Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **4(12),** 9-12, December **(2014)** *Res. J. Chem. Sci.*

Production, Physico-Chemical and Cold-Flow Properties of Biodiesel from Jatropha and Karanja Oils

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Available online at: www.isca.in, www.isca.me
Received 10th January 2014, revised 22nd August 2014, accepted 13th December 2014

Abstract

Biodiesel which is derived from triglyceride by (two step process) esterification and transesterification have attracted considerable attention during the past decade as a renewable, biodegradable, environmental friendly and nontoxic fuel. In India, non-edible oils like JBD and KBD oil are available in abundance, which can be converted to biodiesel. Then the comparison of physicochemical properties of KO and KBD and JO, and JBD were done. The various properties of KBD and JBD are found to be comparable with that of PD fuel. This paper investigation the physical-chemical property of KO, KBD, JO, JBD and KBD and JBD blends with PMA cold-flow improvers. Cold flow properties investigation, cloud point, pours point and kinematic viscosity.

Keywords: Pour point, Cloud point, Kinematic viscosity, Transesterification, Esterification, JBD: Jatropha biodiesel, JO: Jatropha oil, PD: Petroleum diesel, PMA: Polymethacrylate, KO: Karanja oil, KBD: Karanja biodiesel.

Introduction

Biodiesel is a domestic, renewable fuel for diesel engines derived from natural renewable sources. It is produced from virgin or used vegetable oils (both edible and non-edible) and animal fats though various chemical processes. The most common is transesterification process[1-3]. 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 advantage of using biodiesel are its renewability, better quality exhaust gas emissions, its 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 to the green house effect.

The disadvantages of biodiesel are its unfavorable cold-flow properties[4-5]. Since it begins to gel at low temperature which clogs filters or even become so thick that it cannot be pumped from the fuel tank to the engine. There are three important cold-flow properties-cloud point, pour point and cold-filter plugging point and used to asses suitability of biodiesel. Under these condition, the fuel become a suspension of wax crystals in a mixture of shorter-chained n-alkanes, olefins and aromatics, although the crystals are initially submicron in size and invisible to the human eye, they grow in size as temperature drops further when the particle size reaches 0.5µm, the crystals become visible, and 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[6,7].

The viscosity of a fluid plays a major role in its pumping and flow within an engine. Generally, methyl esters have a Newtonian behaviour within typical working temperature. This high viscosity at lower temperature cloud is a result of micro-crystal formation and would cause serious problems in fuel lines and in engine filter[8].

The present work deals with influence of polymeric [PMA] cold flow improvers on the cold-flow properties of JBD and KBD and its blends. The effect of cold-flow improvers on cloud point, pour point and kinematics viscosity. Although some cold flow improvers have so far been reported to be effective in improving the cold-flow properties of biodiesel[7]. Improvement of the low-temperature flow properties of biodiesel by the addition of cold flow improves still remains a challenge and need further investigation. Treatment with chemical cold flow improves is the most convenient and economical way of improving the low temperature properties of diesel fuels. The chemical cold flow improvers are generally referred to as pour point depressants, cold-flow improvers. Most cold flow improvers promote the formation of small [10-100 µm] needle shaped crystals. These crystals experience significantly reduced growth and agglomeration rates as temperature decreases below cloud point[6].

Material and Methods

Materials: Jatropha and Karanja 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 99.9% (Jiangsu huaxi International Trade Co. Ltd made in

China) was purchased from local supplier. Chemical additives PMA was purchased from M/s Pawan and Company, Delhi. The characteristics of these additives and KO and JO and their biodiesel are given in table-1 and 2.

Table-1
Characteristics of PMA[9]

Characteristics	Value for PMA
Density, kg/m^3	0.867
Molecular weight, kg/kmol	2260 [9]
Pour point, ˚C	-6

Table- 2
Characteristics of Jatropha and Karanja Oils and their biodiesel[11,12]

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, ^{o}C	2	5	3	-1
Pour point, ^{o}C	1	1	-5	-7
Kinematic viscosity at 40 ^{o}C, mm^2/s	33.30	30.95	4.16	3.58
Acid value, mg/KOH/g	5.19	4.25	0.61	0.81[13]

Preparation of Jatropha and Karanja Biodiesel: Acid - Catalyzed Esterification Process: A two step process, acid catalyzed Esterification process is followed by base-catalyzed transesterification process. Firstly the oil is esterified with methanol in presence of acid catalyst (i, e. sulfuric acid) for esterifying free fatty acid in the oil. For esterification methanol to oil mole ratio of 6:1has been used with 1% Sulphuric acid (based on weight of the oil). The reaction was allowed to proceed at temperature 60^{o}C with stirring for two hours; contents are 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, it should be less than 2± 0.25 mg KOH/ g for the use in transesterification process otherwise soap formation occur.

Base-Catalyzed Transesterification Process: After acid pretreatment conditions generate for the use of methanol to oil with a molar ratio 6:1 in the presence of 0.55% w/v KOH as an alkaline catalyst. The esterified product from previous step was poured into a reaction glass vessel and heated at 50 ^{o}C. The solution of KOH in methanol based on oil weight is heated to 50 ^{o}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 60-65 ^{o}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. Biodiesel is separated and washed with distilled water to remove alkali (Phenolphthalein test). Biodiesel mixture is then dried with anhydrous sodium sulphate followed by filtration. The mixture is distilled to remove excess methanol. The residue in the flask is only biodiesel. This biodiesel will be used for determination of cloud point, pour point and kinematic viscosity.

Preparation of Blends: JBD and KBD produced in the laboratory have been used for the preparation of its blends with PD by blending technique. Biodiesel and petroleum-based diesel will be blending in a conical flask under continuous stirring to ensure uniform mixing at 45 ^{o}C for 60 minute. These blends are on volume basis and they will be stored in glass bottles.

