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Fatty Acid Methyl Esters from Non Edible Seed Oils : A Potential Biomass for Biodiesel and Possible Industrial Relevance

KEYWORDS: Zinnia elegans Jacq, Salvia farinacea Benth, fatty acids, biodiesel, industrial relevance

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ABSTRACT *The seed oils of Zinnia elegans Jacq [ZE] and Salvia farinacea Benth [SF] plant species are selected for this analytical study. These species yield 27.7% and 27.1% non edible seed oil respectively. The details of component fatty acids [CFA] and other essential analytical data such as iodine value [IV], saponification value [SV] are collected from the literature. The major parameters of bio-diesel viz., cetane number [CN], lower heating value [LHV] and higher heating value [HHV] of the fatty acid methyl esters [FAMEs] are empirically computed. The bio-diesel properties of these seed oils are evaluated with reference to existing bio-diesels. This work reports the suitability of these species for the bio-diesel production.*

INTRODUCTION

Presently, the burning issue is sustainable development. The widest practice of renewable raw materials significantly adds to sustainable progress. Amongst various bio-based products from vegetable resources, plant oils make up the greatest section of the existing utilization of renewable raw materials in the chemical industry as feed stock (Zengshe Liu, 2013).

The utilization of plant seed oils in markets includes a range of products such as, surfactants, soaps, detergents, lubricants, solvents, paints, cosmetics, and chemicals etc. The unusual fatty acids have wider utility in protective coatings, plastics, urethane derivatives, dispersants, cosmetics, lubricant additives, biolubricants, pharmaceuticals, textiles, variety of synthetic intermediates, and stabilizers in plastic formulations etc. (FAO 2008 and M.M. Kucuk 1994).

Due to depletion of resources like petroleum / coal, biodiesel is recently gaining fame as an alternative source of energy. It is derived from biomass like animal fat or from plant seed oil.

The advantages of biodiesel comprises it's; domestic origin, renewability, biodegradability, higher flash point, inbuilt lubricity and blending capability with fossil diesel, reduction in emissions of CO_2 by 80%, high cetane number than that of petro diesel, low viscosity, improved heating value which result in shorter ignition delay and longer combustion duration leading to low particulate emissions.

Recently, various researchers are focusing on non edible seed oils for the biodiesel production (Altun, S. 2011, Balusamy, T.R , Marappan,2010, Banapurmath, N.R et al., 2008.). This is just to mitigate the consequences of usage of edible oils for the production of biodiesel which would lead to adverse effect on food security.

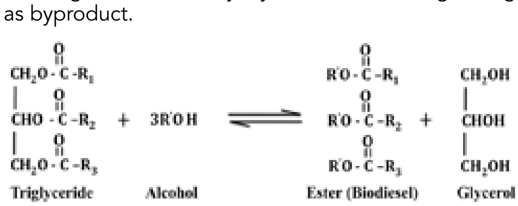
Zinnia elegans Jacq:
It belongs to the family Compositae. It is a native of Mexico, The uncultivated plant grows to about 76 cm in height. It has solitary flower heads about 5 cm across on stems resembling daisies. (Kirkbride, J. H. & J. H. Wiersma. 2007).

Salvia farinacea Benth:
It is a perennial herb belongs to Lamiaceae. Its origin is north America. It is cultivated as a flamboyant plant. It is a useful bedding plant in Deccan gardens, flowering abundantly from September to May (Glossary of Indian medicinal plants 1956).

MATERIALS AND METHODS

Oil extraction: The seeds of ZE and SF were ground, powdered and the oil extracted by light petroleum ether (B.P. 40-60 ^{0}C) in a Soxhelt extractor for 24 hrs. The organic extract filtered and dried over anhydrous Na_2SO_4. The petroleum ether removed under vacuum.

Transesterification: Trigycerides on reaction with alcohol generally methanol or ethanol in presence of strong base / a strong acid as a catalyst yields FAMEs along with glycerol as byproduct.



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R1, R2, and R3 in this diagram represent long carbon chains that are too lengthy to include in the diagram.

Procedure: The seed oil is treated with alcohol (6:1 ratio) usually methanol or ethanol in presence of acid or base as catalyst and refluxed until completion of the esterification reaction. Then the mixture is transferred to separating funnel and 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 washing with de-ionized water. Then, the residual methanol can be removed by rotary evaporation at around 70^{0}C. Thus obtained product containing FAMEs is used as biodiesel (K.S. Katagi, et al 2011).

COMPUTATIONAL ANALYSIS OF BIODIESEL PROPERTIES OF SEED OILS

The selected seed oils were investigated for fuel properties as per ASTM, DIN D6751 and EN 14214 standard methods.

Iodine value and Saponification number: These data extracted from the literature. The SV and IV of fatty acids of these seed oils are calculated to establish their suitability for biodiesel. The SV and IV of seed oils are calculated from the equations [1] and [2] respectively based on component of fatty acid (Krishnangukar, 1986) the results obtained are very close to experimental values.

$$SV = \sum (560 \times Ai) / Mwi \quad [1]$$

$$IV = \sum (254 \times D \times Ai) / Mwi \quad [2]$$

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:

Generally, biodiesel has higher CN than conventional diesel fuel, which results in higher combustion efficiency. Its significance is helpful before selection of FAMEs to use as biodiesel. The CN of FAMEs is computed using the equation [3] and is known closely match to the experimental values (Demirbas Ayhan,1998)

$$CN = 46.3 + (5458 / SV) – 0.225 \times IV \quad [3]$$

Usually, FAMEs with higher CN are preferred but not more than 65.

