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Improvement of Low Temperature Properties of Jatropha-Corn Biodiesel Blend with the Addition of Acrylic Co-polymer

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Abstract: Inevitable low temperature properties is one of the major problems in commercialization of pure biodiesel. Increasing the usage of edible oil in biodiesel production creates the fuel versus food controversy. This paper involves the study of cold flow properties of edible and non-edible oil's biodiesel. Corn biodiesel and jatropha biodiesel are blended respectively. The blend ratio of corn methyl ester and jatropha methyl ester CME: JME (20:80) has the oxidative stability of 6.42 hours and cold filter plugging point value of -2 ºC. An additive of acrylic co-polymer as the cold flow improver (CFI) reduced the CFPP value from -2 ºC to -6 ºC which results in better low temperature properties of corn-jatropha biodiesel blend.

Introduction

Biodiesel is a renewable fuel that comprises of monoalkyl ester of long chain fatty acid derived from the vegetable oils and animal fats [1]. Biodiesel is produced from various types of edible and non edible oils but the fatty acid content varies from source to source and the quality and properties also changed due to the nature of fatty acid methyl ester. More than 95% biodiesel produced are from the edible oils. If such a huge amount of edible oil is used regularly for biodiesel production, it will create the food versus fuel controversy.One of the ways to overcome this crisis is to use non-edible oils for biodiesel production instead of edible oils [2]. As an effort to encourage the usage of non-edible oil as feedstock in biodiesel production, an investigation of the blending of methyl ester of non-edible oils and methyl ester from edible oil is carried out. In this study, refined corn oil and jatropha curcas oil is used. Corn is the third most vital grain in the world after wheat and rice. Corn oil's benefits include its very low level of linolenic acid, contain high amount of unsaturated fatty acids and low content of saturated fatty acids. There is a growing intrest in jatropha curcas L. as the feedstock for biodiesel production. The estimates of the oil content in the seeds range from 35-40% and in the kernels the vary 55-60% [3]. The jatropha curcas L oil contains large amount of unsaturated fatty acids such as oleic and linoleic, thus its cold flow properties are better and oxidative stability is less than the EN 14214 limit [4]. The Jatropha and corn methyl ester show similar fuel properties to conventional diesel compare to Canola and Karanja methyl ester [5]. Last few years, several ways have been studied to resolve the low temperature operability problems of biodiesel. Biodiesel mixed with fossil diesel at various ratios reduced the CP and CFPP [6,7]. Poor cold flow properties have been improved in various ways, such as blending with fossil diesel, using synthetic additives (cold flow improver), by adding a surfactant or winterization additives [8]. The chemical additive treatment is one of the way to improve the cold flow properties. Cold flow improver (CFI) is usually a pour point depressant (PPD) having low molecular weight co-polymers with similar structure and melting point as the n-alkane paraffin molecules which allow them to co-crystallize after nucleation has been initiated [9]. Ploymethacrylates are the most widely used pour point depressants.

In the current study as an effort to support the usage of non-edible feedstock in biodiesel production. Jatropha has been selected as the non-edible oil representative and Corn as representative the edible oil. Jatropha is one of the most important non-edible feedstock for biodiesel production with high amount of free fatty acids and high oil content.

Materials and Methodology

The crude jatropha oil was purchased from Eco Energy Solution Ptv. Ltd. Refined corn oil was obtained from Mazola/Sweet Yet Development Sdn. Bhd purchased from a local store. The chemicals and reagents such as anhydrous methanol (99.8%), sulfuric acid (98%), sodium methoxide (25% in methanol solution) were of analytical reagent grade.

