¹, C Wuwungan¹, H I R Mosey¹, Messiah C Sangian², R
Purwadi³, Z Zulnazri⁴, A Tuhuloula⁵, R Thahir⁶, T Sriana⁷, Z Furqon⁷, S Y
Agnesty⁷, Tri Dianpalupidewi⁷, Arif Nurrahman⁷, Hans F Wowor², Arief Widjaja⁸

¹Department of Physics, Faculty of Mathematics and Science, Sam Ratulangi University, 95115 Manado, Indonesia
 ²Department of Electrical Engineering, Sam Ratulangi University, Manado, Indonesia
 ³Department of Chemical Engineering, Institut Teknologi Bandung, 40132, Bandung, Indonesia
 ⁴Department of Chemical Engineering, Malikussaleh University, 24351, Lhokseumawe, Indonesia
 ⁵Department of Chemical Engineering, Lambung Mangkurat University, 70714 Banjarbaru, Indonesia
 ⁶Department of Chemical Engineering, Politeknik Negeri Samarinda, 75136 Samarinda, Indonesia

⁷Department of Oil and Gas Processing Engineering, Polytechnic of Energy and Minerals, 58315 Cepu Blora, Indonesia

⁸Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, 60111, Surabaya, Indonesia

^{a)} Corresponding author: hannysangian@yahoo.co.id

Abstract. Herein, a brief report of some new blended fuels, one-phase aqueous kerosene-alcohol mixtures, and their compositions is conducted. The procedures of the work were the preparation of ethanol, the separation of kerosene components employing a simple distillation, and the blending process. It was obtained that aqueous ethanol with concentrations of 94 - 98 % could be blended with kerosene to form a single phase. Before mixing, kerosene should be treated or separated thermally based on the boiling temperatures of the component. The process for blending the kerosene and ethanol is described. The compositions of the kerosene and aqueous ethanol blends are presented in the form of tables and triangular graphs. It was measured that the composition of kerosene, pure ethanol, and water in a stable emulsion was 1:4.68:0.19 (in V) in which kerosene was separated at temperature 192 – 198 °C and purity ethanol was 95 % compared to that 1:1.52:0.05 for ethanol 98 % with similar temperature range and the rest of compositions of different temperature range and ethanol concentrations are presented. By adding aqueous ethanol after a stable emulsion was reached, it did not occur a phase separation. Ethanol could be acting as a surfactant that bound the kerosene forming a single phase.

INTRODUCTION

The utilization of renewable resources has recently been receiving attention from investigators [1, 2]. The world is facing an energy crisis, with the depletion of fossil-based fuel resources affecting the global economic turmoil. On the other hand, fossil fuels contribute to an increase in pollutants, especially carbon dioxide, which influences the global climate [3, 4].

Many scientists have proposed ways to overcome the energy crisis and global warming by developing bioenergy [5, 6]. The efficiencies of heat engines using fuel to generate energy can be increased by modifying the internal combustion system [7]. The hybrid engines use both fossil fuel and electrical energy, the latter being obtained from a renewable source. The replacement of fossil fuel with a renewable source of energy (ethanol) to form a blended substance is optional but very important to decrease the carbon dioxide emission.

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Since the use of renewable energy became compulsory, the bioenergy scenario for a sustainable supply has recently been investigated [8]. Blended fuels, which consist of fossil-based and alcohol fuels, have been examined in recent years. The method and operation of the use of a blended fuel of gasoline and ethanol in the internal-combustion engines operating in cold temperatures have been described by authors [9]. The study found that the gasoline blended with 20 and 30 % ethanol (E20, E30) could decline the CO emission significantly.

It had previously been reported that the addition of alcohol to diesel-fuelled to improved combustion performance and a significant decrease in NOx emission. Moreover, it was found that the introduction of ethanol into methyl esters (biodiesel), wherein trans-esterification was performed in the supercritical region without the use of a catalyst, increased the vapor pressure of the blended fuel [10].

The effect of a higher proportion of ethanol, E85, on the starting performance in cold weather has been studied. The investigation showed that with the blended E85, the failure to start was caused by the reduced amount of vapor. The study determined that the use of E85 was difficult in conventional engines unless the compression, pressure, and concentration of the fuel mixture were adjusted [11]. The characterization and feasibility of a palm-oil-based biodiesel fuel were investigated with blend ratios up to 30 %. The study found that a biodiesel 30 % blend could be used in an unmodified engine, but the heat generated was reduced by 1.42 % when the biodiesel proportion was increased to 10 % [12].

