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Tri-fuel (diesel-biodiesel-ethanol) emulsion characterization, stability and the corrosion effect

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Abstract. This paper presents the result of experimenting emulsified tri-fuel in term of stability, physico-chemical properties and corrosion effect on three common metals. The results were interpreted in terms of the impact of five minutes emulsification approach. Tri-fuel emulsions were varied in proportion ratio consist of biodiesel; 0%, 5%, 10%, and ethanol; 5%, 10%, 15%. Fuel characterization includes density, calorific value, flash point, and kinematic viscosity. Flash point of tri-fuel emulsion came with range catalog. Calorific value of tri-fuel emulsion appeared in declining pattern as more ethanol and biodiesel were added. Biodiesel promoted flow resistance while ethanol with opposite effect. 15% ethanol content in tri-fuel emulsion separated faster than 10% ethanol content but ethanol content with 5% yield no phase separation at all. Close cap under static immersion with various ratio of tri-fuel emulsions for over a month, corrosiveness attack was detected via weight loss technique on aluminum, stainless steel and mild steel.

1. Introduction

Diesel engine has been widely used in various industrial sectors due to its durability, better fuel economy and greater fuel to power conversion efficiency as compared to gasoline engine [1]. It is still not the time to give up on diesel engine especially when the demand is still strong and even manifested with market outlook forecasted 9% steady growth of diesel engine demand globally [2]. Furthermore, widely known that diesel engine could support high compression ratio much higher than race car with petrol engine.

Despite the advantages, people with concern over environmental and health have been casting blame and continuously pointing finger to the issue of diesel engine incomplete combustion as part of the serious source of air pollution due to exhaustive hazardous gases emission, including Nitrogen Oxide (NOx), Carbon Monoxide (CO), Carbon Dioxide (CO2) and Sulphur Oxide (SOx). It is disturbing to comprehend that engine emission affects human health on a large scale [3]. Research also shown that widespread especially in compactly populated urban area, regular exposure to diesel exhaust could in due course bring harm to human health [4,5]. Furthermore, diesel engine emissions contain many mutagens, carcinogens and toxic substances such as NOx, SOx, CO and CO2. Moreover, lung cancer has become a major health risk in animal and human research. Studies on railroad workers and truck drivers occupationally exposed to diesel engine emission show that these workers have been found tend to have increasing in getting lung cancer risk with increasing years of work in the exposed job [6].

Bearing in mind the statement that poor air quality mainly caused by the emission of carbon monoxide and carbon dioxide [7], diesel engine emission somewhat partly responsible for the global ecological disturbance. According to the US National Oceanic and Atmospheric Administration (NOAA), it was announced that 2015 was the warmest year in the record, where the global surface temperature was increased by 0.29°F compared to last year and this is the largest margin since records began in 1880s. According to the State of the Climate in 2015, the highest contribution for the annual combined temperature was long term warming and strong El-Nino since records. This is well related to global warming, which causing ice arctic melting, extreme weather events, changing seasons and disruptions to food supplies. Intergovernmental Panel on Climate Change (IPCC) has claimed that the major causes of global sea level rise are thermal expansion of the oceans and the loss of land-based ice due to increased melting. Meanwhile, total dependency on diesel fuel as the only reliable sole source of combustion to the compression ignition engine call for emerging popular biofuel such as biodiesel [8] and bioethanol [9]. Nonrenewable source couple with fear of shortage supply on fossil fuel appeared to be the strong motive to proceed with the research on developing blending solution with conventional diesel fuel.

All the challenges outlined so far offered entree to innovative approach, presenting an opportunity for emulsion fuel technology combo with three fuel composition categories to play key role in automotive. Optimistically, with tri-fuel emulsion, the hope is to become an effective solution as alternative fuel and in time to earn the claim for better fuel efficiency and lesser harmful engine emissions. If not hundred percent. at least, partial replacement with multicomponent biofuel components combined with diesel would be a motivating option. Since bioethanol and diesel got immiscibility issue, biodiesel influence with innovative strategic mixing approach hopefully could be useful. Hagos et al. (2016) signified the possible distinction between blending and emulsion on tri-fuel [10]. Thus, instead of casual mixing, this study experimented emulsification approach on tri-fuel with multiple proportion. As a practical matter, tri-fuels under emulsion category may have some special qualities to contest with tri-fuel blending category [11] on secondary atomization trait.

