Comparative Study on Biodiesel Production from Azadirecta indica and Euphorbia pulcherrima seed oils from western Rajasthan

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Abstract-
Biodiesel is a petroleum-free alternative fuel made from a range of feed-stocks such as animal fats, vegetable oils, and utilised cooking oil. In the current scenario, biodiesel made from food oils is not commercially viable. The widespread usage about edible oils in favor of biodiesel generation may result in a food catastrophe. Low-cost feed-stocks, such as waste cooking oils along with non-edible oils, can be used to alleviate these challenges in biodiesel generation. In the present research the two non-edible seeds oils- Azadirecta indica and Euphorbia pulcherrima were investigated to access their biodiesel potential. The seed oils of both the plant species were converted to biodiesel by base catalyzed trans-esterification.The oil yield for A. indica and E.pulcherrima were 45.65% and 48.50% respectively while the biodiesel yield for both the plant species were 64.50% and 74.60% respectively. GC-MS analysis showed that both the seed oils have higher amount of monounsaturated fatty acids which favor their biodiesel potential.The fuel materialsabout B20 blends of both the species were found almost in the set bounds of ASTM D7467 standards. It has been suggested that B20 blends of A. indica and E. pulcherrima have the potential to be utilized in diesel engine.

Keywords-Azadirecta indica, Euphorbia pulcherrima, trans-esterification, fuel properties and, biodiesel producton.

Introduction-

In modern times diesel vehicles demand a fuel that burns cleanly and consistently under a wide range of operating circumstances. The only alternative to fossil fuels that may be used effectively in any current, unmodified diesel engine is biodiesel. Since it has similar qualities to petroleum-derived diesel, biodiesel could be blended in almost any ratio with it. Biofuel production from biomass is one method to reduce both crude oil use as well as environmental degradation (Ayanoglu and Aksoy 2015). Biodiesel is made when a vegetable oil or animal fat combines with an alcohol (typically methanol) in the presence of a catalyst (usually a base) to generate the appropriate alkyl esters (for methanol, fatty acid methyl esters) [Knothe G. 2010]. Biodiesel is a non-toxic, renewable fuel derived from renewable sources [Selvakumar M J, Alexis S J 2016,Kannahi M, Arulmozhi R (2013)]. It is one of the technically feasible and economically viable solutions to the rapid depletion of fossil fuel reserves and degradation of the environment [Atabani AE et.al 2014]. The majority of biodiesel is now produced from soybean, rapeseed, sunflower, and palm oils [Demirbas MF 2015]. The cost of raw materials is the biggest impediment to the commercialization of biodiesel. Approximately 70%–90% of the cost of biodiesel is due to raw material costs. As a result, producing biodiesel using edible vegetable oils is presently not commercially practicable. Non-edible oil plants are widely available in many countries and are cost-effective when compared to edible plant seed oils. Biodiesel production from various non-edible plant seed oils has been intensively investigated in recent years. Non-edible seed oils are beneficial as a diesel fuel because of their liquid nature, portability, easy accessibility, recyclability, higher combustion characteristics, lower sulfur, and aromatic content, and significantly greater biocompatible [Shikha and Rita, 2012.]Many such non-edible plant seed oils are indeed being researched for their biodiesel suitability based on physicochemical, fatty acid, and other biodiesel properties. Oils from Jatropha, Sclerocaryabirrea, Hevea brasiliensis , Balanites aegyptiaca, Huracrepitans, Huracrepitans have been analyzed so far for their biodiesel potential [Umaru and Aberuagba, 2012, Ejilah et al., 2012, Krishnakumar et al., 2013, Ogala et al., 2018, Sidohounde et al., 2019]. The Azadirachta indica (Neem), is an evergreen Meliaceae family member and is indigenous to India and other tropical and subtropical regions [Abubakar 2016]. Neem is a rapidly growing tree that can reach heights of 15–20 m (49–66 feet) and, in rare cases, 35–40 m (115–131 feet). It is deciduous, with most of its leaves falling off throughout the long dry season. Neem bears fruit in 3 to 5 years and reaches maximum productivity within 10 years, with oil content ranging from 30 to 35 % for kernels and seeds, respectively, and from 35 to 40 % for seeds [Kaura et al. 1998]. These characteristics necessitate considering it as an adequate feedstock for biodiesel.Euphorbia pulcherrima is a small tree or shrub belonging to family Euphorbeacea that grows to a height of 0.6–4 meters (2–13 ft). E.pulcherrima has been shown to have effective larvicidal properties against mosquitos and other insects [De Silva W 2008]. Furthermore, E.pulcherima extracts showed insecticidal activity against fall armyworm with high toxicity and also elevated insect growth regulation (IGR) activity [Almeida VT et.al 2017]. The A. indica and E.pulcherrima plants had that had no known application or appeared on the food menu. In most instances, seeds from these plants are discarded or dumped as waste. Seed oils from both resources are non-edible as well as have good oil content. As a result, the current study evaluates the Physico-chemical, fatty acid compositions and fuel properties of A. indica and E. pulcherrima seed oil extracts from western Rajasthan as prospective biodiesel and commercial substrates.The Graphical representation of Biodiesel production from A.indica and E.pulcherrima seed oils is shown in fig.1.

