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Improvement of Low Temperature Properties of Rubber Seed Oil Methyl Ester by Blending with Fossil Diesel

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A B S T R A C T

Biodiesel is a promising alternative liquid fuel to replace the existing fossil fuel. Biodiesel is an eco-friendly energy source due to less emission of the greenhouse gases. Currently, biodiesel is mostly produced from edible oil. This may create fuel versus food controversy. Malaysia is the second largest rubber producing country in the world and rubber seed oil is underutilized and can be used for biodiesel production because it is non-edible oil. Rubber seed oil methyl ester was characterized by following the EN 14103 method to determine the methyl ester conversion. Methyl ester conversion depicts that rubber seed biodiesel has high content of saturated ester which makes it non convenient in terms of oxidative stability. In current study, low-temperature properties and oxidation stability of biodiesel product are improved by blending with fossil diesel fuel. Pour point, cloud point and cold filter plugging point were analyzed based on ASTM D 6751 standard while oxidation stability and ester content were studied by referring to EN14214 standard. To improve the working ability in a colder region and prolong storage time, biodiesel was blended with fossil diesel at different volumetric ratio. The low temperature properties and oxidation stability results showed that B 20% of rubber seed oil biodiesel is the best blend ratio and meet the ASTM D 6751 and EN 14214 standards for utilization in an engine.

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INTRODUCTION

During the last few decades utilization and demand of energy increased due to the industrial growth, modern life style and also due to increased population of the world. Our main source of energy is fossil fuel. The increasing demand of energy caused serious problems, such as depletions of fossil fuel, increase in the prices of fuels and environmental pollution which causes global warming (Chuah *et al*., 2015a). Transportation and industrial sectors are the major consumer of the fossil fuel. The changes in the global temperature have serious impact on the agricultural production, biodiversity, health and environmental disasters. Increased of sulphate oxides in the air is 23 times in last 20 years (Khan *et al*., 2010). Pollutants like carbon monoxide, carbon dioxide, Ozone and nitrogen oxides emitted from burning of fossil fuel are disturbing the air quality in major cities of the world. Biodiesel is the liquid that has the same combustion properties like fossil diesel (Chuah *et al*., 2015a). Chemically biodiesel is a mixture of fatty acid methyl ester that is produced from the vegetable oil, animal fats and recycled cooking oils by transesterification reaction. (Ahmad *et al*. 2014b). Among all types of available alternative liquid fuels, biodiesel is very famous and growing during the last few years due to its renewable sources and environment friendly nature (Chuah *et al*., 2015b). The low temperature problem of biodiesel in comparison with the fossil diesel is one of the major obstacles after its large scale commercialization around the globe. The vegetable oils can be differentiated based on saturated and unsaturated oil. The saturated fatty acids contain no double bonds in the carbon chain but the unsaturated fatty acids contain the double bounds in the carbon chain. The fuel properties are directly related to the nature of the feedstock used. Higher amount of saturated fatty acid oil when at room temperature becomes solid after some time but reverse case is observed for higher amount of unsaturated fatty acid oil sample. The use of edible oil for biodiesel production at huge scale creates different types of problems such as food versus fuel controversy and deforestation The low temperature problems in

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biodiesel is due to the formation of small crystals (nuclides), that are insoluble and suspended in the fuel lines and clog the fuel line and filters. This problem is prominent in colder region particularly at night time. The low temperature properties can be divided into cloud point (CP), Pour Point (PP) and Cold Filter Plugging Point (CFPP). Different types of triglycerides have different types of fatty acids composition. These properties are related to the nature of the fatty acids present in the feedstock (Bokhari *et al*., 2014). Different types of methods were reported for the improvement of the low temperature properties of the biodiesel such as blending with the fossil diesel and other solvents using different type of the cold flow improver by winterization (Ahmad *et al*., 2014a). These are ways to improve the low temperature properties. Cold flow improver and blending with fossil diesel are the most effective way of improving the low temperature properties (Park *et al*., 2008). Low temperature properties were studied in terms of cloud point, pour point, and cold filter plugging point of pure rubber seed oil biodiesel and after mixing with the fossil diesel in different ratios so that the effect of blending on the low temperature properties can be determined. The oxidation stability of rubber seed oil biodiesel and its blends was studied using the Rancimate method and the storage stability after blending was also determined (Lv *et al*., 2013).