Apart from that, because corrosiveness was mentioned as one of the concern with blended tri-fuel by Zöldy in 2006 and 2011 [12, 13], the study to investigate corrosiveness on mild steel, stainless steel and aluminum by weight loss technique subsequent to the static immersion with various proportion of tri-fuel emulsions was not yet revealed. Number of studies that dogged on corrosion behavior relative to biodiesel have been found in the literatures to date [14-18]. Other example, corrosion of copper in blended tri-fuel category [19] has also been found reported. But corrosiveness effect on common metals such as mild steel, stainless steel and aluminum under tri-fuel emulsion categories according to the best of author knowledge, was never been explored. Hence, it was aimed to fill this gap partially by detecting any weight loss due to corrosiveness consequent to the immersion on various tri-fuel emulsified proportions and compared to one another. At the same time, stability test for different composition ratios was conducted. Last but not least, the study also took some initiative to obtain primary properties of the tri-fuels composition with varies proportion such as density, viscosity, flash point and calorific value. The objective was to provide some rationalization to the influence of tri-fuel components on its fundamental properties.

2. Experimental set up

2.1. Fuel preparation

Conventional diesel, ethanol and biodiesel from palm oil origin were attained from close convenient provider. The amount of biodiesel was varied from 0% to 10%, while ethanol was varied from 5% to 15% as can be seen in Table 1. The tri-fuels were emulsified using Hielscher Ultrasonic Processor UP400S Emulsifier as shown in Figure 1 for 5 minutes with 0.7% cycle and 40% amplitude setting. The temperature of the tri-fuel was observed consistently and not to exceed 50°C using an infrared thermometer.

Table 1. Tri-fuel matrix ratio.

No	Diesel (%)	Biodiesel (%)	Ethanol (%)
1	95	0	5
2	90	5	5
3	85	5	10
4	80	5	15
5	85	10	5
6	80	10	10
7	75	10	15

2.2. Fuel properties

Density of the tri-fuel sample was calculated by measuring the mass and volume in equation (1):

$$\rho = \frac{m}{v} \tag{1}$$

where ρ is the density of the tri-fuel in g/ml, m is the mass of the tri-fuel in g, ν is the volume of the tri-fuel in ml.

(a) (b)

Figure 1. Experimental setup. (a) Hielscher Ultrasonic Processor UP400S Emulsifier (b) Infrared thermometer.

Calorific value of tri-fuel emulsions was determined using oxygen bomb calorimeter and Model 6772 Calorimetric Thermometer observing the standard ASTM-D240. Dynamic viscosity was determined using Brookfield Viscometer Model DV-III ULTRA Programmable Rheometer observing the standard ASTM-D7042. The dynamic viscosity of the tri-fuel was then converted to kinematic viscosity by dividing the density of the tri-fuel sample. Flash point was determined using Koehler K16591 Rapid Flash Point Tester observing standard ASTM D93.

2.3. Fuel stability

To study the stability effect of tri-fuel emulsions, all the samples were monitored by visual observation for any phase separation to occur. 20 ml of all tri-fuel emulsions samples are filled into test tube and observed for 35 days period. The test tubes were examined every 2 hours for the first day, then every day for the first week and every week until 35 days. Result were plotted for analysis.

2.4. Corrosion detection

The fuels used were diesel, biodiesel and ethanol while the metal piece materials used for corrosion testing were mild steel, aluminum and stainless steel. Firstly, all the specimens undergone general procedure of specimen preparation for metallographic examination such as cleaning and surface polishing to obtain scratch free condition. The weight of each metal pieces was measured before immersion. Mild steel, aluminum and stainless steel undergone static immersion into each tri-fuel sample for the period of 2 months and 2 weeks under close cap condition. After immersion, each of the specimen was dried, cleaned, and weighed again.

3. Results and discussion

3.1. Properties

Table 2 shows the density, calorific value, flash point and kinematic viscosity for all tri-fuel samples. Overall, in view of the result obtained, the increase of ethanol content in tri-fuel decrease the density, calorific value, flash point, and kinematic viscosity. The result in this experiment is in agreement to the literatures reviewed due to the characteristics of ethanol [20-22]. In addition, the results are comparable with blending category by Rajesh et al. [23] that studied higher percentage by volume of ethanol and biodiesel into tri-fuel blended category.