Pretreatment. Acid esterification was carried out since the initial acid value of crude jatropha oil was 47 mg KOH/g oil. The initial acid value of refined corn oil was less than 1%. Thus acid esterification for corn oil was not necessary. The reaction was perform by following the previously used method by Khan et. al [10]. The reaction was performed in a three neck round bottom flask, with 250 g of crude jatropha oil in the three neck flask, 1% (by weight of oil) of H_2SO_4 and 10:1 molar ratio of methanol to oil. Methanol and sulfuric acid were poured in a drop wise manner to the oil and were mixed via magnetic stirrer. The mixture was heated at 65 °C. A condenser was used to avoid the loss of methanol. The reaction time was 4 hours and the temperature was maintained at the desired temperature throughout the reaction period. At the end of the reaction duration, the sample was poured into a separating funnel and left for 24 hours for phase separation. After 24 hours, the mixture was separated into two layers, lower layer contained mainly the treated jatropha oil and upper layer contained excess methanol and catalyst. The treated jatropha oil was washed with de-ionized warm water. The remaining methanol and water was removed by using rotary evaporation under vacuum at 70 °C. Finally, the treated jatropha oil was obtained.

Transesterification. Transesterification of treated jatropha and refined corn oil was then performed in a round bottom flask with condenser and thermocouple. Three neck flask was filled with 200g of refined corn oil, 1% (by weight of oil) of sodium methoxide was used as a catalyst and 6:1 molar ratio of methanol to oil mixture was heated at 65 °C for 90 minutes. Sodium methoxide and methanol was mixed and poured into the flask. At the end of reaction time, the sample was cooled down at room temperature and then poured into the separating funnel and left over night. The two layers were obtained where the lower layer is mainly glycerol and the upper layer is mainly corn oil methyl ester (CME). CME is separated and washed with de-ionized water. After washing, the residual methanol and water was removed by vacuum distillation. Similar parametric conditions and method was used to produce the jatropha methyl ester (JME).

Blending of CME and JME. In this study biodiesel blends were prepared in different weight ratio of CME: JME varying from 20:80 to 80:20. Both CME and JME were mixed and stirred for homogenization. The cold flow properties and oxidative stability of blended biodiesel were checked and compared with the B100 sample which represents 100 percent biodiesel.

Results and Disscusion:

Feedstock Analysis. Preliminary analysis of crude jatropha oil (JO) was conducted, and the density of 882.46 kg/m3 at 15 0C and the acid value is 47 mg KOH/g oil were obtained. The corn oil (CO) density is 885.70 kg/m3 at 15 0C and the acid value is 1.6 mg KOH/g oil.

Fatty acid composition. Gas Chromatography was used to analyze the fatty acid composition of JME, CME and the fatty acid composition of each blend. Table 1 listed the major fatty acid composition of JME and CME blend. The composition of saturated fatty acid (SFA) was lower compared to the percentage ofthe unsaturated fatty acid (USFA) for both JME and CME. Table 1 shows the results of JME and CME blends.

Table 1, Fatty Acid Profile of JME: CME blends.

Fatty Acid (wt. %) CME:JME	0:10	20:80	40:60	60:40	80:20	100:0
Palmitic C16:0	22.45	22.08	22.24	22.32	22.70	22.11
Palmitoleic C16:1	3.27	2.84	2.31	1.82	1.42	1.14
Stearic C18:0	10.00	9.19	7.94	6.77	5.42	4.09
Oleic C18:1	8.04	7.63	6.73	7.53	7.49	8.14
Linoleic C18:2	52.90	54.18	55.91	57.18	58.04	59.06
Arachidic C20:0	1.12	1.22	1.26	1.62	1.92	1.95
Saturated Fatty acid	33.57	32.49	31.44	30.71	30.04	28.15
Unsaturated fatty acid	64.21	66.38	64.95	66.52	66.95	68.34

Oxidative Stability. Oxidation of biodiesel can form short chain fatty acids, which can cause the corrosion in the engine. The oxidation stability is determined via the Rancimate method. EN14214 stated that the oxidative stability of biodiesel should be determined at 110 °C and required a minimum value of 6 hours for the induction period.

Figure 1 (a) shows the Induction period (IP) plot against the biodiesel mass fraction of jatropha and corn and their different ratio of weight percentage. At 0.6 and 0.8 ratios represent the CME: JME at (40:60) and CME: JME at (20:80) respectively. The IP of 0.6 and 0.8 are 6.18 and 6.42 hours respectively. The IP escalated as the amount of unsaturated fatty acids increased with the presence of higher amount of JME in the blends. Thus the CME: JME (20:80) is selected for further improvement in the cold flow properties.

