DETERMINATION OF BIODIESEL AMOUNT IN VARIOUS BIODIESEL-DIESEL BLENDS

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Abstract

Biodiesel is an alternative non-toxic fuel with low emission profiles, biodegradable, and environmentally friendly. This study focused in the optimization process of base-catalyzed transesterification of palm oil that produced 97.44 % methyl ester with 60 ºC reaction temperature, 9:1 methanol/oil mass ratio, and 1.2 wt% of catalyst within 1 h. A series of diesel-biodiesel blends of B7, B20, B30, B40, and B100 were prepared by mixing the biodiesel with pure diesel. B100 showed the highest value for all tested parameters (acid value: 0.2596 mg KOH/g; peroxide value: 11.7992 meq/kg; moisture content: 0.45%, flash point: 175 ºC, kinematic viscosity: 5.57 mm^2/g and density: 0.8686 g/cm^3). The correlation coefficient of the relationship between acid value, peroxide value, moisture content, density, and viscosity were 0.9256, 0.8351, 0.8378, 0.8345, and 0.8452, respectively. Nevertheless, all tested parameters were positively accepted according to ASTM - D6751 standard method. Thus, this may benefit the related industries as well as monetary gain in countering any false claim on the % blend.

Keyword: Diesel-biodiesel, blending, methyl ester.

Introduction

Fuels can be categorized into two, which are renewable fuels and non-renewable fuels. Renewable fuels are from renewable sources that can be regenerated in a short period and this is different from the limited non-renewable fuels (Knothe, 2010). Biodiesel, according to ASTM D6751, is alternative fuels that are non-toxic with low emission profiles, biodegradable, and will not pollute the environment (Atabani et al., 2012). Recently, due to the increase in the price of crude oil, environmental concern as well as limited resources of fossil fuels, research has been conducted for alternative biodiesel fuels derived from vegetable oils and animal fats (Singh & Singh, 2010). Continuous and increasing use of petroleum will intensify air pollution and further magnify the effect of global warming due to the emission of carbon dioxide (Ma & Hanna, 1999). Pure biodiesel (B100) does not contain any petroleum diesel, but it is possible to mix and blend the petroleum diesel with biodiesel in any desired percentage. Most diesel equipment requires minor or no modification to use diesel-biodiesel blends ranging from 2% to 20% biodiesel. The B in diesel-biodiesel blends indicates biodiesel fuels and the number represent the percentage amount of biodiesel. Special handling and equipment modification might be needed if the biodiesel blends used is higher than B20 (Scharffbillig & Clark, 2014).

Therefore, it is vital to identify the percentage of diesel-biodiesel blend in order to keep the whole equipment intact and avoiding any damage to the parts. The viscosity, density, moisture content, flow point, and flash point are some properties of the diesel-biodiesel blend that will be affected by the variation of blending percentage.

B7 is a common biodiesel blend in Malaysia provided by petroleum companies including Petronas, Shell, Chevron, Petron, and BHP (Chow, 2016). According to the news article in The Star on 12 September 2016, Malaysia will fully-implement the B10 (10% biodiesel, 90% petroleum diesel) biodiesel in the fourth quarter of 2016 (Adnan, 2016). However, the implementation process is delayed due to several vehicle manufacturers concern on the usage of B10 in their vehicles. Additionally, a few other organisations and associations in Malaysia have urged the government to conduct further testing and discussion. Each percentage of biodiesel used in the blending process will change the properties of the petroleum diesel. In order to gain optimum operation of conventional diesel engine or equipment, reliable data analysis and diesel-biodiesel blends physical properties are required. Each blend of diesel-biodiesel will result in different market price, different emission profiles, viscosity, density, and other related properties. Therefore, this study will evaluate each blend properties in order to ensure the diesel-biodiesel in the market meets the requirement as claimed or labelled. The testing parameters of the diesel-biodiesel properties should be simple with accurate results.

Materials and Methods

Biodiesel (FAME) was prepared through transesterification reaction of palm oil with methanol in a ratio of 9:1 with 1.0 wt.% of potassium hydroxide (KOH) as the catalyst. The catalyst is dissolved in methanol prior to addition into a three-neck round-bottomed flask containing pre-heated palm oil at 60°C. The reaction duration is 60 min in a stirring condition using the magnetic stirrer. After 60 min, the sample was cooled overnight in the fume hood to vaporize the remaining methanol. The separation of the sample will discard the glycerin and the biodiesel obtained was washed and dried for further processing. A series of diesel-biodiesel blends (B7, B20, B30, and B40 blends) were prepared by mixing the pure diesel with the pure FAME in which euro 5M was purchased from the local petrol station.

