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Catalytic Transformation of Four Non-Edible Vegetable Oils into Biodiesel using Egg Shell (CaO) as A Catalyst and Assessment of Their Fuel Properties

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Abstract— Biodiesel has been prepared from four different non-edible oils i.e. Yellow oleander (*Thevetia peruviana*), Nahor (*Mesua ferrea*), Karanja (*Pongamia pinnata*) and Jatropha (*Jatropha curcas*) using egg shell as a catalyst. Egg shell (CaO) catalyst has been prepared from waste egg shells and used as catalyst in these oils. The FAME (Fatty Acid Monoalkyl Ester) produced by this method gives data in accordance with the ASTM D6751 standards. Biodiesel fuel qualities like cloud point (°C), pour point (°C), kinematic (cst), viscosity at 40 °C, flash point (°C), oxidation stability (hours), Calorific value and carbon residue(%wt) are checked using standard test procedures. The heterogeneous catalyst prepared from the egg shell proves to be applicable in all the selected non-edible oil feedstocks to produce biodiesel.

Keywords—Non-edible oil, Egg shell, Heterogeneous catalyst, Biodiesel, Fuel property.

I. INTRODUCTION

The story of bio-based liquid fuel began in 1900 when Rudolf Diesel demonstrated the concept of using biofuels in internal combustion engine at an exhibition in Paris where he used peanut oil effectively in diesel engine. However, due to lower cost and promising supply of petrodiesel at that time, no subsequent research activities were done on biofuels [1]. The ever-increasing fossil fuel costs and austere world principles on exhaust emissions have enhanced the demand for substitution of fossil fuels with non-polluting and widely available renewable fuels for internal combustion engines [2]. Since the world's energy consumption is constantly increasing, environmentally sustainable and cost-effective alternative sources of fuels that can meet the rising demand should be explored and utilized [3]. In recent years, researchers and scientists have been working on biodiesel as an eco-friendly and renewable fuel substitute for petrodiesel. Biodiesel is defined as monoalkyl esters of long chain fatty acids, widely produced through the transesterification of vegetable oils, used cooking oils and animal fats with alcohol using wide range of acid and base catalysts [4].

Biodiesel prepared from low-cost non-edible oils, restaurant waste cooking oils and animal fats can provide viable alternative fuel that is technically as well as environmentally acceptable and economically viable. In USA and Europe, the surplus edible oils like soybean oil, sunflower oil and rapeseed oil are being used as feedstocks for the production of biodiesel. In south Asian countries like India, Sri-lanka, Pakistan etc, biodiesel cannot be produced from edible oils as these countries are the net importers of edible oils. Therefore, biodiesel can be harvested and sourced from non-edible seed oils such as Ratanjyot (*Jatropha curcas*), Mahua (*Madhuca indica*), Rubber seed (*Hevea brasiliensis*), Nahor (*Mesua ferrea*), Karabi (*Thietiva peruviana*) and Karanja (*Pongamia pinnata*) etc. which are naturally grown in these countries. The utilization of biodiesel helps to reduce air pollution and dependency on fossil fuel providing green cover to wasteland as well as supports agricultural and rural economy with reduction in dependency on imported crude oil [5]. Oilseeds e.g. Yellow oleander (*Thevetia peruviana*), Nahor (*Mesua ferrea*), Karanja (*Pongamia pinnata*) and Jatropha (*Jatropha curcas*) etc generally contain triglyceride or oil (lipid) bound to lignocellulosic materials by weak chemical and physical forces. Triglycerides are complex molecules of palmitic, stearic, linolenic, oleic, linoleic, behenic, schrachidic etc. Fatty acids with an attachment to a glyceride molecule [6]. Besides, non-edible oil contains trace amount of some toxic alkaloid components. These oils can be extracted from the oilseeds either by using a mechanical expeller or by dissolving the oil in a suitable solvent e.g. hexane. Recently, biodiesel derived from non-edible oil has been shown to be a viable alternative to the conventional transport fuel. Biodiesel, an alternative and renewable fuel for diesel engines, consists of alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from nontoxic, biological resources such as vegetable oils, or even used cooking oils by transesterification with methanol. Catalysts for transesterification can be acid, base, enzyme, and heterogeneous catalysts.

Transesterification or alcoholysis is the reaction of fat or oil with an alcohol to form biodiesel and glycerol in presence of catalyst. In the biodiesel industry, the most commonly used alcohol is methanol.

