

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



CrossMark

Determination of the Compositions of Gasoline, Aqueous Ethanol, and Butanol, in Stable Emulsions at Low Temperatures

Hanny F. Sangian^{a,*}, Letia R. Benaino^a, Guntur Pasau^a, Messiah C. Sangian^b, Henry F. Aritonang^c, Silvya Yusnica Agnesty^d, Tun Sriana^d, Arief Widjaja^e, Bayu Achil Sadjab^f, Tri Oldy Rotinsulu^g

^aDepartment of Physics, Sam Ratulangi University, Manado, 95115 Indonesia

^b Department of Physics, Institut Teknologi Bandung, Bandung 40132, Indonesia

^c Department of Chemistry, Sam Ratulangi University, Manado, 95115 Indonesia

^d Department of Oil and Gas Processing, Energy and Minerals Polytechnics, Cepu Blora, 58315, Indonesia

e Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya, Indonesia

^f Department of Physics, Halmahera University, Wari, 97762, Indonesia

g Department of Economic Development, Sam Ratulangi University, 95115, Indonesia

Abstract

This study aims to identify and examine the compositions of stable emulsions of gasoline (RON 90), aqueous ethanol, and butanol at low temperatures to improve fuel stability in cold environments. The blending process involved combining gasoline and ethanol in different ratios, followed by the gradual addition of butanol to stabilize the emulsion without using synthetic surfactants. Emulsion stability was evaluated by varying the temperature from 29.0°C to -17.0°C and observing phase separation. The analysis was centered on the volumetric composition and stability of the emulsions over time and across different temperatures. The compositions were documented and the changes in stability were analyzed to understand the effects of temperature and component ratios. The results indicated that at lower temperatures, the volume percentages of gasoline and ethanol in the emulsion decreased, while the percentage of butanol increased. At -17.0°C, the emulsion composition was 33.68% gasoline, 18.13% aqueous ethanol, and 48.19% butanol, highlighting butanol's key role in maintaining stability at low temperatures. These findings suggest that stable emulsions of gasoline, ethanol, and butanol can be achieved at low temperatures, potentially enhancing the performance and reliability of biofuel blends in cold climates. This could contribute to the development of more efficient and environmentally friendly fuel options for automotive and other combustion engines.

Keywords: aqueous ethanol, butanol, emulsion, phase separation, stable emulsion

1. Introduction

People around the world are facing global crises in terms of global warming, energy shortages, and natural disasters. These crises require decisive actions to mitigate their negative impacts on humans. Global warming, which causes annual increases in atmospheric temperature, affects many sectors, including agricultural products, clean water, human health, flash floods, and longer dry seasons. Scientists worldwide are conducting research to utilize renewable and unlimited energy sources.

These new naturally existing energies need to be optimized so they can be applied and used economically by people. The transition from fossil to renewable-based energy is being implemented because it is favorable and feasible on an industrial scale. The increasing demand for sustainable and renewable energy sources has led to significant interest in bioenergy and biofuels as alternatives and substitutes for fossil-based fuels. The use of fuels derived from bio sources has gained significant momentum in recent years due to their potential to reduce carbon dioxide emissions and dependence on conventional fuels [1].

Ethanol and butanol have been considered promising biofuels because of their renewable materials and suitable fuel specifications [2]. Ethanol, commonly synthesized from lignocellulose and starches such as corn and sugarcane, has been widely chosen as a fuel additive since it has a high octane number (RON) and the ability to decrease carbon monoxide emissions [3].

However, the hygroscopic nature and volatility of ethanol pose challenges, especially in cold temperatures, leading to phase separation and reduced fuel stability. Water has a higher affinity, leading to emulsion instability and oxidation problems. Butanol, on the other hand, shows higher energy content and lower hygroscopicity compared to ethanol, making it a more

suitable fuel when blended with gasoline [4]. Because butanol has a lower vapor pressure, it also reduces evaporation, which is beneficial for both environmental and safety reasons [5].

The mixture of gasoline-ethanol and gasoline-butanol has been studied extensively in recent years for their potential to decrease greenhouse gas emissions, replace a portion of fossil fuels, and increase energy security [6-7]. However, the stability of such mixtures, particularly in stable emulsions at low temperatures, remains problematic and influences their practical use in combustion engines. Emulsion stability at low temperatures is especially important to ensure consistent performance and prevent phase separation, which could lead to engine malfunctions [8-11].

The application of blended fuel with gasoline, aqueous ethanol, and butanol is challenging due to its significant water content. Most engines used today require fuel free of water. Gasoline blended with a small part of ethanol and butanol with high purity does not necessitate engine modifications. However, the use of low purity ethanol and butanol with gasoline requires modified engines, which is beyond the scope of this study. Previous studies have explored various blending ratios to optimize engine performance, emissions, and fuel stability.

Therefore, understanding and improving the low-temperature stability of these emulsions is crucial for their broader adoption as sustainable fuel alternatives. This study aims to determine and analyze the compositions of gasoline, aqueous ethanol, and butanol at low temperatures, including the roles of ethanol and butanol as surfactants.