The tested parameters were carried out according to the standards of kinematic viscosity (ASTM 6751), acid value (EN 14214), peroxide value (ASTM D6751), flash point (ASTM D93), moisture content (Karl Fischer Method), and density (ASTM D1480/81). The methyl ester yield was determined following the European regulation procedure EN 14103 by comparing the identified methyl ester peaks with the respective internal standard (Embong et al., 2016).

Result and Discussion

The highest methyl ester yield from transesterification reaction of palm oil at 60 ºC was 97.44% by using 1.2 wt.% of KOH (catalyst), and 9:1 methanol to oil ratio within 60 min showed in **Figure 1**. Rashid et al. (2014) stated that KOH presence helps speeding up the reaction to achieve equilibrium and increased the conversion of reactants to products. The addition of catalyst enhances the solubility of methanol since alcohol is barely soluble in oil and fats thus, increase in the reaction rate. Initially, the increasing amount of catalyst is parallel with the increase of methyl ester conversion until 1.2 wt%. The decreased methyl ester conversion resulted in the formation of soap from the excess amount of catalyst. The same observation was reported by Sabirusta et al., 2016. The excess amount of catalyst also may increase the overall cost and become unfavourable to be used on the industrial scale.

High ratio of methanol to oil will increase the solubility of glycerin in the mixture causing it to remain in the mixture thus, shifting the equilibrium reaction to the left, lowering the ester yield (Anastopoulos et al., 2009). The percentage of FAME produce is 97.44 with catalyst loading of 1.2 wt.% within 60 min. Further increase in the methanol to oil ratio resulted in the decreasing yield of methyl ester yield as the equilibrium state shifted to the left. The 60 min reaction time is the best optimum reaction time to avoid the formation of soap rather than yielding more ester. A longer than 60 min reaction time will decrease the methyl ester yield percentage due to the hydrolysis of ester that will produce more fatty acid (Sinha et al., 2008).

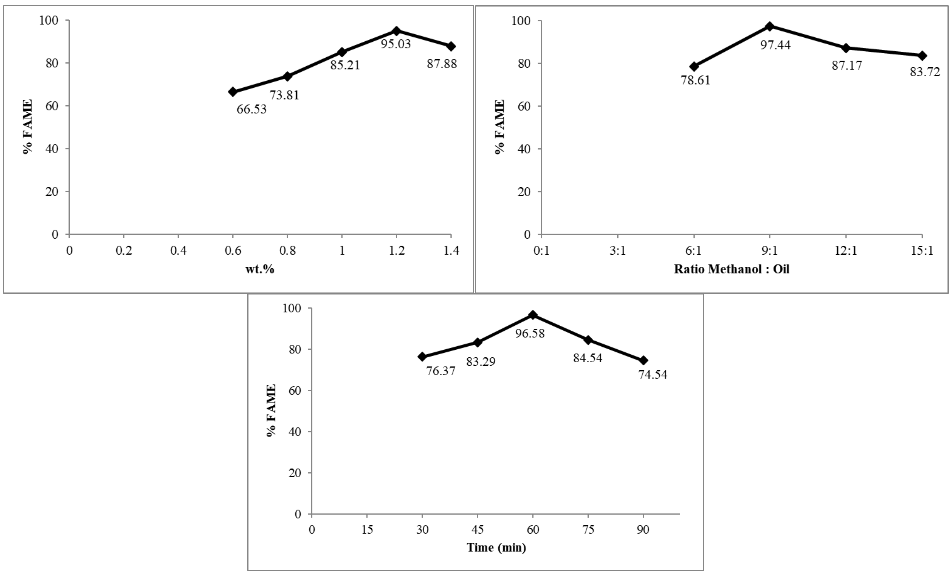

Figure 1 Effect of (a) catalyst amount, (b) methanol/oil molar ratio, and (c) reaction duration on methyl ester yield.

