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# Improvement Of Cold-Flow Properties Of Biodiesel And Its Blends In Petroleum-Based Diesel

Rajesh Kumar[1], Rajneesh Verma[2], Parijat Srivastava[3], Pratima Katiyar[4]

*[1*]Department of Chemical Engineering , H. B. Technical University, Kanpur, India*
*[2]Maharana Pratap Engineering College Kanpur,India*
*[3]Maharaja Ranjit Singh Punjab Technical University, India*
*[4]Research Scholar, DAV- PG College Kanpur Nagar,India*

## ABSTRACT

Biodiesel (fatty acid methyl ester) which is derived from triglycerides by transesterification has attracted considerable attention during the past decade as a renewable, biodegradable and nontoxic fuel. Several processes for biodiesel fuel production have been developed, among which transesterification using alkali as catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in a short duration. This process has therefore been widely utilized for biodiesel fuel production in a number of countries. In India, non-edible oils like karanja oil and jatropha oil are available in abundance, which can be converted to biodiesel. The present work deals with influence of chemical additives polymethyl acrylate (PMA) and poly alpha olefin (PAO) on the flow properties of biodiesel made from Jatropha and Karanja oils and its blends in petroleum based diesel fuels and anhydrous ethanol at low temperatures. Effect of ethanol and commercial additives on cold flow behavior of this biodiesel was studied. A considerable reduction in pour point has been noticed by using these cold flow improvers. The experimental results showed that the poly alpha olefin additive was very effective in the depression of the pour point of jatropha biodiesel and karanja biodiesel and retard viscosity increase of biodiesel at low temperatures when incorporated into biodiesel at the additive contents of 5.0 g/L.

**Keywords:** Biodiesel, Pour point, Cloud point, Kinematic viscosity, Biodiesel-Diesel blends

**Nomenclature**
**KBD= Karanja biodiesel**
**JBD= Jatropha biodiesel**
**PMA= Polymethyl acrylate**
**PAO= Poly alpha olefin**
**KO = Karanja oil**
**JO= Jatropha oil**

## 1. INTRODUICTION

Biodiesel is an alternative fuel for diesel engines derived from natural renewable sources. It is produced from virgin or used vegetable oils (both edible and non-edible oils) and animal fats through various chemical processes. The most common is transesterification process (Srivastava et al., 2002; Otera, 1993; Srivastava et al., 2000; Clements et al., 1998 Fukuda et al., 2001 Yogesh et al., 2014 Meisam et al., 2015 Temitope et al., 2014). Biodiesel can be used as a fuel in its pure from as well as in any concentration with petroleum-based diesel in existing diesel engines with little or no modification. The main advantages of using biodiesel are its renewability, better quality exhaust gas emissions, biodegradability and given that all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere consequently leading to the greenhouse effect Pahan et al., (2005).

The disadvantages of biodiesel are its unfavorable cold-flow properties. Since it begins to gel at low temperature which clogs filters or even becomes so thick that it cannot be pumped from the fuel tank to the engine. Under these conditions, the fuel becomes a suspension of wax crystals in a mixture of shorter-chained n-alkanes, olefins and aromatics, although the crystals are initially to submicron in size and invisible to the human eye. The crystals grow in size as temperature drops further and when the particle size reaches 0.5 µm, the crystals become visible Chuang et al., (2004); Tomas et al., (2010) and Joshi et al., (2009). The temperature at this point is defined as the cloud point. If unchecked, the crystals continue to grow into large flat plate-like structures. As temperature drops below the cloud point the crystals become large enough (0.5- 1.0 mm) to fuse together into large agglomerates and the temperature at this point is defined as the pour point Boshui et al., (2010) and Bhale et al., (2009). The kinematic viscosity of a fluid plays a major role in its pumping and flow within an engine. Generally, methyl esters have a Newtonian behavior within typical working temperatures. However, methyl esters from soybean and mustared oils present pseudoplasstic behavior when temperatures reach values below 5 °C, presenting high viscosity under low shear rates and low viscosity under high shear rates. This high viscosity at lower temperature could be result of micro-crystal formation and would cause serious problems in fuel and in engine filters. One of the most important reasons of the vegetable oils not being used in diesel engines is their high viscosities. High viscosity also causes more problems in cold weather, because viscosity increases with decreasing temperature Alptelan et al., (2008).

It is proposed to study various approaches for improving the cold-flow properties of biodiesel made from different sources of triglycerides. These approaches include, blending with petroleum-based diesel and use of chemical additives in biodiesel Chuang et al., (2004). The use of chemical additives is most convenient and economical way of improving the low temperature properties of diesel fuel. The chemical additives are generally referred to as pour point depressants, flow improvers or wax modifiers. Most chemical additives promote the formation of small (10 -100 µm) needle shaped crystals Dunn et al., (1996). Chemical additives used for diesel fuel are mainly polymeric materials like polyacrylate, polymethacrylate of poly (ethylene-co-vinyl acetate), and poly alpha olefin. A more recent investigation, evaluated the influence of four cold-flow improvers were at 0.1-2% in B80, B90 and B100 blends. Two chemical additives significantly decreased the pour points of soybean biodiesel blends, but all the four cold flow improvers had little effect on cloud points. A mixture of 0.2% chemical additive, 79.8% biodiesel, and 20% kerosene reduced the pour point of B100 by 27 °C Dunn et al., (1996). Taomas et al., (2010) investigated 13 polymers, including alkyl methacrylate homo- and copolymers and it was found that poly (lauryl methacrylate) lowered the pour point by as much as 30 °C and the LTFP by as much as 28 °C. With respect to polymer concentration, it was found that poly (lauryl methacrylate) concentrations of 0.14% performed poorly. The cloud point and pour point of biodiesel (ethyl esters of fish oil), no.2 diesel fuel and B20, B40, B60 and B80 blends were investigated. In all cases the cloud point and pour point of biodiesel decreased with increase in concentration of no.2 diesel Jimenez et al., (2010). The tested fuels were neat mineral diesel fuel (D100), 5% (v/v) ethanol/diesel fuel blends (E05D95), 10% (v/v) ethanol-diesel fuel blend ( E10D90) and 15% (v/v) ethanol-diesel fuel blend ( E15D85). Also, cold weather properties test, such as cloud point and pour point tests are negatively affected by phase separation Jimenez et al., (2011); Kwanchareon et al., (2006). Boshui et al., (2010) and Dunn et al., (2009) evaluated the influence of three cold-flow improvers i.e. olefin-ester copolymers (OECP), ethylene vinyl acetate copolymer (EACP) and polymethylacrylate (PMA) on the cold flow properties of soybean biodiesel. The pour point and cold filter plugging point of neat soybean biodiesel can significantly be inferred from the polarizing microscopic analysis that OECP functioned by reducing the size and amount and altering the shape of the wax crystals of biodiesel. The viscosities of diesel fuels are lower than those of biodiesel. The viscosity of the blend increases with the increasing biodiesel fraction for all the blends. Alptekin et al., (2008) and Dunn et al., (2000) examined 12 chemical additives in methyl soyate. At a 0.1% loading of additives in pure biodiesel, the pour point depression ranged from 2 to 8 °C. Dunn et al., (1996) evaluated the impact of ozonized vegetable oil in lowering the pour point and found the best results occurred with blending of ozonized vegetable oil with the biodiesel derived from the same stock materials. In some cases, it was reported that use of additives and dilution in ≠ 1 resulted in the largest pour point depression. Soriano et al., (2005) and Bhale et al., (2009) studied the effect of ethanol, Lubrizol 7671 and kerosene on the cold-flow properties of neat Madhuca indica biodiesel; Lubrzole 7671 is a pour point depressant. From this study, it was observed that the cloud point was reduced by 10 °C with 20%, ethanol and 13 °C with 20% kerosene, but there was no effect on the cloud point when blended with Lubrizol. Biodiesel Tech Note the effectiveness of four commercially available biodiesel chemical additives (Flozol 503, Bioflow 875, MCC P205, and Arctic Express 0.25%) on the low temperature behavior of soy biodiesel/diesel fuel blends was studied. As expected, the additives had almost no effect on the cloud point. A maximum reduction in cloud point of 1.8 °C was observed with the MCC additive on B20. All of the fuel additives were found to be effective in reducing the pour point for the baseline diesel fuel and the B5 and B20 blend levels with PPs below -36 °C in most cases (ID- 83844-0904). In a more recent investigation, reported that ethyl levulinate as a potential bio-based diluent for biodiesel improved the cold flow properties. Joshi et al., (2010) they also revealed that flash point value decreased with increasing contents of ethyl levulinate

The present work deals with influence of chemical additives PMA (polymethacrylate) and PAO (poly alpha olefin) on the flow properties of biodiesel made from Jatropha and Karanja oils and its blends in petroleum based diesel fuels and anhydrous ethanol at low temperatures. The effects of these chemical additives on the cloud point, pour point and kinematic viscosity of biodiesel and its blends in petroleum based diesel fuels at low temperatures.

## 2. EXPERIMENTAL SECTION

### 2.1 Material

Jatropha (JO) and Karanja (KO) oils were purchased from M/s Jatropha Vikas Sansthan, Delhi. Methanol 99.9% (LR grade) and sodium hydroxide 99.8 (AR grade) were obtained from M/s Ranbaxy Laboratories Limited, Delhi. Petroleum diesel was purchased from Indian Oil Corporation Depot, Kanpur. Ethanol (E) 99.9% (Jiangsu huaxi International Trade Co. Ltd made in China) was purchased from local supplier. Chemical additives PMA and PAO were purchased from M/s Pawan & Company, Delhi. The characteristics of these additives and Jatropha and Karanja oils and its biodiesel are given in Table 1and 2.

**Table1. Characteristics of PMA and PAO**

| Characteristics | Value for | | | |
|---|---|---|---|---|
| | PMA | PAO | Diesel | Ethanol |
| Density, kg/m3 | 0.867 | 0.896 | 0.855 | 0.794 |
| Molecular weight, kg/kmol | 2260 | 1875 | - | - |
| Pour point, °C | -6 | -9 | -18 | < -18 |

**Table 2 Characteristics of Jatropha and Karanja oil and its biodiesel**

| Characteristics | Jatropha oil | Karanja oil | Biodiesel prepared from | |
|---|---|---|---|---|
| | | | Jatropha oil | Karanja oil |
| Free fatty acid, wt.% as oleic acid | 5.2 | 2.5 | 0.31 | 0.42 |
| Cloud point, ˚C | 2 | 5 | 3 | -1 |
| Pour point, ˚C | 1 | 1 | -5 | -7 |
| Kinematic viscosity at 40˚C, $mm^2/s$ | 33.30 | 30.95 | 4.16 | 3.58 |
| Acid value, mg/KOH/g | 5.19 | 4.25 | 0.81 | 0.61 |

### 2.2 Methods

Jatropha and Karanja oils contain free fatty acid usually in the range of (5.2, 2.5 oleic acid). If has to be reduced below acceptable limit for transesterification. Therefore, preparation of JBD and KBD are a two-step processes discussed below.

### 2.3 Preparation of Jatropha and Karanja Biodiesel

### 2.3.1 Acid -Catalyzed Esterification Process

Crude unrefined jatropha and karanja oil were dark greenish yellow in color. Its FFA content was determined by standard titrimetry method. Jatropha and karanja oils had an initial acid value of 5.19 mg/KOH/g and 4.25 mg/KOH/g. The high FFA level of JBD and KBD were reduced to less than 1% by an esterification process. The esterification process was carried out with 0.60 w/w methanol-to-oil ratio (455 g oil and 273 g methanol) in the presence of 1% w/w $H_2SO_4$ (2.3 ml) as an acid catalyst in 2-h reaction at 60 °C. Contents were allowed to cool and transferred to separating funnel for overnight. Methanol-water layer formed at the top was removed. The FFA content of esterified product was determined by standard titrimetric method. The acid value of the esterified product separated at the bottom was also determined. The product having acid value (0.81 mg/KOH/g and 0.61 mg/KOH/g)) was used for the transesterification process.

