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Property Evaluation of Second Generation Biodiesel for Gas Turbine Application

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Alternative fuel in the form of non-crude oil resources are drawing considerable attention as a result of shrinking oil reserves, increasing petroleum costs and the need to reduce emissions of harmful pollutants. Therefore, renewable energy has gained considerable attention to substitute fossil fuels. One of the promising renewable fuel is biodiesel where it has been used successfully in diesel engine to replace diesel fuel. Meanwhile, biodiesel also has potential to replace distillate diesel for gas turbine application. Nevertheless, inherited properties of biodiesel such as high density, surface tension and viscosity impede the fuel compatible for gas turbine application. Thus, in this research microwave distillation method has been deployed to produce second generation biodiesel from waste cooking oils. The improved biodiesel fuel that produced from microwave distillation method is called as “second generation biodiesel” (SGB) and it has shown promising results compared to first generation biodiesel. The fatty acids composition of second generation biodiesel has been evaluated in gas chromatography and the physical properties of second generation biodiesel have been compared with fossil diesel and first-generation biodiesel (FGB). The result shows properties of second generation biodiesel have been improved and meets the standard requirement of gas turbine fuel accordance to ASTM D2880. The most notable is viscosity of second generation reduced to 4.8 mm^2/s compared to neat first-generation biodiesel 6.6 mm^2/s. Overall the properties of second generation biodiesel meets ASTM D2880 standard and more favorable for gas turbine.

1. Introduction

Increasing concerns regarding environmental impacts and the soaring price of petroleum products together with the depletion of fossil fuels have prompted researchers around the world to look for alternative sources of energy which are technically feasible, commercially viable, readily available and environmentally acceptable. One of the most pursued alternatives is biofuel, due its better gas emissions and renewability (Phan and Phan, 2008).

One of the alternative biofuel energy sources that possess a great potential and reachable in near future is biodiesel. Biodiesel is defined as an alternative energy source produced through a chemical process known as the transesterification from vegetable oils and animal fats that meets international standards such as ASTM D6751. On other hand, biodiesel also can be considered a promising fuel for gas turbine application. However, inherited properties of biodiesel such as viscosity, surface tension and density hinder the biodiesel more favorable for gas turbine application. There were few literatures clearly indicated efforts being taken to improvise the fuel for gas turbine application (Gupta et al., 2010).

This is because properties of biodiesel purely influence by origin source of fatty acid composition (Gupta et al., 2010). Biodiesel is mixture of mono alkyl ester composition and each fatty acid monoalkylester has distinct behavior and properties of biodiesel in a direct correlation between the compositions of the fatty acid of the biodiesel (Yang et al., 2010). Biodiesel comprises of saturated and unsaturated compounds. The most predominant compounds that present in biodiesel are Palmitic acids C16: 0, Palmetolic acids C16:1, Stearic acids C18:0, Oleic acids C18:1 and Linoleic acids C18:2. All these compounds have distinct behavior and different boiling point (Goodrum, 2002).

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According to Knothe, the properties of a biodiesel fuel including iodine value, oxidative stability, cetane number, cold flow properties, viscosity and lubricity are directly determined by the degree of unsaturation of its component fatty esters. Yang had reported that, unsaturation compounds have better physical properties compared to saturated compounds in terms of viscosity, density, surface tension and high calorific value. Hence, by selectively separating the mono alkyl ester according to its fatty acid carbon chain the properties of the biodiesel can be controlled and consistent properties can be obtained.

Therefore, in this research microwave distillation method has been used via microwave assisted post treatment scheme (MAPTRES) to separate the FA composition according to its fatty acid carbon chain. This process has slightly increased the saturated compounds in SGB fuel and consequently it has improved the properties of biodiesel such as viscosity and meets the gas turbine fuel standard accordance to ASTM D2880. Interestingly, altering the fatty acids composition has results improvement in surface tension and density. This research opens another avenue for biodiesel as an alternative fuel for gas turbine application for power generation.

2. Methods and materials

2.1 Production of SGB via MAPTRES

SGB fuel produced through selective distillation using microwave energy where conventional household 1100 W microwave was modified to perform the selective distillation. The distillation process was performed in automatic mode where the distillation temperature controlled automatically during distillation. IR sensor was located at bottom of flask to measure and maintain the distillation temperature within (200 °C - 210 °C). Meanwhile, during the distillation process vacuum pressure and air flow rate is maintained at 27cmHg and 20 L/min for entire production period.

