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Transesterification of yellow oleander (*Thevetia peruviana*) seed oil to fatty acid methyl esters (biodiesel) using a heterogeneous catalyst derived from rhizome of *Musa balbisiana* Colla

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Abstract: Transesterification of yellow oleander (*Thevetia peruviana*) seed oil to its fatty acid methyl esters (FAME, biodiesel) was carried out in methanol by batch reaction using a heterogeneous catalyst derived from the rhizome of *Musa balbisiana* Colla (one variety of banana plant). The yield of biodiesel obtained is 95 wt.% at room temperature (32 °C) in 3 h. The catalyst is thermally stable and better catalytic activity is observed when it is activated.

Key words: Transesterification, Biodiesel, *Thevetia peruviana*, *Musa balbisiana* Colla, Banana plant.

Introduction

Consumption and demand of petroleum products have been growing rapidly in recent years due to increase in the number of automobiles and widely use of diesel fuels in transportation, power generation, agriculture vehicles *etc*. Because of unavailability of petroleum crude oil, recent increase in petroleum prices and its non-renewability, there is renewed interest in vegetable oil fuels for diesel engines. Biodiesel is becoming increasingly popular because of its renewable and low environmental impact. Fatty acid methyl esters also known as biodiesel is accepted as a potential green alternative fuel for diesel engine[1-4]. Biodiesel is produced via transesterification of triglycerides present in biological resources such as vegetable oils, animal fats or even used cooking oils by reacting with methanol in the presence of a catalyst[5-11]. Transesterification is a process for transformation of one ester to another with an alcohol and the alcohols used in the transesterification are generally methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are utilized most frequently, especially methanol because of its low cost and its physical and chemical advantages. Transesterification process has been widely employed to reduce the high viscosity of triglycerides thereby making the characteristics of biodiesel close to diesel fuels to improve engine performance[12-16].

The conventional catalysts for transesterification reaction are homogeneous strong bases (such as alkali metal hydroxides and alkoxides) and homogeneous acids (such as H_2SO_4)[13,17-19]. However, basic catalysts are generally corrosive to equipment and also react with free fatty acid to form unwanted soap as by-products that require expensive separation. Homogeneous acid catalysts are difficult to recycle and operate at high temperatures, and also give rise to serious environmental and corrosion problems[20-23]. Therefore, to overcome all these problems and to reduce the present high production cost of biodiesel, the development of economically viable as well as cost-effective heterogeneous catalysts for biodiesel industries is urgently needed. Recently, several heterogeneous catalysts derived from waste biomass have been reported in various literatures for biodiesel synthesis[11] and these are *Musa balbisiana* Colla[24], waste shell of *T. striatula*[25], waste freshwater mussel shell[26], turtle shell[27], waste eggshell[28], waste cockle shell[29], waste shells of mollusk and egg[30], waste fish scale[31], waste mud crab shell[32], chicken eggshells[33], snail shell[34], industrial waste shells of egg, golden apple snail and meretrix venus[35], waste animal bone[36], shrimp shell[37], clamshell (*M. meretrix*)[38], *Pomacea sp*. Shell[39], and oyster shell[40]. These catalysts have very high commercial prospects for biodiesel industries as the catalysts are derived from waste materials making it cost-effective.

Yellow oleander (*Thevetia peruviana* Schum.) is an evergreen ornamental plant which grows to about 2-6 m in height. The plant belongs to the *Apocynaceae* family and is widespread in American, Asian and African continents. The plant starts flowering after one and a half year from plantation and there after blooms thrice a year[41]. The fruits are usually green in colour and become black on ripening. The fruit contains between one to four seeds in its kernel, and the plant bears milky juice in all organs. Mature fruits (**Fig. 1**) contain about 22-23% kernel and seeds have 60-65% oil content[24]. The chemical composition of biodiesel (FAME) of yellow oleander (*Thevetia peruviana*) seed oil determined by GC-MS analysis was reported[24] and it consists of 23.28 wt.% of methyl palmitate (C16:0), 19.85 wt.% of methyl linoleate (C18:2), 43.72 wt.% of methyl oleate (C18:1), 10.71 wt.% of methyl stearate (18:0) and 2.41 wt.% of methyl arachidate (C20:0).