The steps of the present work were as follow: The preparation of ethanol derived from palm tree (*Arenga pinnata*), dilution of ethanol, blending of gasoline, ethanol, and butanol. The determination of composition each component in which the phase was stable, was conducted in the final stage. The analysis of the stability was observed carefully in the precise manner. The measurement of fuel parameters would be conducted in the second part of the study.

2. Experimental

2.1. Materials

The ethanol was obtained through a fermentation of the juice tapped from Arenga pinnata tree. The high purity of ethanol was processed of raw ethanol employing a reflux distillation technique whose column was filled by pores packing materials [12]. The high concentration ethanol was diluted into low purities, 80, 85, and 90%.

The analysis grade butanol 99.50% was purchased from Sigma-Aldrich assigned by Cas No 71-36-3; Product code 00055025500 and Batch No A324972001, Merck KGaA, 64217 Darmstadt Germany. The pure water was produced by investigators using a reflux distillation which was available at laboratory. The commercial unleaded-gasoline, whose RONs value was of 90, was obtained from The Indonesia Petrolium Company (PERTAMINA).

2.2. Equipment

The equipment employed were magnetic stirrer and hot plate, graduated cylinder (10-50 ml), volumetric flask (100, 500, and 1000 ml), pipetts (1-10 ml), digital thermometer (TM-902C), refrigerated incubator/chamber (TCF-210YID, TCL China), and phase separation tools (transparent grad. cylinder).

All flasks used were sterilized by an absolute alcohol and then isolated inside chamber. The graduated cylinder was washed using a high concentration alcohol and the heated before and after experiment. The thermometers used were calibrated at the triple- and boiling points of the water to increase the validity of the experiment.

The all equipment and tools used was handled and kept carefully and stored inside special chamber in which room temperature was controlled by air conditioning.

Table 1: Compositions of gasoline.	aqueous ethanol 80%. an	d butanol 99.50% in stał	ble emulsion at temperatures -17.00
to 29.60°C			

		Volume (ml)					
Time T (min) [°C]	Т [°С]	gasoline	line Aq.Ethanol 80% E	Average	Composition (%v/v)		
		Sussing		Butanol 99.5 %	Gasoline	Aq. Ethanol 80%	Butanol 99.5%
0	29.00	26.00	14.00	27.90	38.29	20.62	41.09
14	12.00	26.00	14.00	29.66	37.32	20.10	42.58
24	1.50	26.00	14.00	30.20	37.04	19.94	43.02
42	-8.50	26.00	14.00	31.70	36.26	19.53	44.21
133	-12.00	26.00	14.00	33.54	35.35	19.04	45.61
390	-15.00	26.00	14.00	35.40	34.48	18.57	46.95
1352	-17.00	26.00	14.00	37.20	33.68	18.13	48.19

Egypt. J. Chem. 68, No. 07 (2025)

2.3. Procedures

The blending of gasoline, ethanol, and butanol followed the procedures as reported previously [13].

The different ethanol concentrations were prepared using the diluting method and then the volumes of ethanol, butanol, and gasoline were measured using graduated cylinders. The gasoline and ethanol were mixed in volumetric flask in desired ratio and total volume and phase was separated initially. The butanol was added gradually while gently stirring until the mixture stabilized. The volumes of gasoline, ethanol, and butanol were measured and the composition was determined. The emulsion stabilized was transferred to the transparent graduated cylinder and then moved to the cold chamber.

Temperature was set to the desired value below room temperature until the phase separation was occurred. The small amount of butanol was added into the mixture to stabilize the emulsion. If the emulsion was stable, each component volume was measured and compositions were calculated with similar way. The temperature was decreased until a certain value and the phase condition was observed carefully. When the stable phase was breaking, some butanol was poured gradually until components were transparent. The volume each component was recorded and compositions were determined.

The blending of gasoline, ethanol, and butanol was proceeded at less temperatures with using similar procedure as described previously. The observation was carried out carefully to watch the stability, cloudiness, and separation of the mixture. The experiment was conducted five times to ensure the accuracy and minimalize the measurement error. The composition analysis in stable emulsion used a simple calculation the component volume divided by total components volume and was multiplied by 100%. The triangular graph analysis in which three components were in equilibrium condition, was employed and used for observing the area in stable- or unstable emulsion. To minimize the error of the observation, the volume of butanol was measured five times as two components (ethanol and gasoline) were kept constant.

3. Results and Discussion

The first study aimed to investigate the stability of gasoline, aqueous ethanol (80%), and butanol (99.50%) emulsions at temperatures ranging from -17.00°C to 29.60°C. The data provided in Table 1 present the compositions of these emulsions at different time intervals and temperatures. The analysis focused on the volumetric composition and stability of the emulsions over time and varying temperatures. The data describe the changes in volumetric composition (%v/v) of gasoline, aqueous ethanol (80%), and butanol (99.50%) in stable emulsions over a temperature range from -17.00°C to 29.00°C.



