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Effect of single double bond in the fatty acid profile of biodiesel on its properties as a CI engine fuel

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Abstract
Fatty acid profile of the vegetable oil and animal fats plays a major role in determining the properties of biodiesel derived from them. Eventhough the type of fatty acids in vegetable oils are similar, their distribution is different. The percentage distribution of fatty acids differs by a significant magnitude with respect to the type of vegetable oil. In the present investigation the effect of single double bond fatty acids in the vegetable oil on its physical and chemical properties are investigated. Different vegetable oils based on the type and geography were selected and the properties of biodiesel derived from it were analysed with respect to its fatty acid of single double bond. From the results of the investigation it is inferred that the fatty acids with single bond plays an important role in determining the properties of biodiesel as a CI engine fuel.

Keywords: Biodiesel; Fatty acid profile; Double bond; Unsaturated fatty acids; Saturated fatty acids.

1. Introduction
Biodiesel, a clean burning renewable fuel, has been paid more attention for the past two decades as an alternative fuel for petroleum diesel [1-8]. As per the ASTM standard 6751 biodiesel is a mixture of long chain fatty acid esters derived from vegetable oils and animal fats that contain only one alcohol molecule on one ester linkage[9]. Fatty acids with glycerine backbone present in the vegetable oil and animal fats are the major resources for the production of biodiesel. Each vegetable oil molecule is made up of a glycerin backbone of three carbons, and each of these carbon atoms is attached to a long chain fatty acid. Varieties of vegetable oils and animal fats (feedstock) which contain fatty acid in its structure are used to produce biodiesel. The chemistry of the feed stocks is similar and contain 10 common types of fatty acids with carbon atoms between 12-22. When comparing these carbon atoms it was found that over 90% are between 16-18. Some of these fatty acids are saturated while others are unsaturated. The level of unsaturation depends upon the number of double bonds present in it. For mono-unsaturation the number of double bonds is 1, and two or more for poly-unsaturation. Each feedstock contains different proportions of saturated, mono-unsaturated and poly-unsaturated fatty acids. The levels of this saturation will affect some of the biodiesel properties. This may also lead to a variation in the engine characteristics when biodiesel is employed as a CI engine fuel. A perfect biodiesel would be made only from mono-unsatuarted fatty acids [9]. Attempts have been made to predict the effect of saturation level on the properties of biodiesel [10]. In the present work attention was focused to investigate the effect of single double bond (mono-unsaturated fatty acids) present in the fatty acid profile of biodiesel on its properties.

2. Experimental programme

2.1 Selection of vegetable oil

Initially three vegetable oils namely cotton seed oil, karanja oil and jatropha oil were chosen for the investigation. Oils were selected such that the variations in unsatuartion and saturation levels between the oils are less in magnitude. Any variation in properties of the biodiesel will be considered as a result of difference in mono-unsaturated fatty acids (MUSFA) present in the biodiesel. Table 1 shows the list of properties tested for biodiesel and their testing method

Table 1. Properties of biodiesel and testing method

Fuel property	Testing method
Viscosity at 40°C (mm^2/sec)	Redwood viscometer
Flash point (°C)	ASTM D 92
Calorific value (kJ/kg)	ASTM D 240-02
Distillation temperature T90 (°C)	ASTM D86
Calculated Cetane Index	ASTM D 4737

This investigation was enriched by including the properties of another five different biodiesels which were reported by the earlier research works [11-15]. These biodiesels were considered since they have higher amount of MUSFA in their fatty acid profile. The testing method followed in the earlier works to determine the properties of biodiesel were similar to that of the present method.

3. Fatty acid profile

Table 2 shows the saturation levels of the selected biodiesels. It can be seen that the difference in unsaturation levels of the cotton seed, jatropha and karanja are lesser in magnitude with significant difference in MUSFA. In other biodiesels like rape seed, corn and olive oil, MUSFA dominates in the fatty acid profile with more than 70 % of unsaturation

Table 2. Saturation levels of biodiesel

Methyl ester	% of Mono unsaturated fatty acid	% of unsaturated fatty acid	% of saturated fatty acid
Cottonseed	19.2	75	23.8
Rubber seed	27.8	78.9	21
Jatropha	42.1	73.2	26.2
Karanja	53.2	72.3	17.8
Rape seed	64.6	94.6	5.4
Corn	66.4	91.7	8
Olive	76	84.4	15.7

4. Results and discussion

Various properties shown in Table 1 for the selected biodiesels given in Table 2 are presented as a function of MUSFA in the biodiesel.