### 2.3.2 Alkali-catalyzed transesterification process

The transesterification process was carried out with 0.24 w/w methanol-to-oil ratio (455 g oil and 109 g methanol) using 0.55 w/w KOH (2.50 g) as an alkaline catalyst. The esterified product from previous step was poured into the flask and heated at 50 °C. The solution of KOH in methanol based on oil weight is heated to 50 °C before addition and then added to heated oil. Excess alcohol was normally used to ensure total conversion of the fat or oil to its esters. The reaction mixture is heated and stirred at 60 °C and 400 rpm for two hours. After completion of reaction the contents were cooled and transferred to separating funnel. The product was allowed to stand overnight for separation of glycerol layer from methyl ester layer of fatty acids on top. JBD and KBD are separated and washed with distilled water 4 to 5 times (approximate 50 ml) to remove alkali (Phenolphthalein test). JBD mixture was then dried with anhydrous sodium sulphate (15 g approximate) followed by filtration. The mixture was distilled to remove unreacted methanol. The residue in the flask was only JBD. This JBD was tested cloud point, pour point and kinematic viscosity.

### 2.4 Preparation of Blends

JBD and KBD produced in the laboratory have been used for the preparation of its blends with petroleum diesel (PD) by blending technique. Biodiesel and petroleum-based diesel is blended in a conical flask under continuous stirring to ensure uniform mixing at 45 °C for 60 minute. These blends were prepared on volume basis and were stored in glass bottles.

### 2.4.1 Preparation of JBD-PD-additive blends

Blends of JBD-PD and KBD-PD were prepared having composition of 100%, 5%, 10%, 15% and 20% v/v. 100 ml of each blends was taken in glass flasks. This was followed by addition of 2.5%, 5.0%, 7.5%, and 10 % w/v PMA and PAO to each flask. Uniform mixing was censured by continuous stirring at 45 °C for 60 minutes.

### 2.4.2 Preparation of JBD and its blends in ethanol and diesel

Blends of ethanol-JBD and diesel were prepared in various proportions on % basis and effect of those blending on cloud point, pour point and kinematic viscosity was investigated. The results are summarized in Table 3 and 4.

### 2.4.3 Preparation of JBD and its blends in oil and diesel

Effect on cloud point, pour point and kinematic viscosity of Jatropha oil-JBD and Diesel blends (% basis) was also investigated. The results are summarized in Table 5 and 6.

### 2.4.4 Preparation of JBD-PD-additive blends

Blends of JBD-PD and KBD-PD were prepared having composition of 100%, 5%, 10%, 15% and 20% v/v. 100 ml of each blends was taken in glass flasks. This was followed by addition of 2.5%, 5.0%, 7.5%, and 10 % w/v PMA and PAO to each flask. Uniform mixing was censured by continuous stirring at 45 °C for 60 minutes.

## 3. RESULTS AND DISCUSSION

### 3.1 Cloud Point and Pour Point

Cloud point, and pour point studies were conducted for JBD-PD and KBD-PD blends with and without cold-flow improvers, in blends of JBD in ethanol and diesel and in Jatropha oil and diesel. Although most of the properties of biodiesel fuels are comparable with that of diesel fuel but cloud point and pour point indicate poor cold-flow behavior. These results are describe in the following figure. The cold-flow properties of biodiesel can be improved using various strategies. Studied related to two common strategies, blending of biodiesel and addition of cold-flow improvers, are discussed below.

It is also common to add cold-flow improvers to biodiesel to prevent galling at low temperatures. The cold-flow improvers can, in some cases, interfere with crystallization, thereby lowering freezing point. However cold-flow improvers generally used as crystal modifiers. For example, in the case of wax formation in petrodiesel, it is known that plate-like crystals as large as 1 mm will form and interconnect into crystal agglomerates Chandler J., E., (1992). The chemical composition of the cold-flow improver is a critical consideration. That is it must be thermodynamically favorable for the polymer to be integrated into the forming crystal in order for the polymer to affect the crystals size and shape. Thus, cold-flow improvers with a variety of chemical structures were screened. The results of three cold flow improvers are summarized in figure 1-22 and listed table 3 and 4. The two main classes cold-flow improvers that were studied were polymethacrylate and poly alpha olefin because these are known to successfully modify crystal growth in petrodiesel. As expected, almost all the cold-flow improvers had no impact on the cloud point temperature Dunn et al., (1996).

Measurement of the pour point temperature provides a fairly clear understanding of which cold-flow improvers the cold-flow properties of biodiesel. The fundamental finding was that poly alpha olefin and polymethylacrylate significantly lowered the pour point of biodiesel. As was described above, the ability of cold-flow improvers to properly modify crystal growth strongly depends on the polymers chemical structure. Thus, increasing cold-flow improvers concentration and mixing the sample are expected to improve the dispersing properties of a polymer that has an appropriate chemical structure. On the other hand, it is noted that 7.5 g/L additive concentration may represent an excessive biodiesel treat rate, since many manufactures of commercial pour point dispersant recommend 1000ppm treat rates. It is possible that low concentration cloud perform better, since pour point dispersant themselves often have poor cold flow properties.

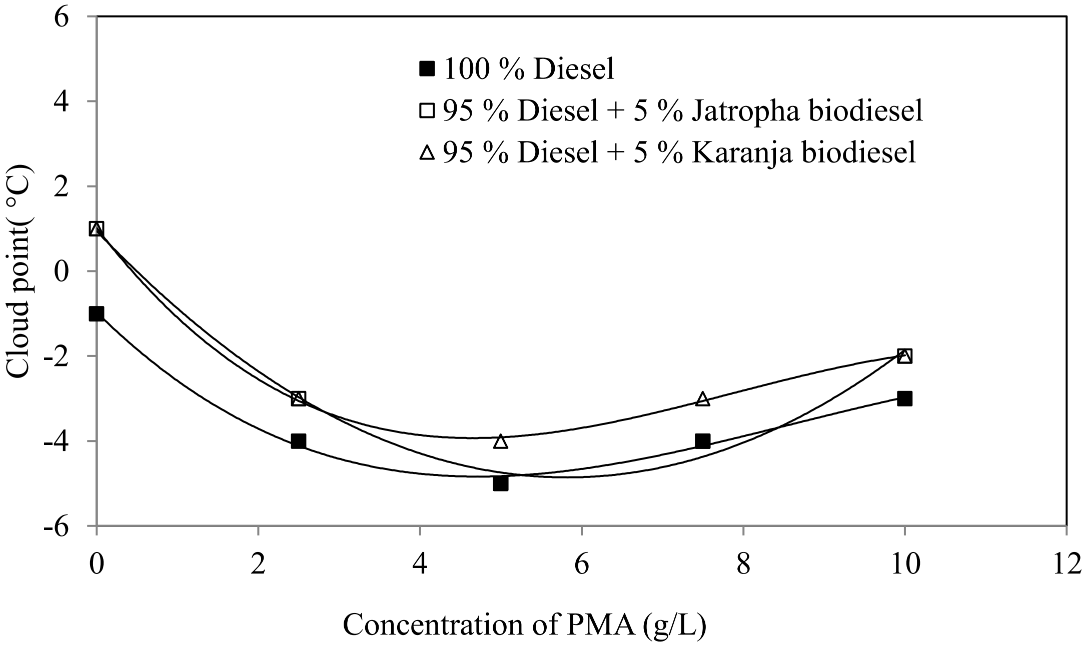

Fig. 1Variation of cloud point of diesel and their blends with concentration of PMA

Fig.1. Shows variation of cloud point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PMA cloud point increases with constant in jatropha biodiesel composition. For a given composition biodiesel blends cloud point decreases with increasing concentration of PMA. There appeared to be no benefit of treatment levels beyond 5.0 g/L. Adding 5.0 % PMA additive with 5% biodiesel and 95% diesel produced a cloud point -5 $^{O}$C –a significant reduction in these properties over the neat biodiesel. The additives had essentially little or no effect on cloud point.

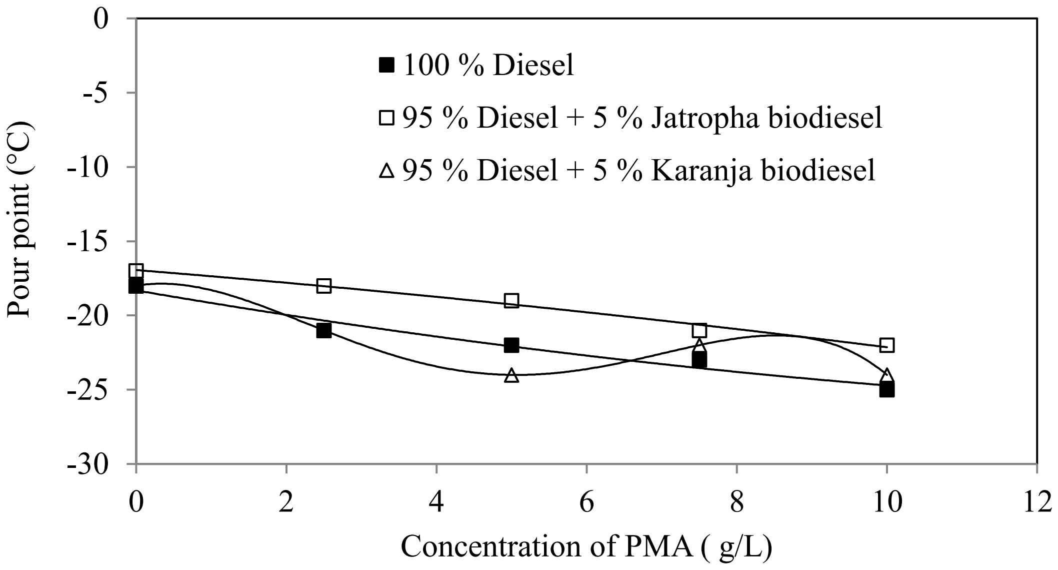

Fig. 2 Variation of pour point of diesel and their blends with concentration of PMA

Fig.2. Shows variation of pour point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PMA pour point increases with constant in jatropha and karanja biodiesel composition. For a given composition of biodiesel blends pour point decreases with increasing concentration of PMA. Adding 5.0 g/L additive with 5% jatropha biodiesel blends produced pour point (-24 °C). Composition between jatropha and karanja biodiesel blends in same concentration, karanja biodiesel shows best result. Karanja biodiesel is more effective blending of petroleum diesel.

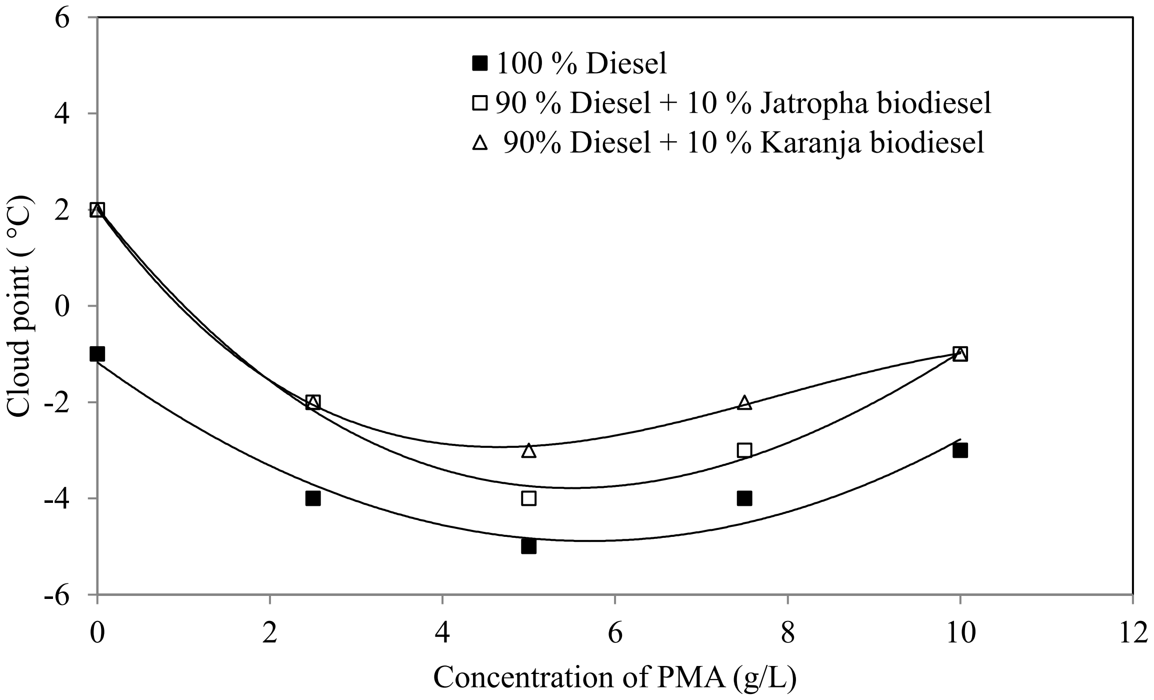

Fig. 3 variation of cloud point of diesel and their blends with concentration of PMA

Fig.3. Shows variation of cloud point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PMA cloud point increases with constant in jatropha biodiesel composition. For a given composition biodiesel blends cloud point decreases with

increasing concentration of PMA. There appeared to be no benefit of treatment levels beyond 5.0 g/L. Adding 5.0 % PMA additive with 10% biodiesel and 90% diesel produced a cloud point -4 °C jatropha and -3 °C karanja biodiesel –a significant reduction in these properties over the neat biodiesel. The additives had essentially little or no effect on cloud point.