The distillate product collected for every 30 min from round flask and conical flask while same amount of FGB added into distillation flask to prevent overheating. Two flasks have been used because during distillation, some distillate product collected at round bottom flask which is the nearest flask and the remaining distillate that continue vaporized condensed at conical flask.

Samples from round flask and conical was analyzed separately in gas chromatography (GC) to determine whether there are any changes in fatty acids composition between 2 flasks. The GC results and property analysis of SGB fuel samples presented in the subsequent section.

2.2 GC Analytical method for FAME composition

The fatty acid (FA) profile of fatty acid methyl ester (FAME or Biodiesel) was analyzed by Agilent 7890A series GC equipped with hydrogen flame ionization detector (FID). The separation was carried out on a DB-Wax capillary column (30 mm x 0.25 mm (id) x 0.25-µm, Agilent Tech). The temperature of sampling inlet was 250 °C and detector temperature was 280 °C.

Meanwhile, the starting temperature of the column was 50 °C and then increased at 25 °C/min up to 200 °C and later the temperature was increased at 3 °C/min up to 230 °C and maintained at 230 °C for 18 min. The split ratio was 100:1 and helium was used as carrier gas with purity level 99.90 %. A 20 mL of biodiesel (SGB) has been heated up to 100 °C to remove moisture content. Then 100 µL of biodiesel (SGB) transferred into 2 mL vial and mixed with 1000 µL of hexane.

The mixture was shock vigorously and 1 µL of sample was injected into GC. FAME peaks were identified by comparison to the retention times of known reference standard which is 37 FAME mix solutions (Brand: Supelco). The analytical software (Chemstation Version 3.0.31) has been used to identify the peaks and to calculate the percentage of fatty acids composition. The GC run for 30 to 45 min per injection and similar steps were repeated for all fuel samples.

2.3 Property evaluation of SGB fuel sample

All fuel samples were sent to third party laboratory accredited by National Laboratory Accreditation Scheme (SAMM) to perform the fuel property analysis. Stabinger Viscometer has been used to measure the dynamic viscosity and density of the fuel accordance to ASTM D7042. The measurements results obtained via Stabinger Viscometer are equivalent to ISO 3104 and ASTM D445.

Meanwhile, the surface tension of biodiesel measured with Du Nouy Ring method. The gross heat of combustion of biodiesel was measured using Bomb Calorimeter accordance to procedure established in ASTM D3286.

3. Results and findings

This section provides the results and findings from this research. Section 3.1 shows the results from the gas chromatography analysis on the fatty acid profile of Malaysian waste cooking oils (MWCO), first generation biodiesel (FGB) and SGB. Section 3.2 shows the density of the SGB fuels. Section 3.3 shows the surface tension of the fuels. Section 3.4 shows the gross heating value of the fuels.

3.1 Gas chromatography analysis: fatty acid profile

The fatty acids composition of MWCO, FGB and SGB was determined using gas chromatography analysis at UNITEN laboratory. Based on GC analysis, the fatty acid (FA) distribution of MWCO biodiesel is almost identical to palm oil biodiesel because most the MWCO that collected from local restaurants and food outlets are palm oil based (Kumaran et al., 2011). On the other hand, the GC results also indicated the FA composition before and after transesterification remain the same (Keera et al., 2011).
Figure 1 shows that there were significant changes found on distillate samples. Selective distillation significantly increased the saturated compounds from 50 % to average 55 % to 65 % in comparison to FGB fuel. Monounsaturated compounds have reduced from 49 % to average 30 % to 35 %. Finally, di-unsaturated and tri-unsaturated compounds have consistently decreased for all distillate samples compared to FGB. Selective distillation has reduced the unsaturated compounds in biodiesel (FGB) from 49 % to average 43 % to 32 % and substantially increased the saturated compounds from 50 % to 65 %.
The results obtained through microwave distillation meet in good agreement with Malheiro et. al. (2010), who have studied the effect of microwave on organic materials, saturation compounds did not suffer significant changes when exposed to microwave while both unsaturated and polyunsaturated will reduce significantly due to oxidation.