Experimental

Materials and Methods-

The A.indica seeds and E. pulcherrima were collected from various locations of Jodhpur (Rajasthan).

Extraction of seed oils.

To extract oil from ground seeds of A.indica and E. pulcherrima, the soxhlet extraction method was used, along with n-hexane (40-60ºC) as solvent. After the extraction of oils, the solvents were evaporated using a rotary evaporator.

Investigation of physicochemical characteristics of the oils-

Standard AOCS methods were used to estimate the moisture content, iodine value, and saponification value of the oil [AOCS 1997]. Abbe's refractometer was used to measure the refractive index.

Examination of the fatty acid profile

The FAMEs were obtained separately from both the seed oils using a base-catalyzed trans-esterification method. To achieve this aim 25 µl of extracted seed oils were mixed with 10 ml CH_3OH and 2 ml NaOH in a round bottom flask. Thereafter it was refluxed for about 2-4 hrs at 70^0-80^0C to get FAMEs of the respective seed oils. The resulting mixture was cooled and separated with a separating funnel containing 5ml distilled water and 2ml hexane into two phases. The higher phase covered the thing of biodiesel and the lower one covered the glycerin items(through product).

FAMEs GC-MS analysis-

FAMEs' GC-MS analyses were collected from sections A along with E. Pulcherrima seed oils were carried out using a scientific thermo TSQ 800 gas spectrophotometer of mass chromatographic. Moreover, a column that is capillary generated about polysilphenylenesiloxane(length is 25 m, 0.22 mm in internal diameter, 0.25 mm is the thickness and BPX is 70 TM) was utilised.Furthermore, helium was utilised as the gas of carrier and the rate of flow was 1 ml/min. Apart from that, the injector temperature, as well as the detector chambers, were controlled among 250 degrees c to 260 degrees c respectively.

Analysis of fuel properties of FAMEs-

Biodiesel (FAMEs) so prepared were tested for their fuel properties including Kinematic Viscosity, Specific gravity, Cetane number, Flash Point, Cloud point, etc. The fuel properties analysis were carried out for B-10 and B-20 blends of A.indica oil biodiesel (AIOB) and E. pulcherrima oil biodiesel (EPOB) with petroleum diesel and compared them with the American Society for Testing Materials (ASTM) D7467 standards.[ASTM D7467 2020]

Results and Discussion-

Table.1 illustrates the oil content of A.indica (45.65%) and E. pulcherrima (48.50%). The significantly good oil yield obtained from both the non-edible seed oils indicates that their use in the production of biodiesel would be cost-effective. Moisture content was found to be 0.27% in A.indica and 0.25% in E. pulcherrima oils. Significantly low moisture content extends the shelf life, prevents corrosion In the middle of engines of internal combustion, along with aids within the transesterification procedure about these oils.A.indica seeds oil was found to have 64.50% and E. pulcherrima seeds oil have 72.60% biodiesel yield. Alkali-based transesterification was used to maximize biodiesel yield from non-edible oilseeds as it would be much more rapid than catalyzed of acidtrans esterificationas well as has been secondhandwithin commercial biodiesel manufacture.