Fig. 1. The triangular graph of the compositions of gasoline. aqueous ethanol 80%. and butanol 99.50% in stable emulsion blended at temperatures of 29.00, 12.00, 1.50, -8.50, 12,00, -15.00, and -17.00 °C.

Egypt. J. Chem. 68, No. 07 (2025)

The initial volumetric composition of the emulsion was 38.29% gasoline, 20.62% ethanol, and 41.09% butanol (99.50%) at 29.00°C. This composition served as a baseline to understand the effect of temperature changes on emulsion stability and composition. As the temperature decreased, the percentages of gasoline and aqueous ethanol in the emulsion declined, while the percentage of butanol increased significantly. This trend continued consistently as the temperature decreased to -17.00°C.

The composition changed to 36.26% gasoline, 19.53% aqueous ethanol, and 44.21% butanol at -8.50°C after the sample was stored in cool storage for 42 minutes. The compositions shifted to 35.35% gasoline, 19.04% aqueous ethanol, and 45.61% butanol at -12.00°C after 133 minutes. When blended at -17.00°C (after 1352 minutes), the compositions were 33.68% gasoline, 18.13% aqueous ethanol (80%), and 48.19% butanol.

The increase in butanol composition corresponded to a decrease in gasoline and aqueous ethanol contents, suggesting that lower temperatures promoted phase separation. This behavior indicated that the emulsion's stability depended on temperature, and the decrease in temperature was countered by adding butanol. Over the course of the experiments, it was evident that emulsion stability was influenced by both composition and temperature. For instance, blending conducted at -15.00°C after 390 minutes resulted in compositions of 34.48% gasoline, 18.57% aqueous ethanol, and 46.95% butanol (99.50%). The continuous adjustment and stabilized equilibrium in volumetric composition with respect to time and temperature highlighted the dynamics of emulsion stability. The blended fuels was kept at lower temperatures in long time resulted in a more probable to phase separation in which it was indicative that time was also critical variable in maintaining stable emulsions in low climate [14]. Fig. 1 plots that represents the compositions of gasoline, aqueous ethanol (80%), and butanol (99.50%) at temperatures variation and time intervals. The solid circles show the compositions of three components inside the emulsion changing with respect to time and temperatures. As the temperature decreased, the circles of the points shifted which were an indication the relative contents of gasoline, aqueous ethanol, and butanol. The temperatures were just close to room temperature recorded at 29.00°C and 12.00°C which the emulsions were stable. The compositions of gasoline, aqueous ethanol, and butanol were relatively balanced without significant shifts. It was found that butanol added was functioning to bridge between polar and non-polar parts of the water, ethanol and gasoline. The property belonged to butanol was called as surfactant whereby it was very important role in stabilizing the substances involved in weak interactions.

			Volume (ml)				
Time T (min) [°C]	gasoline	A.a. Ethanol 90%	Average Butanol	Composition (%v/v)			
	Γ-]	gasonne	rq. Ethanor 9070	99.5 %	Gasoline	Aq. Ethanol 90%	Butanol 99.5%
0	29.50	26.00	14.00	12.90	49.15	26.47	24.39
16	9.60	26.00	14.00	15.36	46.97	25.29	27.75
21	-2.00	26.00	14.00	18.38	44.54	23.98	31.48
31	-4.20	26.00	14.00	21.00	42.62	22.95	34.43
40	-6.10	26.00	14.00	25.92	39.44	21.24	39.32

Table 2: Compositions of gasoline,	aqueous ethanol 90%.	, and butanol 99.50% in	n stable emulsion a	at temperatures -6.10
to 29.50°C				

The short exposure times noted at 24 min and at slightly lower temperature, at 1.50°C also indicated that emulsion was stabilized, as seen in figure 1. At temperatures below 0°C, the compositions show significant changes, indicating instability. The emulsion tends to separate into its components, with butanol becoming more predominant as seen at -8.50°C, -12.00°C, -15.00°C, and -17.00°C. Extended exposure to low temperatures exacerbates phase separation, leading to non-stable emulsions. This is evident from the data at -12.00°C (133 min), -15.00°C (390 min), and -17.00°C (1352 min). The addition of butanol into the mixture gradually could stabilized the emulsion stability in each temperature.

The findings from the data analysis revealed several critical insights into the behavior and stability of gasoline, aqueous ethanol (80%), and butanol (99.50%) emulsions at low temperatures. The stability of the emulsions was highly sensitive to temperature changes. Lower temperatures favor the phase separation of gasoline from the mixture, leading to an increase in butanol volumetric percentage. The stability was also influenced by the duration of exposure to low temperatures [15]. Prolonged exposure exacerbated phase separation, indicating that maintaining stable emulsions requires not just optimal initial compositions but also controlled environmental conditions over time [16].

The findings underscored the need for careful consideration of temperature and time when using such emulsions in practical applications, particularly in colder climates. Enhancing the stability of these emulsions could involve the use of surfactants or additives that mitigate phase separation and improve compatibility between the components [17].

