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Biodiesel properties of *Putranjiva roxbhurghii* and *Plumieria rubra* seed oils: Evaluation based on fatty acid chemistry

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ABSTRACT

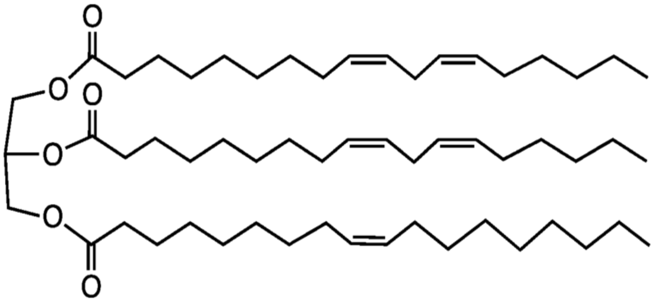
In this work new feedstock for biodiesel production has been screened. Non edible seed oil species like Putranjiva roxbhurghii (PRO) and Plumieria rubra (PR) plant species which yields 22% and 40% seed oil respectively. The molecular weight of oil is calculated based on the percentage component fatty acids of the seed oils. The prominent parameters of bio-diesel such as cetane number (CN), lower heating value (LHV) and higher heating value (HHV) of these Fatty Acid Methyl Esters (FAMEs) are empirically determined. The bio-diesel property of Fatty Acid Methyl Esters (FAMEs) of these seed oils is compared with existing bio-diesels which confirmed the suitability of these seed oils for the generation of biodiesel. The seed oils selected in this investigation convene the major specification of biodiesel standards organizations like American (ASTM), Germany (DIN) and European (EN). This work reports the suitability of these candidates for the bio-diesel productivity.

Keywords: *Putranjiva roxbhurghii*, *Plumieria rubra*, unusual fatty acids, industrial utilization, biodiesel.

INTRODUCTION

The global plant oils production over last 40 years has amplified from 23 million metric tons in 1967 to 129 million metric tons in 2007 [1]. It is estimated that about 90% of world's population will be located in developing countries by 2050. The seed oils have much higher density than starch and hence more energy per volume is obtainable. The seed oil has 2.25 times more energy than starch or proteins [3]. The application of plant seed oils includes surfactants, soaps, detergents, lubricants, solvents, paints, cosmetics, and chemicals. In addition there is good number of *unusual fatty acids* produced by wild plant species or minor seed oils (non edible). The unusual fatty acids include those with chain lengths amid 8 and 22 carbons containing double bonds or conjugated systems or with functional groups such as a*cetylenic* bond or epoxy group or *hydroxyl* group or *cyclopropenoid* entity. The seed oils containing unusual fatty acids have wider industrial applications like protective coatings, plastics, urethane derivatives, dispersants, cosmetics, lubricant additives, pharmaceuticals, textiles, variety of synthetic intermediates, and stabilizers in plastic formulations etc.[4].

Fossil fuels are depleting in a very high-speed. Alternative energy sources are the only solution to alleviate energy crisis. Bio-fuels are dragging much attention worldwide. Animal fats and vegetable oils are most widely occurring lipids. Chemically, vegetable oils / animal fats are triglyceride molecules wherein three fatty acid groups / esters attached to glycerol molecule.



Trigylceride of sunflower seed oil; represents 90 % unsaturated fatty acids

Vegetable oils could only replace a small fraction of transport fuel. But the major problem posed by direct use of vegetable oil is its higher viscosity compare to common diesel fuel. The methods applied to reduce the viscosity of seed oil are; dilution, microemulsification, pyrolysis, catalytic cracking and transesterification [5]. Transesterification consists of a sequence of three consecutive reversible reactions involving conversion of triglycerides to diglycerides, and diglycerides to monoglycerides. Finally, glycerides are converted into glycerol and one ester molecule in each step. The transesterification method is vastly practiced throughout the globe for the production of biodiesel.