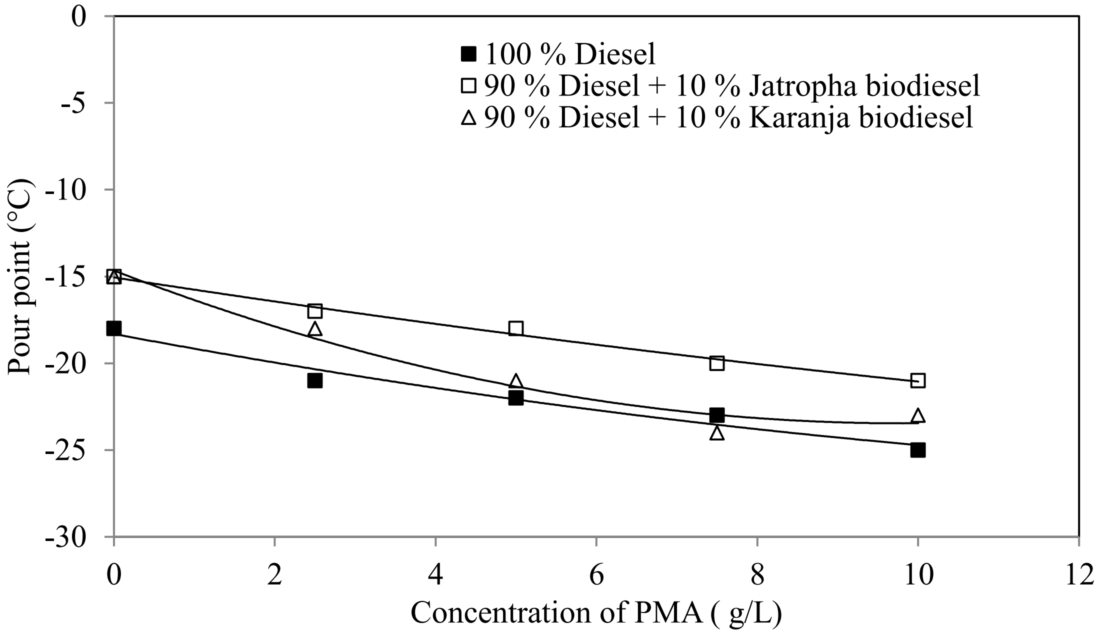

Fig. 4 Variation of pour point of diesel and their blends with concentration of PMA

Fig.4. Shows variation of pour point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PMA pour point increases with constant in jatropha and karanja biodiesel composition. For a given composition of biodiesel blends pour point decreases with increasing concentration of PMA. Adding 0 to 10 g/L additive with 10 % jatropha biodiesel blends produced pour point continuous increases. While adding 7.5 g/L PMA additive with 10 vol. % karanja biodiesel blends produced pour point -24 °C. Composition between jatropha and karanja biodiesel blends in same concentration, karanja biodiesel shows best result. Karanja biodiesel is more effective blending of petroleum diesel.

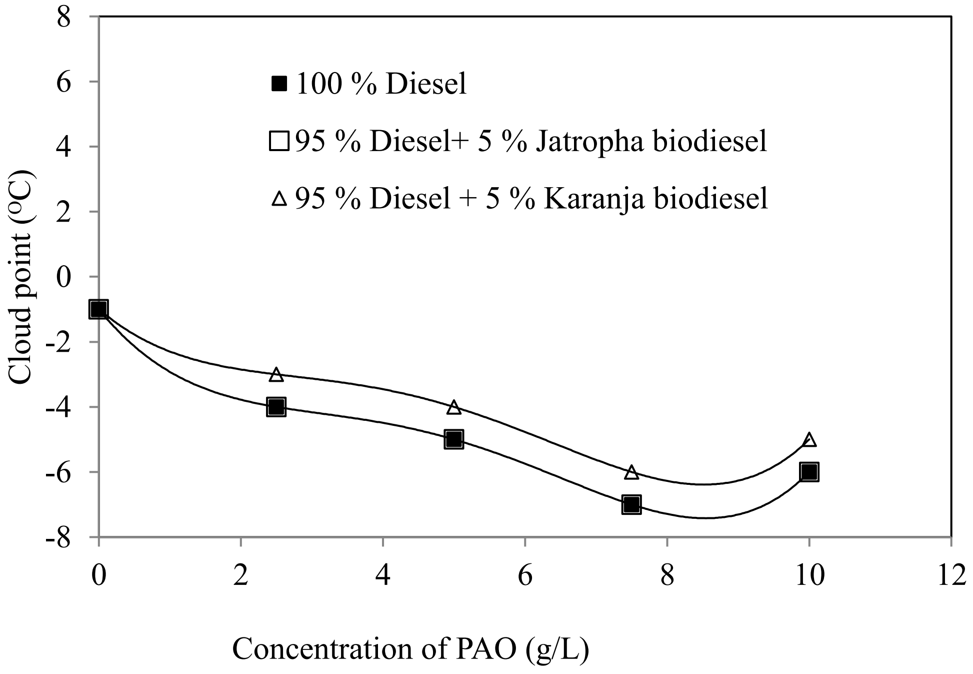

Fig. 5 variation of cloud point of diesel and their blends with concentration of PAO

Fig.5. Shows variation of cloud point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PAO cloud point increases with constant in jatropha biodiesel composition. For a given composition biodiesel blends cloud point decreases with increasing concentration of PAO. There appeared to be no benefit of treatment levels beyond 7.5 g/L. Adding 5.0 % PMA additive with 5 % biodiesel blends produced a cloud point -7 °C jatropha and -6 °C karanja biodiesel –a significant reduction in these properties over the neat biodiesel. The additives had essentially little or no effect on cloud point.

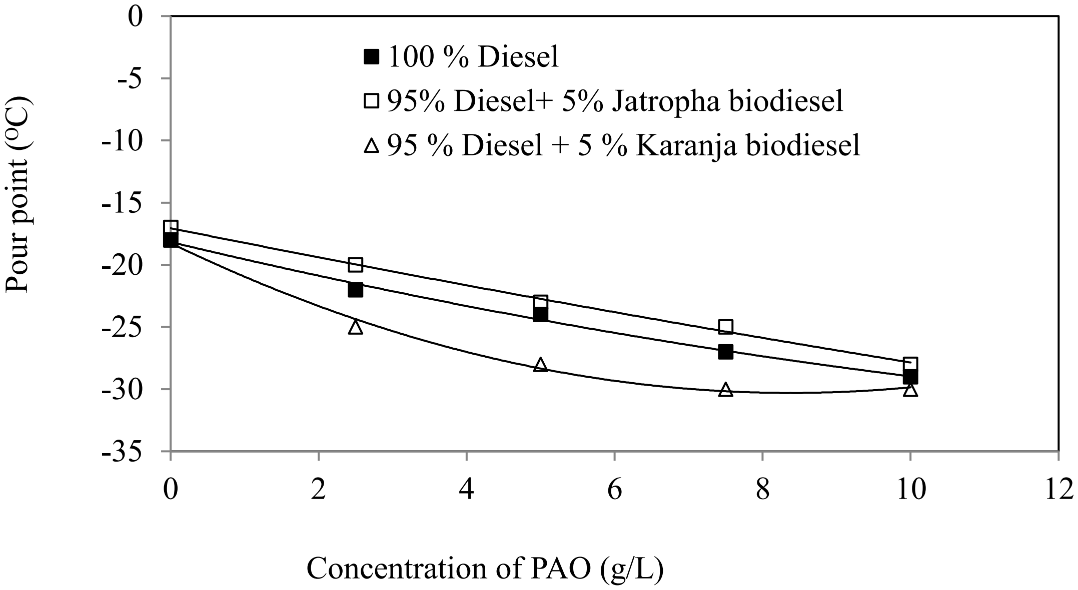

Fig. 6 Variation of pour point of diesel and their blends with concentration of PAO

Fig.6. Shows variation of pour point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PAO pour point increases with constant in jatropha and karanja biodiesel composition. For a given composition of biodiesel blends pour point decreases with increasing concentration of PAO. Adding 0 to 10 g/L PAO additive with 5% jatropha biodiesel blends produced pour point continuous increases. While adding 7.5 g/L PAO additive 5 vol. % karanja biodiesel -30 °C. compressions between jatropha and karanja biodiesel blends in same concentration, karanja biodiesel shows best result. Karanja biodiesel is more effective blending of the petroleum diesel.

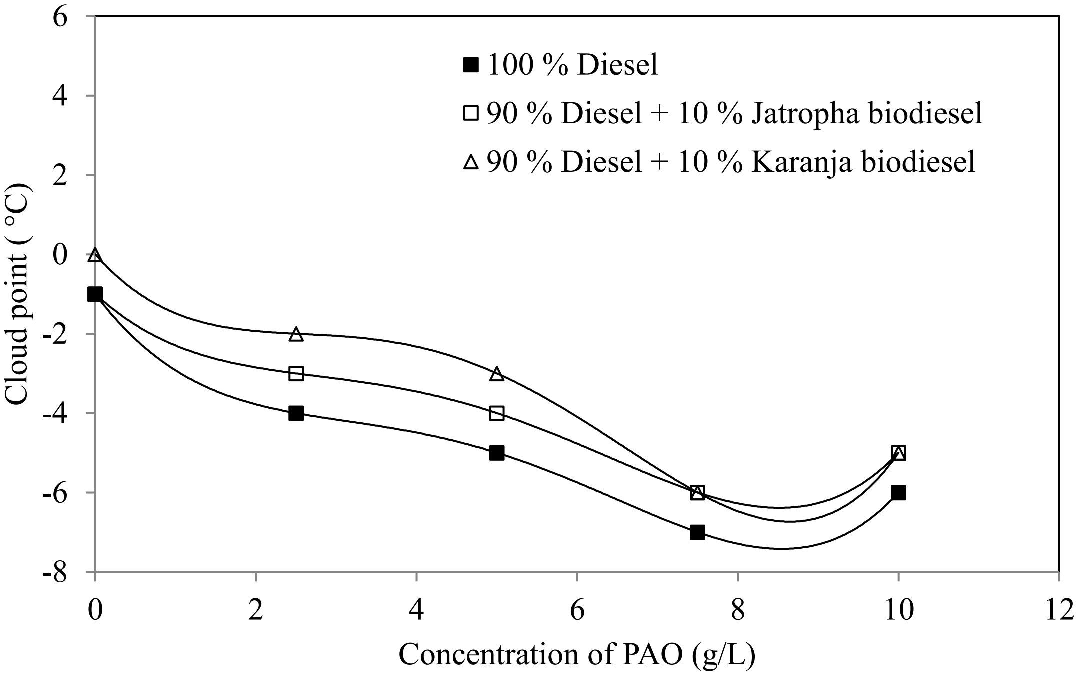

Fig. 7 Variation of cloud point of diesel and their blends with concentration of PAO

Fig.7. Shows variation of cloud point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PAO cloud point increases with constant in jatropha biodiesel composition. For a given composition biodiesel blends cloud point decreases with increasing concentration of PAO. There appeared to be no benefit of treatment levels beyond 7.5. g/L. Adding 7.5.0 g/L PAO additive with 10% biodiesel and produced a cloud point -6 $^{0}$C jatropha and karanja biodiesel – a significant reduction in these properties over the neat biodiesel. The additives had essentially little or no effect on cloud point.

