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Characterization of neem seed oil and de-oiled cake for its potentiality as a biofuel and biomanure.

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Abstract

The draining crude oil reserves concurrently with a growth in population bang, consumption of energy, automobile usage and price hike results in energy crisis in emerging economies. For the past few decades efforts are on the way to find out new alternatives to diesel since depletion of crude oil would cause a major impact on the transportation sector. Amidst of the various alternative source, biodiesel from non-edible oils ascertain the promising outburst. Biodiesel is biodegradable, easily available, economic, eco-friendly and offers lubricity to extend the durability of engine. In the current study, the oil from the traditional revered tree of India – *Azadirachta indica* was scrutinized for the competent biodiesel production to meet the ASTM standard for biodiesel. The neem oilcake was assessed and it was observed to control the weeds, diseases and it is a proficient biofertilizer.

Keywords: Biodiesel, neem seed oil, neem oilcake, B10, B20 blends, biofertilizer.

INTRODUCTION

Over the past few decades, energy is the backbone of technology and economic development. Hence, our energy requirements have increased in the years following the industrial revolution. This rapid increase in use of energy has created problems of demand and supply. With the depletion in fossil fuel resources, it is a need of today's world to concentrate on renewable energy source to satisfy the demand and conserve our finite natural resources for the forth-coming generations. The depleting fossil fuel reserves, increasing demand for diesels and ambiguity in their availability, greater environmental impact are considered to be the important trigger for many initiatives to search for the alternative source of energy which can supplement or replace fossil fuels. In recent years, research has been directed to explore plant- based fuels and plant oils and fats as fuels. Of the various alternate fuels under consideration, biodiesel derived from vegetable oils, appears to be the most promising alternative fuel to diesel. More than 95% of the world's biodiesel is produced from edible vegetable oils, thereby increasing demand throughout the worldwide for vegetable oil production.

The contributions of non-edible plant oils as a new source for biodiesel production have the advantage of not competing with edible oils produced from crop plants. A lot of research work has already been carried out to use vegetable oil both in its pure form and also in modified form. Studies have shown that the usage of vegetable oils in pure form is possible but not preferable [1]. Biodiesel can be used in pure form (100%) or blended with the conventional diesel fuel up to 20% to create a biodiesel blended fuel for its use in the compression ignition engines [2]. Biodiesel, defined as simple mono alkyl esters of long chain fatty acids prepared from vegetable oils or animal fats, possesses a number of technical advantages over petro diesel, such as derivation from renewable and domestic feed stocks, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, superior flash point and biodegradability, reduced toxicity, as well as reduction in most regulated exhaust emissions.

Neem seed oil has a great potential to become a prominent resource because of its non-edible property. The neem tree found in abundance in tropical and semi-tropical regions, produce 350,000 tons of oil per annum. Neem seed contains the following compounds and they are 17, beta hydroxyl azadiradione, 17 epiazadiradione, 7 decacetyl 7 benzoyl azadiradine, 1- alpha methoxy 1,2 dihydro epoxyazadiradione, diepoxyazadiradione, 7 desercetyl 7 benxoyl epoxy azadiradione, 7 acetyl neo trichillinone, 7 diacetyl , 7 benzoyl gedunin. Neem seed cake contain the compounds namely azadirachtin, nitrogen, phosphorous, potassium, carbon, sulphur, calcium and magnesium. Major fatty acid composition : Palmitic acid, Stearic acid, Oleic acid, Linoleic acid, Arachidic acid [3, 4, 5].

The oil cake obtained from the neem seed after oil extraction is rich in proteins, carbohydrates, minerals, and is a suitable material for the formulation of nitrogenous

fertilizer [6]. In India, the byproduct of the neem tree the neem seed oil finds its utility as biocide rather than as a biofuel. In the present study, the physico-chemical properties of neem seed oil and its blended biodiesel at B10 and B20 proportions were analysed for its potentiality as a biodiesel resources and it was compared with the ASTM standard. Also the neem oil cake was analysed for its efficacy as biofertilizer by pilot studies.