Biodiesel fuels obtained from different sources, varies with fatty acid profiles. Generally it contains C_{14}–C_{22} lower alkyl fatty acid esters. FAMEs of vegetable oils have outstanding advantages over clean engine fuel alternatives. It contains about 77% carbon, 12% hydrogen by weight [6]. Compare to direct seed oil biodiesel has low viscosity and improved heating value which result in shorter ignition delay and longer combustion duration thus low particulate emissions. Biodiesel has become more attractive recently because of its eco-friendly nature. Its advantages includes; its domestic origin, renewability, biodegradability, higher flash point, inbuilt lubricity and blending capability with petro diesel. The use of pure bio-diesel especially in the transport sector brings down the emissions of CO_2 by 80%. It has high cetane number than that of petro diesel. Biodiesel is a realistic fuel for future. It has more or less analogous properties to that of petro diesel, but low exhaust emissions, non-toxic, free of sulfur and aromatics. It has more than 10% oxygen weight which reduces the carbon monoxide, oxides of sulphur and volatile organic content. Its flash point is more (423 K) compared to petro diesel (337 K). It is non-flammable hence non-explosive also. The mechanical problems associated with biodiesel are oxidative stability, poor low-temperature properties, and bit higher NO_x exhaust emissions. The latter problem may be solved over time with the introduction of new exhaust emission control technologies [7,8,9].

To reduce the processing and raw material cost of biodiesel it is recommended to use *non edible seed oils* as raw materials, if unusual fatty acids are identified during analysis of seed oil, prior to transesterification process the isolation of industrially important unusual fatty acid/s to be carried out. Then, the rest of the material subjected for transesterification. Finally, the recovery of glycerol is important. Glycerol may be used as a chemical feedstock in the various products like polyurethanes, polyesters, polyethers, lubricants, wrapping and packaging materials, foods, drugs, cosmetics, tobacco products and products that displace existing petroleum derived materials. The manifestation of the biodiesel industry has generated a additional glycerol, which has initiated numerous efforts to find new products, and newer markets using glycerol as the resourceful chemical [10-13].

Currently, the commonly occurring fatty esters in biodiesel are those of palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. Usually, *Soyabean, palm, sunflower, safflower, cottonseed, rapeseed,* and *peanut* oils are considered potential alternative fuels for diesel engines. The major seed oils sources like *Coconut, corn, cottonseed, canola , olive, peanut , safflower, soyabean,* and *sunflower* species are the multipurpose oils which are used for both biodiesel purpose as well as edible purpose. This created more demand, escalating price, etc., of these seed oils due to competition of these seed oils for food and fuel. On the other hand the non edible seed Oils which are used for the production of are *babassu , copaiba, honge, jatropha , jojoba, karanja, pongamia, mahua, nagchampa, neem, petroleum nut, rubber tree seeds, nicotinica tabacum, deccan hemp, cerebra oddulum* etc., Researchers are looking forward to new avenues for raw materials, especially non-edible materials for the production of biodiesel [14]. Biodiesel can provide just such an interim solution. However, no feed stock seems to exist that fulfils all requirements. It is becoming apparent that there may be an optimal fatty acid profile that provides optimal fuel properties while minimizing environmental risks and other negative effects. Knoth suggested that a mixture consisting primarily of methyl oleates and mixture of shorter chain esters derived from palmitoleic acid and esters derived from decanoic acid might be an ideal mixture. To meet this requirement transgenic crops are suggested [15-18].

The aim of this paper is to apply the already developed theoretical models (substantiated with experimental results) of fuel parameters on selected non edible seed oils. The individual non edible seed oils and their readily available fatty acid profile are utilized for assessment of their biodiesel profile. The non edible seed oils which yield more than 20% seed oil have been selected and subjected for screening their candidature for biodiesel. After the meticulous survey we have selected *Putranjiva roxbhurghii* (PRO*)* and *Plumieria rubra* (PR) for this investigation.

Putranjiva roxbhurghii: It belongs to the family *Euphorbiaceae*. This plant family consists of about 200 genera with species numbering to 3000. A mostly dioecious, evergreen tree with pendant branches found wild or cultivated almost in all parts of India. The leaves are reported to be applied on swollen throats of cattle. Leaves are also lopped for fodder [19].