The data of physicochemical properties tested were used to determine the correlation for each test. As expected, the same observation was recorded throughout the parameters tested. B100 gives the highest data while the diesel fuel for the lowest data. The highest acid value is the pure palm oil biodiesel (B100) with a value of 0.2596 mgKOH/g. While the lowest acid value is the pure diesel with the value of 0.0921 mgKOH/g. As for B7 Euro 5M, B7, B20, B30, and B40, the acid value is 0.1200 mgKOH/g, 0.1591 mgKOH/g, 0.1870 mgKOH/g, 0.2037 mgKOH/g, and 0.2149 mgKOH/g, respectively. The acid value increase as the amount of biodiesel increases in the diesel-biodiesel blends. The correlation coefficient of the relationship between acid value and biodiesel content is 0.9256. The same observation was reported by Ali et al. (2016). All of the diesel-biodiesel blend samples meet the ASTM D 7467 acid value requirement. The peroxide values were measured in milliequivalents of peroxide per kilogram of a sample. The highest peroxide value is the pure biodiesel (B100) with 11.7992 meq/kg and the lowest peroxide value is the pure diesel with 0.7448 meq/kg. As for B7 Euro 5M, B7, B20, B30, and B40, the peroxide value is 1.1368 meq/kg, 1.6660 meq/kg, 2.9008 meq/kg, 4.2140 meq/kg, and 5.4488 meq/kg, respectively.
The correlation coefficient of the relationship between peroxide value and biodiesel content is 0.8351. Bouaid et al. (2007) stated that the presence of water trace can cause sample oxidation resulting in high peroxide value. Since pure biodiesel has the highest tendency to absorb water due to FAME hygroscopic properties, it contributes to the high peroxide value compared to other blends that have different diesel-biodiesel blends. Pure biodiesel (B100) has the highest water content value of 0.45 while the pure diesel has the lowest water content value of 0.03. The correlation coefficient of the relationship between moisture content and biodiesel content is 0.8378. Meanwhile, only 0.1% difference percentage between the tested B7 samples with the commercial B7, which could be due to the moisture trap during storage

duration. The other blends have almost the same data.

The pure biodiesel has the highest flash point and the pure diesel has the lowest flash point with a value of 170-175 ºC and 70-75 ºC, respectively. The B7 and B20 blend have the same range value of flash point (90-95 ºC) and the B7 Euro 5M, B30, and B40 have the range value of flash point (95-100 ºC). The higher the biodiesel content in the blended fuel, resulting in increase in its flash point (Shang et al. 2010). The result shows the flash point increases as the percentage of biodiesel in each diesel-biodiesel blend increases. Higher flash point results in less dangerous fuel due to the slow evaporation process making it safer for storage and transport (Gülüm et al., 2017). Kinematic viscosity of pure biodiesel (B100) is the highest with a value of 5.57 mm^2/s. As for pure diesel, B7 Euro 5M, B7, B20, B30, and B40, the viscosity is 3.60, 4.09, 4.27, 4.24, 4.46, and 4.61, respectively. The correlation coefficient of the relationship between kinematic viscosity and biodiesel content is 0.8452. The viscosity of fuel is important to be considered as it can affect the fuel injection system and output performance of an engine. The kinematic viscosity of biodiesel is greatly higher than pure diesel but is approximately less than vegetable oils. One of the benefits of transesterification is it reduces the desired oil viscosity to be used as biodiesel (Ali et al., 2013).

The density of the fuel is the weight of a unit of volume of fuel. Low density value is desirable in order to obtain a maximum engine output through the fuel flow control in the fuel injection system (Ali et al., 2013). Biodiesel is much denser than pure diesel due to the presence of long chain fatty acid, thus any addition of biodiesel to pure diesel will alter the density to a higher value than the initial density. The density of pure biodiesel is 0.8686 g/cm3, which is the highest among other results. The correlation coefficient of the relationship between density and biodiesel content is 0.8345. **Table 1** tabulated the data of the biodiesel-diesel blends.

Table 1 Characterization of a series of biodiesel-diesel blends

	Result							Standard Method
Test	Pure diesel	B7 Euro 5M	B7	B20	B30	B40	B100	
Acid value (mgKOH/g)	0.0921	0.1200	0.1591	0.1870	0.2037	0.2149	0.2596	0.5
Peroxide value (meq/kg)	0.7448	1.1368	1.6660	2.9008	4.2140	5.4488	11.7992	-
Moisture content (%)	0.03	0.20	0.10	0.21	0.23	0.21	0.45	300 mg/kg
Flash point (ºC)	75	100	95	95	100	100	175	125
Kinematic Viscosity (mm^2/s)	3.60	4.04	4.27	4.24	4.46	4.61	5.57	6
Density (g/cm^3)	0.8320	0.8338	0.8362	0.8405	0.8439	0.8475	0.8686	0.86-0.9