The feasibility of biodiesel fuels has been studied and reported over the years since they became compulsory, before a scale-up. The technology requirements and raw material availability for biofuel production, and engine performance, are the factors that influence the product's feasibility. The lubricity, corrosion, combustion, power, and emissions were analyzed in assessing the feasibility. The study showed that biodiesel increased lubricity and corrosion but decreased NOx emission [13].

In an investigation into the technical possibility of a blend of alcohol (butanol) and gasoline, the combustion performance, pollution, ignition, and engine efficiency of the fuel were evaluated. It was found that the engine performance using the butanol-gasoline blend was similar to that of using gasoline [14]. A feasibility study of dieselbiodiesel-ethanol mixtures used in unmodified compression ignition (CI) engines showed that the main problem was the separation and instability of ethanol and diesel that occurred at low temperatures [15].

The addition of 25 % biodiesel and 5 % ethanol to diesel fuel has been shown to lead to improvement. The combustion characteristics of an ethanol-kerosene blend were studied and compared with those of kerosene. The wall and exit emission temperatures were found to be reduced, and the brightness and carbon dioxide produced were also decreased compared with those of kerosene [16]. A machine performance prediction for a diesel–kerosene–ethanol blend, using a fuzzy-based optimization technique showed that the fuel parameters, such as the thermal brake efficiency, brake specific energy consumption, and the emission of oxides of nitrogen, total hydrocarbon, and carbon monoxide from the engine, were all expected to be significantly increased [17].

The previous works were not yet exploring the mixture between aqueous ethanol and kerosene in a wide range of compositions. The alcohol employed, however, was pure ethanol (anhydrous alcohol), which is expensive and difficult to prepare. As a consequence, attempts to scale up the use of aqueous ethanol blended with fossil-based fuels have presented a significant challenge in many countries like Indonesia. These earlier studies showed that the use of anhydrous ethanol was not feasible on an industrial scale. The present study is aimed at reporting the composition of a stable emulsion whereby kerosene was blended with aqueous ethanol concentration 93 - 98 %. The ethanol used in our work was prepared from *Arenga pinnata* sap that was yeasted naturally and had an alcohol content of about 7 % (V/V).

MATERIALS AND METHODS

Chemicals

The ethanol can be prepared easily by starting with biomass such as corn, sugarcane, cassava, or rice. Cellulosebased biomass, however, has also interested scientists recently as an ethanol raw material [18, 19]. The present study was employed ethanol purified from the yeasted Arenga pinnata sap applying a reflux distillation and adapted the previous report [20]. While. Ethanol 97-98% were obtained from the molecular sieve technique employing an activated lime, and the commercial kerosene was purchased from the market.

Kerosene treatment

Fossil fuels, except for gasoline, are very difficult to blend with aqueous ethanol to produce a one-phase solution since the carbon chains in kerosene and diesel fuels are much longer than that in ethanol, which has only two carbon atoms. The kerosene must first be conditioned in its properties, especially by separating its components based on the length of the carbon chain, using a distillation method.

As much as 1.5 L of kerosene was poured into a reactor with volume 2 L, and the reactor temperature was increased to 192 °C so that the kerosene was just boiling. The separation was divided into 12 ranges of temperature (in °C): 192-198, 198-204, 208-210, 214-216, 218-222, 224-228, 230-234, 236-242, 244-250, 252-258, 262-270, and 272-276.

The boiler was connected to a simple distillation apparatus equipped with a condenser, whereby the gas phase of the kerosene was transformed into a liquid. A sample of distillate was taken periodically in each temperature segment, as previously explained. The kerosene was collected and kept in an isolation bottle before being blended with aqueous ethanol. (In an industrial-scale process, the kerosene should be obtained from a refinery to reduce the preparation cost.)

The distillation was stopped at 276 °C, since above this temperature; kerosene was found not to form a one-phase solution with aqueous ethanol. The cracking of 1.5 L kerosene using a simple distillation apparatus and stove (capacity 3 kg) consumed around 0.05 kg of gas within 60 min. The distillation process was straightforward and occurred very fast, especially below 250 °C. It was found that the more the temperature was increased, the more separation time and gas were required. The amount of separated kerosene taken periodically was 150 mL in each different range of time. In the first range, cracking took just 1 to 5 min, but the time then increased linearly as the temperature went up.