Table 2. Physical characteristics of tri-fuel emulsions.

Tri-fuel	**Density (kg/m^3)**	**Calorific value (MJ/kg)**	**Flash point**
D95E5	838.6	48.6673	86°C - 90°C
D90B5E5	833.1	48.4884	78°C - 80°C
D85B5E10	818.0	47.5606	80°C - 85°C
D80B5E15	814.9	46.5904	85°C - 90°C
D85B10E5	834.7	47.7769	110°C - 115°C
D80B10E10	827.3	45.7008	85°C - 90°C
D75B10E15	815.3	44.4648	65°C - 70°C

Tri-fuel	**Kinematic viscosity at 30°C (mm^2/s)**	**Kinematic viscosity at 40°C (mm^2/s)**	**Kinematic viscosity at 50°C (mm^2/s)**
D95 E5	4.2323	3.5639	2.8236
D90 B5 E5	4.2872	3.5957	2.8760
D85 B5 E10	4.0213	3.4340	2.7313
D80 B5 E15	3.8164	3.1851	2.5965
D85 B10 E5	4.2946	3.6147	2.9099
D80 B10 E10	4.0758	3.4112	2.6606
D75 B10 E15	3.8001	3.2671	2.5967

3.2. Calorific value

Calorific value of tri-fuel emulsions was found apparently degrading as can be seen in Figure 2. The degradation is inevitable considering biodiesel is known with slightly lower calorific value as compared to diesel. Moreover, ethanol carries substantial lower level of calorific value compared to the two fuels individually. Thus, this possibly explain the degradation. Meanwhile, D95E5 and D90B5E5 calorific value were not much different from PD100 as the base fuel. D75B10E15 is the composition with the lowest calorific value among all, 44.4648 MJ/kg. Despite of the calorific value decreases, the level is still within the range of 40 MJ/kg to 49 MJ/kg for the used in diesel engine as stress out in the previous literature [24].