MATERIALS AND METHODS

Neem seed (*Azadirachta indica* Adr. Juss.) was collected. The seeds were processed and crushed mechanically to collect the oil. The explicit remnant - the residual oil cake was collected and stored in an airtight container.

Blend preparation

The blends were made on a volume basis. Biodiesel is used as B100 or in a blend with diesel. A blend of 20% biodiesel with 80% diesel by volume, is ‘‘B20” and a blend of 10% biodiesel with 90% diesel by volume, is ‘‘B10” is prepared using neem seed oil and conventional diesel.

Physico-chemical analysis

Normal titrimetric method was used to measure the acid value. Saponification number was determined by refluxion followed by the titration. Estimation of iodine number was done by the Wij’s method. The cetane number was empirically determined by [7]. The ultrasonic studies were carried out using Ultrasonic interferometer (Mittal & Co.) with a frequency of about 3 MHz. Density and viscosity was measured using specific gravity bottle and Ostwald viscometer respectively. The other properties such as pH, conductivity, total dissolved solids, and dissolved oxygen were measured using Systronics analyzer.

Oil cake analysis

The oil cake obtained after the extraction of oil is dried, preserved and used for field study. The nutrient in the oil cake namely the nitrogen content was estimated through Kjeldhal’s method, phosphorous by Olsen et al., method and potassium by flame photometry. Vegetable crops like chilly, onion and paddy were planted in pots and the neem oilcake was applied to the potted plants as biofertilizers and macro and micronutrient contents of the soil was analysed before and after the application of neem oil cake.

RESULTS AND DISCUSSION

The physical properties namely density, viscosity, pH, conductivity, total dissolved solids and dissolved oxygen for neem seed oil and its blends of B10 and B20 were anticipated and the results were depicted in the Table-1.

Table 1: Physical properties of Neem seed oil and its blends.

Parameters	B10	B20	B100
Density (g/ml)	1.08 ± 0.01^{c}	1.13 ± 0.02^{b}	1.24 ± 0.02^{a}
Viscosity ($Nm^{-2}s$)	3.43 ± 0.21^{c}	4.46 ± 0.20^{b}	6.37 ± 0.21^{a}
pH	2.53 ± 0.05^{c}	2.78 ± 0.04^{b}	3.78 ± 0.08^{a}
Conductivity (µs)	0.56 ± 0.02^{b}	0.59 ± 0.03^{b}	0.63 ± 0.01^{a}
Total dissolved solids (ppm)	0.09 ± 0.01^{c}	0.15 ± 0.01^{b}	0.37 ± 0.01^{a}
Dissolved oxygen (ppm)	5.43 ± 0.25^{b}	6.50 ± 0.20^{a}	6.80 ± 0.17^{a}

Values are expressed as average of triplicates ± standard error.

In order to find out the fuel efficiency, the ultrasonic parameters such as ultrasonic velocity, adiabatic compressibility, acoustic impedance and relaxation time were estimated and are tabulated in Table-2.

Table 2: Ultrasonic properties of Neem seed oil and its blends.

Parameters	B10	B20	B100
Ultrasonic velocity ($10^{6}m/s$)	1.22 ± 0.01^{c}	1.45 ± 0.12^{b}	1.65 ± 0.01^{a}
Adiabatic compressibility ($kgm^{-1}s^{-2}$)	0.51 ± 0.06^{a}	0.36 ± 0.06^{b}	0.29 ± 0.07^{b}
Acoustic impedance ($10^{6}kgm^{-2}s^{-1}$)	1.17 ± 0.03^{c}	1.32 ± 0.07^{b}	1.71 ± 0.10^{a}
Relaxation time (sec)	3.06 ± 0.05^{c}	3.37 ± 0.03^{b}	3.84 ± 0.01^{a}

Values are expressed as average of triplicates ± standard error.