Future studies could explore the role of different surfactants, the impact of varying ethanol and butanol concentrations, and the potential of other biofuels in creating more stable emulsions. Additionally, investigating the mechanical and thermal properties of these emulsions under real-world conditions would provide deeper insights into their practical applicability. This analysis highlighted the significant impact of temperature and time on the stability of gasoline, aqueous ethanol (80%), and butanol (99.50%) emulsions. Understanding these factors is crucial for developing stable biofuel blends that can perform reliably across a range of environmental conditions. Further research and optimization are essential to enhance the viability of these emulsions as sustainable fuel alternatives.

Table 2 presents the compositions of gasoline, aqueous ethanol (90%), and butanol (99.50%) in stable emulsions over a range of temperatures from -6.10°C to 29.50°C across five experiments. The data captures how the volumetric composition of the emulsion changes with time and temperature, providing insights into the stability of the emulsion under different conditions.

At room temperature (29.50°C), the emulsion was stable with a balanced composition of 49.15% gasoline, 26.47% aqueous ethanol (90%), and 24.39% butanol (99.50%). This indicated good miscibility among the components at higher temperatures. As the temperature decreased to 9.60°C, there was a slight reduction in gasoline content to 46.97%, with aqueous ethanol and butanol percentages adjusting to 25.29% and 27.75%, respectively. This minor shift suggests the emulsion remains relatively stable with moderate cooling.

At -2.00°C (21 min), the gasoline content decreased to 44.54%, while butanol increased to 31.48%. This indicated the beginning of phase separation as the temperature dropped below freezing. Further decreased in gasoline (42.62%) and increased



Fig. 2. The triangular graph of the compositions of gasoline, aqueous ethanol 90%, and butanol 99.50% in stable emulsion blended at temperatures of 29.50, 9.00, -2.00, -4.20, and -6.00 °C.

in butanol (34.43%) highlighted increasing the stability blended at -4.20°C (31 min). The most significant shift occurred with gasoline dropping to 39.44% and butanol rising to 39.32%, suggesting marked the stability at this temperature mixed at -6.10°C (40 min). At room temperature (29.50°C), the

emulsion maintained stability with a balanced composition, indicating that the components are well-mixed and stable under these conditions. The slight changes in composition at 9.60°C showed that the emulsion could remain stable with moderate cooling, in which this was favorable for applications in climates with mild temperature variations. As temperatures dropped below freezing, significant changes in composition were observed. The decrease in gasoline and aqueous ethanol percentages, coupled with an increase in butanol, indicated that butanol became more predominant. If the composition was constant and temperature decreased, it was leading to instability in the emulsion and phase separation.

Initial changes in composition occurred gradually, suggesting that the emulsion could tolerate short-term exposure to moderately low temperatures without significant stability issues. Prolonged exposure to low temperatures exacerbated phase H.F. Sangian et.al.

separation, leading to more pronounced shifts in composition and reduced stability [18]. To back the emulsion stability of gasoline, aqueous ethanol, and butanol blended at low temperatures, butanol must be added into mixture gradually.

For practical applications in cold climates, it was crucial to ensure the stability of gasoline-ethanol-butanol emulsions. The data indicated that these emulsions were stable at higher temperatures but require careful formulation and potentially the use of additives to maintain stability at lower temperatures. Ensuring stable storage conditions for fuel emulsions was essential to prevent phase separation and maintain performance. Emulsions stored at lower temperatures may need additional stabilization measures [19-20].

Fig. 2 describes the triangular graph of the blended fuel of the gasoline, aqueous ethanol 90%, and butanol 99.50% mixed at temperatures 29.50, 9.00, -2.00, -4.20, and -6.00 °C. At room temperature, the emulsion was stable with a balanced composition, indicating good miscibility among the components.

Table 3: Compositions of gasoline, aqueous ethanol 96%, and butanol 99.50% in stable emulsion at temperatures -0.0
to 26.90°C

		Volume (ml)					
Time T (min) [°C]	gasoline Aq.Ethano 96%	Aq.Ethanol	Average Butanol 99.5 % [—]	composition (%v/v)			
		96%		Gasoline	Ethanol 96%	Butanol 99.5%	
0	26.90	26	14	1.43	62.76	33.79	3.45
60	16.80	26	14	1.90	62.05	33.41	4.53
100	10.00	26	14	2.39	61.34	33.03	5.64
150	5.00	26	14	2.74	60.83	32.75	6.42
200	0.00	26	14	3.16	60.24	32.44	7.32

The relatively high gasoline content showed that it was well-mixed with aqueous ethanol and butanol. As the temperature dropped to 9.60°C, there was a slight decrease in gasoline content, with a corresponding slight increase in butanol content. This indicated that the emulsion remained relatively stable, suggesting it could tolerate moderate cooling. The gasoline content decreased further, indicating the beginning of phase separation. Butanol content must be increased aiming to stabilized the emulsion and showing its increasing dominance in the mixture. Further decrease in gasoline content and increase in butanol content indicated growing instability ata -2.00 °C. The emulsion was becoming more prone to phase separation as temperature decreased to -4.20 °C. Significant shifts in composition were observed, with the gasoline content reducing further and butanol content increasing significantly, whereby this suggested the marked phase separation and reduced stability at this low temperature.