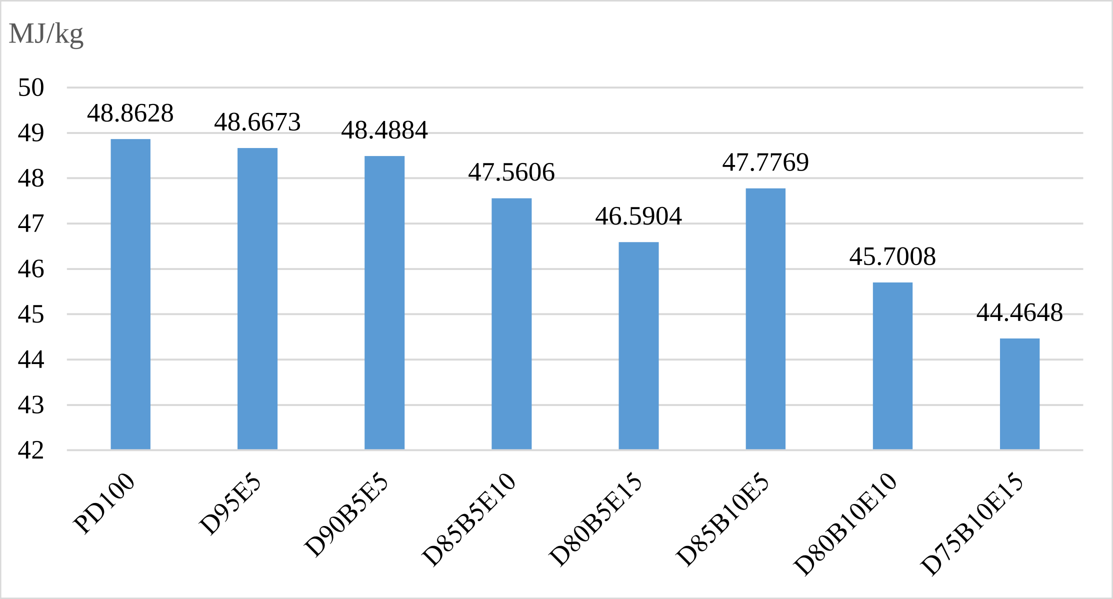

Figure 2. Calorific value of tri-fuel emulsions

3.3. Kinematic viscosity and density

Keep in mind that higher viscosity means weaker fuel injection as the fuel are more viscous and adherent [24]. Figure 3 shows the kinematic viscosity of all the composition at 3 different temperatures. But, it is important to look deeper by carefully track and appreciate the source of influence to the differential value between the ups and down of viscosity level with either 5% ethanol or 5% biodiesel increment gap. Hence, side by side variant assessments were done as in Table 3 for kinematic viscosity and table 4 for density. It is well known individually that density of ethanol is lesser than diesel and much lower than biodiesel. Biodiesel in fact carry higher density than diesel. The highest variant detected between D90B5E5 and D85B5E10 with 15.1 kg/m^3 density drop as 5% of ethanol was added. From viscosity reading, this is the second biggest drop among all with 0.2659 mm^2/s at 30 ºC. The highest drop detected on the viscosity reading was between D80B10E10 and D75B10E15 with 5% ethanol addition for 0.3615 mm^2/s changed. Again, comparing in term of density, the smallest variant detected between D80B5E15 and D75B10E15 with 5% biodiesel add on with influence only 0.4 kg/m^3 density increment. D95E5 which by right under bi-fuel emulsion category was compared with tri-fuel emulsion with the presence of 5% biodiesel (D90B5E5), yield density drops of 5.5 kg/m^3. Furthermore, increasing 5% biodiesel by comparing D85B5E10 and D80B10E10 yield increase in density of 9.3 kg/m^3. Meanwhile, second highest density drop (12 kg/m^3) can be seen on D80B10E10 versus D75B10E15 with 5% ethanol influence. While biodiesel increase the density level, ethanol compelled on shifting the reading the other way around. Nevertheless, back to back trait between ethanol and biodiesel can be noticed in the viscosity reading between D85B5E10 and D80B10E10 at different temperatures. At 30ºC, viscosity increased by 0.0545 but at 40ºC and 50ºC, viscosity drop for 0.0228 mm^2/s and 0.0707 mm^2/s respectively. The rest of the viscosity reading appeared regular as expected.