II. MATERIALS AND METHOD

Soxhlet apparatus, rotary vacuum evaporator, heating mantle, hexane, various oil bearing seeds such as Yellow oleander (*Thevetia peruviana*), Nahor (*Mesua ferrea*), Karanja (*Pongamia pinnata*) and Jatropha (*Jatropha curcas*) were collected from different localities of Assam. *Jatropha curcas* and *Pongamia pinnata* seeds were supplied by Kaliabor Nursery, Nagaon (Assam).

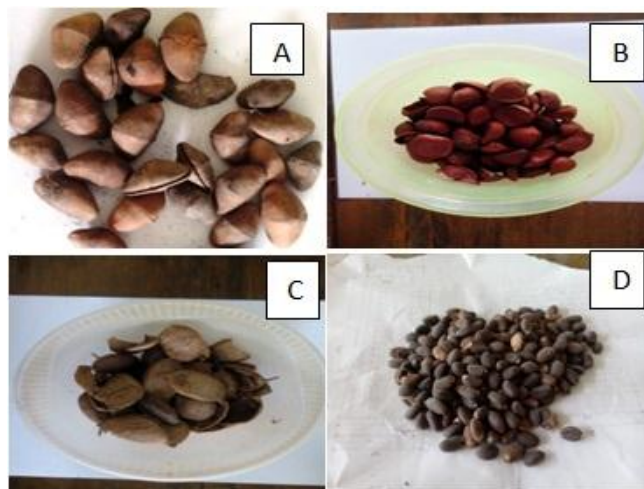


Fig.1 A: Yellow oleander B: Nahor C: Karanja and D: Jatropha seeds

About 2 kg of ripe oilseeds were taken and sun dried for 3 days and oven dried below 50°C for 24 hrs to remove any traces of moisture. Then, the dried oilseeds were shelled and milled separately, grinded to powdery (small size) form using attrition mill or by mixer-grinder. We place accurately weigh amount of oilseed (*w1*) powder inside the soxhlet apparatus (100 g).

Filling the flask about half with hexane (60-80°C) and placing it appropriately upon the heater and wait until the temperature reaches to the boiling point of hexane. We continue the process for about 6-8 hrs until the colour of the solvent is retained with the constant flow of water.

The oil contents of oilseeds are thus the maximum amount of oil that can be extracted from a known amount of oilseed, expressed as wt. Percentage.

$$\% \text{ Recoverable oil content} = \frac{\text{Wt. of oil extracted (w1 - w2)}}{\text{Wt. of dry ground oilseed (w1)}}$$

Catalyst Preparation

The egg shells catalyst was prepared by calcination method. The collected eggshells were cleaned properly at first with tap water to remove the organic impurities adhered to its inner surface and then rinsed with double distilled water for 6-8 times. Then it was dried in oven overnight at 180°C. Then the crushed eggshells were sieved (100-200 mesh) and subjected to heat treatment at 900°C for 4hrs in the muffle furnace [7].

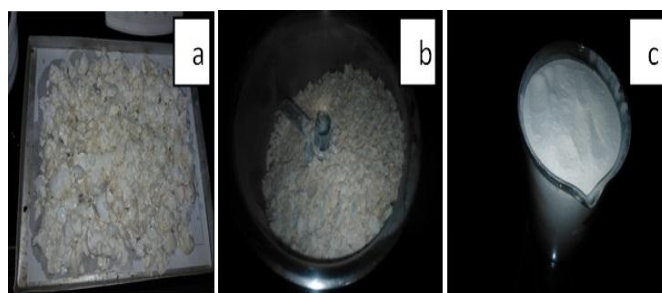


Fig.2 a: Raw egg shell b: oven dried egg shells and c: powdered and egg shell catalyst CaO.

Biodiesel preparation from vegetable oil:

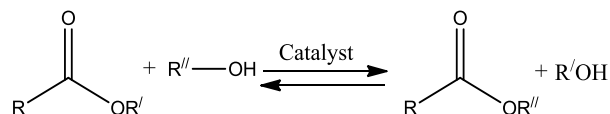


Fig.2 General equation of transesterification reaction



Fig.3 Experimental setup for transesterification reaction

A one step transesterification reaction was performed to prepare biodiesel using egg shell as catalyst. (70:30% by volume oil: alcohol) was mixed with CaO (egg shell) catalyst (2 wt. % of oil) and added slowly to the reactor containing oil along with stirring. The reaction mixture was heated at 70 °C for 3 h. After completion of the reaction, the reaction mixture was transferred to separating funnel and both the phases were separated. Upper phase was biodiesel and lower phase contained glycerin. Alcohols from both the phases were distilled off under vacuum. The glycerine phase was neutralized with acid and stored as crude glycerine. Upper phase i.e. methyl ester (biodiesel) was washed with the water to remove the traces of glycerin, unreacted catalyst and soap formed during the transesterification[8]. For all the four different feedstocks the same procedure of biodiesel production has been followed. Biodiesel fuel properties have been assessed according to the standard test method ASTM-D 6751. Fuel properties analysed herein are Viscosity measured by – Falling ball viscometer company – Thermoscietic, Pour point and cloud point measured by- Pour and cloud point bath Company-Reico, Flash and fire point measured by – flash and fire point apparatus as per ASTM-D92 company-Hamco, Oxidation stability measured by Rancimat743 Company-metrohm and Carbon residue analysed by carbon residue apparatus..

III. RESULT AND DISCUSSION

The production of biodiesel starts with the choice of feedstock. One of the distinctive characteristic of biodiesel with respect to other bio fuels is that it can be produced from a number of feedstocks. Several issues are to be considered while identifying feedstock for biodiesel production and most important factor is the oil content of the seed. The oil contents of the selected seeds are as follows: Nahor containing 73%, yellow oleander containing 61%, jatropha containing 57% and karanja containing 35%. Non-edible vegetable oils are promising feedstocks for biodiesel production as they are renewable in nature.

Table I
OIL CONTENT OF THE COLLECTED SEED

Serial No.	Seed	Oil content (%)
1	Yellow oleander (<i>Thevetia peruviana</i>)	61
2	Karanja (<i>Pongamia pinnata</i>)	35
3	Nahor (<i>Mesua ferrea Lin.</i>)	73
4	Jatropha (<i>Jatropha curcas</i>)	57

Another important factor in biodiesel production is the selection of catalyst. Renewable heterogeneous catalyst is desirable as they are naturally available and non-toxic. The use of Egg shell as catalyst for biodiesel production is in progress in recent times. This study may prove to be beneficial in terms of using this catalyst in various non-edible oils from north-east India. The biodiesels produced using egg shell as catalyst has been shown in the fig.4 and the fuel properties are given in the table II.

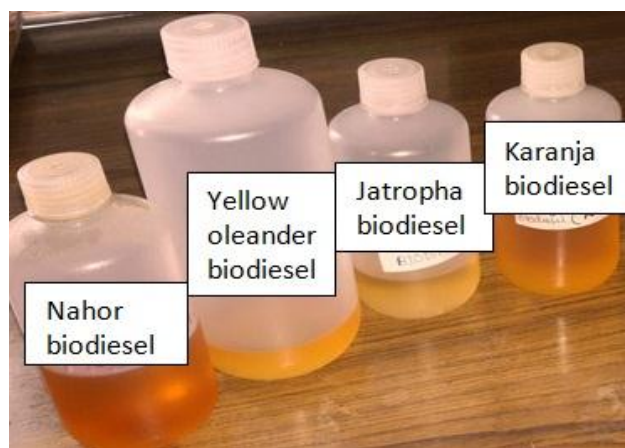


Fig. 4 Biodiesel produced from the non-edible oil feedstock

Table II
BIO DIESEL FUEL PROPERTIES OF N: NAHOR, Y: YELLOW OLEANDER K: KARANJA AND J : JATROPHA BIODIESEL

Fuel properties	N	Y	K	J	ASTMD 6751 standards (Units)
Viscosity	6.01	5.2	3.27	4.5	1.9-6.0(cst)
Flash point	136	132	131	137	130 min
Cloud point	6	5	12	7	---(°C)
Pour point	2	-9	5	-2	---(°C)
Carbon residue	0.03	0.027	0.042	0.047	0.050max(% mass)
Oxidation stability	5	5.7	6	3.5	3min (hour)
Calorific value	39.8	39.6	40.2	40.32	---(MJ/kg)



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From the table II. It can be observed that the produced biodiesel using egg shell as catalyst is meeting the given standards. It has been seen that the catalyst works on all of the non-edible vegetable oil and emerged as effective catalyst for performing transesterification. This catalyst is beneficial to avoid undesired saponification reactions as the catalyst is heterogeneous catalysts. Bio-diesel production using solid catalysts could also take to cheaper production costs because of renewable nature of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously.

IV. CONCLUSION

- Locally available non-edible oil feedstock should be explored for possible utilization in biodiesel production.
- The catalyst is non-selective in nature. The biodiesel production is complete irrespective of the feedstocks.
- Here in this study it has been seen that the biodiesel produced using egg shell as catalyst demonstrates good fuel quality.
- The use of biodiesel and heterogeneous catalyst is beneficial because of their non-toxic nature.

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