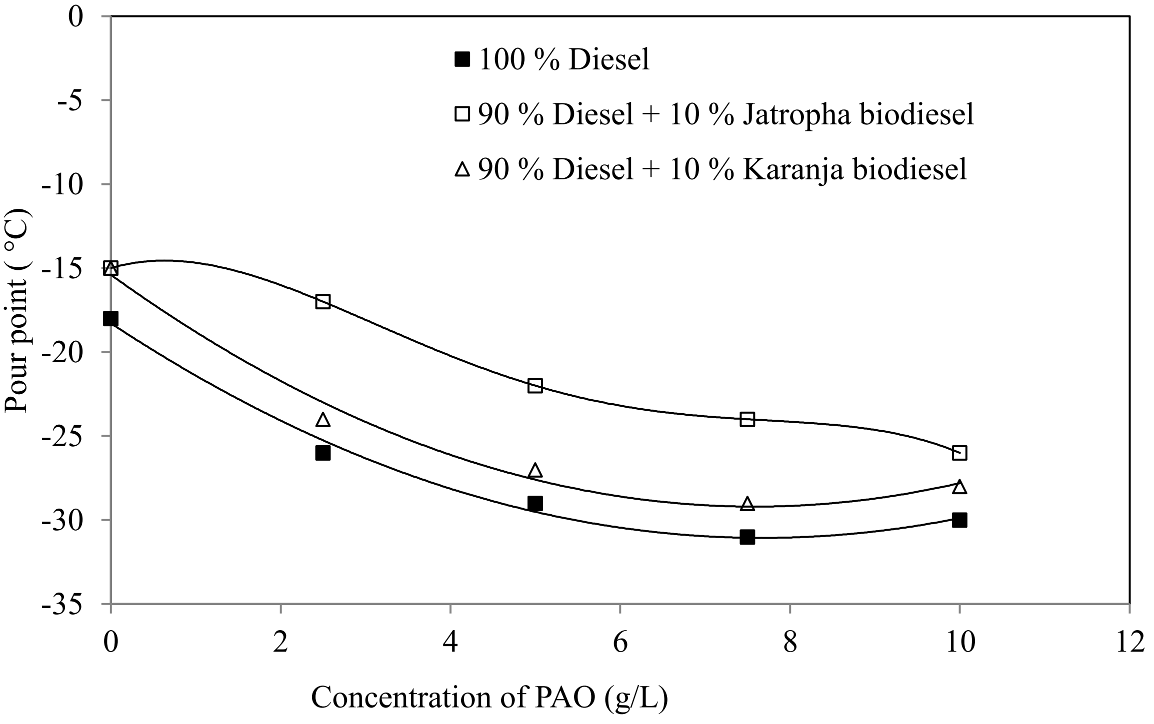

Fig. 8 Variation of pour point of diesel and their blends with concentration of PAO

Fig. 8 shows variation of pour point of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PAO pour point increases with constant in jatropha and karanja biodiesel composition. For a given composition of biodiesel blends pour point decreases with increasing concentration of PAO. Adding 0 to 10 g/L additive with 10 % jatropha biodiesel blends produced pour point continuous increases. While adding 7.5 g/L PAO additive with 10 vol. % karanja biodiesel blends produced pour point -29 $^{0}$C. Composition between jatropha and karanja biodiesel blends in same concentration, karanja biodiesel shows best result. Karanja biodiesel is more effective blending of petroleum diesel.

### 3.2 Kinematic Viscosity:

Kinematic viscosity is the primary reason why biodiesel is used as an alternative fuel instead of neat vegetable oils or animal fats. Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. Kinematic Viscosity of the biodiesel, diesel fuel and their blends can be measure by IS: 1448 (P: 25)-1976, Bureau of Indian Standards, New Delhi 1977 test methods. The Viscosity ranges have given as per the ASTM D445 standard 3.5 to 5.0 mm$^2$/s and as per the EN ISO 3104, 05 standards 1.9 to 6.0 mm$^2$/s and IS: 1448 (P: 25)-1976 1.9-6.0 mm$^2$/s . Here we have measured the kinematic viscosity in mm$^2$/s by Saybolt viscometer used. We have used this formula while calculating the kinematic viscosity of karanja oil methyl ester: **Kinematic viscosity = Calibration constant (mm$^2$/s$^2$) x mean time of flow (s) in mm$^2$/s.** The Karanja biodiesel blends kinematic viscosity increases as the fossil diesel percentage decreases or the biodiesel percentage increases in the blends. For Kinematic Viscosity we have taken here blends in the step of 6, like B00 (Diesel), B5, B10, B15, B20, B100.

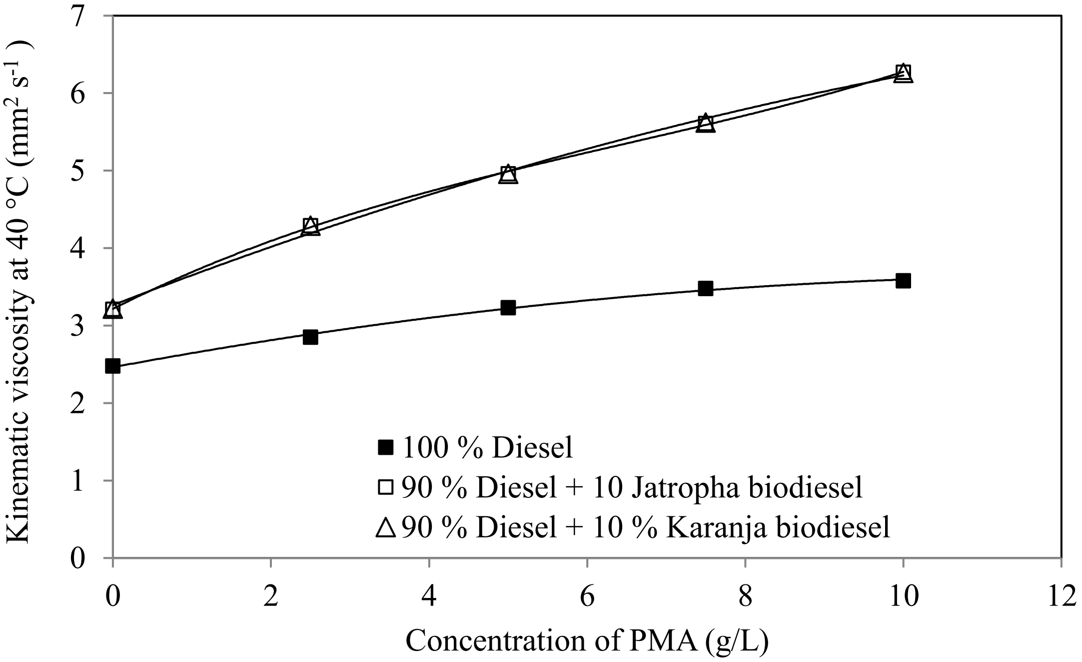

Fig. 9 Variation of kinematic viscosity of diesel and their blends with concentration of PMA

Fig.9. Shows variation of kinematic viscosity of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PMA pour point increases with constant in jatropha and karanja biodiesel composition. For a given composition of biodiesel blends kinematic viscosity increases with increasing concentration of PMA. Adding 0 to 10 g/L additive with 10 % jatropha biodiesel blends produced kinematic viscosity continuous increases. Composition between jatropha and karanja biodiesel blends in same concentration, karanja biodiesel shows best result. Karanja biodiesel is more effective blending of petroleum diesel.

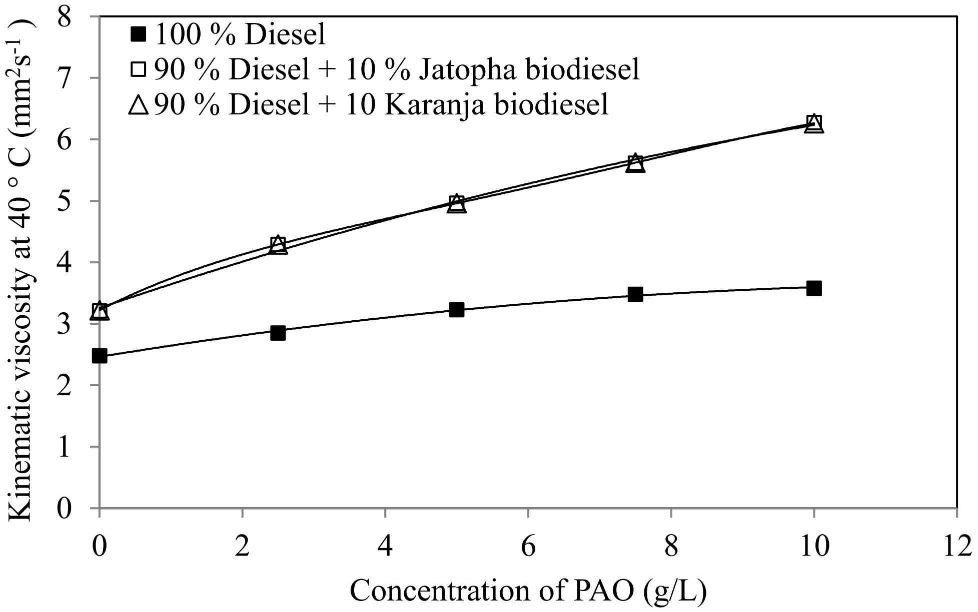

Fig.10. Shows variation of kinematic viscosity of jatropha and karanja biodiesel blends constant. It concentration has been varied 0 to 10 g/L. It can be seen that a given concentration of PAO pour point increases with constant in jatropha and karanja biodiesel composition. For a given composition of biodiesel blends kinematic viscosity increases with increasing concentration of PAO. Adding 0 to 10 g/L additive with 10 % jatropha biodiesel blends produced kinematic viscosity continuous increases. Composition between jatropha and karanja biodiesel blends in same concentration, karanja biodiesel shows best result. Karanja biodiesel is more effective blending of petroleum diesel.

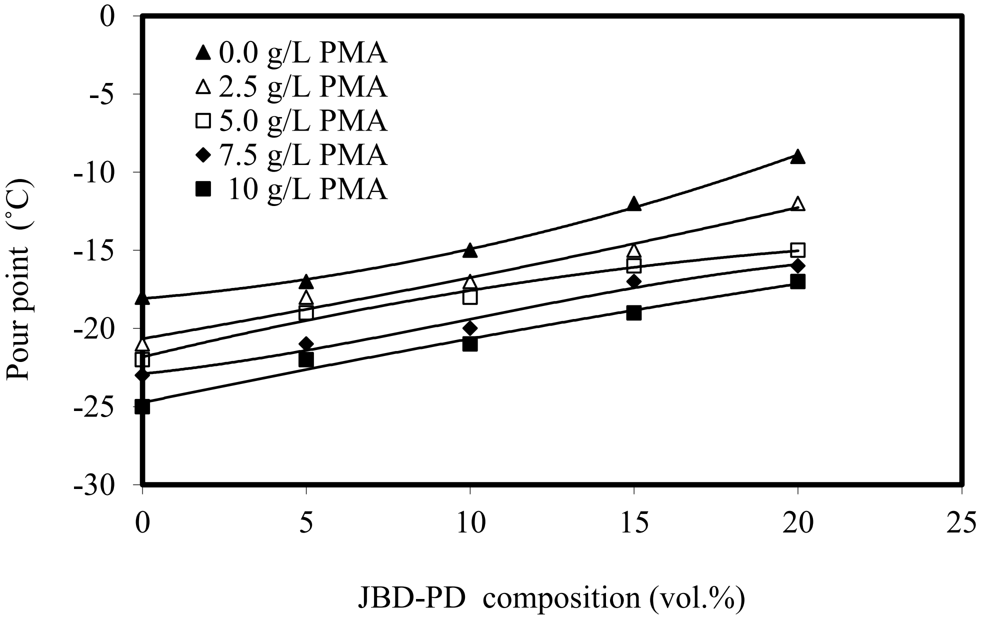

Fig.11 Variation of cloud point of JBD-PD blends with PMA concentration as a parameter.

Figure 11 shows variation of cloud point of biodiesel blends from 0 to 20 Vol. %. PMA of average molecular weight of 2260 has been use as cold flow property improver. Its concentration has been varied from 0 to 10 g/L. It can be seen that a given concentration of PMA cloud point increases with increment in biodiesel composition. For a given composition of biodiesel blends, cloud point decreases with increasing concentration of PMA. It can be seen that the pour point increases with increases the concentration of cold-flow improvers. There appeared to be no benefit of treatment levels beyond 7.5 g/L. adding 7.5 % PMA cold flow improvers with 5 % biodiesel and 95 % diesel produced a pour point (-21 ºC).