Table-2 showed the Uncorrected weight percentage of fatty acids in A. indica and E. pulcherrima seeds oil.The GC-MS spectra of A. indica and E. pulcherrima FAMEs were given in fig.2 and fig. 3. From GC –spectra it was found that both the oils A. indica and E. pulcherrima contained a higher amount of mono unsaturated fatty acids (oleic acid) 49.90% and 58.38% respectively as compared to polyunsaturated fatty acids (linoleic and linolenic). The A.indica seed oil contained 18.00% linoleic acid and 3.70% linolenic acid whereas E. pulcherrima found to have 14.28% linoleic acid and 3.85% linolenic acid. Numerous research findings recommended that the best vegetable oil used for biodiesel production contains a higher proportion of monounsaturated fatty acids than polyunsaturated fatty acids because oil containing a high proportion of polyunsaturated fatty acids has poor oxidation stability and can compromise fuel properties including kinematic viscosity and degrade fuel quality [Emil A et.al, 2010, Saravanan S, Nagarajan G 2011, Ejikeme PM et.al. 2011].

The fuel materials about blends of biodiesel AIOB along with EPOB were contrasted by the ASTM D7467 standard given in Table 3. Blending oils with petroleum diesel has been discovered to be an effective method for reducing choking and extending engine life. Gerpenalong with Zhang explored the usage of blended fuels of fatty acids soybean methyl esters diesel and oil, which resulted within relatively short ignition timing and combustion and emission characteristics comparable to diesel[Zhang Y, Van Gerpen JH 1996]. With the increase in biodiesel proportion within mixtures, viscosity increases slightly. Yet, this occasion does not impact the characteristics of atomization. In addition, the B20's viscosity of both the non-edible oils seemed to be very similar to that of ASTM standards. As a result, biodiesel blends B20 of AIOB and EPOB could be used with any heating configuration or engine modification. As shown in Table.3 the specific gravity of the AIOB and EPOB blends B10 and B20 were in the range of 0.857–0.887g/cm^3, which is close to the standard range of 0.87–0.90 for biodiesel [Knothe G 2002]. The Ash content for B10 and B20 blends of AIOB and EPOB were shown in fig.6.The ash content for the B20 blends of the AIOB (.015 %) and EPOB (.014%) was slightly higher than the ASTM D7467 standard of 0.01 maximum. The iodine values for both AIOB and EPOB blends were found to be in the range of 98-118, which was close to the expected iodine value for biodiesel set by Europe's EN 14214 specification of 120 [Fangrui M, Hanna MA 1999]. Based on Iodine values A.indica seed oil was categorized under non-drying oils whereas E. pulcherrima seed oil was categorized as semi-drying oil. The drying and semi-drying oils have resistant to rancidity, therefore they have longer shelf lives. The comparison of acid values for B10 and B20 blends of AIOB and EPOB were shown in fig.5 .Acid values for the B20 blends of AIOB and EPOB were 0.5 mgKOH/g. and 0.4 mgKOH/g respectively, which were very much closer to ASTM standards of 0.3 mgKOH/g. The acid value measures the presence of corrosive free fatty acids and oxidation products. This is an important factor to consider when evaluating oil quality because the lower the free fatty acid content, the higher the quality of the oil. Oils with a low free fatty acid content not only promote transesterification but also do not interfere with the separation of FAMEs and glycerol. Saponification values for AIOB and EPOB blends B10 and B20 were in the range of 164-187mg KOH g^{-1}, which was quite comparable to the 193.55 mg KOH g^{-1} reported by Akbar et al. for Jatrhopa seed oil [Akbar E, 2009]. The fact that a low saponification value favors the separation of biodiesel and glycerol implies that it could responsible for the good yields of biodiesel.