In this study, an environmentally benign highly active heterogeneous catalyst derived from the rhizome of *Musa balbisiana* Colla (one variety of banana plant) for biodiesel synthesis is reported. It is observed that the catalyst can catalyze transesterification of *Thevetia peruviana* seed oil with methanol in a highly efficient manner at room temperature (32 ºC) into its corresponding fatty acid methyl esters (biodiesel).

Fig. 1. Yellow oleander fruits with seeds and kernels

Experimental Section

Materials

The yellow oleander (*Thevetia peruviana*) fruits were collected from Gauhati University Campus, Guwahati, Assam, India. The pulps were removed, seeds dried in sunlight, deshelled and the kernel crushed using a grinder prior to oil extraction. Solvents and other chemicals used were of analytical grade, and they were procured from commercial sources (Merck, Rankem, Sigma Aldrich, Qualigens) and used as such without further treatment.

Oil extraction

Crushed kernel in petroleum ether (bp 40-60 ºC, 10 mL/g) was magnetically stirred at room temperature (22-23 ºC) for 3 h, filtered and solvent was removed at 45 ºC using a rotary vacuum evaporator to yield the crude oil. The oil was purified prior to transesterification done, by column chromatography over silica gel (60-120 mesh) using a mixture of petroleum ether and ethyl acetate (20:1) as the eluent.

Catalyst preparation and characterization

The rhizome of *Musa balbisiana* Colla (one variety of banana plant) was cut into thin pieces and air dried under sun for several days. Dry material was ignited, and allowed to burn and cool down to ambient temperature in its own. The ash was then preserved in an air tight plastic container for use as and when necessary. Burning is usually expected to complete within half an hour, but cooling down process may take hours.

BET surface area, pore volume and pore size of the catalysts were determined using TriStar 3000 V6.08 A. TGA spectra of the catalysts were recorded with TGA/DSC-1, METTLER TOLEDO, STAR^e SW 9.10 from room temperature to 900 ºC at a scanning rate of 10 ºC/min under nitrogen atmosphere.

Composition of the catalyst

The chemical composition of the catalyst was estimated by chemical analysis, atomic absorption spectroscopy and flame photometry[42]. Major components present are K^+, Na^+, CO_3^{2-} and Cl^- along with eleven other metals *viz*. Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, which are present only in trace amounts (ppm level). Metals are present as their carbonates, chlorides or oxides. Finely divided carbon particles are also present[24].

Activation of catalyst

The catalyst was activated by heating at 400 ºC and 700 ºC in a programmable muffle furnace (LAB TECH). About 1.5-2.0 g of the catalyst was taken in a silica crucible (preheated and weighted) and then heated in a muffle furnace to either 400 ºC for 2 h or 700 ºC for 3.5 h, and kept at the temperature for about 1.5 h. After the heating was completed, the catalyst was allowed to cool to room temperature inside a desiccator, and preserved there until used.

Transesterification of seed oil

The purified yellow oleander seed oil was transesterified to fatty acid methyl esters using the catalyst derived from rhizome of *M. balbisiana*. A mixture of oil in methanol (10 mL/g of oil) and the catalyst (20 wt.% of oil) was magnetically stirred at room temperature (32 ºC) and the conversion was monitored by TLC (**Fig. 2**). The reaction mixture was filtered under vacuum pump and the residue washed with petroleum ether and the combined filtrate was partitioned between water and petroleum ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to yield the crude product which was further purified by column chromatography over silica gel using 20:1 petroleum ether and ethyl acetate as the eluent. The purified product was further subjected to high vacuum to remove the last traces of solvents to yield pure biodiesel.

