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Improving Cold-Flow Propertiws of Jatrpha and Karanja Biodiesel

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Abstract

In this paper, the low temperature properties of jatropha methyl ester and karanja methyl esters. Cold-flow improvers poly methyl acrylate and poly alpha olefin were tested at 0g to 10 g in 5 ml, 10 ml, 15 ml, and 100 ml. PMA and PAO additives reduced the pour point and cloud point jatropha and karanja methyl esters mixture and its blend petroleum diesel with cold flow improvers shows very little effect on cloud point. A considerable reduction in pour point has been noticed by using cold flow improvers. The experimental result showed that the poly alpha olefin cold flow improvers was very effective in the depression of the pour point of jatropha methyl ester and karanja methyl ester and retard viscosity increase of jatropha and karanja methyl esters.

Keywords: Jatropha oil, CP, Pour point, Kinematic Viscosity.

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

Introduction

Efforts are under way in many countries including India to search for alternatives of hydrocarbon-base fuels such as biodiesel, bioethanol, etc. The need for the alternative biodiesel fuels arises mainly from the standpoint of preserving the global environment and the concern about long term supplies of conventional hydrocarbon-based diesel and biodiesel fuels. Various alternatives of bio fuels have been suggested as a blending component for ethanol and biodiesel fuels[1]. Biodiesel is one of the biofuels produced today. Biodiesel is an alternative fuel for diesel engines derived from natural renewable sources. Biodiesel can be used as a fuel in its pure form as well as any concentration with petroleum-based diesel in existing diesel engines with little modification.

Biodiesel is gaining attention as an alternative fuel and is typically obtained by transesterification of vegetable oils, animal fats or used frying oils that comprise mainly of triglycerides[1-4]. In the India and other cold regions of the world, one of the greatest concerns of biodiesel users is its unfavorable cold weather operability. Biodiesel has a higher cloud point (CP) and pour point (PP) than regular diesel fuel. The cold filter plugging point (CFPP) temperature is more closely related to the actual cold weather operability of biodiesel, but it has been shown that CFPP correlates well to CP. Since CP and PP are easy to measure, they are routinely used to characterize the cold flow operability of diesel fuels[5].

In previous studies in order to address this challenge, various strategies have been proposed, such as winterization, blending with Diesel fuel, and use of chemical additives (CA). The cloud point, which usually occurs at higher temperature than the pour point, is the temperature at which a liquid fatty material become cloudy due to the formation of crystals and solidification of saturates. Crystallization of the saturated fatty acid methyl ester components of biodiesel during cold seasons causes fuel starvation and operability problems as solidified materials clog fuel lines and filters with decreasing temperature more solids from and mutual approaches the pour point[6].

Different chemical additives are available to improve the cold flow properties of diesel and biodiesel. In general, these additives act by distorting the wax crystal shape and size to inhibit crystal growth and thereby reducing PP temperatures.

The additives contain proprietary components that are usually copolymers of ethylene and vinyl acetate or other olefin-ester copolymers. Fuel additives are available in the market for pure biodiesel and biodiesel-diesel blends that are supposed to reduce the pour point temperature of the fuel so it can be used at low temperature.

In this paper discussed the cold-flow improvers' poly methylacrylate and poly alpha olefin on the low temperature characteristics of jatropha methyl ester and karanja methyl ester made from JO and KO. The effects of these cold flow improvers on the CP, PP and KV methyl ester and its mixture in petroleum based diesel fuels at low temperature.

Materials and Methods

Materials[7]: The properties of these cold flow improvers and jatropha oil, karanja oil and its derivatives methyl esters given in Table-1 and 2.

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

Preparation of jatropha and karanja biodiesel[7]: Preparation of biodiesel mixture and its blends in diesel[7]: The biodiesel mixtures were prepared by measuring the appropriate amounts of Jatropha biodiesel and Karanja biodiesel and then mixing in a conical flask at 45^0C for 45 minute with continuous stirring to ensure uniform mixing. Similarly, the appropriate amounts of biodiesel mixture and chemical additive to produce mixture containing chemical additive in the range of 0-10 g/L were mixed in a conical flask at 45^0C for 45 minute with continuous stirring.