Per oxide values (PV) of the AIOB and EPOB blends ranged between 3.56- 4.75 mEq/kg oil were shown in fig.4. The PV (3.56 mEq/kg oil) was found in a B20 blend of EPOB. It was found comparable to the PV value for Jatropa oil (1.2-3.7 mEq/kg oil). [Jonas M et.al 2020]. Therefore, the B20 blend of EPOB was found suitable for using biodiesel as it may prevent erosion of both engine components along with the fuel system.

The flashpoint is the temperature that signifies the overall flammability risk in the air atmosphere; higher flash points allow for secure biodiesel storage and transportation [Hossain AK, Davies PA 2010]. The flashpoints of B20 blend of AIOB and EPOB were 192.5^{0}C and 198.8^{0}C respectively, which were much higher than those of ASTM (52 min.). The flashpoint about non-edible seed oils is upper than thatabout fossil diesel [REN21. 2008, Pramanik K 2003, Ziejewski M, Goettler HJ 1992]. The Cetane number (CN) for B10 and B20 blends of AIOB and EPOB were varied from 47-58, which were also higher than ASTM standard values. A relatively high CN for these blends results in a relatively short ignition delay and timeframe of the combustion period, minimal knocking, and lower nitrogen oxide formation (NOx) [Bello EI et.al 2012, Barabas I 2010]. The viscosity of B20 blends of AIOB and EPOB were 3.5mm^2/s and 3.9mm^2/s which also met the ASTM limits. The cloud point for B10 and B20 blends of AIOB and EPOB were 2^{0}C and 1^{0}C respectively.

Conclusion- A comparative study on biodiesel production from non-edible oilseeds ofA.indica and E. pulcherrima was conducted in this research. Both theA.indica and E. pulcherrima seeds oils showed a high oil yieldand a good amount about fatty acids related to monounsaturated. Both B10 as well as B20 blends related to AIOB and EPOB were found to have lower CO and NOX emissions. Further due to low PV and Acid value as well as comparatively lower ash content for the B20 blends of AIOB and EPOB, they are found to have a higher potential for biodiesel production. They also prevent corrosion about both the engine components and fuel system , accelerate the trans-esterification process, and also do not interfere with the separation of FAMEs and glycerol. Thus it is concluded that the production of biodiesel from the B20 blend of AIOB and EPOB was environmentally friendly, cost-effective and feasible.

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Table 1- Physical properties of A.indica and E. pulcherrima seed oils

S.No.	Name/Family	Local Name	Oil %	Moisture %	Biodiesel %
1.	Azadirecta indica	Neem	45.65	0.27	64.50
2.	Euphorbia pulchherima	Poensettia	48.50	0.25	74.60

Table 2- Uncorrected weight percentage of Fatty acids in A.indica and E. pulcherrima seed oils determined by GC-MS

Fatty acids	Carbon number	Azadirecta indica	Euphorbia pulchherima
Palmitic acid	C16:0	1.95	-----

Stearic acid	C18:0	25.70	23.02
Oleic acid	C18:1	49.90	58.38
Linoleic acid	C18:2	18.00	14.28
Linolenic acid	C18:3	3.70	3.85
Eicosenic acid	C20:1	-----	------
others	others	0.75	0.47

Table-3 Fuel properties OF B10 AND B20 BLENDS of AIOB and EPOB compared with ASTM-D7467 Biodiesel standards.