Preparation of JBD and KBD bends: JBD and KBD blends were mixed with cold-flow improvers (the additive purchased from M/s Pawan and company Delhi) before adding it to diesel. The appropriate amount of JBD and KBD were measured in masses of 100, 75, 50 and 25 ml, placed into glass flask. The appropriate amounts of cold-flow improver were added to each flask (0, 2.5, 5.0, 7.5 and 10 g). JBD and KBD-PD-Additive will be blending in a conical flask under continuous stirring to ensure uniform mixing at 45 ^{o}C for 60 minute.

Results and Discussion

Fatty Acid Composition of KO and JO: The percentage composition of fatty acids present in KO and KO was determination by GCMs and represented in the table-3 given below.

Comparison of Fuel Properties of KO, KBD, JO, JBD and PD: Comparison of fuel properties of KO, KBD, JO, JBD done with diesel and the result are shown in the table-4 given below.

Table-3
Fatty Acid Composition of KO and JO

Fatty Acid Structure		Fatty Acid %	
		KO	JO
Palmitic	16:0	11.56	14.1
Stearic	18:0	7.4	7.1
Eicosanoic acid	20:0	1.35	0.4
Dosocasnoic acid	22:0	4.45	-
Tetracosanoic acid	24:0	1.08	2.4
Oleic	18:1	52.3	42.8
Linoleic	18:2	16.46	33.1
Residual		**5.40**	0.10

Table-4
Comparison of Fuel Properties of KO, KBD, JO, JBD and PD[14,15]

Properties	KO	KBD	JO	JBD	PD
Density (15°C, kg/m^3)	0.905	0.797	0.911	0.798	0.850
Kinematic viscosity at 40 °C, mm^2/s	30.95	3.58	33.30	4.16	2.33
Flash Point °C	205	97.8	232	98.0	70.0
Cloud Point °C	5	-1	12	2	-1
Pour Point °C	1	-7	1	-5	-18
Acid value, mg/KOH/g	4.25	0.81	5.19	0.61	0.35
Iodine Value	90.8	91	89.0	89	-
Saponification Value	189.7	180.0	190	187	--
Calorific Value Kcal/kg	8742	3712	3860	3934	4290
Cetane Number	38	42.9	37	43	46

Cloud Point, Pour Point and Kinematic Viscosity: Results are shown in the table 5. It can be seen variation of cloud point of JBD and KBD blends from 0 to 100 Vol. % PMA of average molecular weight of 2260 has been use as cold-flow property improver. It has been varied from 0 to 10 g per 100 ml. At a given concentration of PMA cloud point increases with increment in JBD composition. For a given composition of KBD blends, cloud point decreases with increment concentration of PMA.

Table- 5
Cloud Point of JBD and KBD blends

Sample composition		Cloud point at additive concentration of PMA				
JBD	KBD	0	2.5	5.0	7.5	10
100	0	3	2	1	1	1
75	25	5	5	5	4	3
50	50	7	5	5	4	4
25	75	4	4	4	4	3
0	100	3	2	1	1	1

Table- 6
Pour Point of JBD and KBD blends

Sample composition		Pour point at additive concentration of PMA				
JBD	KBD	0	2.5	5.0	7.5	10
100	0	-5	-9	-12	-12	-12
75	25	-6	-7	-8	-10	-10
50	50	-6	-7	-9	-11	-10
25	75	-6	-8	-9	-11	-11
0	100	-7	-10	-12	-15	-15

Results are shown in the table 6. It can be seen variation of pour point of JBD and KBD blends from 0 to 100 Vol. % PMA of average molecular weight of 2260 has been use as cold-flow property improver. It has been varied from 0 to 10 g per 100 ml. At a given concentration of PMA pour point increases with increment in JBD composition. For a given composition of KBD blends, pour point decreases with increment concentration of PMA.

Table -7
Kinematic viscosity of JBD and KBD blends

Sample composition		Kinematic viscosity at 40°C, mm^2/s at additive concentration of PMA				
JBD	KBD	0	2.5	5.0	7.5	10
100	0	4.16	3.45	3.45	3.09	3.09
75	25	3.39	3.55	3.57	3.49	3.50
50	50	3.40	3.54	3.55	3.47	3.48
25	75	3.40	3.53	3.54	3.45	3.46
0	100	3.45	3.09	2.71	2.33	2.33

Results are shown in the table 7. It can be seen variation of kinematic viscosity of JBD and KBD blends from 0 to 100 Vol. % PMA of average molecular weight of 2260 has been use as cold-flow property improver. It has been varied from 0 to 10 g per 100 ml. At a given concentration of PMA kinematic viscosity increases with increment in JBD composition. For a given composition of KBD blends, kinematic viscosity increases with increment concentration of PMA.

Conclusion

Thus this study suggests that KO and JO can be used as a source of triglycerides in the manufacture of JBD and KBD by esterification and transesterification. In the present work, it has been shown that physical-chemical properties of KO, KBD and JO, JBD compared to those of pure diesel fuel, because all properties investigated, excepting flash point, were within the diesel fuel standard limits. At a given concentration of PMA cloud point increases with increment in JBD composition. For a given composition of KBD blends, cloud point decreases with increment concentration of PMA. At a given concentration of PMA pour point increases with increment in JBD composition. For a given composition of KBD blends, pour point decreases with increment concentration of PMA. At a given concentration of PMA kinematic viscosity increases with increment in JBD composition. For a given composition of KBD blends, kinematic viscosity increases with increment concentration of PMA. While the pour point decreases with respect to that of diesel fuel that cloud point increases.

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