4.1 Effect of MUSFA on viscosity of biodiesel

Figure 1 shows the variation of viscosity of biodiesels with respect to its MUSFA. It is observed that MUSFA of biodiesel has an influence on its viscosity since the curve is not a horizontal line. It can be seen that as the MUSFA of biodiesel increases its viscosity also increases till 35% of MUSFA and decreases with further increase in MUSFA. It can also be seen from Table 1 that for biodiesel with low MUSFA (cotton seed, rapeseed) the percentage of saturated fatty acid has also increased with increase in MUSFA which leads to an increase in viscosity. For the biodiesels from other oils the increase in MUSFA causes a decrease in viscosity. Since the saturated fatty acid content of olive oil (15.7 %) is more than corn oil (8 %) it shows an increase in viscosity with increase in MUSFA. In general the presence of higher unsaturated fatty acids will decrease the viscosity of biodiesel since the molecular weight of unsaturated fatty acids investigated is lower than that of the saturated fatty acids.

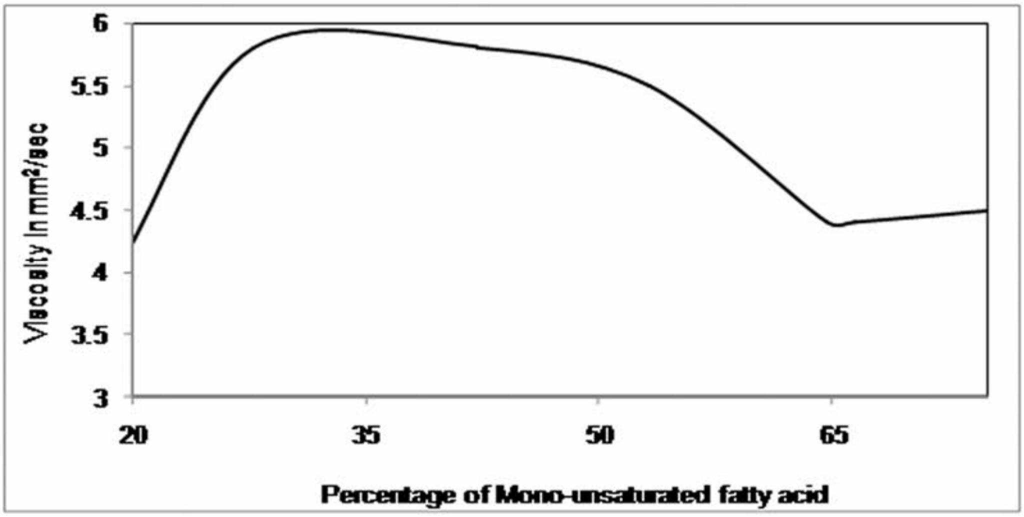

Figure 1. Variation of viscosity with MUSFA

4.2 Effect of MUSFA on calorific value of biodiesel

The variation of calorific value of biodiesels with MUSFA is shown in Figure 2. It can be seen that an increase in MUSFA of biodiesel decreases its calorific value. It can also be seen that the variation is inconsistent in nature which is due to the influence of saturated fatty acid in the structure. In general, the energy content of saturated fatty acid is more when compared with unsaturated fatty acids. As the unsaturation increases it will lead to a decrease in calorific value of the biodiesel. It is observed that the calorific value of biodiesel not only depends on MUSFA in biodiesel but also the percentage of saturated fatty acids as evident from Figure 2 and Table 2.