The analysis of the data from Table 2 demonstrates that gasoline, aqueous ethanol (90%), and butanol (99.50%) emulsions exhibit temperature-dependent stability. They are stable at higher temperatures but become increasingly unstable as temperatures drop below freezing. This underscores the need for optimized formulations and potential additives to maintain stability in cold climates, ensuring the practical viability of these biofuel emulsions [21].

The Table 3 provides a detailed account of the compositional changes of a stable emulsion of gasoline, aqueous ethanol (96%), and butanol (99.5%) over time and across a temperature gradient from 26.90°C to 0.00°C and the data captures these changes at specific time intervals (0, 60, 100, 150, and 200 minutes). The initial temperature was 26.90°C, and it gradually decreased to 0.00°C over 200 minutes. The temperature drop indicated a controlled cooling process, allowing the observation of compositional changes over time. The volumes of gasoline (26 ml), aqueous ethanol (14 ml), and butanol (1.43-3.16 ml) remained constant throughout the experiments. This suggests that the primary focus is on the relative compositional changes rather than volumetric variations.

The percentage of gasoline slightly decreased from 62.76% to 60.24% that indicated that gasoline's relative proportion in the emulsion diminished as the temperature dropped. The percentage of ethanol showed a steady decline from 33.79% to 32.44%. This trend was less pronounced than gasoline but still significant. The butanol exhibited an increasing trend, rising from 3.45% to 7.32%. This sharp increase suggested butanol's stability and potential role in maintaining emulsion properties at lower temperatures.

The stability of the emulsion was likely influenced by the relative proportions of its components. As temperature decreased, the solubility and interaction of ethanol and butanol with gasoline could alter, impacting the overall composition. Butanol's increasing proportion might indicate its superior stabilizing properties in lower temperatures, potentially acting as a co-solvent (surfactant) that enhanced emulsion stability [22].

The decrease in gasoline and ethanol percentages might be attributed to phase separation or the reduced solubility of these components at lower temperatures. Butanol, with its higher boiling point and better solubility in both polar and non-polar phases,

could be compensating for the reduced solubility of ethanol and gasoline, thereby increasing its relative percentage. Understanding these compositional changes was crucial for applications requiring stable emulsions-



Fig. 3. The triangular graph of the compositions of gasoline, aqueous ethanol 96%, and butanol 99.50% in stable emulsion (equilibrium state) at temperatures -0.00 to 26.90°C

over varying temperatures. For instance, in fuel blends, maintaining stability at lower temperatures can be critical for performance and efficiency. The results suggest that increasing butanol content could be a strategy to enhance low-temperature stability of gasoline-ethanol mixtures.

Investigating the molecular interactions at play could provide deeper insights into the mechanisms driving these compositional changes. Additional experiments could explore a wider range of temperatures and time intervals to map out a more detailed stability profile. Comparative studies with different alcohols or solvents could help identify optimal compositions for specific applications.

The data in Table 3 and Fig. 3 illustrate how temperature variations impact the compositional stability of a gasoline-ethanolbutanol emulsion. The gradual decrease in gasoline and ethanol percentages, coupled with the increase in butanol, highlights the importance of butanol in maintaining emulsion stability at lower temperatures. This analysis underscores the need for strategic formulation adjustments in temperature-sensitive applications, paving the way for further research into optimizing fuel blends for varying environmental conditions.

Here is the triangular plot illustrating the compositional changes of gasoline, ethanol, and butanol over time. The Fig. 3 shows the relative proportions of each component as the temperature decreases from 26.90°C to 0.00°C in which each point on the plot is labeled with the corresponding time in minutes, indicating how the composition evolves over the experiment duration. The movement of points on the plot showed a gradual shift from higher ethanol content towards higher butanol content. Gasoline content remained relatively stable but showed a slight decrease, evidenced by the clustering of points. As butanol increased, it demonstrated its role in stabilizing the emulsion at lower temperatures. Ethanol and gasoline contents were seen to decrease in relative proportions, aligning with the data from the table. The triangular plot visualized the stability trends and could help in formulating mixtures that maintain desired properties over temperature changes. It provided a clear picture of the compositional dynamics, useful for applications requiring precise control over emulsion stability. This plot effectively summarized the data and highlighted the important trends and interactions between the components over the observed time and temperature range.

The three tables provided give a comprehensive overview of the compositional changes in emulsions containing gasoline, aqueous ethanol, and butanol at various concentrations and temperatures. By examining these tables collectively, we can gain insights into how different ethanol concentrations and temperature ranges impact the stability and composition of the emulsions over time. As the temperature decreases, the gasoline and ethanol percentages decreased, while the butanol percentage increased.