The chemical properties like acid value, saponification number, iodine value, average molecular weight and the cetane number was analyzed and its was tabulated in Table-3.

Table 3: Chemical properties of Neem seed oil and its blends.

Parameters	B10	B20	B100
Acid value(mg KOH/g)	0.61 ± 0.10^{b}	0.74 ± 0.04^{ab}	0.80 ± 0.07^{a}
Saponification number (mg KOH/g)	295.27 ± 1.95^{c}	312.27 ± 1.97^{b}	339.46 ± 2.56^{a}
Iodine value (mg iodine /100g)	73.14 ± 2.15^{b}	77.27 ± 2.22^{b}	87.78 ± 1.91^{a}
Cetane number	48.33 ± 0.60^{a}	46.39 ± 0.61^{b}	42.63 ± 0.50^{c}

Values are expressed as average of triplicates ± standard error.

Macro and micro nutrient status of the oilcake was analysed before and after planting the vegetable crops. The results were given in Table-4.

Table 4: Evaluation of oilcake through field studies.

Parameters		Before planting	After planting chilli	After planting onion	After planting paddy
pH		8.12 ± 0.11^{a}	7.45 ± 0.05^{b}	7.92 ± 0.08^{a}	7.55 ± 0.05^{ab}
EC (µS)		0.52 ± 0.03^{a}	0.39 ± 0.02^{b}	0.47 ± 0.01^{ab}	0.38 ± 0.02^{b}
Macro nutrients	**N**	171.7 ± 3.16^{a}	171.7 ± 7.02^{a}	168.8 ± 3.98^{ab}	151.0 ± 3.63^{b}
	P	8.32 ± 0.26^{a}	7.73 ± 0.29^{b}	6.07 ± 0.12^{bc}	8.17 ± 0.21^{ab}
	K	414.8 ± 2.25^{a}	394.9 ± 5.40^{b}	364.6 ± 6.70^{b}	364.2 ± 6.38^{b}
Micro nutrients	**Fe**	9.53 ± 0.05^{a}	7.13 ± 0.15^{b}	6.06 ± 0.08^{c}	7.26 ± 0.07^{b}
	Mn	14.07 ± 0.12^{a}	12.72 ± 0.33^{ab}	7.66 ± 0.06^{b}	7.68 ± 0.06^{b}
	Zn	6.05 ± 0.04^{a}	6.03 ± 0.12^{a}	3.70 ± 0.14^{c}	4.21 ± 0.05^{b}
	Cu	0.84 ± 0.05^{a}	0.77 ± 0.04^{ab}	0.71 ± 0.02^{ab}	0.67 ± 0.05^{b}

Data represents the mean value of three replications, for the cultivation of three set of vegetable crops. Mean values within each column followed by the same letter in superscript are not significantly different (Duncan's New Multiple Range Test).

The increase in density may be due to the increase in structural changes as there is an increase in saturation composition of the biofuel [8]. Similar results were found by [9,10,11]. The viscosity of the biodiesel feedstock can be reduced by dilution, pyrolysis, transesterification, and emulsification process [12,13] and the results of the current study coincide with the findings of [14,15,16,17]. The higher water levels in biodiesel can exacerbate problems with corrosion, wear, suspension of solids, and microbial growth [18]. The biodiesel obtained by blending is free from catalyst, water content and other residual chemical. Hence it is safe to the engine. Conductivity increases with increase in temperature which implies high energy consumption. Similar results were observed by [19]. Thermal efficacy was improved with lower concentrations of biodiesel blends while with higher concentrations of biodiesel in the blend, there was a reduction of smoke density in exhaust gas [2]. Total dissolved solids were in very trace amounts in vegetable oils [20]. The ester formed during the production of biodiesel reduces energy content and makes the biodiesel polar, through the hydroxyl (-OH) hydrogen bond. The polarity gives the properties of solvency, detergency, wet ability and conductivity [21]. The oxygen molecules present in the fuel enhances the combustion resulting in higher thermal efficiency [22]. The results obtained goes equivalently with the findings of [23, 24].