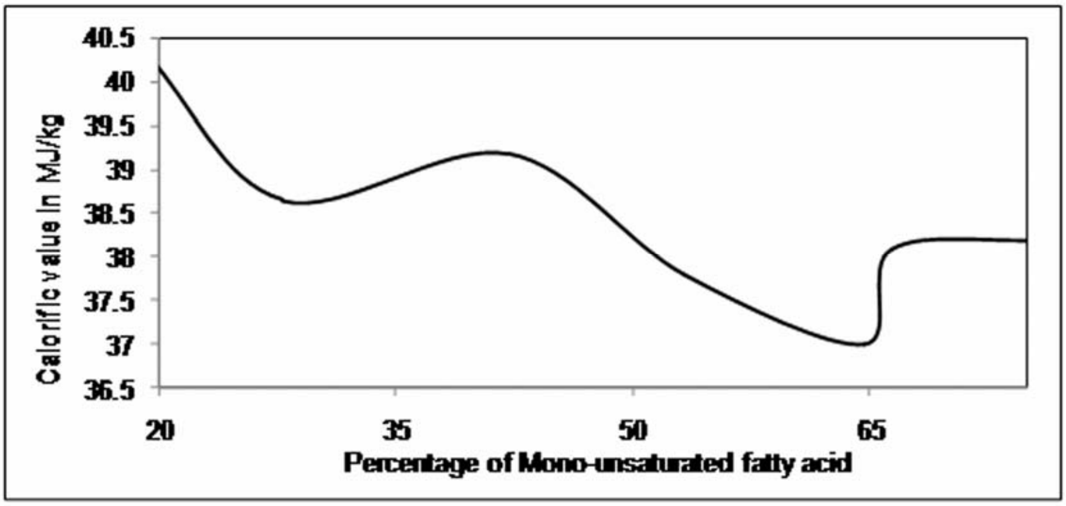

Figure 2. Variation of calorific value with MUSFA

4.3 Effect of MUSFA on flash point of biodiesels

Figure 3 shows the variation of flash point (FP) of biodiesels as a function of MUSFA .It can be seen that as MUSFA increases the FP of biodiesel decreases at lower levels and at higher levels the FP of biodiesel increases with increase in MUSFA in it. At lower percentage levels even though the MUSFA increases, the percentage of poly unsaturated are more which results in a decrease in FP. At higher percentage levels increase in MUSFA decreases the poly-unsaturated fatty acids which have lower molecular weight than MUSFA. This results in an increase in FP with increase in MUSFA.

4.4 Effect of MUSFA on Cetane index of biodiesel

Figure 4 shows the variation of calculated Cetane index (CCI) as a function of MUSFA of biodiesel. It shows an erratic variation which shows that CCI not only depends on MUSFA but also on other saturation and unsaturation levels. Cetane number of saturated fatty acids is higher than unsaturated fatty acids and the presence of more unsaturated fatty acids will have lower cetane index. This can also be evident from Figure 4 that biodiesel of higher MUSFA have lower CCI than that of lower MUSFA. The variation of CCI of biodiesel with respect to MUSFA depends upon the associated variation of saturated and unsaturated fatty acids. If the increase in MUSFA is associated with increase in saturated fatty acid, the CCI of the biodiesel will increase.