NMR data of the FAME mixture: ^1H NMR (300 MHz; $CDCl_3$; Me_4Si) δ= 0.87 (m, 3H: -C-C$\boldsymbol{H}_3$), 1.24 (m, -(C$\boldsymbol{H}_2$)$_n$-), 1.60 (m, 2H: -C$\boldsymbol{H}_2$-C-COOMe), 2.02 (m, 2H: -C$\boldsymbol{H}_2$-C=C-), 2.29 (t, 2H, ^3J = 7.5 Hz: -C$\boldsymbol{H}_2$-COOMe), 2.75 (t, 2H, ^3J = 6.9 Hz: -C=C-C$\boldsymbol{H}_2$-C=C-), 3.65 (s, 3H: -CO-OC$\boldsymbol{H}_3$) and 5.33 (m, 2H, -C$\boldsymbol{H}$=C$\boldsymbol{H}$-); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ= 14.04-34.01 (-($\boldsymbol{C}H_2$)$_n$, -$\boldsymbol{C}H_3$), 51.36 (-O$\boldsymbol{C}H_3$), 127.8-130.1 (olefinic carbons), 174.34 (-$\boldsymbol{C}$O-OCH$_3$).

Results and Discussion

Transesterification of seed oil to fatty acid methyl esters

Biodiesel consists of methyl esters of long chain fatty acids. Conversion of oil to biodiesel is achieved by reacting with methanol in the presence of a catalyst. In this paper, transesterification of yellow oleander (*Thevetia peruviana*) seed oil to fatty acid methyl esters (FAME, biodiesel) using a heterogeneous catalyst derived from the rhizome of *Musa balbisiana* Colla is presented (**Table 1**). For transesterification reaction, a mixture of oil in methanol (10 mL/g of oil) and the catalyst (20 wt.% of oil) was taken in 250 mL RB flask and magnetically stirred at room temperature (32 ºC). The conversion of triglyceride to biodiesel was monitored by TLC (**Fig. 2**). Using the catalyst derived from rhizome of *Musa balbisiana* Colla, the yield of FAME (biodiesel) from yellow oleander seed oil was 95 wt.% at room temperature (32 °C) within 3 h (**Table 1, Entry 1**). The ^{1}H and ^{13}C NMR spectra of yellow oleander biodiesel (FAME) are presented in **Figs. 3 & 4** respectively. In **Fig. 3**, a singlet signal at δ 3.65 ppm represents the methoxy protons (-CO-OC$\boldsymbol{H}_3$) of the ester functionality of the yellow oleander biodiesel. In ^{13}C NMR spectrum of biodiesel (**Fig. 4**), the signal at δ 51.36 ppm is due to methoxy carbon (-O$\boldsymbol{C}$H$_3$) which is indicative enough for the desired transformation.