Fuel Property	Units	ASTM D7467 Limits	AIOB		EPOB	
			B10	B20	B10	B20
Flash point	^0C	52 min	188.2	192.5	185.5	198.8
Cetane number (CN)		40 min	58	48	55	47
Kinematic Viscosity, 40^0C	mm^2/s	1.9-4.1	1.5	3.5	1.7	3.9
Specific gravity	g/cm^3	--------	0.867	0.875	0.857	0.887
Ash content	% mass	0.01max	0.023	.015	0.021	.014
Sulphur content	ppm	15 max (S 15)	24	12	21	14
Per oxide value (PV)	mEq Kg/oil	-------	4.75	3.15	4.32	3.56
Cloud point	^0C	Only guidance provided	2	1	2	1
Pour Point	^0C	-------	5.3	5.5	5.8	5.9
Acid value	mg KOH/g	0.30 max	0.7	0.5	0.6	0.4
Saponification value	mg KOH/g	-----	164	178	174	187
Iodine Value	$gI_2/100g$	------	56	98	105	118
Refractive index		-------	1.431	1.472	1.421	1.475

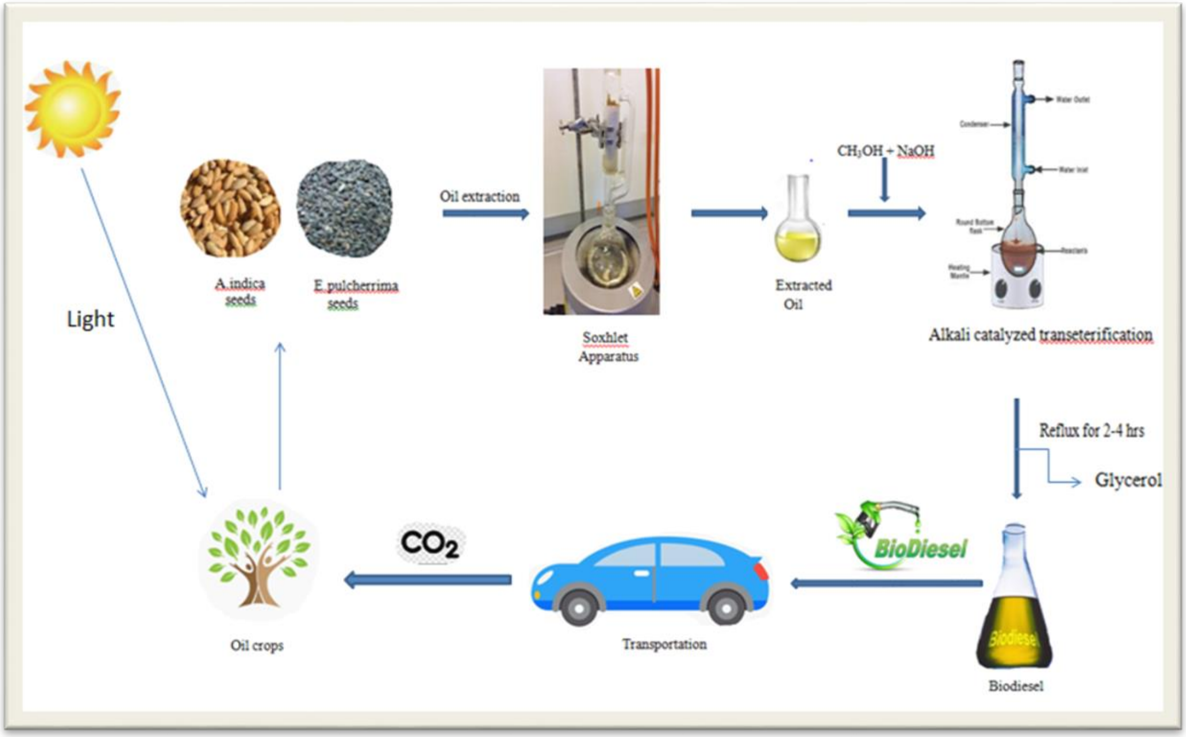

Fig.1- Graphical representation of Biodiesel production from A.indica and E.pulcherrima seed oils