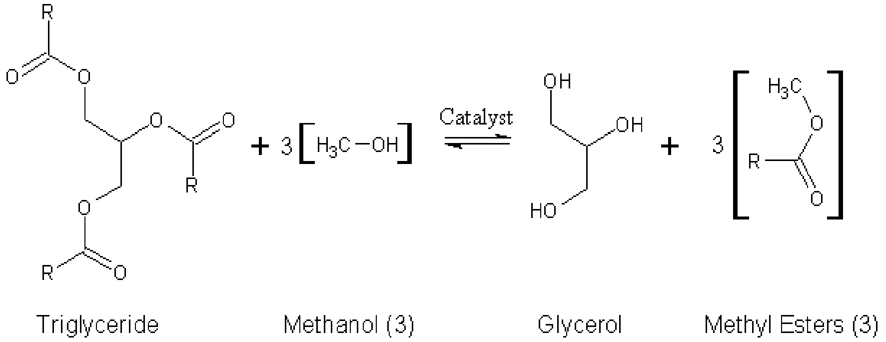
Plumieria rubra: It belongs to the family *Apocynaceae*. This plant family consists of about 110 genera with more than 900 species. It is a small tree, grown in gardens. The white latex is used for trothache and for carious in teeth [20].

MATERIALS AND METHODS

Oil extraction: The seeds of *Putranjiva roxbhurghii* and *Plumieria rubra* were ground, powdered and the oil content extracted by extraction with light petroleum ether (B.P. 40-60 ^{0}C) in a Soxhelt extractor for 24 h. The organic extract has to be filtered and dried over anhydrous Na_2SO_4. The petroleum ether removed under vacuum. The % oil for each 100 grams of dry seeds is calculated.

Transesterification: This is a reversible reaction. A strong base / a strong acid are used as a catalyst. Sodium or potassium methanolate can be used for efficient conversion of fatty acids present in oils to their corresponding FAMES.

Procedure: The seed oil and the alcohol (methanol / ethanol) in the ratio is1:6. In presence of acid or base as catalyst and refluxed until completion of the esterification reaction. Then the mixture is transferred to separating funnel then it is allowed to stand for overnight. The lower layer containing glycerol, methanol and most of the catalysts was drained out. The upper layer containing methyl esters, some methanol, traces of the catalyst are cleaned thoroughly by washed with warm de-ionized water. Then, the residual methanol is removed by rotary evaporation at around 70^{0}C. Thus obtained product containing FAMEs is used as biodiesel.



Transesterification reaction

The selected seed oils were investigated for fuel properties as per American (ASTM), Germany (DIN D6751) and European (EN 14214) standards. The highly useful analytical data for this work such as % SFAs, %USFAs, IV, SN, CN, LHV, HHV are deployed in this work. The SN and IV were calculated empirically with the help of equations (1) and (2) respectively or referred from the literature. SN depends upon the molecular weight and the percentage concentration of fatty acid components present in FAMEs of oil. However, IV, according to equation (2), depends upon three variables those are percentage concentration, molecular weight and the number of double bond(s) present in the corresponding fatty acid. Percent seed oil content SN, IV and fatty acid compositions of the selected seed oils is collected from the literature [21].

Screening of biodiesel property of *putranjiva roxbhurghii* and *plumieria rubra* seed oils based on their component fatty acids/fames: The selected seed oils were investigated for fuel properties as per American (ASTM), Germany (DIN D6751) and European (EN 14214) standards.

Iodine value (IV) and Saponification number (SN): The IV and SN of fatty acid of these seed oils are calculated and used to establish their suitability for biodiesel. Thus, IV and SN of seed oil are calculated from the equations (1) and (2) respectively based on compositions of fatty acid methyl ester [22] results obtained are very close to experimental values.

$$SN = \sum (560 \times A_i)/ Mw_i \qquad (1)$$

$$IV = \sum (254 \times D \times A_i)/ Mw_i \qquad (2)$$

where, Ai is the percentage of component fatty acids, D is the number of double bonds and Mwi is the molecular mass of each component.