Blending

The method of blending kerosene and aqueous ethanol was straightforward and did not require complicated technology. In this study, the aqueous ethanol used had various concentrations, namely 98, 97, 96, 95, 94, and 93 %. Initially, 7 mL kerosene was placed in a flask, and aqueous ethanol was then mixed in gradually with gentle shaking until it dissolved completely.

TABLE 1. Compositions of blended fuels (kerosene, pure ethanol, and water) in the one-phase solution obtained using ethanol
concentrations of (a) 98 $\%$ and (b) 97 $\%$ under distillation temperatures 192-276 $^{\circ}$ C

	(;	a)			-	(b)	
Temp. [°C]	Compositions [in V]			Temp.	Compositions [in V]		
	Kero	Pure Ethanol	H ₂ O	[°C]	Kero	Pure Ethanol	H_2O
192-198	1	1.52	0.05	192-198	1	2.10	0.04
198-204	1	1.94	0.06	198-204	1	2.38	0.05
208-210	1	2.22	0.07	208-210	1	2.52	0.05
214-216	1	2.63	0.08	214-216	1	2.80	0.06
218-222	1	2.77	0.09	218-222	1	2.94	0.06
224-228	1	3.19	0.10	224-228	1	3.22	0.07
230-234	1	3.46	0.11	230-234	1	3.36	0.07
236-242	1	3.74	0.12	236-242	1	3.64	0.07
244-250	1	4.02	0.12	244-250	1	3.92	0.08
252-258	1	4.43	0.14	252-258	1	4.2	0.09
262-270	1	4.99	0.15	262-270	1	4.48	0.09
272-276	1	5.54	0.17	272-276	-	-	-

The phase existence has been observed by seeing for months. The volume of pure ethanol was determined by multiplying its purity by its total capacity, the remainder being the water content, and the compositions are the ratio (in V) of kerosene, pure ethanol, and water.

The composition in the triangular graph was defined as component volume per total volume, multiplied by 100 %. When the concentration of ethanol was decreased to 94, and 93 %, the proportions of the three substances were changed significantly. The ethanol was added to kerosene in a procedure similar to that previously described.

RESULTS AND DISCUSSION

Tables 1a and 1b show the volume ratios, in the blended fuels, of kerosene, pure ethanol, and water in a stable emulsion (one-phase solution), employing ethanol with concentrations of 97 and 98 % and separation temperatures in the range 192-276 °C. At all the separation temperatures, the proportions of kerosene, pure ethanol, and water were similar, as shown in the table for both 97 and 98 % ethanol. At a separation temperature of 192-198 °C, the relative volumes (mL) of kerosene, pure ethanol, and-water in one phase were, respectively, 1, 1.52, and 0.05 for 98 % ethanol and 1, 2.1, and 0.04 for 97 % ethanol.

TABLE 2. Compositions of blended fuels (kerosene, pure ethanol, and water) in the one-phase solution obtained using ethanol concentrations of (a) 96 % and (b) 95 % under distillation temperatures of 192-276 °C

	(a))				b)	
Temp.	Compositions [in V]			Temp.	Compositions [in V]		
[°C]	Kero	Pure Ethanol	H ₂ O	[°C]	Kero	Pure Ethanol	H ₂ O
192-198	1	3.28	0.17	192-198	1	4.68	0.19
198-204	1	4.54	0.24	198-204	1	5.48	0.23
208-210	1	4.75	0.25	208-210	1	5.62	0.23
214-216	1	4.84	0.25	214-216	1	5.76	0.24
218-222	1	5.56	0.29	218-222	1	5.90	0.24
224-228	1	6.06	0.32	224-228	1	6.4	0.27
230-234	1	7.87	0.41	230-234	1	6.56	0.27
236-242	1	8.55	0.45	236-242	1	6.03	0.25
244-250	1	10.04	0.53	244-250	1	6.17	0.26
252-258	1	11.40	0.60	252-258	1	6.44	0.27
262-270	1	11.52	0.61	262-270	1	7.13	0.30
272-276	1	12.35	0.65	272-276	1	7.68	0.32

It was found that the higher the separation temperature, the higher the ethanol content that blended, but the water content was relatively constant. Table 2 shows the compositions of kerosene, ethanol, and water in the one-phase solution using ethanol of concentration 96 (a) and 95 % (b) conducted at 192-276 °C.