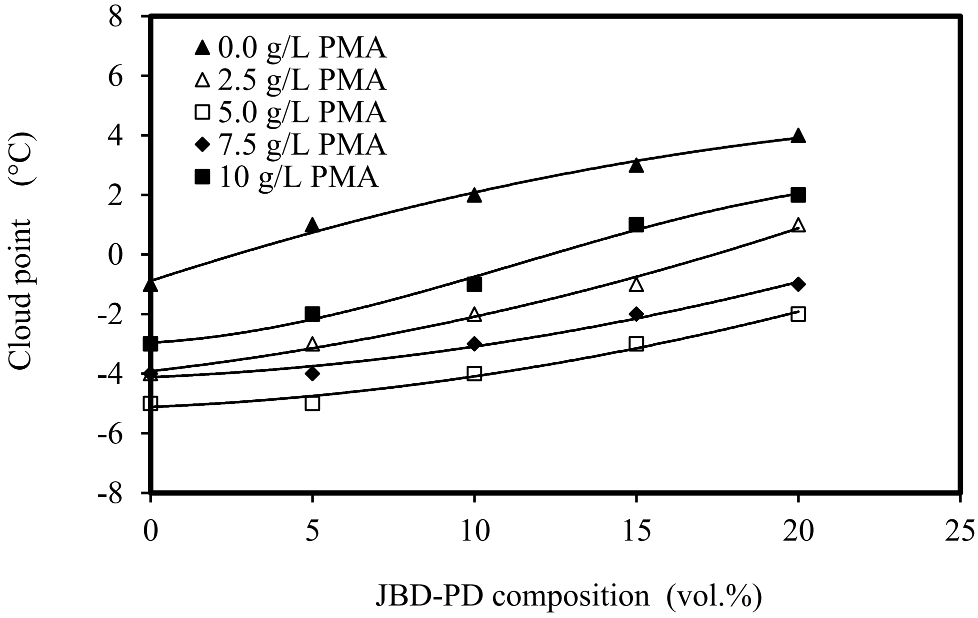

Fig. 12 Variation of pour point of JBD-PD blebds with PMA concentration as a parameter.

Figure 12 shows variation of pour point of biodiesel blends from 0 to 20 Vol. %. PMA of average molecular weight of 2260 has been use as cold flow property improver. Its concentration has been varied from 0 to 10 g/L. It can be seen that a given concentration of PMA pour point increases with increment in biodiesel composition. For a given composition of biodiesel blends, Pour point decreases with increasing concentration of PMA. It can be seen that the cloud point increases with increases the concentration of cold-flow improvers. There appeared to be no benefit of treatment levels beyond 5.0 g/L. adding 5.0 % PMA cold flow improvers with 5 % biodiesel and 95 % diesel produced a pour point (-5 ºC)- a significant reduction in these properties over the neat biodiesel. The cold flow improvers had essentially little or no effect on cloud point.

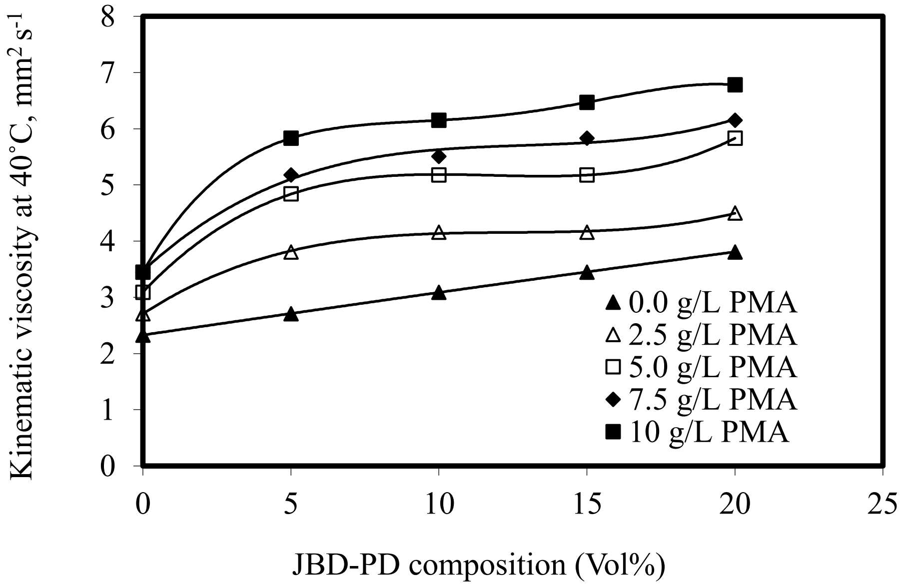

Fig.13 Variation of Kinematic viscosity of JBD-PD blends with PMA concentration as a parameter.

Figure 13 shows Variation of kinematic viscosity of biodiesel blends from 0 to 20 Vol.%. PMA of average molecular weight of 2260 has been use as cold-flow property improver. Its concentration has been varied from 0 to 10 g/L. It can be seen that a given concentration of PMA kinematic viscosity increases with increment in biodiesel composition. For a given composition of biodiesel blends,kinematic viscosity increases with increasing concentration of PMA.

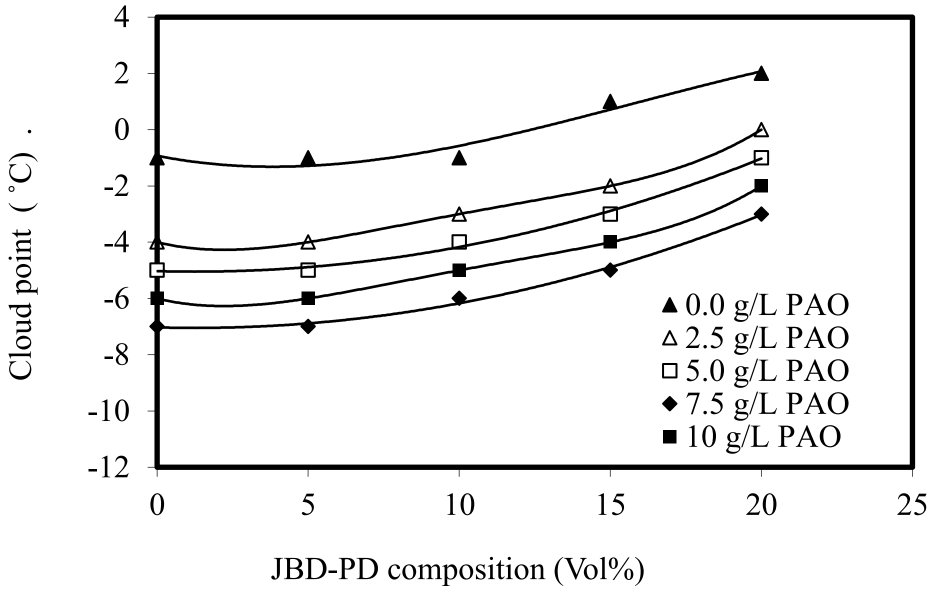

Fig.14 Variation of cloud point of JBD-PD blends with PAO concentration as a parameter.

Figure 14 shows variation of cloud point of jatropha biodiesel blends from 0 to 20 Vol. % PAO of average molecular weight 1875 has been use as cold-flow property improver. It concentration has been varied from 0 to 10 g/L. It can be seen that a given concentration of PAO cloud point increases with increment in biodiesel composition. For a given composition of biodiesel blends, cloud point decreases with increasing concentration of PAO. It can be seen that the cloud point increases with increases the concentration of cold-flow improvers. There appeared to be no benefit of treatment levels beyond 7.5 g/L. adding 7.5 % PMA cold flow improvers with 5 % biodiesel and 95 % diesel produced a pour point (-7 ºC)- a significant reduction in these properties over the neat biodiesel. The cold flow improvers had essentially little or no effect on cloud point.

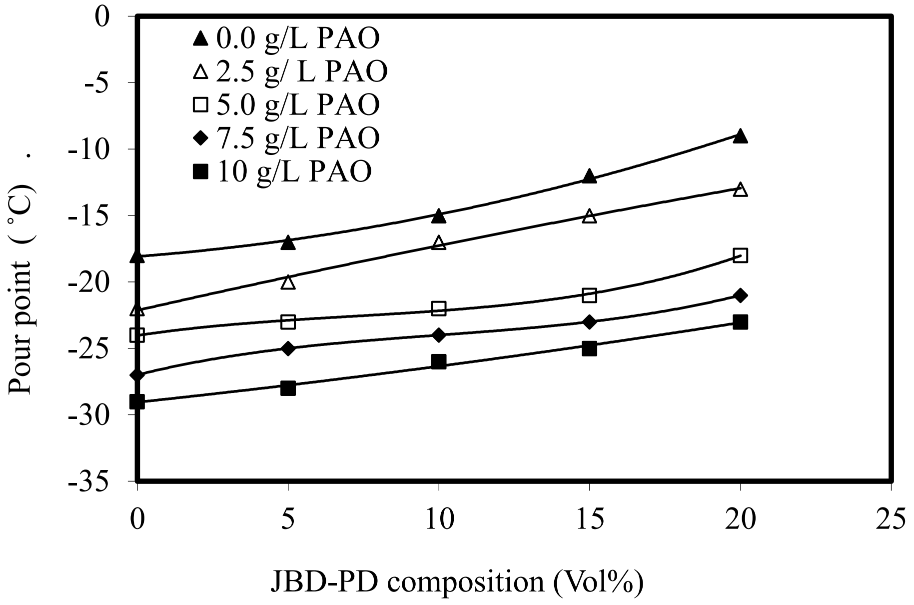

Fig. 15 Variation of pour point of JBD-PD blends with PAO concentration as a parameter.

Figure 15 shows variation of pour point of jatropha biodiesel blends from 0 to 20 Vol. % PAO of average molecular weight 1875 has been use as cold-flow property improver. It concentration has been varied from 0 to 10 g/L. It can be seen that a given concentration of PAO pour point increases with increment in biodiesel composition. For a given composition of biodiesel blends cloud point decreases with increasing concentration of PAO. It can be seen that the pour point deceases with increases the concentration of cold-flow improvers.

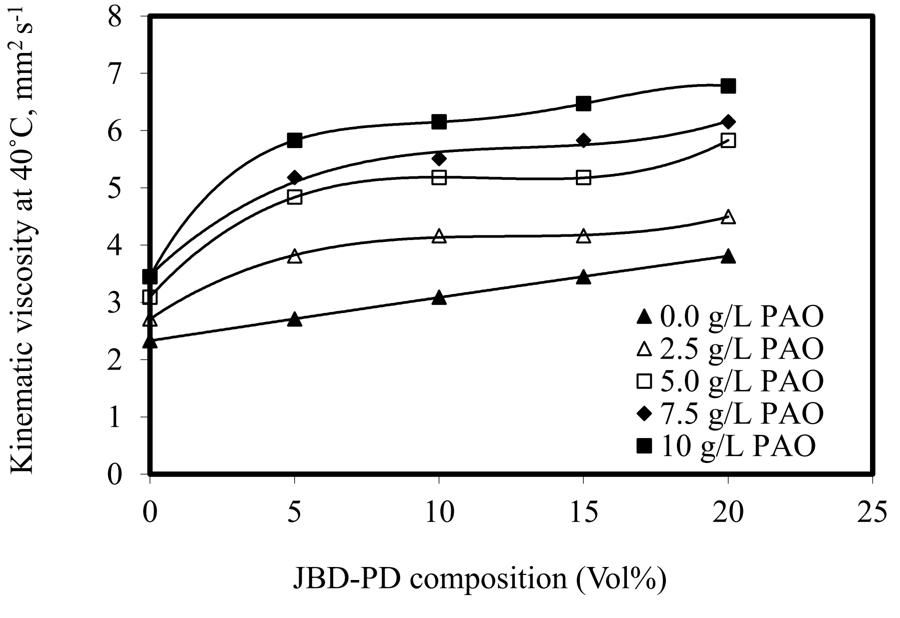

Fig.16 Variation of Kinematic viscosity of JBD-PD blends with PAO concentration as a parameter

Figure 16 shows variation of kinematic viscosity of biodiesel blends from 0 to 20 Vol.%. PAO of average molecular weight of 1875 has been use as cold-flow property improver. Its concentration has been varied from 0 to 10 g/L. It can be seen that a given concentration of PAO kinematic viscosity increases with increment in biodiesel composition. For a given composition of biodiesel blends,kinematic viscosity increases with increasing concentration of PAO.