Conclusion

In this study, the reaction of palm oil biodiesel was conducted through base-catalyzed transesterification for the purpose of blending with petroleum diesel. Base-catalyzed transesterification is chosen instead of acid-catalyzed transesterification since the raw material used is palm cooking oil that does not have high free fatty acid. For catalyst loading, the highest percent yield of FAME is 95.03 % with 1.2 wt. % of KOH catalyst with respect to the weight of the oil with the highest percentage yield of FAME is 97.44 % with 9:1 methanol to oil ratio and lastly, the highest yield of FAME is 96.58 % within 60 min. Meanwhile, the tested parameters of biodiesel-diesel blends results were in the accepted data range according to the ASTM standard method.

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Conflict of interests

The authors declare that there is no conflict of interest.

References

Adnan, H. (2016). All systems go for B10 biodiesel ; shoring up CPO prices, reducing stock seen. The Star Online, pp. 1–10. Kuala Lumpur. Retrieved from http://www.thestar.com.my/business/business-news/2016/09/12/all-systems-go-for-b10-biodiesel. [31 June 2019].

Ali, O. M., Mamat, R., & Faizal, C. K. M. (2013) Influence of oxygenated additive on blended biodiesel-diesel fuel properties. *Applied Mechanics and Material*, *39*3,487–492.

Ali, O. M., Mamat, R., Abdullah, N. R., & Abdullah, A. A. (2016) Investigation of blended palm biodiesel-diesel fuel properties with oxygenated additive. *ARPN Journal of Engineering and Applied Sciences*, *11*(8), 5289–5293

Anastopoulos, G., Zannikou, Y., Stournas, S., & Kalligeros, S. (2009). Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. *Energies*, *2*(2), 362–376.

Atabani, A. E., Silitonga, A. S., Badruddin, I. A., Mahlia, T. M. I., Masjuki, H. H., & Mekhilef, S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. *Renewable and Sustainable Energy Reviews*, *16*(4), 2070–2093.

Bouaid, A., Martinez, M., & Aracil, J. (2007). Long storage stability of biodiesel from vegetable and used frying oils. *Fuel*, *86*(16), 2596–2602.

Chow, E. (2016). Update 2-Malaysia in talks to move startup of B10 biodiesel programme to July. Retrieved from http://uk.reuters.com/article/malaysia-palmoil-biodiesel-idUKL4N19C1QM. [31 June 2019].

Gülüm, M., Bilgin, A., Çakmak, A. (2017). Production of the Lowest Viscosity Waste Cooking Oil Biodiesel by Using Ethanol and Potassium Hydroxide. *Journal of Clean Energy*

Technologies, *5*(4), 289–293.

Knothe, G. (2010). Biodiesel and renewable diesel: A comparison. *Progress in Energy and Combustion Science*, *36*(3), 364–373.

Ma, F., & Hanna, M. A. (1999). Biodiesel production: A review. *Bioresource Technology*, *70*(1), 1–15.

Rashid, W. N. W. A., Uemura, Y., Kusakabe, K., Osman N. B., & Abdullah, B. (2014). Synthesis of Biodiesel from Palm Oil in Capillary Millichannel Reactor: Effect of Temperature, Methanol to Oil Molar Ratio, and KOH Concentration on FAME Yield. *Procedia Chemistry*, *9*, 165–171.

Sabirusta, M., Mathur, Y. B., & Samad, A. (2016). Optimization of Transesterification Process for Production of Thumba Methyl Ester. *International Journal of Innovative Research in Science, Engineering and Technology*, *5*(1), 311–316.

Scharffbillig, J., & Clark, E. (2014). A Biodiesel Blend Handling Guide. Minnesota Biodiesel Technical Cold Weather. Retrieved from http://www.biodiesel.org/docs/using-hotline/a-biodiesel-blend-handling-guide.pdf?sfvrsn=4. [31 June 2019].

Singh, S. P., & Singh, D. (2010). Biodiesel production through the use of different sources and characterization of oils and their esters as the substitute of diesel: A review. *Renewable and Sustainable Energy Reviews*, *14*(1), 200–216.

Sinha, S., Agarwal, A. K., & Garg, S. (2008). Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. *Energy Conversion and Management*, *49*(5), 1248–1257.