Cetane number (CN): The CN measures how easily ignition occurs and the smoothness of the combustion. The CN affects a number of engine performance parameters like combustion, stability, drivability, white smoke, noise and emission of carbon monoxide and hydrocarbon. Generally, biodiesel has higher CN than conventional diesel fuel, which results in higher combustion efficiency. It is an important parameters of the biodiesel / petro diesel fuel. It's significance is useful during selection of FAMEs to use as biodiesel. The CN of FAMEs is calculated [23] using the equation (3) and is known closely match to the experimental values.

$$CN = 46.3 + (5458 / SN) – 0.225 \times IV \qquad (3)$$

Usually, FAMEs with higher CN are preferred. But the increase of CN thereby IV decreases it means degree of unsaturation goes down leading to the solidification of FAMEs at elevated temperature. To avoid this situation, US biodiesel standard specified the upper limit of CN up to 65 only [24].

Higher heating value (HHV): It is known that straight and processed vegetable oils used in diesel engines are the complex chemical mixture of FAMEs. The HHV of biodiesel is calculated using equation (4) in accordance with regression model [25].

$$HHV = 49.43 – (0.015 \times IV) – (0.041 \times IV) \qquad (4)$$

Lower heating value (LHV): The LHV of straight and processed vegetable oils is estimated with respect to equations (5) and (6) respectively based on bond energy values of chemical structure of different FAMEs. The method established for the calculation of lower heating value is quite general and its predictive ability is more precise [5].

For FAMEs,

$$LHV = 0.0109(C/O)^3 - 0.3516(C/O)^2 + 4.2000(C/O) + 21.066 - 0.100\ Ndb \qquad (5)$$

$$LHV = 0.0011(H/O)^3 - 0.0785(H/O)^2 + 2.0409(H/O) +20.992 - 0.100\ Ndb \qquad (6)$$

Where C is the number of carbon atoms, H is the number of hydrogen atoms, O is the number of oxygen atoms, and Ndb is the number of double bonds.

RESULTS AND DISCUSSION

The component fatty acids present in PRO seed oil are oleic acid (59.2%) stearic acid (23%), linoleic acid (11%) and palmitic acid (3.7%). The seed oil of PR comprised of linoleic acid (40.5%) lauric acid (23.1%) and palmitic acid (19.7%) and stearic acid (4.2%) and arachidic acid (2.7%). The industrially important unusual fatty acids such as malvalic acid (1.5%) and sterculic acid (1.6%) are reported from the seed oil of PRO. In case of PR seed oil the ricinolic acid (7.7%) is identified. The data extracted from the literature [21]. Details of component fatty acids in above said seed oils and structure of corresponding fatty acids are shown in tables 1 and 2 respectively.

Table 1 Fatty acid profile of seed oils of *Putranjiva roxbhurghii* and *Plumieria rubra* [21]

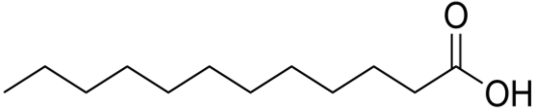
Sp. No.	**Seed species**	**% Oil**	**Fatty acid % composition in the corresponding seed oils**								
			SFAs				**USFAs**		**UFAs**		
			12:0 Lauric $C_{12}H_{24}O_2$	**16:0** Palmitic $C_{16}H_{32}O_2$	**18:0** Stearic $C_{18}H_{36}O_2$	**20:0** Arachidic $C_{20}H_{40}O_2$	**18:1** Oleic $c_{18}H_{34}O_2$	**18:2** Linoleic $C_{18}H_{32}O_2$	**M**	**S**	**R**
1.	*Putranjiva roxbhurghii*	22.0	-	3.7	23.0	-	59.2	11.0	1.5	1.6	-
2.	*Plumieria rubra.Linn*	40.0	23.1	19.7	4.2	2.7	-	40.5	-	-	7.7