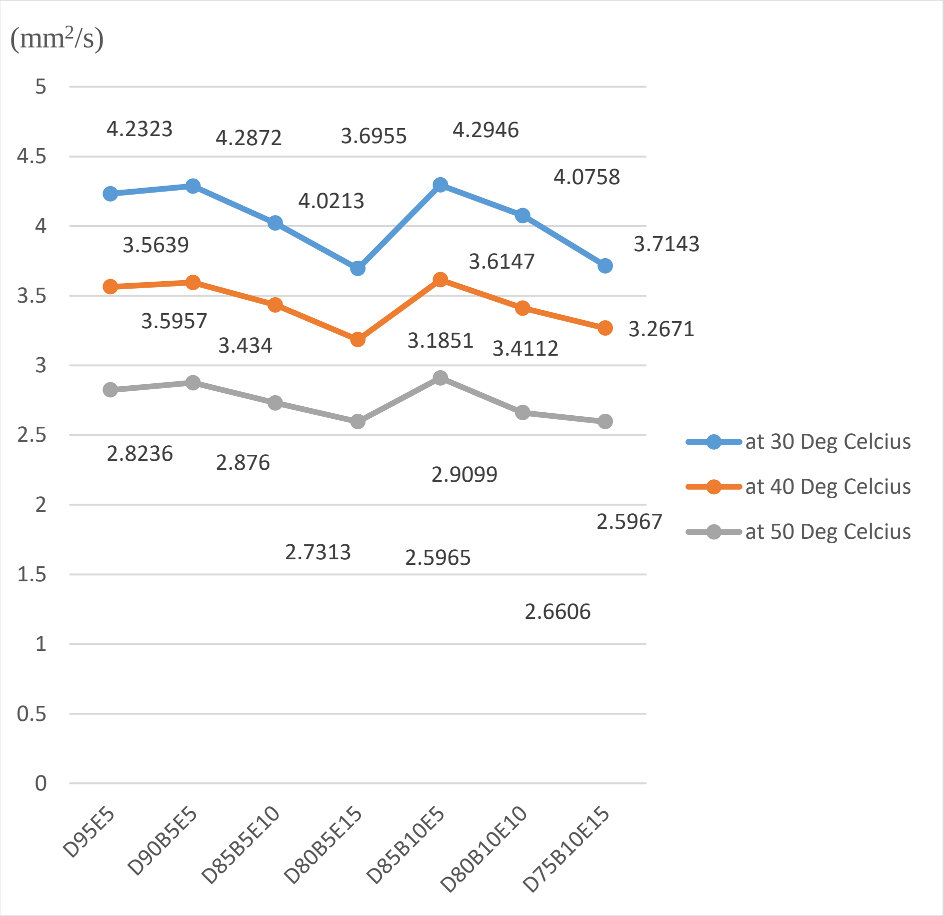

Figure 3. Kinematic viscosity of tri-fuel emulsions at 3 different temperature.

3.4. Flash point

As expected, Table 2 also suggests that ethanol content has significant effect on the flash point of tri-fuel emulsions. Flash point of all proportion were observed appeared with range and with increasing trend parallel to the increasing level of ethanol content. As compared to the well-known conventional diesel flash point base with over 52°C, the range for all the samples tested are under acceptable practical level. The lowest range detected for D75B10E15 with the range from 65°C to 70°C. Providentially, it is well known that flash point has no significant effect on engine performance [25] but the issue lies on safety concern with regards to handling, producing and storing.

3.5. Emulsification stability

Tri-fuel emulsions appeared to be transparent and was observed with noticeable cloudy look occurred upon emulsified but only last temporarily and not on all samples. Sometimes, the samples turned to cloudy appearance the next day with no consistency detected. Perhaps this is some grey areas that require intense observation and further investigation under microscope is needed. The range of appearance detected probably subject to droplet size and difference in refractive indices between the phases. Perhaps, optical microscope can be used in the future to determine the size and distribution upon physical appearance variation. The stability of tri-fuel emulsions of different proportion was studied for 35 days as shown in Table 5 and Figure 4. The study indicates that as ethanol content increase, the tri-fuel undergone phase separation faster, especially for tri-fuel D75B10E15 and D80B5E15. Tri-fuel with ethanol content of 5% did not experience phase separation until the end of observation of 35 days. As indicated, composition with highest ethanol content 15% initiated as early as before it reaches 24 hours. As evident from the figure, five minutes preparation tri-fuel emulsions were seeming to be inadequate to stabilize the composition against the effect of gravitational separation. Perhaps, considering the use of surfactant addition would not be a bad idea after all as demonstrated in the recent study by Tan et al. [26] on engine performance and emissions test with tri-fuel emulsions. In other word, the result in this experiment is comparable to Tan et al. [26].

Table 3. Analysis of biodiesel and ethanol influence on kinematic viscosity.

Temp at (^{o}C)	D95E5	D90B5E5	Influence	Viscosity	Variant
30	4.2323 mm^2/s	4.2872	Biodiesel	Increment	0.0549
40	3.5639 mm^2/s	3.5957	Biodiesel	Increment	0.0318
50	2.8236 mm^2/s	2.876	Biodiesel	Increment	0.0524
Temp at (^{o}C)	D90B5E5	D85B5E10	Influence	Viscosity	Variant
30	4.2872 mm^2/s	4.0213	Ethanol	Decrement	-0.2659
40	3.5957 mm^2/s	3.434	Ethanol	Decrement	-0.1617
50	2.876 mm^2/s	2.7313	Ethanol	Decrement	-0.1447
Temp at (^{o}C)	D85B5E10	D80B10E10	Influence	Viscosity	Variant
30	4.0213 mm^2/s	4.0758	Biodiesel	Increment	0.0545
40	3.434 mm^2/s	3.4112	Biodiesel	Decrement	-0.0228
50	2.7313 mm^2/s	2.6606	Biodiesel	Decrement	-0.0707
Temp at (^{o}C)	D80B5E15	D75B10E15	Influence	Viscosity	Variant
30	3.6955 mm^2/s	3.7143	Biodiesel	Increment	0.0188
40	3.1851 mm^2/s	3.2671	Biodiesel	Increment	0.082
50	2.5965 mm^2/s	2.5967	Biodiesel	Increment	0.0002
Temp at (^{o}C)	D80B10E10	D75B10E15	Influence	Viscosity	Variant
30	4.0758 mm^2/s	3.7143	Ethanol	Decrement	-0.3615
40	3.4112 mm^2/s	3.2671	Ethanol	Decrement	-0.1441
50	2.6606 mm^2/s	2.5967	Ethanol	Decrement	-0.0639

Table 4. Analysis of biodiesel and ethanol influence on density.