Results and Discussion

The effect of concentration of two chemical additives PMA and PAO on the cloud point, pour point and kinematic viscosity of Jatropha biodiesel, Karanja biodiesel and their mixture has been studied. The concentration of chemical additives has been varied in the range of 0 – 10 g/L. The experimental results are discussed below:

Cloud Point, Pour Point and Kinematic Viscosity[8, 9, 10]: It can be seen variation, the concentration of cold-flow improver, the cloud point value reverse. There appeared to be no benefit of treatment levels beyond 5.0 g/L. Adding 5.0 % PMA cold-flow improvers with 5 % biodiesel mixture (75J+25K) and 95 % diesel produced a cloud point (-5°C). The cold-flow improver had essentially little or no effect on cloud point. Comperision between diesel and biodiesel it can be seen in the table the results are shown nearly the same blending with 5 % biodiesel with 5.0 % PMA cold flow improver.

It can be seen variation, the concentration of cold-flow improver the pour point value continuous increases. Comparison between diesel and biodiesel it can be seen in the Table-4 the results are shown nearly the same blending with 15% biodiesel (75K + 25J) with 10% poly methylacrylate cold flow improver.

Its concentration has been varied from 0 to 10g per 100 ml. At a given concentration of PMA, kinematic viscosity increases with increment in biodiesel mixture composition. For a given composition of biodiesel mixture blend, kinematic viscosity increases with increment concentration of PMA (Table-5).

Table-1
Properties of PAO[11]

Properties	Properties of cold flow improver
	PAO
Density, kg/m^3	0.896
Molecular weight, kg/kmol	1875[17]
Pour point, °C	-9

Table-2
Characteristics of Jatropha oil and its biodiesel[7]

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

Table-3
Cloud points of biodiesel mixture and its blends in diesel

Composition		CP at cold flow improver composition of poly methylacrylate				
diesel	Biodiesel mixture	0 g/L	2.5g/L	5.0g/L	7.5g/L	10g/L
100	0	-1	-4	-5	-4	-3
95	5(75 J+25K)	1	-3	-5	-4	-2
90	10(50J+50K)	1	-3	-4	-3	-2
85	15(75K+25J)	2	-2	-3	-2	-1
0	100(J)	3	2	1	1	1

Table-4
PP of jatropha and karanja methyl esters mixture and its blends in Petroleum diesel

Composition		**PP at cold flow improver composition on poly methylacrylate**				
Diesel	**Biodiesel mixture**	**0g/L**	**2.5g/L**	**5.0g/L**	**7.5g/L**	**10g/L**
100	0	-18	-21	-22	-23	-25
95	5(75 J+25K)	-17	-19	-21	-22	-23
90	10(50J+50K)	-16	-18	-21	-21	-22
85	15(75K+25J)	-12	-15	-21	-23	-24
0	100(J)	-5	-9	-12	-12	-12

Table-5
Kinematic viscosity of jatropha and karanja methyl ester mixture and its blends In petroleum diesel

Composition		**KV at 40 ^{o}C, mm^2/sat cold flow improver composition on poly methylacrylate**				
Diesel	**Biodiesel mixture**	**0g/L**	**2.5g/L**	**5.0g/L**	**7.5g/L**	**10g/L**
100	0	2.48	2.85	3.29	3.48	3.58
95	5(75 K+25J)	2.95	3.80	4.89	5.20	6.10
90	10(50K+50J)	3.08	4.25	5.40	5.70	6.18
85	15(75J+25K)	3.70	4.53	5.51	5.89	6.30
0	100 (J)	4.16	3.45	3.45	3.13	3.09

Table-6
CP of jatropha and karanja methyl ester mixture and its blends in Petroleum diesel