Where M= Malvalic acid ($C_{18}H_{32}O_2$), S= Sterculic acid ($C_{18}H_{32}O_2$), R= Ricinolic acid $C_{18}H_{34}O_3$
SFAS = saturated fatty acids, USFAs =Unsaturated fatty acids, UFAs=Unusual fatty acids

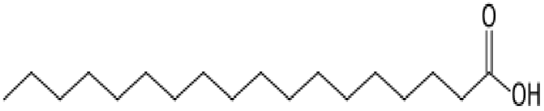
Table 2. Structure of component fatty acids in respective seed oils of PRO and PR

Saturated Fatty Acids

Lauric acid ($C_{12}H_{24}O_2$)



Steraic acid ($C_{18}H_{36}O_2$)

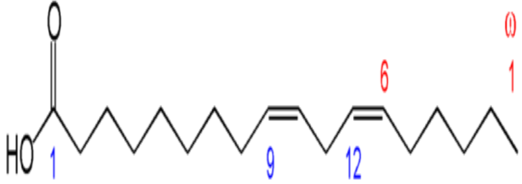


Palmitic acid ($C_{16}H_{32}O_2$)

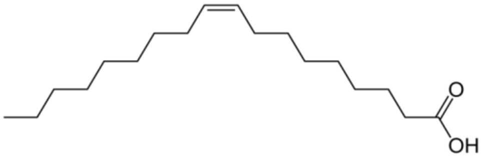
Arachidic acid ($C_{20}H_{40}O_2$)

Unsaturated Fatty acids and Unusual fatty acids

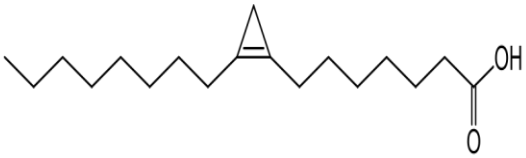
Linoleic acid ($C_{18}H_{32}O_2$)



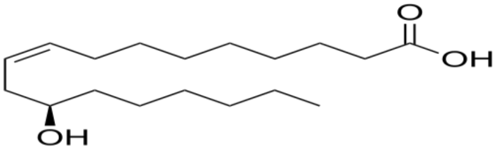
Oleic acid ($C_{18}H_{34}O_2$)



Malvalic acid ($C_{18}H_{32}O_2$)



Ricinoleic acid ($C_{18}H_{34}O_3$)



The molecular weight (MW) of individual seed oil is calculated based on component fatty acids. The MW of PRO and PR is 855.64 and 883.71 g/mol respectively. Iodine value of d these seed oils is not exceeding 120 which best fit as per the limitation laid by EN 14214 for biodiesel. There is consistency in the SN. Generally, the FAMEs, which are mainly comprised of carbon chain lengths from 16 to 18, have boiling points in the range of 330–357^{0}C; thus the specification value of 360^{0}C is easily achieved. In the same context the FAMEs of these species meet the specification of 90/95% boiling point limit of 360^{0}C specified in ASTMD6751 and in other biodiesel standards.

The CN of the FAMEs of these oils are 58.53 and 51.99 respectively. Biodiesel standards of USA (ASTMD 6751), Germany (DIN 51606) and European Organization (EN 14214) have set CN value as 47, 49 and 51, respectively [23]. The upper limit of CN (65) has been specified in US biodiesel standard (ASTMPS 121–99). Moreover, the CN of petro diesel is 42.6. Overall the empirically calculated CN value of FAMEs of PRO and PR meet the requirement of biodiesel standards.