Density	D95E5	D90B5E5	Variant	Add Biodiesel
	838.6 kg/m^3	833.1 kg/m^3	-5.5	
Density	D90B5E5	D85B5E10	Variant	Add ethanol
	833.1 kg/m^3	818 kg/m^3	-15.1	
Density	D85B5E10	D80B10E10	Variant	Add biodiesel
	818 kg/m^3	827.3 kg/m^3	9.3	
Density	D80B5E15	D75B10E15	Variant	Add biodiesel
	814.9 kg/m^3	815.3 kg/m^3	0.4	
Density	D80B10E10	D75B10E15	Variant	Add ethanol
	827.3 kg/m^3	815.3 kg/m^3	-12	

Table 5. Phase separation of all tri-fuel samples for 35 days.

	Phase separation (cm)							
Fuel types	**2 hrs**	**4 hrs**	**6 hrs**	**8 hrs**	**10 hrs**	**12 hrs**	**2 days**	**3 days**
D95 E5	0	0	0	0	0	0	0	0
D90 B5 E5	0	0	0	0	0	0	0	0
D85 B5 E10	0	0	0	0	0	0	0	0
D80 B5 E15	0	0	0	0	0	0	0.10	0.16
D85 B10 E5	0	0	0	0	0	0	0	0
D80 B10 E10	0	0	0	0	0	0	0	0
D75 B10 E15	0	0	0	0	0	0	0.14	0.14
	Phase separation (cm)							
	4 days	**5 days**	**6 days**	**7 days**	**14 days**	**21 days**	**28 days**	**35 days**
D95 E5	0	0	0	0	0	0	0.20	0.30
D90 B5 E5	0	0	0	0	0	0	0	0
D85 B5 E10	0	0	0	0	0	0.20	0.30	0.40
D80 B5 E15	0.16	0.16	0.20	0.30	0.60	0.70	0.80	0.80
D85 B10 E5	0	0	0	0	0	0	0	0
D80 B10 E10	0	0	0.08	0.16	0.34	0.40	0.40	0.40
D75 B10 E15	0.18	0.18	0.30	0.40	0.60	0.60	0.80	0.80