The first eleven milliliters of kerosene at 192-198 °C was poured into a tube, and then ethanol 95, or 96 %, was added gradually. When the substance was observed to be almost thoroughly mixed, the tube was shaken gently by hand. It was found that the volume of 96 % ethanol needed to be utterly liquefied with kerosene was 38 mL (consisting of pure ethanol 36.1 and water 1.9 mL). By dividing by 11, the volume ratios of kerosene, absolute ethanol, and water are seen to be 1:3.28:0.17, while for ethanol 95 %, the proportions were 1:4.68:0.20. If kerosene at a higher temperature was used, the balances with 95 and 96 % ethanol increased, as shown in the table.

Table 3 shows the ratios of fuel components distilled kerosene, pure ethanol, and water in the one-phase solution, using ethanol with concentrations of 93 % and 94 %, and temperature ranges between 192 and 276 °C. The same trend was also observed using ethanol with a concentration of 93 %, as shown in Table 3a, in which the boiler temperature was similar. The first row shows that the proportions of kerosene separated at the first range of temperature, pure ethanol, and water were in the ratio 1:7.31:0.55. It was found that for ethanol 94 %, the proportions of kerosene distilled at 192-198 °C, pure ethanol, and water were 1:6.18:0.39 (Table 3b).

The content of absolute ethanol increased to 6.18 compared to 3.28 (V/V) shown in the data recorded for ethanol 95 %. The kerosene separated at 198-204 °C mixed ultimately with pure ethanol and water in a ratio of 1:6.44:0.41, which was comparable to the previous experiment with a similar concentration of ethanol. The higher the distillation temperature, the more ethanol was needed to mix with kerosene to produce a blended fuel, as displayed in all data.

With aqueous ethanol and kerosene distilled above 252 °C, dissolution was no longer observed. It could because the carbon chain was not long enough for interaction with ethanol, with its short carbon chain, to occur. The critical finding is that as the amount of ethanol decreased, the kerosene and aqueous ethanol eventually separated into two phases. In contrast, if sufficient ethanol was present, the mixture remained in a single phase. As the blending process was carried out using only a manual procedure, the practical utility was not calculated.

	()	a)		(b)				
T	Compositions [in V]			Town	Compositions [in V]			
Temp. [°C]	Kero	Pure Ethanol	H ₂ O	Temp. [ºC]	Kero	Pure Ethanol	H ₂ O	
192-198	1	7.31	0.55	192-198	1	6.18	0.39	
198-204	1	7.57	0.57	198-204	1	6.44	0.41	
208-210	1	7.97	0.6	208-210	1	7.12	0.45	
214-216	1	8.37	0.63	214-216	1	7.25	0.46	
218-222	1	8.63	0.65	218-222	1	7.38	0.47	
224-228	1	8.90	0.67	224-228	1	7.65	0.49	
230-234	1	9.30	0.7	230-234	1	7.92	0.50	
236-242	1	9.43	0.71	236-242	1	8.19	0.52	
244-250	1	9.56	0.72	244-250	1	8.59	0.55	
252-258	-	-	-	252-258	1	9.13	0.58	
262-270	-	-	-	262-270	1	9.67	0.62	
272-276	-	-	-	272-276	1	10.88	0.69	

 TABLE 3. Compositions of blended fuels (kerosene, pure ethanol, and water) in the one-phase solution using ethanol concentrations 93 % (a) and 94 % (b) and distillation temperatures 192-276 °C

On an industrial scale, this mechanism uses low electrical energy and almost zero waste because it does not employ fresh water. The blended fuel prepared in this investigation has the potential to be developed into fuel for a modified jet engine. The emulsion fuel previously reported required absolute ethanol, which is expensive and difficult to extract from liquor. An aqueous emulsion fuel is optimal for future jet fuel technology, as its price is much lower than that of an anhydrous one.

Figure 1 presents the requirements for stable one-phase solutions of the fuels, drawn as triangular graphs of the kerosene-pure ethanol-water proportions, for ethanol of concentrations 94 (A), 95 (B), 96 (C), 97 (D), and 98 % (E). Compositions were transformed into percentages (%) by dividing volume each component by the total volume of all components and multiplying by 100 %. With the ethanol having a purity of 93-98 %, the points representing the proportions of kerosene, pure ethanol, and water almost overlap. As described previously, ethanol 93 % was the minimum purity at which aqueous ethanol and kerosene mixed thoroughly. The solid area marked in black is the region in which the blended fuel is a one-phase solution. The points were separated slightly when the ethanol purity was increased to 97 and 98 %, but the area on the right side becomes narrower.