MATERIALS AND METHODS

RSO is used in this study for in addition to analytical grade methanol, potassium hydroxide and anhydrous sodium thiosulphate. Biodiesel is produced from rubber seed oil by following the two steps acid esterification followed by the transesterification due to rubber seed oil has acid content around 20 to 30% (Yusup *et al*. 2015). In acid esterification 10 wt % of the sulfuric acid is used as acid catalyst with methanol to oil molar ratio of 15:1, reaction time of 90 min and reaction temperature of 45°C. In the transesterification, 1 wt% of base catalyst (KOH) was used with methanol to oil molar ratio of 6:1, reaction time of 67 min and reaction temperature of 55°C. These parameters were optimized by using the central composite design approach. The byproduct was separated from the methyl ester by the gravity method and the methyl ester was washed to remove the un-reacted catalyst. After washing, the colour of biodiesel was faint due the trapped water molecule and dissolved methanol. A rotary evaporator is used for evaporation of the water and methanol under reduced pressure. The produced rubber seed oil methyl ester (RSOME) was analyzed by using Agilent 7890A GC FID (Gas Chromatography Flame Ionization Detector) for the composition of the fatty acid profile. The low temperature properties such as cloud point, pour point CPP 5Gs and cold filter plugging point were analyzed by using the ISL FPP 5Gs analyzer.

RESULTS AND DISCUSSION

The fatty acid composition is the most important property since all biodiesel properties depend on the fatty acids composition. The fatty acid profile of rubber seed oil was analyzed by following the EN 14103 method and it was observed that the unsaturated fatty acid composition are high than the saturated acid. Similar result was reported by the (Khan *et al*., 2010). The chromatogram of fatty acids from RSO is shown in Figure1.

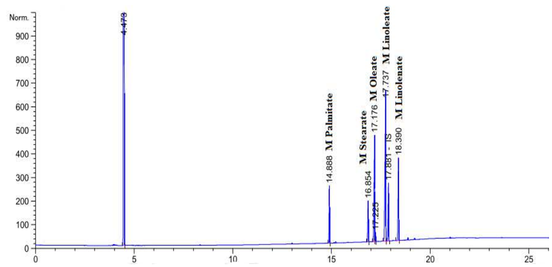

Fig. 1: Chromatogram of rubber seed oil methyl ester

Table 2: Fatty acid methyl ester composition of rubber seed oil

Compositions of fatty acid methyl ester	Percentage (wt.%)
Palmitic acid	9.44
Stearic acid	8.95
Oleic acid	41.41
Linoleic acid	23.08
Linolenic acid	17.12

The low temperature properties of biodiesel depend on the fatty acid composition of the feedstock. It was observed that higher concentration of the un-saturated fatty acid rich biodiesel shows better low temperature properties as compared to the saturated fatty acid methyl ester. Rubber seed oil methyl ester has 81.61 wt.% unsaturated fatty acid methyl ester and 18.39% of saturated fatty acid methyl ester (Yusup and Khan, 2010). A better low temperature property of the unsaturated fatty acids is observed due to the structure and orientation of the double bonds in the carbon chain. RSO methyl ester contains the methyl oleate (C18:1) with 41.41 wt.%, methyl linoleate (C18:2) of 23.08 wt.% and methyl linolenate (C18:3) of 17.12 wt.%.

The melting point of the unsaturated fatty acid is increased by increasing the number of the double bond. The melting point of the methyl oleate (C18:1) is -20°C, methyl linoleate (C18:2) is -35°C and methyl linolenate (C18:3) is -52°C. RSO methyl ester shows pour point of -2°C, cloud point of 3.2°C and CFPP of 0°C. These results are better than the palm oil methyl ester (Ahmad *et al*., 2014a). To improve the low temperature of the RSOME, blend is with the fossil diesel at different ratios and the improvement in CP, PP and CFPP were analyzed. The blending result is shown in Figure 2.

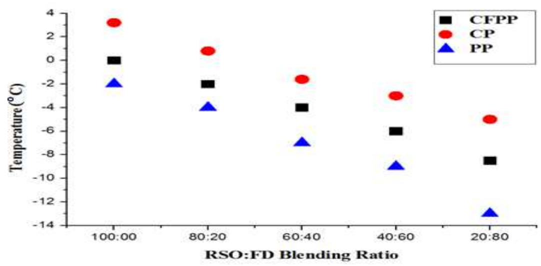

Fig. 2: Blending effect on the low temperature properties.

Figure 2 shows the result of pour point, cloud point and cold filter plugging point of different blending ratio of the rubber seed oil biodiesel with the fossil diesel. It was observed that by increasing the concentration of the fossil diesel in blend, the low temperature properties increased. The fossil diesel shows better low temperature properties than the biodiesel.