This suggested that at lower temperatures, butanol contributed significantly to the stability of the emulsion, possibly due to its higher boiling point and solubility characteristics. Similar to Table 1, the gasoline and ethanol percentages decreased as the temperature lowers, while the butanol percentage increased.

The higher initial ethanol concentration (90% compared to 80%) aimed to maintain a higher relative percentage of ethanol in the emulsion, although butanol still increased substantially at lower temperatures. The data followed the trend observed in Tables 1 and 2, with gasoline and ethanol percentages decreasing as temperature decreased, while butanol increased. The highest initial ethanol concentration (96%) resulted in the lowest butanol content at higher temperatures, but butanol increased more rapidly compared to the other tables as the temperature dropped.

Lower ethanol concentrations (80% in Table 1) lead to higher initial butanol content to achieve stable emulsions, as observed by comparing initial compositions across the tables. Higher ethanol concentrations (96% in Table 3) showed lower initial butanol but more significant increased in butanol content with temperature reduction. All tables showed that as temperature decreased, butanol percentage increased, indicating its crucial role in stabilizing emulsions at lower temperatures. Gasoline and ethanol proportions decreased consistently with temperature, indicating potential phase separation or decreased solubility.

Butanol acted as a stabilizer in the emulsion, compensating for the decreased solubility of ethanol and gasoline at lower temperatures. Its increasing percentage across all tables highlighted its importance in maintaining stability. The compositional changes suggested that butanol's higher boiling point and better solubility in both polar (ethanol) and non-polar (gasoline) phases made it an effective stabilizer in varying ethanol concentrations and temperatures. The need for more butanol in higher ethanol concentrations (as seen in Table 3) at lower temperatures pointed to its role in preventing phase separation and maintaining a homogenous mixture.

Understanding these relationships was crucial for formulating stable fuel blends that could withstand temperature variations. For instance, in colder climates, increasing butanol content might be necessary to ensure stability. The data could inform industrial practices where precise control over emulsion composition is necessary, such as in biofuel production or other chemical processes involving mixed solvents.

Investigating the molecular interactions and specific phase behaviors at microscopic levels could provide deeper insights into the mechanisms behind these compositional changes. Expanding the temperature range and including additional solvents or co-solvents could help in developing more robust formulations for various applications.

The relationship between the data in Tables 1, 2, and 3 revealed a clear pattern of how ethanol concentration and temperature influence the stability and composition of gasoline-ethanol-butanol emulsions. Butanol emerged as a critical component for maintaining stability, especially at lower temperatures, across different ethanol concentrations. These findings were essential for optimizing fuel blends and other industrial applications requiring stable emulsions under varying environmental conditions.

The findings showed that when the temperature of the stable emulsion fuel decreased, phase separation occurred, forming aqueous ethanol-butanol and gasoline layers. However, gradually adding butanol stabilized the emulsion again. It was also discovered that increasing the emulsion temperature prevented phase separation.

The formation of a stable emulsion differs from reaction kinetics, which involve chemical reactions that produce new substances. In this case, the components—aqueous ethanol, butanol, and gasoline—undergo weak interactions and dissolution.

The stability of the emulsion was highly dependent on temperature and composition, rather than time exposure. The dependence of the composition in stabilizing of the emulsion was reported previously [23]. At low temperatures, the interactions weakened due to changes in density, indicating that gravitational forces became more dominant than the interactions between the components. The emulsion instability was recovered by adding butanol gradually by stirring until emulsion was stable.

The addition of butanol aimed to restore the stability of the emulsion. Butanol functioned by bonding polar-polar and nonpolar-nonpolar components in water, ethanol, and gasoline. This behavior occurs because butanol has a dual structure: a nonpolar hydrocarbon chain (C-C-C-C) interacting to gasoline and a polar hydroxyl group (-O-H). This behavior was close to the previous works employing cellulose and chloropyrifos to bond oil-water in forming emulsion [24-25]. Without the addition of butanol, the emulsion remained unstable. In practical applications, electronic devices must be installed inside the fuel tank equipped with temperature controller to prevent phase separation, which will be explored in future studies.

4. Conclusions

This study successfully determined and analyzed the compositions of gasoline (RON 90), aqueous ethanol, and butanol in stable emulsions at low temperatures. The objectives were met by establishing a method to blend these components without synthetic surfactants and by identifying the critical role of butanol in stabilizing emulsions at reduced temperatures. The blending procedure revealed that gradual addition of butanol to the gasoline-ethanol mixture effectively prevented phase separation and maintained emulsion stability. As temperatures decreased, the emulsion's stability was notably influenced by the increase in butanol content, which compensated for the decreasing solubility of gasoline and ethanol. At the lowest observed temperature of -17.0°C, the stable emulsion composition of 33.68% gasoline, 18.13% aqueous ethanol, and 48.19% butanol highlighted the temperature-dependent nature of the emulsion stability. The study's findings underscored the importance of butanol as a stabilizing agent in low-temperature environments. These conclusions indicated that stable gasoline-ethanol-butanol

emulsions could be achieved at low temperatures, providing valuable insights for the development of biofuel blends. The potential applications of this research included improving the performance and reliability of biofuels in automotive engines and other combustion systems, especially in cold climates. This work paved the way for further research into optimizing biofuel compositions and exploring the use of other renewable additives to enhance fuel stability and efficiency.

Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript. The reviewers and the funder had no involvement in the study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Acknowledgments

We gratefully acknowledge the financial support provided by the Indonesia Higher Education, Research and Technology Department (*Direktorat Jenderal Pendidikan Tinggi, Riset, Dan Teknologi*) under Research Project with a contract No: 084/E5/PG.02.00.PL/2024 and 1878/UN12.13/LT /2024. We also extend our sincere appreciation to the PIC of Lab of The State Polytechnic in Samarinda and the Lab of Oil and Gas of PEM AKAMIGAS Cepu Blora in Central Java for generously providing the laboratory facilities that were essential for the successful completion of this research project. We highly also appreciate the support the Rector of Sam Ratulangi University, Prof. Dr. Ir. Oktovian Berty Alexander Sompie, M.Eng., IPU, ASEAN Eng., who permitted authors in using laboratory. The hard-work of Head of LPPM, Prof. Dr. Ir. Jeffrey I. Kindangen, in managing and selecting of research proposal was highly appreciated.

References

- R.C. Rial, Biofuels versus climate change: Exploring potentials and challenges in the energy transition, Renew. Sustain. Energy Rev. 196 (2024) 114369. https://doi.org/10.1016/j.rser.2024.114369.
- [2] W. Qi, Q. Deng, N. Du, W. Hou, Surfactant-free microemulsions of n-butanol, ethanol, and water, J. Mol. Liq. 390 (2023) 122980. https://doi.org/10.1016/j.molliq.2023.122980.
- [3] P.P. Sanap, A.G. Diwan, Y.S. Mahajan, Ethanol blending in petrol: A techno-commercial overview, Mater. Today Proc. (2023). https://doi.org/10.1016/j.matpr.2023.04.055.
- [4] I.E. Yousif, A.M. Saleh, Butanol-gasoline blends impact on performance and exhaust emissions of a four-stroke spark ignition engine, Case Stud. Therm. Eng. 41 (2023) 102612. https://doi.org/10.1016/j.csite.2022.102612.
- [5] A. Mejía, M. Cartes, A. Velásquez, G. Chaparro, V. Sanhueza, Vapor-liquid phase equilibria, liquid densities, liquid viscosities, and surface tensions for the ternary n-hexane + cyclopentyl methyl ether + 1-butanol mixture, Fluid Phase Equilib. 558 (2022) 113444. https://doi.org/10.1016/j.fluid.2022.113444.
- [6] Z. Fan, L. Zhang, W. Di, K. Li, G. Li, D. Sun, Methyl-grafted silica nanoparticle stabilized water-in-oil Pickering emulsions with low-temperature stability, J. Colloid Interface Sci. 588 (2021) 501-509. https://doi.org/10.1016/j.jcis.2020.12.095.
- [7] W. Cai, F. Yang, X. Xia, Z. Zhao, B. Yao, C. Li, Y. Zhao, G. Sun, Effects of solvent composition and test temperature on the stability of water-in-model waxy crude oil emulsions, Geoenergy Sci. Eng. 234 (2024) 212617. https://doi.org/10.1016/j.geoen.2023.212617.
- [8] M. Amine, E.N. Awad, V. Ibrahim, Y. Barakat, Effect of ethyl acetate addition on phase stability, octane number, and volatility criteria of ethanol-gasoline blends, Egypt. J. Petrol. 27 (2018) 567-572. https://doi.org/10.1016/j.ejpe.2017.08.007.
- [9] K. Chinnadurai, N. Kasianantham, Impact on combustion stability, fuel economy, and emission compliance with butanol enleanment strategy in gasoline engine – A drop-in fuel approach, Fuel Process. Technol. 246 (2023) 107756. https://doi.org/10.1016/j.fuproc.2023.107756.
- [10]S. Kumaravel, C.G. Saravanan, V. Raman, M. Vikneswaran, J. Sasikala, J.S.F. Josephin, S. Alharbi, A. Pugazhendhi, H.F. Oztop, E.G. Varuvel, Experimental investigations on in-cylinder flame and emission characteristics of butanol-gasoline blends in SI engine using combustion endoscopic, Therm. Sci. Eng. Prog. 49 (2024) 102449. https://doi.org/10.1016/j.tsep.2024.102449.
- [11]R. Li, C. Zhong, Y. Ning, Y. Liu, P. Song, R. Xu, H. Mao, Exhaust and evaporative volatile organic compounds emissions from vehicles fueled with ethanol-blended gasoline, Environ. Pollut. 124163 (2024). https://doi.org/10.1016/j.envpol.2024.124163.
- [12]H.F. Sangian, G.H. Tamuntuan, H.I.R. Mosey, V. Suoth, B.H. Manialup, The utilization of Arenga pinnata ethanol in preparing one phase-aqueous gasohol, ARPN J. Eng. Appl. Sci. 12 (2017) 7039-7046. https://www.arpnjournals.org/jeas/research papers/rp 2017/jeas 1217 6582.pdf.
- [13]H.F. Sangian, D. Lestari, G. Pasau, G.H. Tamuntuan, A. Widjaja, R. Purwadi, S.Y. Agnesty, B. Sadjab, M.C. Sangian, R. Thahir, Identifying the compositions of the blended fuels of butanol, gasoline, and water stabilized at low temperatures, East.-Eur. J. Enterp. Technol. 1 (6) (2023) 22-32. https://doi.org/10.15587/1729-4061.2023.272512.