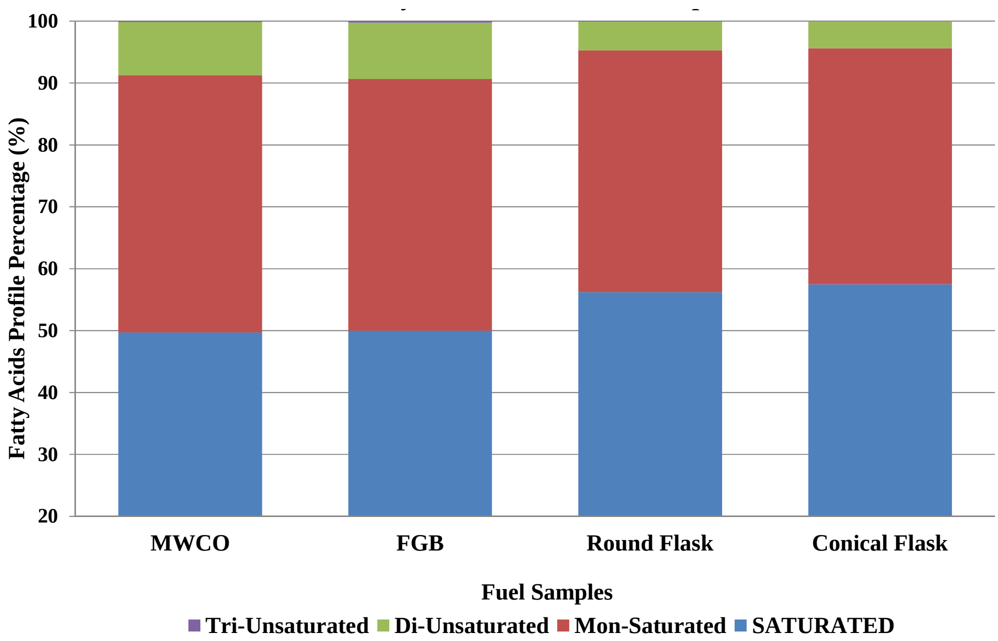

Figure 1: Fatty acid profile of fuel sample

Besides that, boiling points of saturated compounds are lower than unsaturated compounds. In addition to this, boiling points also influenced by the carbon chain number where normal boiling points increase linearly with increasing carbon chain number (Yuan et al., 2005). This could be the reason all other minor FA composition with longer carbon number could not be distillate by MAPTRES.
Meanwhile, the FA profile that obtained from selective distillation contradict with Refaat, (2009), who had suggested a good compromise fuel property can be obtained by fuel with high in the mono-unsaturated fatty acids and low in both saturated and polyunsaturated fatty acids. However, it is worthwhile to note that properties of biodiesel are not only dictated by the FA composition alone but it is also influenced by structural features such as chain length, degree of unsaturation and branching of the chain (Knothe, 2005). Moharam et. al. (2010) had reported properties of edible oils have changed due to change in structural features of polar molecules as result of high frequency oscillation under microwave irradiation. Thus, MAPTRES has

successfully changed the fatty acids composition of FGB by reducing the unsaturated compounds while slightly increased the saturated compounds. Besides that, the fatty acid profile for sample from conical flask and round flask is identical; thus, only one sample sent for property analysis at SAMM accredited laboratory.

3.2 Density of SGB fuel

Fuel density is a key property that affects engine performance because fuel injection pumps measure fuel by volume not by mass. Thus, greater or lesser mass of fuel is injected depending upon it density (Alptekin and Canakci, 2008). Furthermore, the air fuel ratio and energy content within the combustion chamber are influenced by the fuel density (Hoekman et al., 2012). Table 1 shows the ASTM D2880 gas turbine fuel specification standard.

Table 1: Properties of ASTM D2880

Properties	ASTM D2880
Blending ratio	Limit
Density (g/cm^3)	0.8760
Viscosity (m^2/s)	4.4
Surface tension (N/m)	N/A
Calorific value (kJ/kg)	40,000

Table 2 shows the results of this research. The results show that the density are within the ASTM D2880 gas turbine fuel specification standard. The results in Table 1 shows that, biodiesel is denser than distillate diesel (DD), where the density of SGB, FGB and its blends increase linearly as percentage of biodiesel increased in DD.

Table 2: Variation of Density, Viscosity, Surface Tension and Calorific value with increasing blend percentage of biodiesel

Properties	Type of Fuel									
	DD	FGB					SGB			
Blending ratio	0	10	20	50	80	100	10	20	50	80	100
Density (g/cm^3)	0.845	0.848	0.851	0.860	0.869	0.875	0.845	0.848	0.851	0.860	0.868
Viscosity (m^2/s)	3.90	4.00	4.00	4.30	4.50	4.60	3.90	3.96	4.00	4.15	4.30
Surface tension (N/m)	23.0	23.7	24.4	26.5	28.6	30.0	23.5	24.0	25.5	27.0	28.0
Calorific value (kJ/kg)	45,088	44,588	44,088	42,588	41,088	40,088	44,572	44,067	42,510	40,963	39,932

Generally, biodiesel has a higher density than petrol diesel because it's strongly influenced by the degree of unsaturation with higher unsaturation leading to increased density (Refaat, 2009). FGB has higher unsaturation compounds the density FGB slightly higher than SGB. Thus, by decreasing the unsaturated compounds the density of biodiesel can be control.
Therefore, SGB fuel has slight advantage over FGB in terms of density and more favorable for gas turbine application.