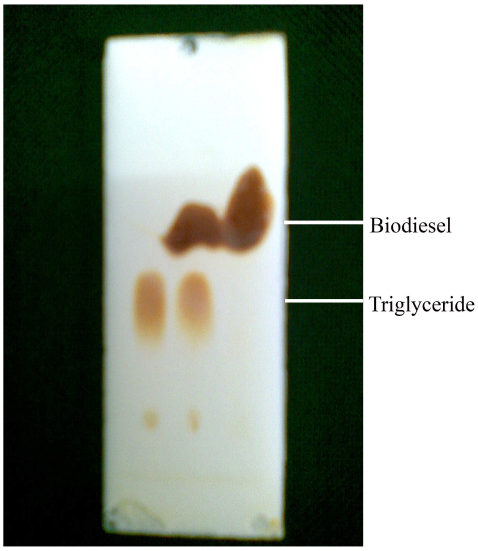
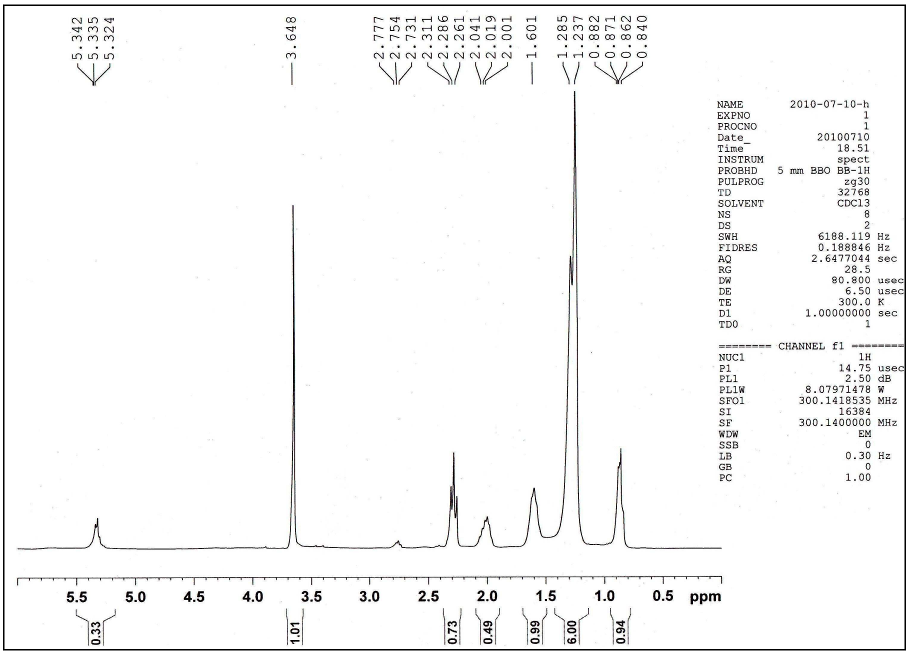


Fig. 2. TLC showing the conversion of triglyceride to biodiesel



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TD                  32768
SOLVENT             CDCl3
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DS                      2
SWH              6188.119 Hz
FIDRES           0.188846 Hz
AQ              2.6477044 sec
RG                   28.5
DW                 80.800 usec
DE                   6.50 usec
TE                  300.0 K
D1             1.00000000 sec
TD0                     1

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P1                  14.75 usec
PL1                  2.50 dB
PL1W           8.07971478 W
SFO1          300.1418535 MHz
SI                  16384
SF            300.1400000 MHz
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LB                   0.30 Hz
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PC                   1.00
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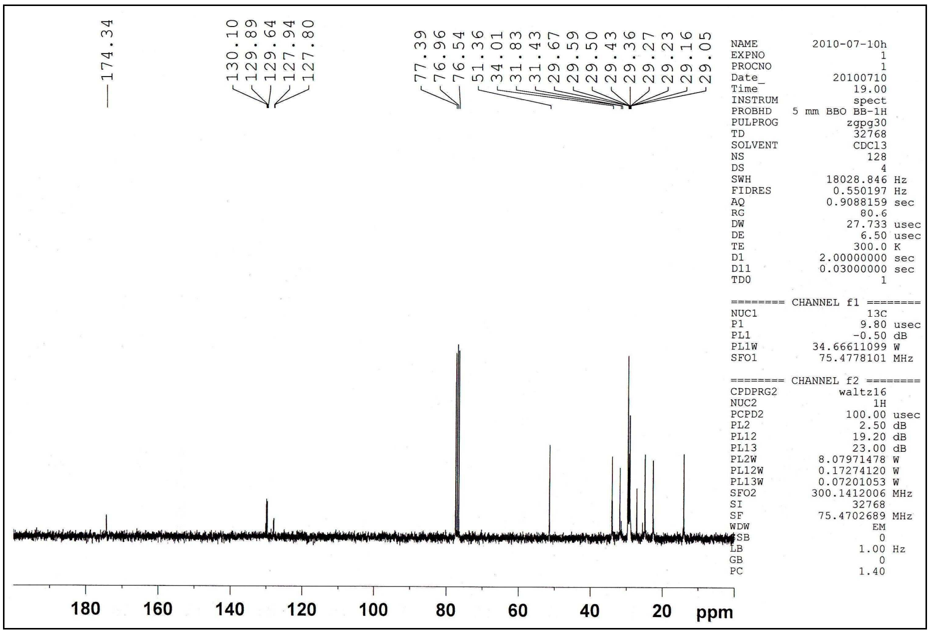
Fig. 3. ^{1}H NMR spectrum of the biodiesel from yellow oleander seed oil