Though the regions in which the three components are dissolved completely are narrow for all triangular graphs, there is an infinite number of combinations of kerosene, pure ethanol, and water forming one phase. When kerosene or water was added, aqueous ethanol and kerosene would become separated. If the three components were mixed perfectly, the addition of ethanol did not change the one-phase state, as shown in Fig. 2a and 2b.

The dissolution of the cracked kerosene into aqueous ethanol in a single phase can be explained with the surfactant theory. The ethanol molecule consisted of two parts, polar- and non-polar sections represented by -OH and -R. The first section (-OH) interacted with -H and -OH sections of water molecule. Meanwhile, the -R section of ethanol interacted weakly with a kerosene molecule which had a long carbon chain. The electrical interaction between kerosene and aqueous ethanol was easy broken by changing of composition as described previously.

The -R number of ethanol should be comparative with kerosene molecules in order to the bonds would not be broken. According to the figure revealed that the composition of pure ethanol was higher than kerosene. The single phase attained when some -R of ethanol interacted with a single kerosene molecule. The increase of kerosene composition caused the -R sections were not enough to bind the long carbon chain resulting a phase separation.

The increase of ethanol composition effected the kerosene bound and trapped perfectly inside aqueous ethanol but phase was separated when water composition was added. When the ethanol purity decreased the gravity interaction would be more dominant compared to the electrical one in which the components were separated, aqueous ethanol and kerosene.

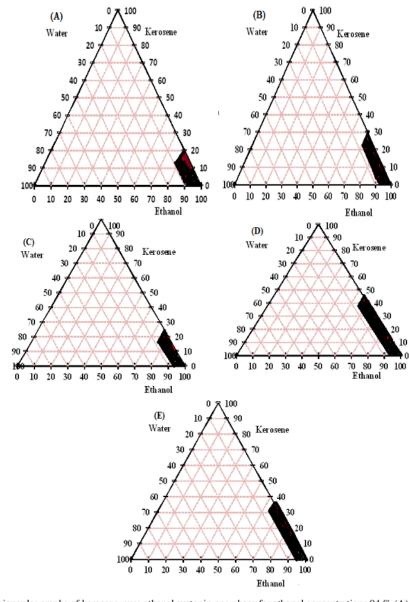


FIGURE 1. Triangular graphs of kerosene-pure ethanol-water in one phase for ethanol concentrations 94 % (A), 95 % (B), 96 % (C), 97 % (D), and 98 % (E) with separation temperatures 192-276 °C

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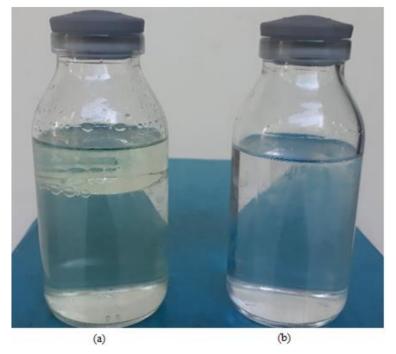


FIGURE 2. The aqueous ethanol and kerosene in two phases (a) and one phase (b)

The separation was started with appearing of droplets which were distributed uniformly throughout the mixture. The droplets appeared clear when ethanol purities were at 93, 94 and 95% but disappeared in higher concentrations, 96-98%. The contents of droplet could be consisting of the aqueous ethanol, or pure water that it was still under investigating.

CONCLUSIONS

Aqueous emulsion fuels composed of kerosene, ethanol, and water in one phase were blended successfully for ethanol concentrations 93 - 98 %. Before blending, the kerosene component was cracked or separated based on boiling temperature using simple distillation. It was found that ethanol, kerosene, and water could be forming a single phase in a specific composition. Generally, the more ethanol concentration was used, the less kerosene was needed to create a stable emulsion. When the stable emulsion was obtained, adding aqueous ethanol continually into solution was not occurred a phase separation. The compositions of kerosene, ethanol, and water were attained at 1:3.28:0.17 and 1:4.68:0.19 employing ethanol 96 and 95%, which distillation temperature of kerosene was held at 192 – 198°C.

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