3.3 Surface tension of SGB fuel

Surface tension of liquid is considered to be one of the critical properties that affect its atomization characteristics (Lin and Lin, (2010), claimed that the quality of atomization is highly dependent on the chemical properties of the fuel such as viscosity, density and surface tension.
Furthermore, high surface tension tends produce larger droplets during spray and eventually leads to incomplete combustion and higher emission pollutant (Park et al., 2010). Generally, surface tension of biodiesel is 22 % higher than fossil diesel (Ejim et al., 2007).
Although, surface tension is considered to be important property but it is not covered in any of biodiesel standard and also gas turbine fuel requirement standard. However, in this current study the surface tension of SGB and FGB evaluated accordance Du Nuoy Ring method to perform SMD analysis and also to determine the impact of fatty acids composition surface tension.
According to the results in Table 1, distillate diesel has the lowest surface tension and followed by SGB and FGB. Meanwhile, the surface tension of fuel increased as the ratio of biodiesel increased in DD. The results

meet in good agreement with Tan, (2012), where the sauter mean diameter (SMD) of biodiesel blend increased linearly as the ratio of biodiesel increased in DD due to higher surface tension.
However, the surface tension of SGB slightly decreased compared to FGB due to lower di-unsaturated compounds especially linoleic acids C18:2. Allen et. al. (1999) claimed that surface tension of di-unsaturated compounds C18:2 is greater than saturated compounds C18:0 and mono-unsaturated compounds C18:1. In conclusion, by reducing the di-unsaturated linolenic acids C18:2 in FGB have improved the surface tension of SGB.

3.4 Gross heat of combustion (heating value)

The heat of combustion measures the energy content in a fuel and it is referred as calorific value or heating value (Demirbas, 2008). The heating value of biodiesel from all sources is 10 % lower than petroleum diesel due to high oxygen content (Hoekman et al., 2012).
In addition, being a lower heating value of fuel biodiesel requiring more fuel in the range 10 %-50 % compared to diesel flow to deliver same output. Consequently, the fuel delivering system required different setting or new hardware to compensate higher fuel flow (Prussi et al., 2012). Since, heating value is an important parameter; hence heating value of SGB and FGB evaluated accordance ASTM D5865 and the results presented in Table 1.
The results meet in good agreement with most reported work where the gross heat of combustion decreases linearly as the volumetric ratio for biodiesel is increased from 10 % biodiesel concentration to 100 % biodiesel concentration (Tan, 2008).
SGB100 has obtained the lowest heating value and followed by FGB100. It is worthwhile to note that, with higher saturation level SGB100 should have higher heating value than FGB100 because esters of saturate fatty acid compound have more energy content than unsaturated esters (Knothe, 2005). Unfortunately, higher moisture content in SGB attributed to low energy content.
Tan (2008) reported that, moisture content affects other properties of the fuel like calorific value, density and cetane index. Additionally, higher oxygen content in SGB due to additional oxygen molecule that presence in water is another factor that attributed to lower energy content in SGB.
Hoekman et. al. (2012) have reported biodiesel has lower energy mass value than petroleum diesel due to high oxygen content. In conclusion, the energy content of SGB can be improved further or even better compared to FGB by removing the excess water.

4. Conclusions

Fuel property analyses have been carried out for distillate diesel (DD), SGB100 and FGB100 accordance to ASTM D2880 gas turbine fuel specification standard and ASTM D6751 biodiesel fuel specification standard. The property analysis was conducted only for neat SGB and FGB because properties of biodiesel have a linear correlation with percentage of biodiesel blends with diesel/distillate. The property results show that, SGB has better physical properties than FGB in terms of viscosity, density, surface tension and meets ASTM D2880 gas turbine fuel specification standard. However, gross heating value of SGB is lower than FGB fuel due to presence of moisture content in SGB.
Overall, this research has proved that by altering the fatty acids composition of biodiesel the property of biodiesel can be controlled and desired properties can be obtained. Besides that, this research has utilized microwave energy for the selective distillation instead of conventional heating. In future, comprehensive property analysis in accordance to ASTM D2880 is needed to ensure the compatibility of SGB fuel for gas turbine application.

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