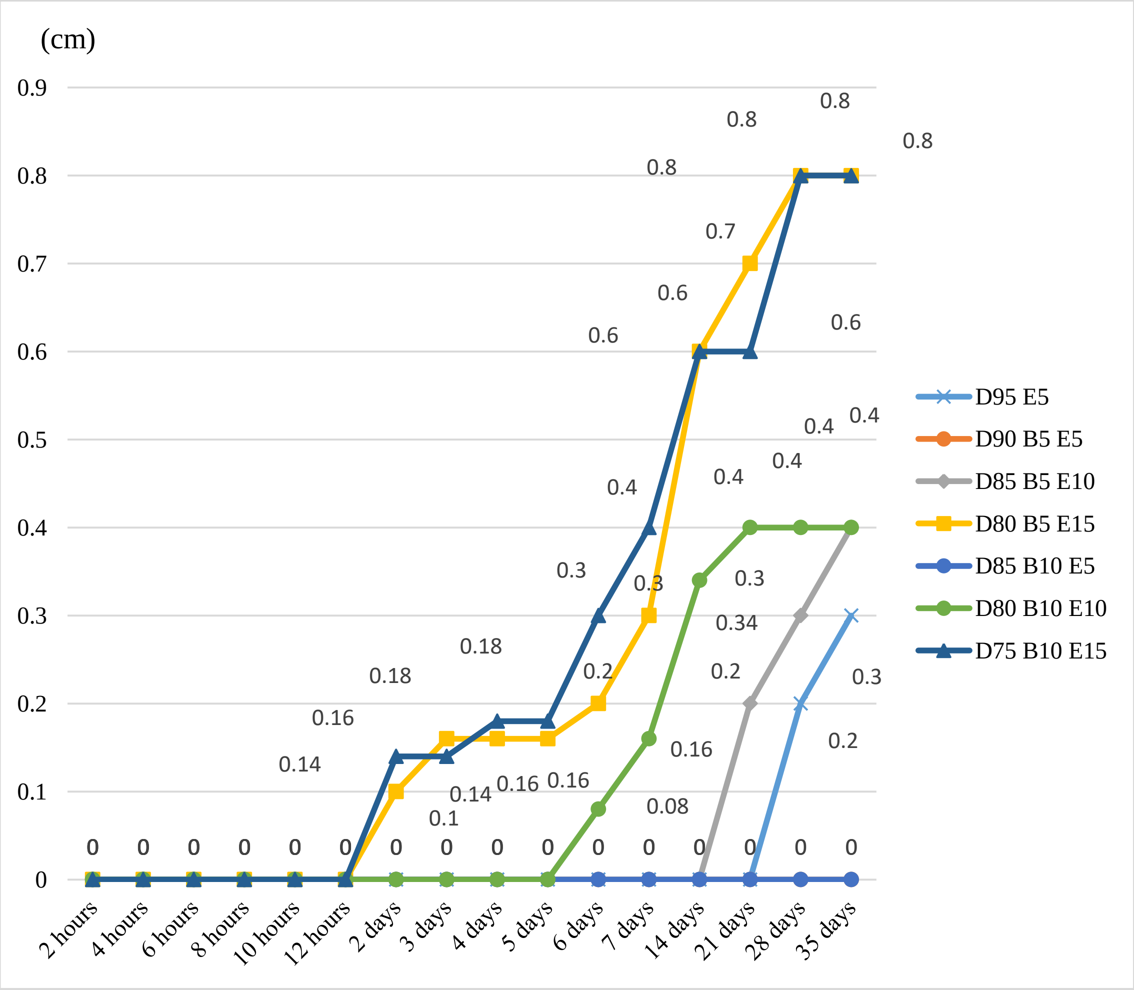

Figure 4. Stability of tri-fuel emulsions.

3.6. Corrosion detection

In this section, it is important to stress that upon corrosion, decreasing in weight should be expected due to metal loss because of the unwanted oxidation activity. Chromium, nickel content in the stainless steel supposed to act as corrosion resistance. Back then, Torres et al. [27] and Hansen et al. [28] outlined ethanol corrosion under 3 categories caused by water content cause, ionic impurities and polarity of ethanol molecule. Less corrosion attack because of low acid content in biodiesel also mentioned in the recent study by Gautam [29] but the fact that weight loss was detected considering brief period of 2 months under close cap room temperature, the plot suggested that corrosion could happened for all three types of metal immersed in tri-fuel emulsions. The data however is not sufficiently enough for deeper comparison for addressing the question on which different proportion ratio contribute more or less to the corrosiveness of the three metals. It was suspected that corrosion mechanism in stainless steel was due to the contact with tri-fuel emulsions D95B0E5 and this could explain with the 0.0125 g weight loss. Further work is required to verify all the finding in this section. Table 6 shows there is significant weight loss on aluminum and stainless steel for D95E5 and this is the highest weight loss among all the tri-fuel samples. The weight loss for most of the metal pieces for all tri-fuel samples between 0.0001 g and 0.0002 g could be neglected and consider none corrosiveness attack detected. The weight losses were too small to consider due to the short immersion period 2 months and 2 weeks for close cap condition. The unnoticed but present of contaminant could also play a role in the detected weight loss. Therefore, it is wise to consider reading above 0.0002 g. It is believed that weight loss suspected of corrosion attack on all the samples mostly under crevice corrosion group. The geometry of the surface of the sample with limited oxygen content because of the emersion plus close cap condition fit into the classification criteria. Further work is required to validate this. Detection of weight loss was recognized on aluminum emersion with B80B10E10 and D90B5E5 while stainless steel emersion with D80B5E15 and D95B0E5. Weight loss of mild steel was noticeable with the emersion in D85B5E10 as depicted in Figure 5. The limitation of the study however that the detection is not by stages within the time frame. Longer period is needed for more significant weight loss on the metal piece to be traced. Hence it is not possible to track which of the composition contribute to the corrosiveness strike first. It would also be useful to obtain a more quantitative understanding of the influence of the component to the corrosiveness of metals that subject to tri-fuel blending immersion. Comparison of weight loss of the complete five standard known types of stainless steel will be also the recommended future study. Finally, in the future, surface analysis is suggested with Scanning Electron Microscope and Energy Dispersive X-Ray Spectroscopy for detail element detection and identify corrosion initiation hot spot on metal pieces.