Egypt. J. Chem. 68, No. 07 (2025)

- [14]Y. Cao, H. Zhao, S. Zhang, X. Wu, J.E. Anderson, W. Shen, T.J. Wallington, Y. Wu, Impacts of ethanol blended fuels and cold temperature on VOC emissions from gasoline vehicles in China, Environ. Pollut. 348 (2024) 123869. https://doi.org/10.1016/j.envpol.2024.123869.
- [15]V. Hönig, Z. Linhart, J. Táborský and J. Mařík. Determination of the phase separation temperature and the water solubility in the mixtures of gasoline with biobutanol and bioethanol. Agronomy Research 13(2), (2015) 550–557,. https://agronomy.emu.ee/vol132/13 2 32 B5.pdf.
- [16]Y. Cao, H. Zhao, S. Zhang, X. Wu, J.E. Anderson, W. Shen, T.J. Wallington, Y. Wu, Impacts of ethanol blended fuels and cold temperature on VOC emissions from gasoline vehicles in China, Environ. Pollut. 348 (2024) 123869. https://doi.org/10.1016/j.envpol.2024.123869.
- [17] M.G.A. Kassem, A.M. Ahmed, H.H. Abdel-Rahman, A.H.E. Moustafa, Use of Span 80 and Tween 80 for blending gasoline and alcohol in spark ignition engines, Energy Reports 5 (2019) 221-230. https://doi.org/10.1016/j.egyr.2019.01.009.
- [18]Z. Mužíková, P. Šimáček, M. Pospíšil, G. Šebor, Density, viscosity, and water phase stability of 1-butanol-gasoline blends, J. Fuels 2014 (2014) 459287. https://doi.org/10.1155/2014/459287.
- [19]I. Gorbatenko, A.S. Tomlin, M. Lawes, R.F. Cracknell, Experimental and modelling study of the impacts of n-butanol blending on the auto-ignition behaviour of gasoline and its surrogate at low temperatures, Proc. Combust. Inst. 37 (2019) 501-509. https://doi.org/10.1016/j.proci.2018.05.089.
- [20]H.F. Sangian, D. Lestari, G. Pasau, G.H. Tamuntuan, A. Widjaja, R. Purwadi, S.Y. Agnesty, B. Sadjab, M.C. Sangian, R. Thahir, Identifying the compositions of the blended fuels of butanol, gasoline, and water stabilized at low temperatures, East.-Eur. J. Enterp. Technol. 4 (2023) 6-17. https://doi.org/10.15587/1729-4061.2023.286349.
- [21]B. Strus, A. Sobczyńska, M. Wiśniewski. Solubility of water and association phenomena in gasoline modified with hydrophilic additives and selected surfactants. Fuel, 87(6), (2008), 957-963. https://doi.org/10.1016/j.fuel.2007.05.047.
- [22]C. Jin, Z. Geng, X. Liu, J.D. Ampah, J. Ji, G. Wang, K. Niu, N. Hu, H. Liu, Effects of water content on the solubility between Isopropanol-Butanol-Ethanol (IBE) and diesel fuel under various ambient temperatures, Fuel 286 (2021) 119492.https://doi.org/10.1021/acs.energyfuels.9b02150.
- [23] N. Saleh, M. Betiha, N.A. Negm, Preparation, characterization, and rheological behavior of O/W and W/O non-Newtonian emulsions using surface-modified nano-silica and non-ionic surfactant, Egypt. J. Chem. 66 (2023) 15–24. <u>https://doi.org/10.21608/EJCHEM.2022.105977.4877</u>.
- [24]M. El-Sakhawy, S. Kamel, A. Salama, M.A. Youssef, W. Elsaid Teyor, H.S. Tohamy, Amphiphilic cellulose as stabilizer for oil/water emulsion, Egypt. J. Chem. 60 (2017) 181–204. <u>https://doi.org/10.21608/ejchem.2017.544.1002</u>.
- [25] A.F. Aly, N.A. Ibrahim, S.S. Hafez, Z.K. Elkhiat, Formulations of chlorpyrifos-ethyl in non-conventional water-based oil in water emulsion (EW) and micro emulsion (ME), and their insecticidal evaluation against pink bollworm (P. gossypiella) and migratory locust (L. migratoria), Egypt. J. Chem. 66 (2023) 311–323. https://doi.org/10.21608/EJCHEM.2022.147912.6404.