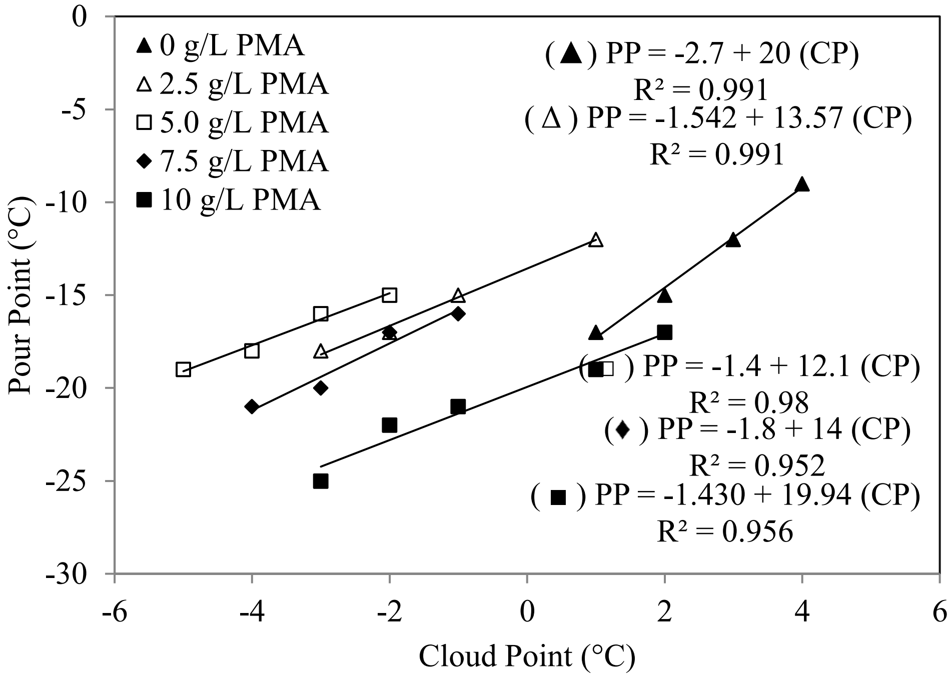

Fig. 17 Relation between Pour point and Cloud point of JBD and 0 g/L to 10 g/L PMA

The reference study showed that PP was nearly a linear fuction of CP. Figure 17 is a graph of PP vs. CP data that B5, B10, B15, B20 and B0 jatropha biodiesel blends adding with the 0 g/L to 10 g/L PMA cold flow improvers. Least- squeres regression yielded the following mathmatical expression are summerized in the table 3.

**Table 3 Relation between Cloud point and Pour point**

| Sample composition (%) | Additive PMA and PAO in g/L | Equation | $R^2$ |
|---|---|---|---|
| 0 | 0 | PP = -2.7+20 (CP)<br>PP = -2.259 +13.81 (CP) | 0.991<br>0.937 |
| 5 | | | |
| 10 | | | |
| 15 | | | |
| 20 | | | |
| 0 | 2.5 | PP = - 1.54+13.57 (CP)<br>PP = - 1.685+12.45 (CP) | 0.991<br>0.929 |
| 5 | | | |
| 10 | | | |
| 15 | | | |
| 20 | | | |
| 0 | 5.0 | PP = -1.4+12.1 (CP)<br>PP = -1.257+16.91 (CP) | 0.98<br>0.987 |
| 5 | | | |
| 10 | | | |
| 15 | | | |
| 20 | | | |
| 0 | 7.5 | PP = -1.8+14 (CP)<br>PP = -1.4+16.4 (CP) | 0.952<br>0.914 |
| 5 | | | |
| 10 | | | |

| | | | |
|---|---|---|---|
| 15 | | | |
| 20 | | | |
| 0 | 10 | PP = -1.430+19.94 (CP)<br>PP = -1.2 +16.4 (CP) | 0.956<br>0.969 |
| 5 | | | |
| 10 | | | |
| 15 | | | |
| 20 | | | |

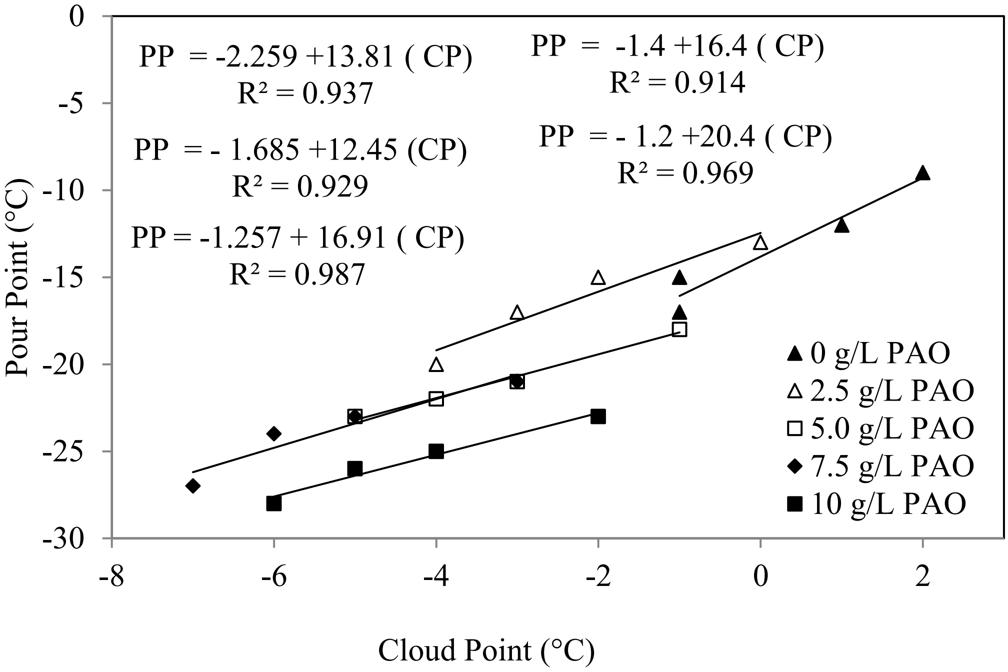

Fig.18 Relation between Pour point and Cloud point of JBD and 0 g/L to 10 g/L PAO

The reference study showed that PP was nearly a linear fuction of CP. Figure 18 is a graph of PP vs. CP data that B5, B10, B15, B20 and B0 jatropha biodiesel blends adding with the 0 g/L to 10 g/L PAO cold flow improvers. Least- squeres regression yielded the following mathmatical expression are summerized in the table 3.

It can be seen Fig. 19 shows variation of cloud point of biodiesel blends from 0 to 20 Vol. %. PAO of average molecular weight of 1875 has been use as cold flow property improver. Its concentration has been varied from 0 to 10 g/L. At a given concentration of PAO cloud point increases with increment in biodiesel composition. For a given composition of biodiesel blends, Cloud point decreases with increment concentration of PAO.

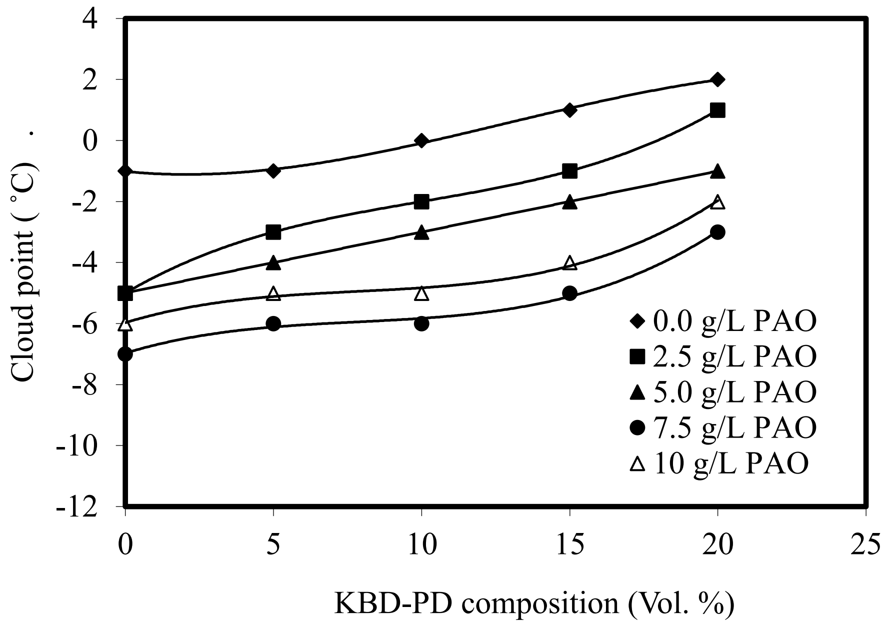

Fig. 19 Variation of cloud point with biodiesel blends composition with PAO concentration as a parameter.

It can be seen Fig. 20 shows variation of pour point of biodiesel blends from 0 to 20 Vol. %. PAO of average molecular weight of 1875 has been use as cold flow property improver. Its concentration has been varied from 0 to 10 g/L a given concentration of PAO pour point increases with increment in biodiesel composition. For a given composition of biodiesel blends, pour point decreases with increment concentration of PAO.

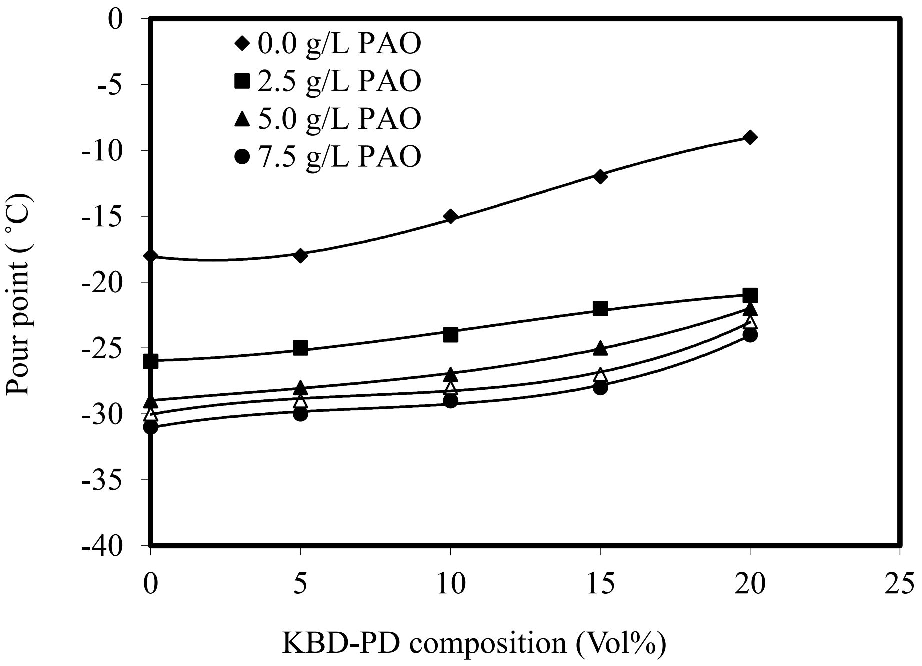

Fig. 20 Variation of pour point with biodiesel blends composition with PAO concentration as a parameter.

It can be seen Fig. 21 shows variation of cloud point of biodiesel blends from 0 to 20 Vol. %. PMA of average molecular weight of 2260 has been use as cold flow property improver. Its concentration has been varied from 0 to 10 g/L. At a given concentration of PMA cloud point increases with increment in biodiesel composition. For a given composition of biodiesel blends, Cloud point decreases with increment concentration of PMA.

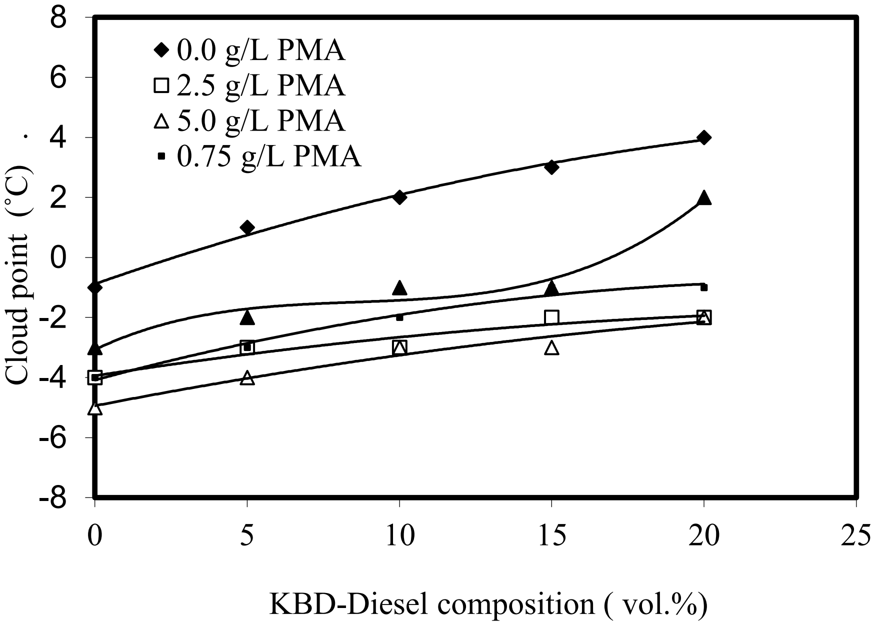

Fig. 21 Variation of cloud point with biodiesel blends composition with PMA concentration as a parameter.