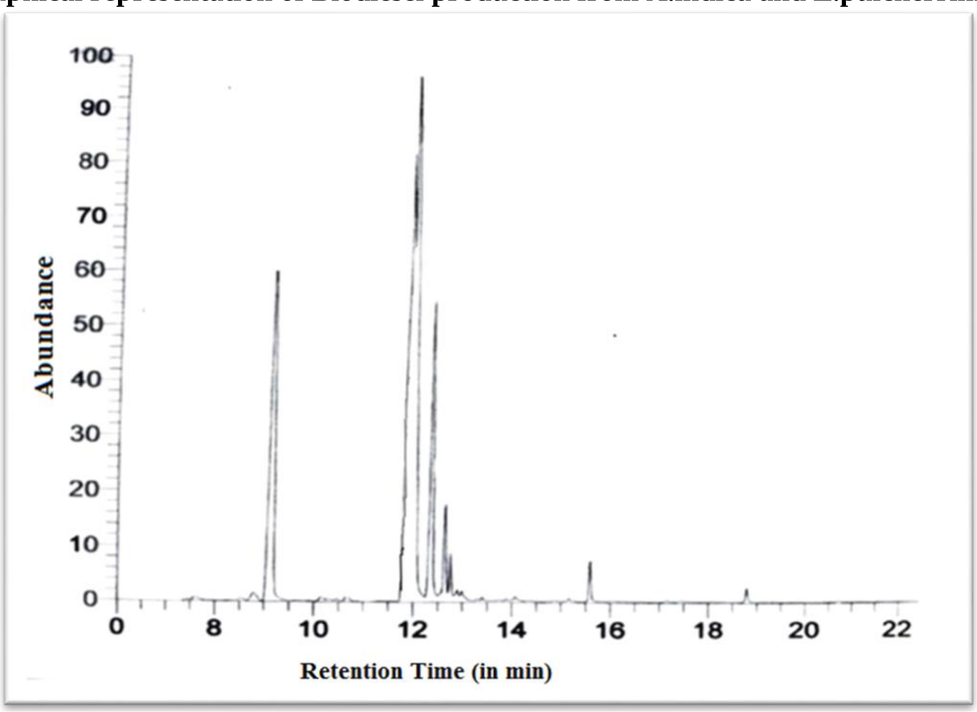

Fig.2- GC-MS spectra of FAMEs of A.indica

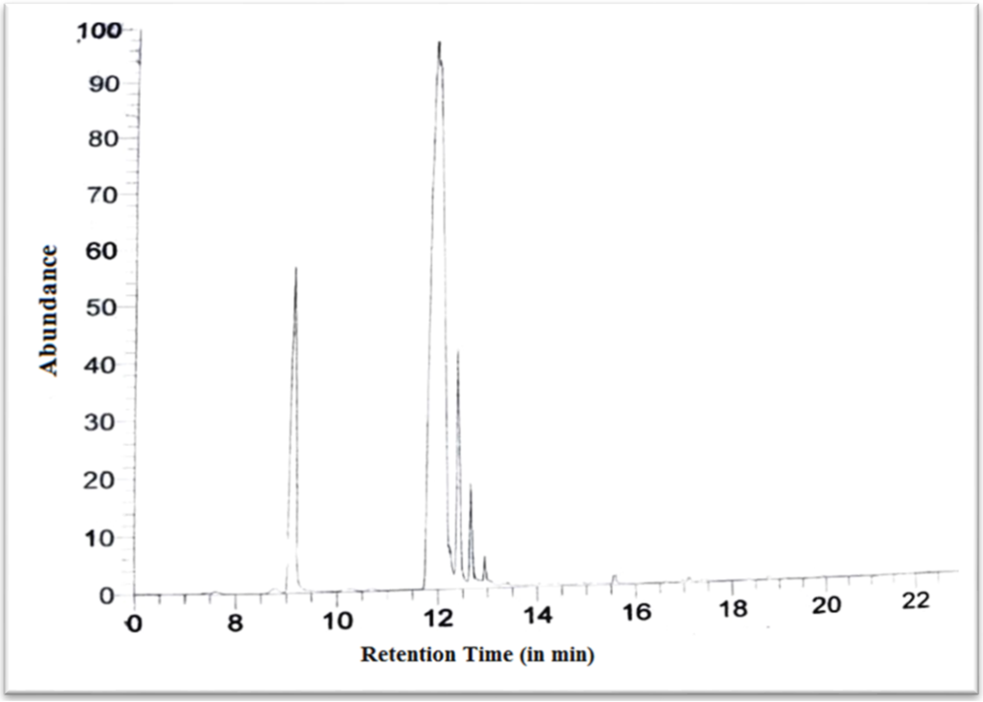

Fig.3- GC-MS spectra of FAMEs of E.pulcherrima