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DS                     4
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RG                  80.6
DW                27.733 usec
DE                  6.50 usec
TE                 300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

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NUC1                 13C
P1                  9.80 usec
PL1                -0.50 dB
PL1W         34.66611099 W
SFO1          75.4778101 MHz

======== CHANNEL f2 ========
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NUC2                  1H
PCPD2             100.00 usec
PL2                 2.50 dB
PL12               19.20 dB
PL13               23.00 dB
PL2W          8.07971478 W
PL12W         0.17274120 W
PL13W         0.07201053 W
SFO2         300.1412006 MHz
SI                 32768
SF            75.4702689 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Fig. 4. ^{13}C NMR spectrum of the biodiesel from yellow oleander seed oil

Table 1. Activity of catalyst in transesterification of *Thevetia peruviana* seed oil to its FAME

Entry	Catalyst from Rhizome of *M. balbisiana*	Reaction time (h)	Yield (wt.%)
1	Normal	3.0	95
2	Activated at 400 ºC	2.50	95
3	Activated at 700 ºC	2.25	96

Reaction conditions: *Thevetia peruviana* seed oil 2 g; catalyst 20 wt.%; methanol 20 mL; reaction temperature 32 ºC.

Effect of activation of the catalyst in transesterification of seed oil

The catalyst derived from rhizome of *M. balbisiana* was activated at 400 °C and 700 °C in a muffle furnace and transesterification reaction of *Thevetia peruviana* seed oil was performed with the activated catalyst under nitrogen atmosphere. The results are shown in **Table 1**. It is seen that a maximum of 96 wt.% conversion could be achieved with both normal and activated catalysts but activated catalysts demand slightly lower duration of reaction time. Activation temperature, 400 °C *vs*. 700 °C practically makes no difference except that reaction time with the catalyst activated at 700 ºC is marginally reduced. The increase in activity after heating the catalyst at 400 °C may be due to more free surface area availability for catalytic activity. As the catalyst is hygroscopic, it absorbs moisture from the atmosphere which is easily removed by heating the catalyst. Only a marginal increase in activity of the catalyst after heating at 700 ºC reaffirms our hypothesis. There is no substantial change either in physical state or chemical structure of the catalyst after heating either at 400 °C or 700 °C.