The oxidation stability of RSOME was determined by using the Rancimate method described in EN 14112. The oxidation stability is the most important factor with respect to storage and performance of fuel. The increase in viscosity, gumming and deposition of unwanted particle during storage results in poor oxidation stability of biodiesel (Park *et al*., 2008). Oxidation stability depends on the composition of the fatty acids. Most of the vegetable oils are poly-unsaturated and have low oxidative stability. The un-saturation (C=C) in the vegetable oil is due to the presence of oleic acid, linoleic acid and linolenic acid. These unsaturated acids provide active site and promote the oxidation. The unsaturated fatty acid reacts with the oxygen through free radical mechanism and produces the hydro peroxide. This hydro peroxide further decomposed and started to form the cross linkage or polymeric gel. This process is called the auto-oxidation. Biodiesel has some problems and the low oxidative stability is one of the major problems for its commercialization. Figure 3 shows the oxidation stability of RSOME was 8.54 h for this work and is higher than all of previous studies represented on the rubber seed oil biodiesel. This value meets both the standard values of ASTM D 6751 and EN 14214.

Improvement in the oxidation stability using different methods such as using synthetic antioxidant and blending with the fossil diesel showed better oxidation stability of biodiesel which has higher amount of the saturated fatty acids instead of un-saturated fatty acids such as palm based biodiesel (Ahmad *et al*., 2014a). Best way to improve the oxidation stability is to synthetic antioxidant and blending with fossil diesel.

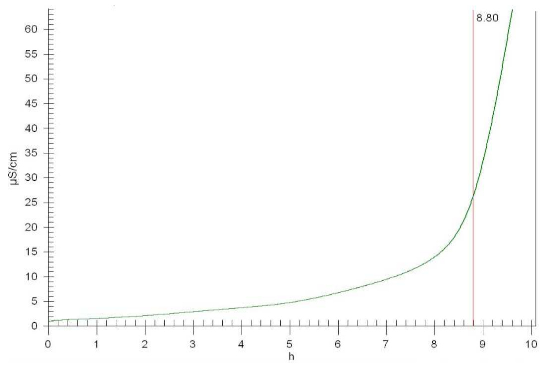

Fig. 3: Oxidation stability trend by Rancimat for rubber seed oil methyl ester

In this study blending method is used to improve the oxidation stability. It was observed in Figure 4, by increasing the amount of fossil diesel, the oxidation stability also increased because due to reduced the chances of auto-oxidation (Bokhari *et al*., 2014). Oxidation stability is the property of biodiesel. All types of vegetable oil have some natural antioxidant. These natural antioxidants help to decrease the oxidation of vegetables oil during long storage. Biodiesel is prepared by using the alcohol and a catalyst. The reaction of alcohol and vegetable oil at high temperature in the presence of catalyst affected the activity of the naturally present antioxidant. Oxidation stability of biodiesel depends on the nature of fatty acids present in the feedstock and also depends on the nature of naturally present antioxidant. The oxidation stability is higher if the amount of saturated fatty acids.

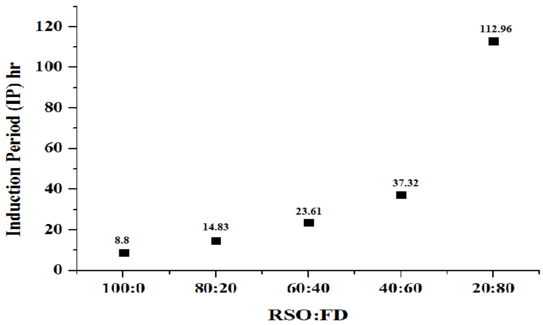

Fig. 4: Oxidation stability of rubber seed oil methyl esters post blended with fossil diesel

Conclusion:

An investigation on the blending of RSOME with fossil diesel has been performed to improve the low temperature properties such as cloud point, pour point and cold filter plugging point. The study showed that by increasing the concentration of the fossil diesel. The low temperature properties increased and storage ability is more stable. Rubber seed oil has higher amount of the unsaturated fatty acids and due to this, the low temperature properties such as CP, PP and CFPP of the rubber seed oil biodiesel is better but with poor oxidation stability. To improve the low temperature properties and storage duration, rubber seed oil biodiesel was blended with the fossil diesel (FD) and the improvement was analyzed and results showed that 20:80 (RSOME: FD) can be used easily in colder region with prolong storage of products.

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