It can be seen Fig. 22 shows variation of pour point of biodiesel blends from 0 to 20 Vol. %. PMA of average molecular weight of 2260 has been use as cold flow property improver. Its concentration has been varied from 0 to 10 g/L. At a given concentration of PMA pour point increases with increment in biodiesel composition. For a given composition of biodiesel blends, pour point decreases with increment concentration of PMA.

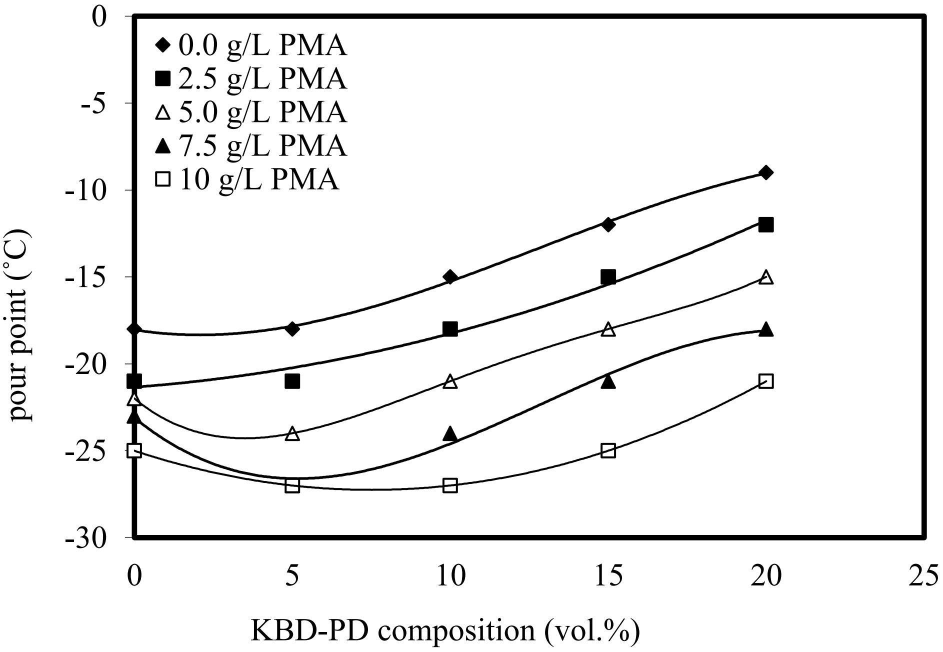

Fig.22 Variation of pour point with biodiesel blends composition with PMA concentration as a parameter.

From Figure 23 it can be seen that effect of PAO on the kinematic viscosity of jatropha biodiesel. Variation of kinematic viscosity of biodiesel blends from 0 to 20 Vol. %. PAO of average molecular weight of 1875 has been use as cold-flow property improver. Its concentration has been varied from 0 to 10 g/L. At a given concentration of PAO kinematic viscosity increases with increment in biodiesel composition. For a given composition of biodiesel blends, kinematic viscosity increases with increment concentration of PAO.

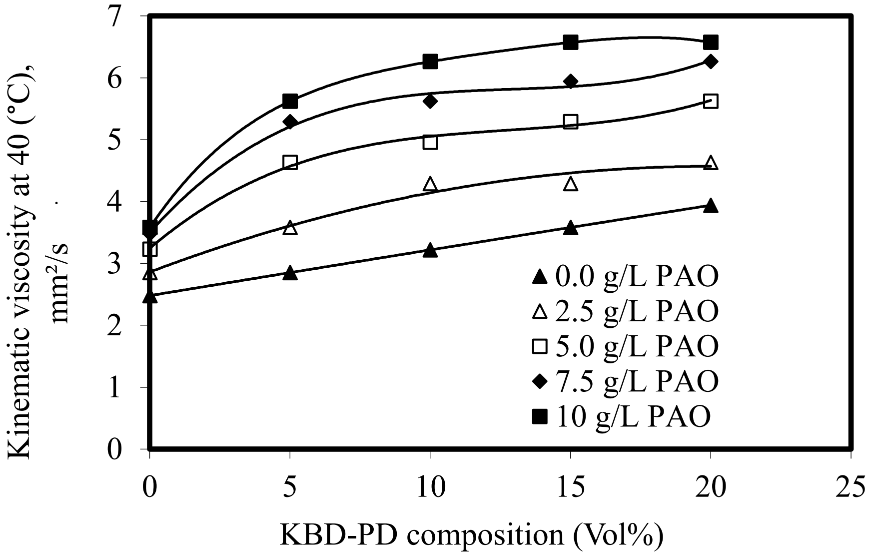

Fig. 23 Variation of kinematic viscosity with biodiesel blends composition with PAO concentration as a parameter

From Figure 24 it can be seen that effect of PMA on the kinematic viscosity of jatropha biodiesel. Variation of kinematic viscosity of biodiesel blends from 0 to 20 Vol. %. PMA of average molecular weight of 2260 has been use as cold-flow property improver. Its concentration has been varied from 0 to 10 g/L. At a given concentration of PMA kinematic viscosity increases with increment in biodiesel composition. For a given composition of biodiesel blends, kinematic viscosity increases with increment concentration of PMA.

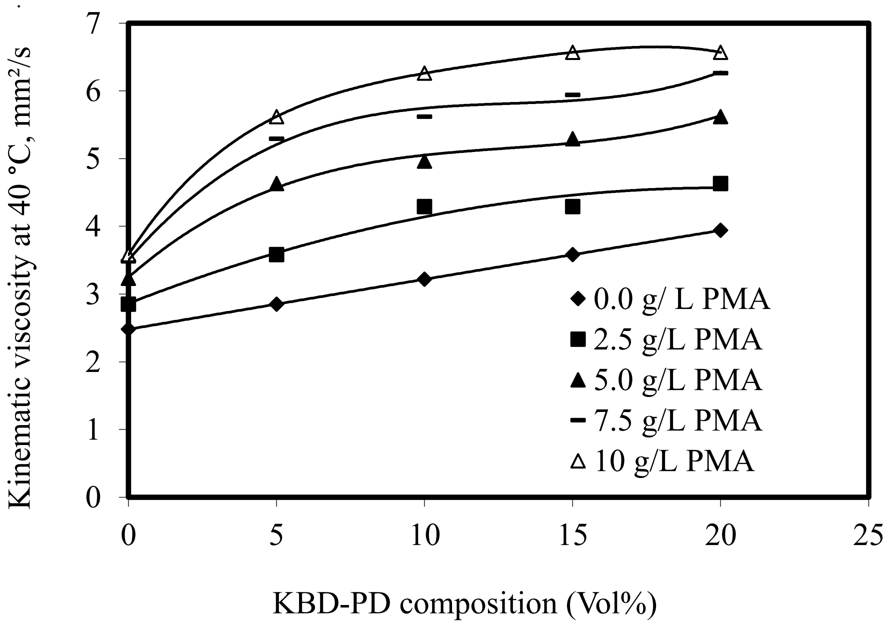

Fig. 24 Variation of Kinematic viscosity with biodiesel blends composition with PMA concentration as a parameter.

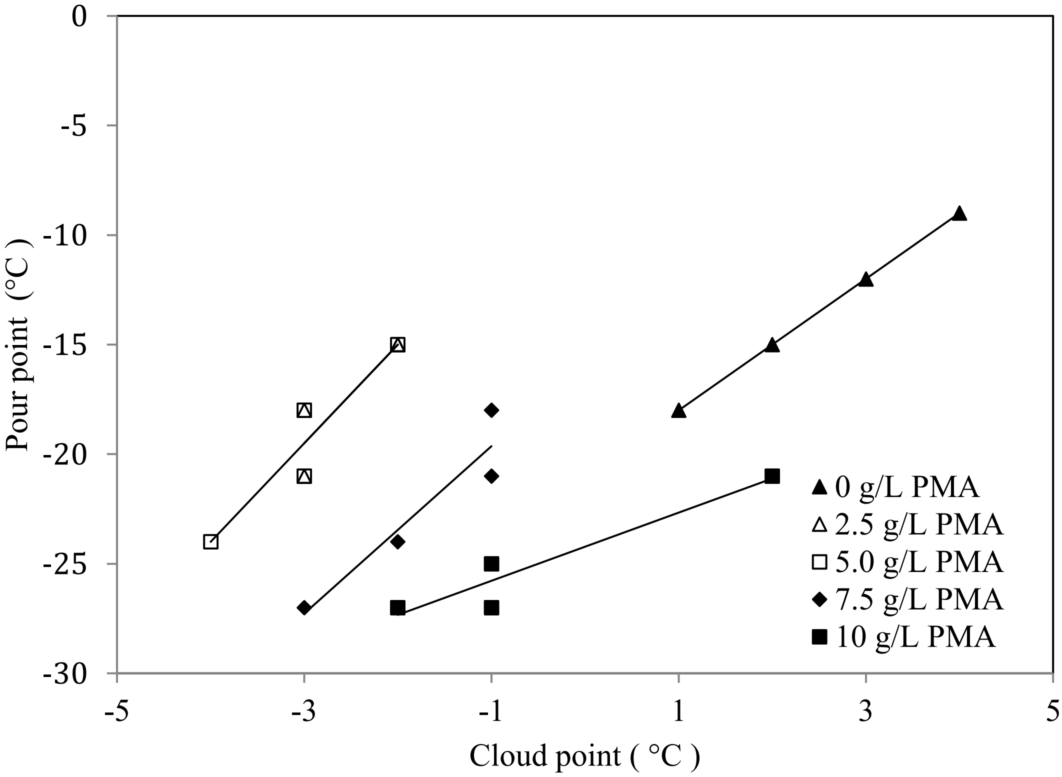

Fig. 25 Relation between Pour point and Cloud point of KBD and 0 g/L to 10 g/L PMA

The reference study showed that PP was nearly a linear fuction of CP. Figure 25 is a graph of PP vs. CP data that B5, B10, B15, B20 and B0 karanja biodiesel blends adding with the 0 g/L to 10 g/L PMA cold flow improvers. Least- squeres regression yielded the following mathmatical expression are summerized in the table 4.