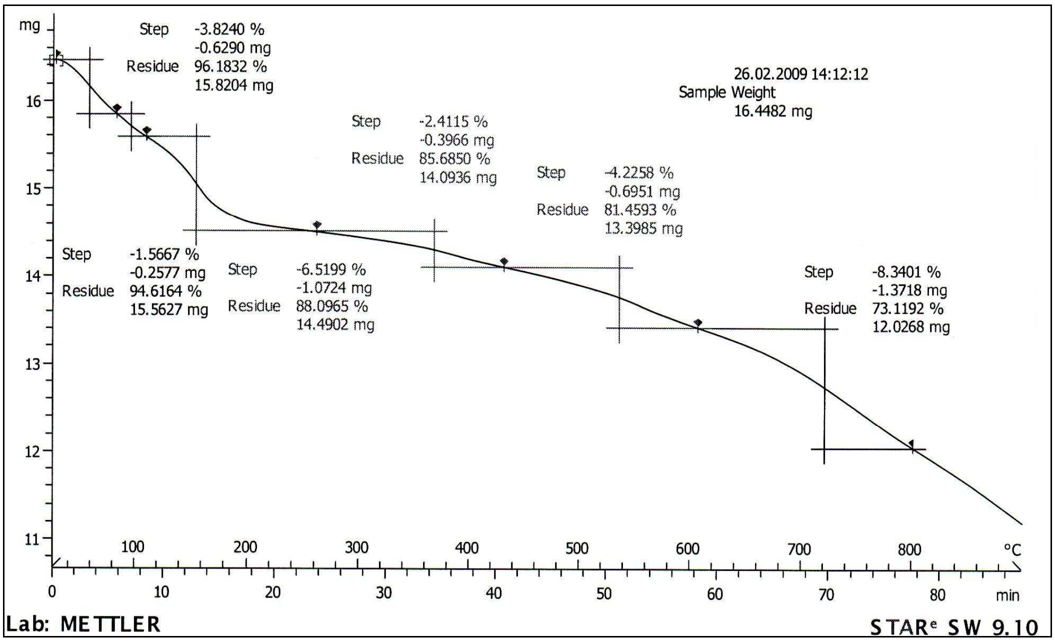

Fig. 5. TGA spectrum of catalyst from the rhizome of *M. balbisiana*

Table 2. Weight loss of activated catalyst

Catalyst from rhizome of *M. balbisiana*	Initial wt. (g)	Wt. after heating (g)	Wt. loss (g)	Wt. loss (wt.%)
Activated at 400 ºC for 3.5 h	1.550	1.335	0.215	13.87
Activated at 700 ºC for 5 h	2.093	1.633	0.460	21.97

Thermal stability and characterization of catalyst

To observe the thermal stability of the catalyst, the TG measurement for the catalyst was conducted. The TGA of the catalyst (**Fig. 5**) shows that the catalyst starts losing weight on heating till about 200 °C. From about 200 °C to about 400 °C, the catalyst is almost stable as indicated by near constant weight in this range of temperature. Beyond 400 °C, the catalyst starts losing weight again albeit at slow rate. Beyond 700 °C, catalyst continues to lose weight at somewhat increased rate. The loss of weight in the early part of heating *i.e.* to about 400 °C is due to loss of physically adsorbed water from the surface of the mass. Loss of weight beyond 400 °C may be due to slow loss of water of crystallization as no chemical change is expected in this range of temperature. Loss of weight due to chemical decomposition is expected at a temperature beyond 700 °C.

The catalyst derived from rhizome of *M. balbisiana* was activated at 400 °C and 700 °C. The results of weight loss of the catalyst at those temperatures are summarized in **Table 2**. When the catalyst is activated at 400 °C, a weight loss of about 14% in 3.5 h is observed. Similarly, a weight loss of about 22% is observed on heating at 700 °C for about 5 h.

The BET surface area, pore volume, and pore size of the catalyst derived from the rhizome of *Musa balbisiana* Colla were determined using TriStar 3000 V6.08 A and found to be 0.5790 m^2/g, 0.010196 cm^3/g, and 70.44064 nm respectively.

Conclusion

In this study, highly active and low-cost heterogeneous catalyst derived from the rhizome of *Musa balbisiana* Colla (one variety of banana plant) for conversion of yellow oleander seed oil to biodiesel has been established. Using this catalyst, 95 wt.% yield of biodiesel is achieved at room temperature (32 °C) in 3 h. The catalyst is thermally stable and better catalytic activity is observed when it is activated by heating in the range of 400 °C to 700 °C. The catalyst has very high commercial prospects, especially in biodiesel industries, as the catalyst can be prepared at nominal cost from the waste of post-harvest banana plants and the discovery means a value addition to banana cultivation. The banana plant is an excellent raw material for the large scale preparation of the catalyst for biodiesel production due to its easy availability. Biodegradability and environmental acceptability are other two factors in favour of the catalyst as its large scale use will pose no disposal problem.

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