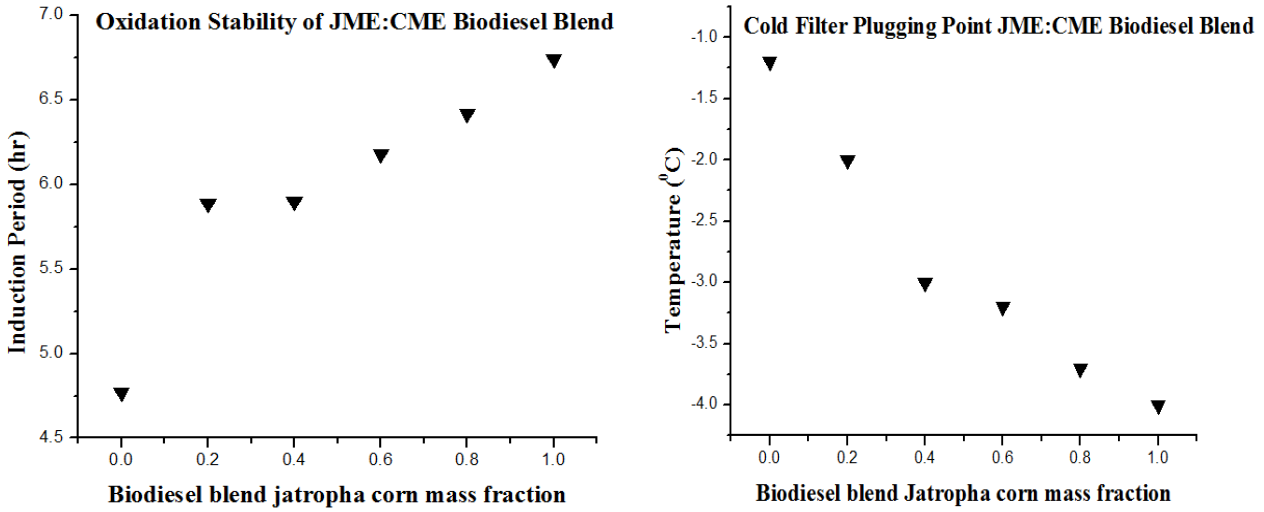

Fig. 1 (a) Oxidation stability of JME:CME biodiesel blend, (b) Cold Filter Plugging Point of JME:CME biodiesel blend

Cold Filter Plugging Point. The CFPP was analyzed by using ISL FPP 5Gs by following the ASTM method. Figure 1(b) shows that pure CME has a CFPP value of -4 ºC which is lower than pure JME which has a value of -1.2 0C. It can be seen that the edible oil has a better CFPP value as compared to non-edible JME [11]. The blend ratio of 20:80 (JME: CME) from the lowest CFPP value of -3.7 ºC. The CFPP value increased by increasing the weight fraction of CME in the blend. Although the blend ratio of 20:80 (JME: CME) has the lowest CFPP, the oxidation stability of this blend is 5.80 hours less than that specified in EN 14214 standard limit. Thus the blend of 80:20 (JME: CME) with an oxidation stability of 6.42 hours and -2 0C CFPP was used to further investigate the performance of cold flow improver (CFI).

Performance of Cold Flow Improver (CFI). The acrylic co-polymer was used as a CFI in this study. The acrylic co-polymer acts as cold flow improver and it significantly reduces the growth and agglomeration rates and thus prevents the crystal growth but does not prevent the crystal

initiation. They have little effect on the temperature at which crystal already formed [12]. The effect of an acrylic co-polymer on the CFPP of the 80:20 (JME:CME) at different mass ratio of 0%, 0.5% and 1% of acrylic co-polymer was studied and 1% mass ratio of CFI is found to be the effective percentage. The CFPP of the 80:20 (JME:CME) blend decreased from -3.7 0C to -6 0C.

Conclusion

An investigation on the blending of CME with JME was performed to improve the cold flow properties of JME. The study showed that the blend ratio of 20:80 (CME: JME) has the CFPP value of -2 ºC and oxidation stability of 6.42 hours. With the addition of the CFI, the CFPP value decreased from -2 ºC to -6 ºC.

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