Table 6. Weight loss for several types of metal piece for all tri-fuel samples.

Fuel type	Weight loss (g)		
	Mild steel	Aluminium	Stainless steel
D95 B0 E5	0.0001	0.0049	0.0125
D90 B5 E5	0.0001	0.0021	0.0002
D85 B5 E10	0.0024	0.0001	0.0000
D80 B5 E15	0.0001	0.0001	0.0038
D85 B10 E5	0.0001	0.0001	0.0000
D80 B10 E10	0.0001	0.0040	0.0001
D75 B10 E15	0.0002	0.0001	0.0002

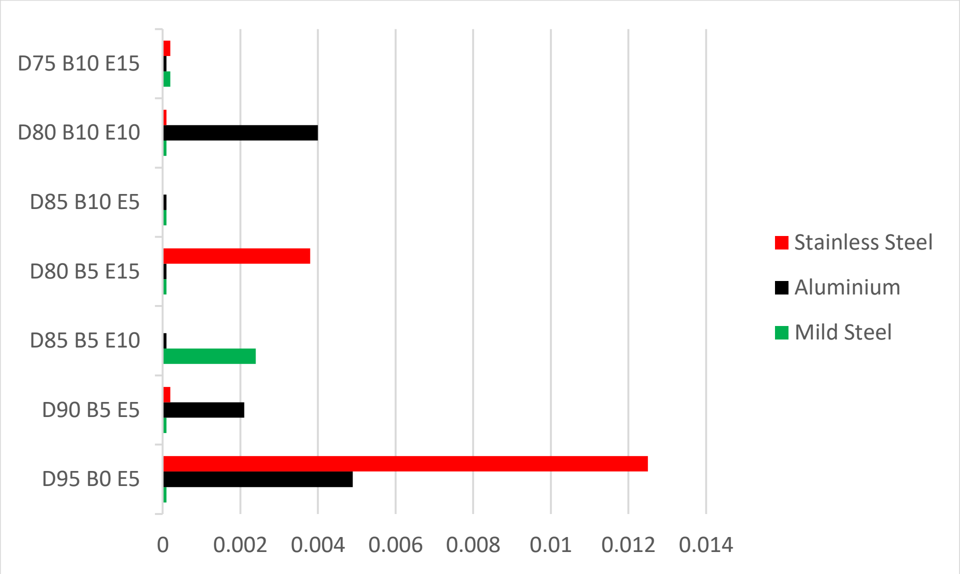

Figure 5. Weight loss detection.

4. Conclusions

Partial key properties, stability and corrosion effect of seven various tri-fuel emulsions ratios were determined in this paper. The highest density reading was the one with the highest biodiesel content and lowest ethanol content. Furthermore, the calorific value degraded as the biodiesel and ethanol content level is amplified but comparatively still under acceptable limit. Flash point of tri-fuel emulsion came with range classification and decreases as more ethanol is added. In other word, more ethanol meant lower flash point. The level however is comparable with diesel standard limit and worth noting for safe handling. Meanwhile, ethanol content pulled the level of kinematic viscosity down whereas biodiesel influence on the opposite direction. Meanwhile, information about the kinetic of cloudy appearance of tri-fuel emulsions mentioned ought for future research consideration to obtain better insight. Tri-fuel emulsion with higher ethanol content could undergo phase separation faster. In summary, 15% ethanol content in tri-fuel emulsion separate faster than 10% ethanol content but ethanol content of 5% yield satisfactory result with no phase separation up to 35 days experimentation period. Weight losses were detected on all three metals under close cap static immersion with tri-fuel emulsion which an indicator to the corrosive initiation. The section on corrosiveness effect can be improved further in the future with comparison between immersion under close and open cap. Perhaps, it is more effective to conduct similar future work with frequent weight loss inspection on weekly basis to know which metal corrode first among all. Furthermore, extended time frame is highly recommended in addition to metallographic study upon significant weight loss detection.

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