Ultrasonic velocities of blended neem seed oil concur with [25]. Acoustic impedance is almost reciprocal of adiabatic compressibility. Compressibility decreases with the increase of

concentration, whereas the acoustic impedance increases [26].Compressibility is inversely proportional to the velocity. It is primarily compressibility that changes with structure. This leads to a change in ultrasonic velocity. The greater the attractive forces among the molecules of a liquid, the smaller will be compressibility. It shows the reverse effect as that of impedance which produces the peaks which again confirms the formation of complex molecule which is due to the ion-solvent interactions [26]. The ultrasonic values obtained in this study coincide with the results of [27]. The dispersion of ultrasonic velocity in a mixture reveals information about the characteristic time of the relaxation process that causes dispersion [28].

As oil-fats rancidify, triglycerides are converted into fattyacids and glycerol, causing an increase in acid number. The acid value of the neem oil biodiesel is within the ASTM limits and also it coincides with the reported value [29]. The non-fatty impurity and the amount of alkali that would be required by the fat for its conversion to soap are determined by the saponification value. The present study coincides with the reported value [30]. The iodine value is a measure of unsaturation. The higher the iodine number, higher will be the amount of iodine needed to break the double bonds and also higher is the efficiency of that oil as a biodiesel and the findings coincides with [31], Cetane number plays the important role governing the suitability of fuel in C. I. engines. Ignition quality of the fuel is given in terms of cetane rating. Higher CN is a desirable property in diesel engine, indicates shorter time between ignition and initiation of fuel injection into the combustion chamber. The higher CN is correlated with the reduction of nitrogen oxides and unburnt hydrocarbon exhaust emissions which is important for alleviating air pollution [21,32,33]. The results of the current study coincide with the studies of [14,34]. The macro and micro nutrient contents of the soil samples after the application of selected de-oiled cakes had been significantly increased. Also these nutrients were utilized by the planted crops to certain extent. The oilcake analysis showed that the neem oil cake efficiently controls weeds and diseases and was found to be a potent biofertilizer and biocide. The cake left after extraction of oil from Neem is excellent organic manure with insecticidal properties significantly reducing the number of soil insects and nematodes [35]. Neem is very effective against grasshoppers, leaf hoppers, plant hoppers, aphids, jassids, and moth caterpillars [36,37,38,39,40,41]. Due to the perennial nature of most of the second generation bioenergy crops, field resistance against diseases and pests should be multigenic [42]. In the present study, the oil cake was applied to Chilly, onion and paddy and it was found that the oil cakes controls the weeds as well as protect the plants from pests and diseases. Usually the oilcakes such as neem, cottonseed, castor, sesame, mustard, coconut, linseed, soyabean are used as concentrated organic manures for the cultivation of crops because of their valuable N, P, K contents. According to [43, 44,45], the decomposition rate of seed cakes are relatively higher, due to its lower C:N ratio and quickly mineralized, releasing appreciable amounts of inorganic Nitrogen supply. Oilcakes are rich in fibre, protein and energy contents. Moreover the seedcakes were used in the production of chemicals and biomolecules such as enzymes.

CONCLUSION

The physical, chemical and ultrasonic properties of neem biodiesel in B10 and B20 proportions falls within the range of ASTM specifications and the biodiesel blends B10 and B20 can be used in conventional diesel engine without much modification. The present study proves that *Azadirachta indica* can produce biodiesel more efficiently than the routine bioenergy crops used in the manufacture of biofuel. The remnant after the extraction of oil from oilseeds of *Azadirachta indica* emerges to be a superior biomanure and biocide. Furthermore, positive impacts on biodiversity may be realized as a result of ameliorating the rate of change of atmospheric composition and global climate and bioenergy crops and cropping systems mainly help to reduce the green house gases emission, utility of waste lands, improves land fertility by reducing the soil erosion and perk up economic status of the country.

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