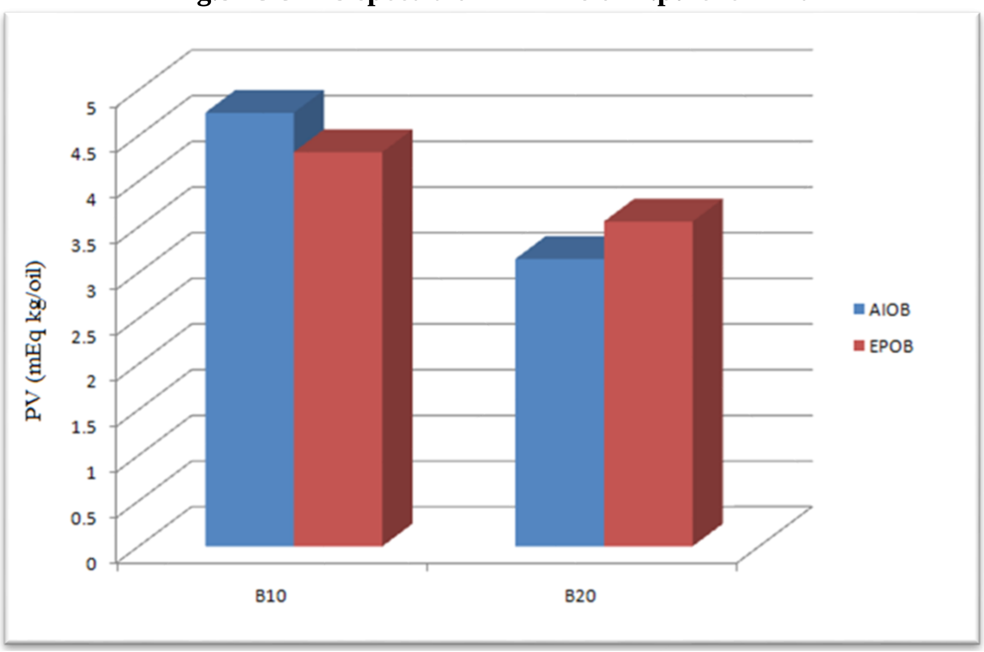

Fig.4 – Peroxide Values (PV) for B10 and B20 blends of AIOB and EPOB

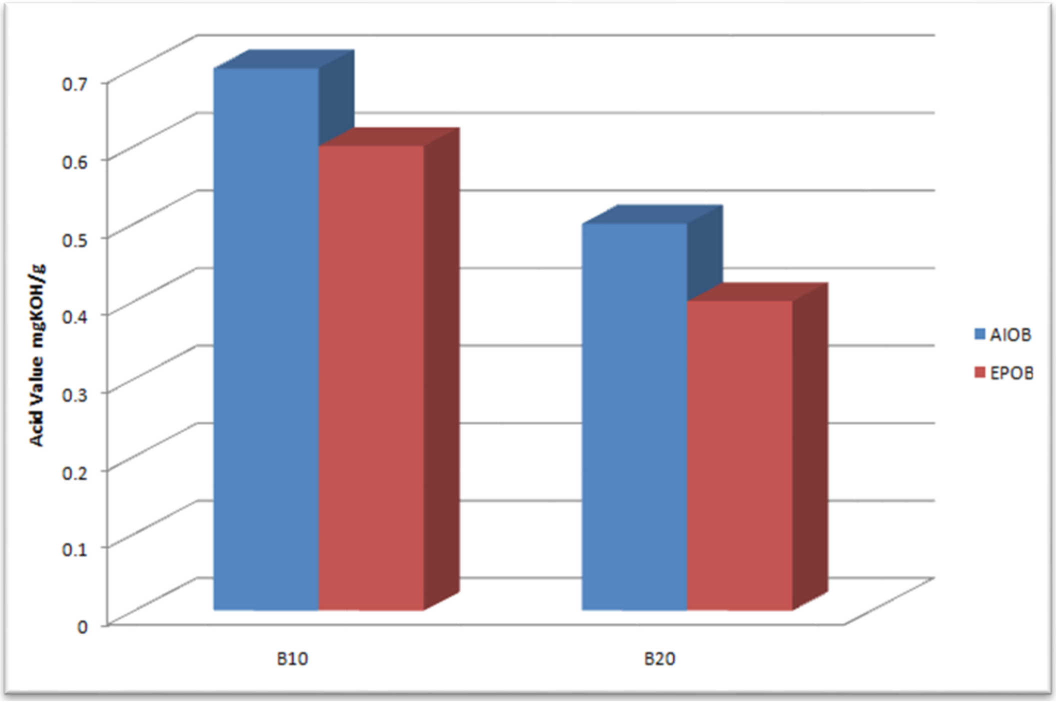