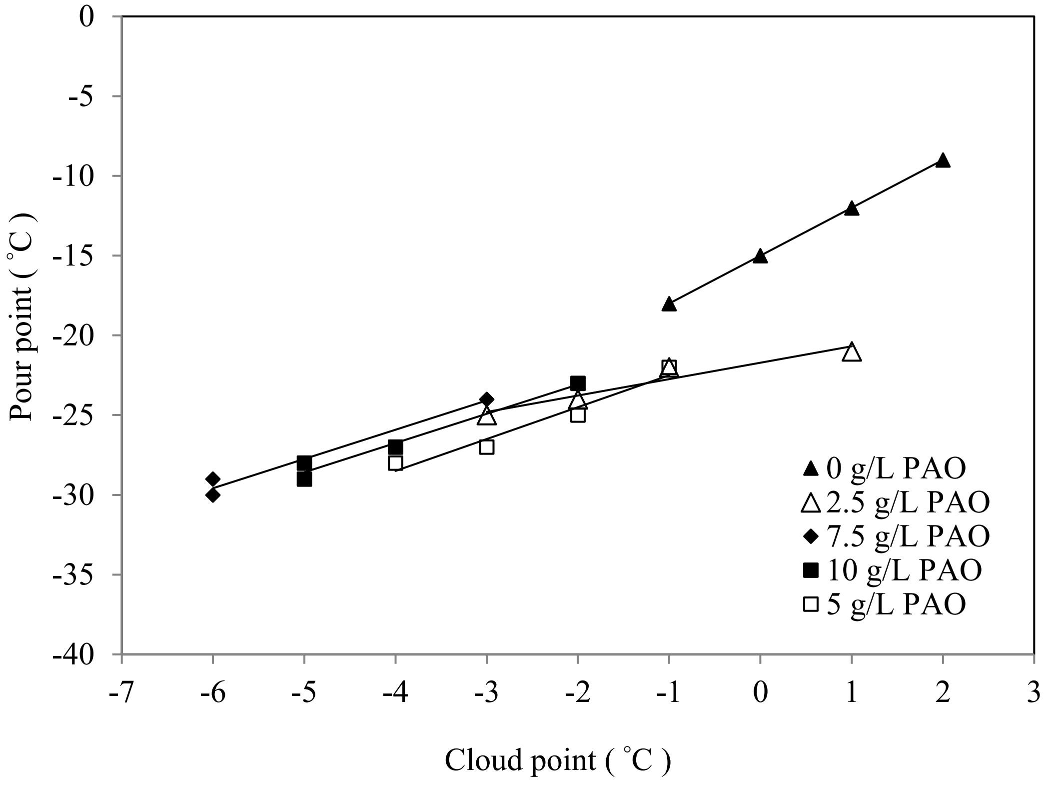

Fig. 26 Relation between Pour point and Cloud point of KBD and 0 g/L to 10 g/L PAO

The reference study showed that PP was nearly a linear fuction of CP. Figure 26 is a graph of PP vs. CP data that B5, B10, B15, B20 and B0 karanja biodiesel blends adding with the 0 g/L to 10 g/L PAO cold flow improvers. Least- squeres regression yielded the following mathmatical expression are summerized in the table 4.

**Table 4 Relation between Pour point and Cloud point of KBD**

| KBD % | Additive g/L | | Equation | $R^2$ |
|---|---|---|---|---|
| 0-20 | 0 | PMA | PP= - 3+21 (CP) | 1.000 |
| | | PAO | PP= -3+15 ( CP ) | 1.000 |
| 0-20 | 2.5 | PMA | PP= -4.5+6 ( CP) | 0.818 |
| | | PAO | PP= -1.028+21.71 (CP ) | 0.925 |
| 0-20 | 5.0 | PMA | PP= -4.5+6 ( CP) | 0.90 |
| | | PAO | PP= -2+20.5 ( CP ) | 0.952 |
| 0-20 | 7.5 | PMA | PP= -3.818+15.81 ( CP ) | 0.890 |
| | | PAO | PP= -1.833+18.58 (CP ) | 0.971 |
| 0-20 | 10 | PMA | PP= -1.555+24.22 (CP ) | 0.90 |
| | | PAO | PP= -1.833+19.41 (CP ) | 0.971 |

**Table 5 Cloud point, pour point and Kinematic viscosity of biodiesel and its blends in ethanol and diesel**

| Sample Composition (%) | | | Cloud Point, °C | Pour point, °C | Kinematic viscosity at 40 °C, $mm^2/s$ |
|---|---|---|---|---|---|
| Ethanol | Jatropha Biodiesel | Diesel | | | |
| 0 | 0 | 100 | -1 | -18 | 2.48 |
| 0 | 5 | 95 | 2 | -18 | 2.84 |
| 5 | 0 | | 1 | -18 | 2.71 |
| 0 | 10 | 90 | 2 | -15 | 3.21 |
| 5 | 5 | | 1 | -18 | 3.09 |
| 10 | 0 | | 1 | -18 | 2.71 |

| | | | | | |
|---|---|---|---|---|---|
| 0 | 15 | 85 | 2 | -15 | 3.58 |
| 5 | 10 | | 1 | -15 | 3.09 |
| 10 | 5 | | 1 | -15 | 3.09 |
| 15 | 0 | | 1 | -18 | 2.71 |
| 0 | 20 | 80 | 2 | -12 | 3.94 |
| 5 | 15 | | -1 | -12 | 3.45 |
| 10 | 10 | | -1 | -14 | 3.45 |
| 15 | 5 | | -1 | -15 | 3.09 |
| 20 | 0 | | -2 | -18 | 2.71 |
| 100 | 0 | 0 | -5 | -18 | 3.09 |
| 0 | 100 | 0 | 3 | -5 | 4.16 |

The cloud point and pour point of PD, JBD, Ethanol and their blends have been determined experimentally. These Results are summarized in the Table **5**. It can be seen that the pour point decreases significantly compared to that of PD while the cloud point increases, which is in concordance with earlier results. Consequently, cloud point for E05JBD15PD80, E10JBD10PD80 and E15JBD5PD80 is similar to that of neat diesel fuel (Table 5). Table 5 shows that cloud point decreases with ethanol concentration increases. In fact E100PD0JBD0 shows a great decrease in cloud point values.

Due to the very low pour point of ethanol (< -18 °C) relative to that of diesel fuel, it can be expected that ethanol-diesel fuel blends will depict a lower value compared to that of diesel fuel. This improvement is possible as long as ethanol remains soluble in diesel fuel. Table 5 shows that pour point decreases when ethanol concentration increases with fuel flow improving in the fuel injection system. Except samples containing E0PD85JBD15, E0PD90JBD10 E5PD85JBD10, E0PD85JBD15 and E15PD80JBD5 were found to have the same pour point at -15 °C. E0PD80JBD20 and E5PD80JBD15 were found to have the same pour point at -12 °C. The reason is that the ethanol has a very low pour point and biodiesel normally has pour point higher than conventional diesel. But all of the blends have diesel as a major component, and therefore the pour point of the fuel blends were found to be not much different conventional diesel. The kinematic viscosity of PD, JBD, Ethanol and their blends have been determined experimentally. The results are summarized in the table 5 it can be observed that in general the kinematic viscosity of the blends increased with an increase in ethanol composition in the blends however in absence of JBD. When the percentage of biodiesel was increased, the viscosity increased, which is due to the fact that the JBD has a higher viscosity than the other two components. These findings suggest that the higher viscosity can lead to inferior fuel injection.

**Table 6 Cloud point, pour point and Kinematic viscosity of biodiesel and its blends in oil and diesel**

| Sample Composition (%) | | | Cloud Point, °C | Pour point, °C | Kinematic viscosity at 40 °C, mm$^2$/s |
|---|---|---|---|---|---|
| Jatropha Oil | Jatropha Biodiesel | Diesel | | | |
| 0 | 0 | 100 | -1 | -18 | 2.48 |
| 0 | 5 | 95 | 2 | -18 | 2.84 |
| 1 | 4 | | -1 | -18 | 3.09 |
| 2 | 3 | | -1 | -18 | 3.09 |
| 3 | 2 | | -1 | -18 | 3.17 |
| 4 | 1 | | -1 | -18 | 3.25 |
| 5 | 0 | | 0 | -18 | 3.45 |
| 0 | 10 | 90 | 2 | -15 | 3.21 |
| 2 | 8 | | -1 | -15 | 3.45 |
| 4 | 6 | | -1 | -15 | 3.45 |
| 6 | 4 | | 1 | -15 | 3.45 |
| 8 | 2 | | 1 | -12 | 3.65 |
| 10 | 0 | | 1 | -12 | 3.81 |
| 0 | 15 | | 3 | -15 | 3.58 |
| 3 | 12 | | 1 | -12 | 3.45 |

| | | | | | |
|---|---|---|---|---|---|
| 6 | 9 | 85 | 1 | -12 | 3.81 |
| 9 | 6 | | 1 | -12 | 3.81 |
| 12 | 3 | | 2 | -12 | 4.16 |
| 15 | 0 | | 1 | -12 | 4.58 |
| 0 | 20 | 80 | 4 | -9 | 3.94 |
| 4 | 16 | | 1 | -9 | 6.78 |
| 8 | 12 | | 1 | -9 | 8.00 |
| 12 | 8 | | 1 | -8 | 8.29 |
| 16 | 4 | | 3 | -7 | 9.17 |
| 20 | 0 | | 3 | -7 | 9.74 |
| 0 | 100 | 0 | 2 | -5 | 4.16 |
| 100 | 0 | 0 | 12 | 1 | 33.30 |

The cloud point, pour point and kinematic viscosity of PD, JBD, JO and their blends have been determined experimentally. The results are summarized in the table 6. It can be observed that the cloud point and pour point of the blends increase with increasing percentage of JO in the blends which is due to the fact that the JO has a higher cloud point and pour point than the other two components. It can be observed that the kinematic viscosity of the blends increased with increasing percentage of JO in the blends. But when the percentage of JBD was increased, the kinematic viscosity increased which is due to the fact that the JO biodiesel has higher kinematic viscosity than the other one component.

**Impact of additive loading in Jatropha and Karanja biodiesel blends**

Additives for improving the cold-flow properties of diesel fuel have been extensively studied. Generally, additives are developed to distort the crystals shape and to some extent alter the size, or directly inhibit their growth habit, thereby reducing pour point temperatures. Many additives contain proprietary components, and copolymers of ethylene and vinyl acetate or other olefin-ester copolymers. In addition to dilution, it is also common to add polymers to biodiesel to prevent gelling at low temperatures. The polymers can, in some cases, interfere with crystallization, thereby lowering the freezing point. However, polymer additives are typically used as crystal modifiers that integrate into the crystal surfaces (i.e. they are activated by crystal nuclei). In diesel fuels, a few polymer additives having long hydrocarbon chain have been observed to delay observable crystal formation as a petroleum diesel is cooled. These additives tend to reduce the visibility of the crystals and not their formation. Similar approaches will be considerably more challenging to develop for biodiesel blends because biodiesel has less chemical diversity-biodiesel is comprised of fewer chemical components present in higher composition than petroleum diesel.

## 4. **Conclusions**

Chemical additives can reduce pour point temperature in biodiesel blends. In the most chemical additives, pour point of JBD and KBD blends deceased with increasing chemical additive loading although this depression in pour point is nearly proportional to chemical additive loading, its magnitude varied between chemical additives. The action of the mechanism for PMA and PAO to improve the cold-flow properties of JBD and KBD can be ascribed on one hard to the reduction of kinematic viscosity increase. The results are summarized in the table 3 it can be observed that in general the kinematic viscosity of the blends increased with an increase in ethanol composition in the blends however in absence of JBD. When the percentage of biodiesel was increased, the viscosity increased, which is due to the fact that the JBD has a higher viscosity than the other two components. These findings suggest that the higher viscosity can lead to inferior fuel injection. It can be observed that the kinematic viscosity of the blends increased with increasing percentage of JO in the blends. But when the percentage of JBD was increased, the kinematic viscosity increased which is due to the fact that the JO biodiesel has higher kinematic viscosity than the other one component.

**Uncertainty in additive concentration**

Mass additive m = 0.2500 g

Uncertainty in weighing Δm = 0.0010 g

Volume of biodiesel v = 100 ml

Uncertainty in volume Δv = 1.0 ml

$$\sigma_{c,\,r\,(C\,pm)} = \sqrt{(\frac{\Delta m}{m})2 + (\frac{\Delta v}{v})2}$$

$$= \sqrt{\left(\frac{0.0010}{0.25}\right)2 + \left(\frac{1}{100}\right)2}$$

$$= \quad 0.016$$

**Table-1 Uncertainty in additive concentration (PMA and PAO)**

| Blend | At additive concentration (PMA and PAO g) | | | |
|---|---|---|---|---|
| | 0.25 | 0.50 | 0.75 | 1 |
| B100 | 0.25±0.04 | 0.50±0.01 | 0.75±0.04 | 1±0.01 |

**Blend uncertainties** B10

Uncertainty in measurement of volume of biodiesel $\Delta v_1 = 0.2$

Volume measured $v_1 = 10$ ml

Uncertainty in total volume $\Delta v_2 = 1$ ml

Volume measured $v_2 = 90$ ml

$$\sigma_{c\,,\,r}(B_{10}) = \sqrt{\left(\frac{\Delta v1}{v1}\right)2 + \left(\frac{\Delta v2}{v2}\right)2}$$

$$= \sqrt{\left(\frac{0.2}{10}\right)2 + \left(\frac{1}{90}\right)2}$$

$$= \quad 0.023$$

**Table-2 Blend uncertainties**

| Blend | Uncertainties |
|---|---|
| $B_{20}$ | 0.026 |
| $B_{15}$ | 0.034 |
| $B_{10}$ | 0.023 |
| $B_5$ | 0.022 |

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