Composition		**CP at cold flow improver additive composition of poly alpha olefin**				
Diesel	**Biodiesel mixture**	**0g/L**	**2.5g/L**	**5.0g/L**	**7.5g/L**	**10g/L**
100	0	-1	-4	-5	-7	-6
95	5(75 J+25K)	1	-3	-4	-6	-6
90	10(50J+50K)	1	-3	--3	-5	-6
85	15(75K+25J)	2	-1	-2	-3	-4
0	100 (J)	3	1	0	-1	-2

It can be seen variation, the concentration of cold-flow improver, the cloud point value reverse. There appeared to be no benefit of treatment levels beyond 7.5 g/L. Adding 5.0 % PMA cold-flow improvers with 5 % biodiesel mixture (75J+25K) and 95% diesel produced a cloud point (-6 ˚C). The cold-flow improver had essentially little or no effect on cloud point. Comperision between diesel and biodiesel it can be seen in the Table-6 the results are shown nearly the same blending with 5 % biodiesel with 7.5 % PMA cold flow improver.

Table-7
PP of jatropha and karanja methyl ester mixture and its blends in Petroleum diesel

Composition		**PP at cold flow improver composition on poly alpha olefin**				
Diesel	**Biodiesel mixture**	**0g/L**	**2.5g/L**	**5.0g/L**	**7.5g/L**	**10g/L**
100	0	-18	-22	-24	-27	-24
95	5(75 J+25K)	-18	-21	-23	-27	-24
90	10(50J+50K)	-17	-20	-22	-26	-23
85	15(75K+25J)	-16	-19	-22	-25	-22
0	100 (J)	-5	-9	-12	-15	-15

Table-8
Kinematic viscosity of jatropha and karanja methyl ester mixture and its blends In petroleum diesel

Composition		**Kinematic viscosity at 40 ^{o}C, mm^2/sat cold flow improver on poly alpha olefin**				
Diesel	**Biodiesel mixture**	**0g/L**	**2.5g/L**	**5.0g/L**	**7.5g/L**	**10g/L**
100	0	2.48	2.85	3.29	3.48	3.58
95	5(75 K+25J)	2.98	3.90	4.89	5.23	6.12
90	10(50K+50J)	3.10	4.30	5.45	5.78	6.28
85	15(75J+25K)	3.78	4.55	5.92	6.10	6.35
0	100 (J)	4.16	3.45	3.45	3.13	3.09

It can be seen variation, the concentration of cold-flow improver, the pour point value reverse. There appeared to be no benefit of treatment levels beyond 7.5 g/L. Adding 7.5% PAO cold-flow improvers with 5% biodiesel mixture (75J+25K) and 95% diesel produced a cloud point (-27˚C). Comperision between diesel and biodiesel it can be seen in the table the results are shown nearly the same blending with 5% biodiesel with 7.5% PAO cold flow improver (Table-7).

Its composition has been varied from 0 to 10g per 100 ml. At a given composition of PAO, kinematic viscosity increases with increment in biodiesel mixture composition. For a given composition of biodiesel mixture blend, kinematic viscosity increases with increment composition of PAO (Table-8).

Comparison between PMA and PAO Chemical Additive: 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.

Conclusion

The effect of poly methacrylate and poly alpha olefin on the low temperature properties of jatropha and karanja methyl esters blend composition were different of which poly alpha olefin was most effective with 8°C decreases in the cloud point and 13°C decreases in the pour point, PAO was very efficient in decreasing both cloud point and pour point of biodiesel blend composition of the chemical additive content of 7.5 g/L, it provided little effect on cloud point. Pour point continuous increases with increment composition of cold flow improvers. Kinematic viscosity increases with increment in biodiesel mixture composition. For a given composition of biodiesel mixture blend, kinematic viscosity increases with increment composition of poly methylacrylate and poly alpha olefin.

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-9
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-10
Blend uncertainties

Blend	Uncertainties
B_{15}	0.034
B_{10}	0.023
B_5	0.022

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