Fig 5- Acid values for B10 and B20 blends of AIOB and EPOB

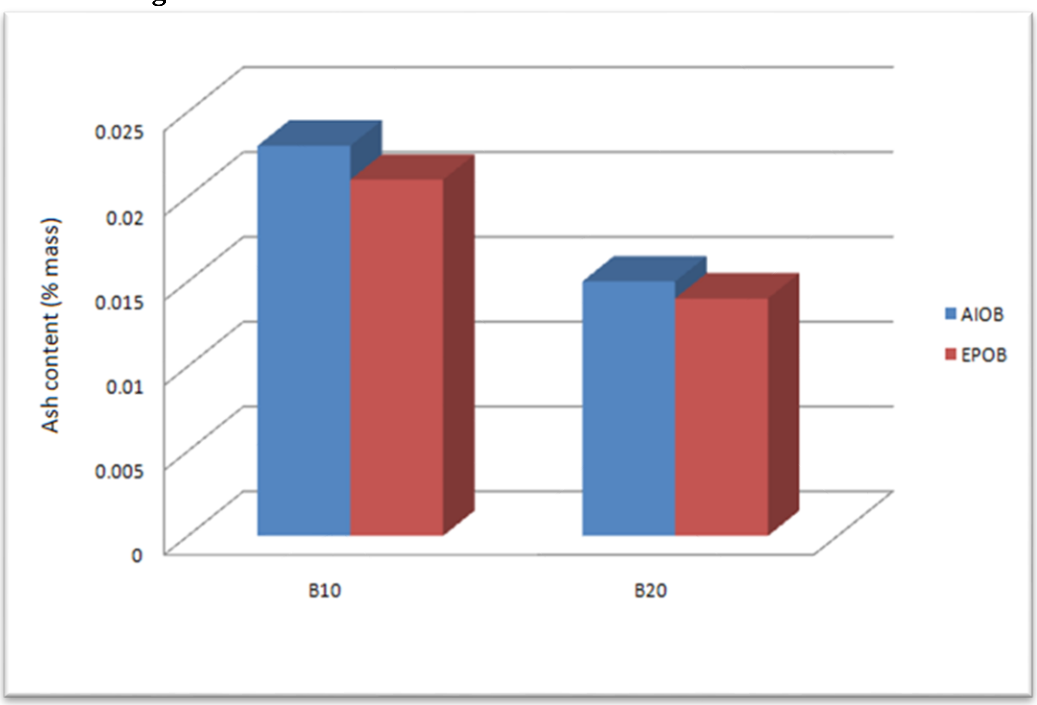

Fig.6- Ash content for B10 and B20 blends of AIOB and EPOB