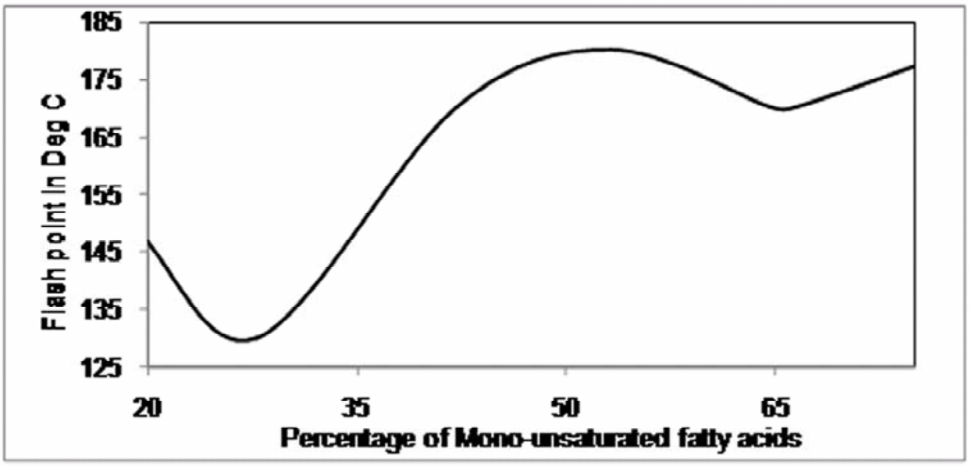

Figure 3. Variation of flash point with MUSFA

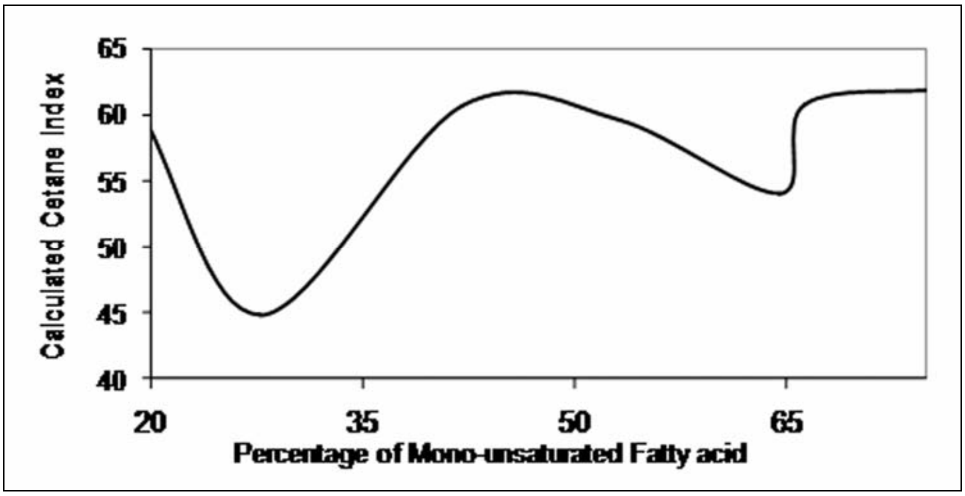

Figure 4. Variation of cetane index with MUSFA

4.5 Effect of MUSFA on T90 of biodiesel

Figure 5 shows the variation of 90 % recovery temperature on distillation curve (T90) for biodiesels as a function of MUSFA. It can be seen that as the MUSFA increases the T90 of biodiesel increase initially and shows wavy nature of variation with further increase in MUSFA. As the MUSFA increase it decreases the percentage of poly-unsaturated fatty acids present in the biodiesel which causes an increase in T90 since the molecular weight of MUSFA is higher than poly-unsaturated fatty acids. The increase in T90 of biodiesel depends upon the associated increase in saturated and poly unsaturated fatty acids. If the increase in MUSFA is associated with saturated fatty acids T90 of biodiesel will increase.

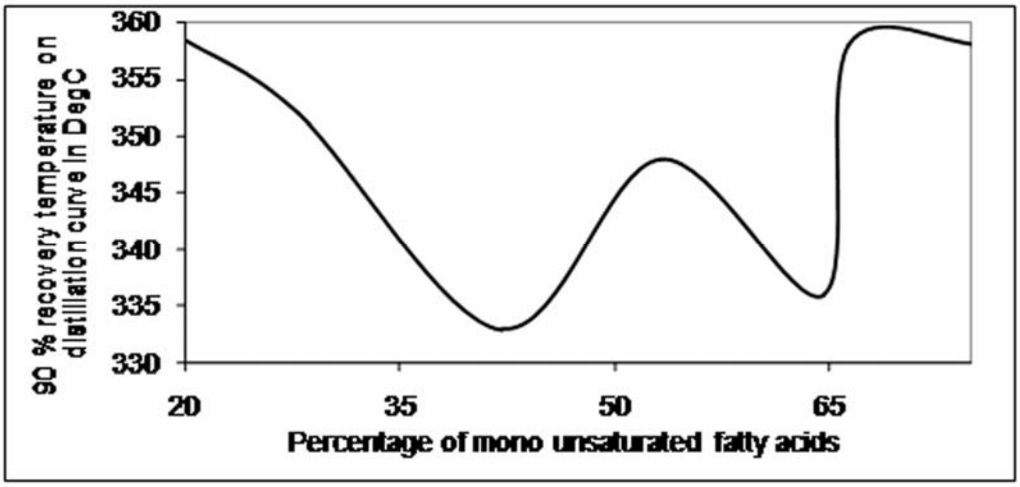

Figure 5. Variation of T90 with MUSFA

5. Conclusion

From the investigation the following conclusions are drawn

(i) Properties of biodiesel depends upon their fatty acid profile and their saturation and unsaturation levels

(ii) Variation of MUSFA shows a significant variation in the properties of biodiesel

(iii) variation in properties with MUSFA depends upon the associated variation of poly- unsaturated and saturated fatty acids.

(iv) To throw more light on the effect of MUSFA, deeper investigation with biodiesels produced from a wider variety vegetable oils and fats with close levels of saturation and unsaturation, where variation in MUSFA is the only significant parameter, is suggested

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