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 (Demirbas Ayhan, 1998).

$$HHV = 49.43 – (0.015 \times IV) – (0.041 \times SV) \quad [4]$$

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 (S.Mehta Pramod, K. Anand, 2009).

For FAMEs,

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

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

Where, CHO are the number of carbons, hydrogen and oxygen respectively. Ndb is the number of double bonds.

RESULTS AND DISCUSSION

Biodiesel property of selected seed oils of ZE and SF are computed based on the data from the literature (Mohan R. Shanbhag 1974, Jayshree K. Thakkaar,1983). Details of CFAs and other analytical values of seed oils and their biodiesel properties depicted in Table -1 and Table - 2 respectively.

Iodine value of these seed oils is not exceeding 120 mg I_2/g which best fit as per the limitation laid by European standard organization EN 14214 for biodiesel. There is consistency in the SN. Further, it is supported that, both the seed oils contain higher percentage of oleic acid 39.7% and 82.2% in ZE and SF seed oils respectively. This signifies the ideal mixture for the biodiesel as per the conclusion derived by G. Knoth (G. Knothe 2008).

Biodiesel standards of USA (ASTMD 6751), Germany (DIN 51606) and European Organization (EN 14214) have set CN value as 47, 49 and 51, respectively (K. Krisnangkura 1986). The CN of the FAMEs of ZE and SF seed oils are 47 and 48.5 respectively. Moreover, the CN of petro diesel is 42.6. Over all the empirically calculated CN value of FAMEs of ZE and SF meet the ASTM standard, however, the values are more than the CN of petro diesel.

HHV is evaluated using the equation [4]. 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 according to equations [5] and [6] respectively. There is uniformity of LHV that is with 38 MJ/Kg in both the species under this investigation. The European Biofuels Technology Platform 2011 reported the LHV for biodiesel as 37.1 MJ/Kg (Biofuels Technology Platform 2011). This is slightly lower than the LHV of petro diesel [43 MJ/Kg]. The HHVs of biodiesels for these species are 36.974 MJ/kg and 36.838 MJ/kg respectively which are slightly lower than those of petro diesel [43 MJ/kg], or petroleum [42 MJ/kg], but are higher than that of HHV of coal [32–37 MJ/kg]. Table 2 shows various fuel properties of FAMEs of these seed oils.

Table - 1. Analytical valuesof Zinnia elegans Jacq [a] and Salvia farinacea Benth seed oils[b]

Source/Seed species	Zinnia elegans	Salvia farinacea
% Seed oil	27.7	27.4
Saponification number (mg KOH / g)	277.3	278.9
Iodine value (mg I_2/g)	82.1	77.1
% CFAs; 12:0	NA	2.3
14:0	1.6	2.3
16:0	22.3	2.6
18:0	3.8	2.7
18:1	39.7	82.2
18:2	25.2	1.9
18:3	NA	NA
20:0	3.0	1.1
22:0	4.4	4.9

Table - 2. Computed biodiesel properties of Zinnia elegans and Salvia farinacea seed oils

Source/Seed species	Zinnia elegans	Salvia ferinesia
Molecular weight of oil (g/mol)	880.54	828.86
TSFA (%)	35.1	15.9
TUSFA (%)	64.9	84.1

Cetane number	47.0	48.5
Lower heating value (MJ/Kg)	38.49	38.68
Higher heating value (MJ/Kg)	36.974	36.838

Table - 3. Comparison of biodiesel properties of Zinnia elegans Jacq and Salvia fernecia Benth with existing biodiesels

Biodiesel property	Seed oil species under this investigation		Existing biodiesel / Diesel			
	Zinnia elegans	Salvia fernesia	Glycin max. * (Soyabean)	Brassica nepus* (Rapeseed)	Helianthus annus* (Sunflower)	Petro Diesel
% Seed oil	27.7	27.4	19.0	43.0	44.0	NA
Iodine Value (mg I_2 /100g)	82.1	77.1	120.50	108.05	132.32	NA
% TSFAs	35.1	15.9	14.90	4.34	10.00	75
% TUSFAs	64.9	84.1	86.44	94.93	90.00	
Cetane Number	47.0	48.5	50	52.0	47.0	42.0
Lower Heating Value (MJ/kg)	38.49	38.68	33.50	32.80	33.50	43.1
Higher Heating Value (MJ/kg)	36.974	36.838	39.50	37.60	40.56	46.0

*** indicates some of the data obtained from, Ref. (A S Ramadas , 2005) NA=Not applicable**

CONCLUSION

The FAMEs of seed oils of ZE and SF meet the major specifications of US biodiesel standard and European Standard organizations. Therefore, these species can be utilized for the production of biodiesel and also have the possible industrial relevance. However, still further research is required to evaluate these FAMEs for other property measures like, tribological studies, and long term engine testing.

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