The LHV and HHV of the FAMEs are quite appreciable in these seed oil species. For HHV, equation 4 shows that, the increase in the value due to increasing chain length in the fatty acid. The decrease is due to increase in the number of double bonds. The HHV of a fuel is a function of its carbon, hydrogen and oxygen content. The LHV of straight and processed vegetable oils is estimated with respect to equations (5) and (6) respectively based on bond energy values of chemical structure of different fatty acids or FAMEs. The calculated results of both the species reflects that there is a consistency of LHV of 38 MJ/Kg in all the species under this investigation. This is slightly lower than the LHV of petro diesel (43 MJ/Kg). The European Biofuel Technology Platform 2011 reported the LHV for biodiesel as 37.1 MJ Kg^{-1} [27]. The HHVs of biodiesels are relatively high. The HHVs of these species is 40.35 MJ Kg^{-1}and 36.45 MJ Kg^{-1}respectively which are slightly lower than of petro diesel (43 MJ Kg^{-1}), or petroleum (42 MJ Kg^{-1}), but are higher than coal (32–37 MJ Kg^{-1}). Table 3 shows various fuel profile of FAMEs of these seed oils.

Table 3. Biodiesel properties of *Putranjiva roxbhurghii and Plumieria rubra* seed oils

Sp. No.	**Source/Seed species**	**M.W of oil (g mol^{-1})**	**SN (mg KOH / g)**	**IV (mg I_2 /g)**	**TSFA (%)**	**TUSFA (%)**	**CN**	**LHV MJKg^{-1}**	**HHV MJKg^{-1}**
1.	*Putranjiva roxbhurghii.*	883.71	195.8	69.5	26.6	73.3	58.53	38.47	40.35
2.	*Plumieria rubra.*	855.64	197.5	97.5	49.1	50.9	51.99	38.61	36.45

Where, MW=mol.wt, IV=iodine value, SN=saponification number, TSFAs=Total saturated fatty acids TUSFAs=Total unsaturated fatty acids,CN=Cetane number, LHV=Lower heating value, HHV=Higher heating value

The overall screening of these selected species of the seed oils for biodiesel properties compared as shown in table 4 with the already existing biodiesels so also with the common diesel. The calculated values are very close to the standards. This reveals that both selected seed oils at this effort are potential feed stock for the purpose.

Table 4. Comparision of biodiesel properties of selected seed oils with existing biodiesels

Biodiesel property	**Seed oil species under this investigation**		**Existing biodiesel / Diesel**			
	Putranjiva roxbhurghii	**Plumieria rubra**	**Soyabean***	**Rapeseed***	**Sunflower***	**Petro Diesel**
% seed oil	22.0	40.0	19.0	43.00	44.0	NA
Iodine Value (mg I_2/100g)	69.50	97.50	120.50	108.05	132.32	NA
% TSFAs	26.60	50.90	14.90	4.34	10.00	75

% TUSFAs	73.30	40.50	86.44	94.93	90.00	
Cetane Number	58.53	51.99	50.90	52.00	47.00	42.6
Lower Heating Value (MJ kg^{-1})	38.47	38.61	33.50	32.80	33.50	43.1
Higher Heating Value (MJ kg^{-1})	40.35	36.45	39.50	37.60	40.56	46.0

* indicates some of the data obtained from, Ref. [29] NA=Not applicable

APPLICATIONS

The high saponification value of both PRO and PR seed oil can be used in the manufacture of shoe polish, liquid soap and shampoo production, cosmetic applications, high oleic oil is an excellent emollient. The linoleic acid occure in cream which are essential in the human diet, infants grow poorly and develop skin lesion if fed a diet of non fat milk for prolonged period [28]. The byproducts of the transesterification industrially important glycerol. The purified glycerol can be applied in the food/ cosmetic industries, so also in the oleochemical based industry. Isolated unusual fatty acids can be utilized for possible industrial applications [29].

CONCLUSIONS

The FAMEs of PRO and PR seed oil meet the major specifications of American biodiesel standard (ASTMD 6751-02, ASTMPS 121-99), Germany (DIN V 51606) and European Standard Organization (EN 14214). The FAMEs of these seed oils are found to be the most suitable feed stock for biodiesel production. However, still further research work is needed, to evaluate these FAMEs for other property measures like, tri bological studies, and long-term engine testing before full-fledged alternative fuel. If many of such plants are grown in large scale on suitable wastelands, the bio-diesel produced from such seeds can supplement or replace the petro-diesel.

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