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Research Article

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Transesterification with a green catalyst obtained from post harvest Banana plant waste

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ABSTRACT

A simple, efficient and cost effective method for the transesterification of structurally varied aromatic esters is described. Transesterification is carried out in presence of a highly active heterogeneous base catalyst developed from post-harvest banana plant. The catalyst derived from different parts of the post-harvest plant waste of the Musa balbisiana and Musa acuminata varieties of banana. Successful transesterification of a variety of esters have been achieved to the corresponding methyl esters using the catalyst at ambient temperature. The catalyst is renewable, cost-effective and non-polluting. Post-harvest banana has no commercial value and available at no cost. It has potential applications in biodiesel industries.

Keywords: banana plant; transesterification; *Musa balbisiana; Musa acuminata*; heterogeneous; biodiesel.

INTRODUCTION

Transesterification is an important synthetic transformation by which an ester is transformed into another. It involves the exchange of the alkoxy group of an ester with that of an alcohol. Transesterification is one of the prominent organic reactions that has entertained considerable attention and emerged as the most significant and easiest procedure having boundless applications in academic as well as industrial research [1]–[6]. General technique of conversion of one ester to another ester involves two steps: (a) conversion of the ester to the corresponding carboxylic acid and (b) re-esterification of the acid. Transesterification reaction is a single pot equilibrium reaction which can be accomplished by simply mixing the reactants. However, presence of a catalyst speeds up the reaction. Transesterification is a preferred process to the esterification of carboxylic acids of low solubility, because esters that are starting materials for transesterification are commonly soluble in most of the solvents[7]. Transesterification has numerous application in biodiesel industries [8]–[11] as well as in paint industry [2]. Transesterification is a significant pathway in the synthesis of biologically active compounds and drugs [2], [11]. The transesterification reaction can be catalysed by a variety of protic and Lewis acids, organic and inorganic bases, enzymes and antibodies [4], [12]–[14]. Bronsted acid catalysed transesterification reactions occur slowly and high product yields are achieved at high temperature and pressure [14]–[16]. Base catalysed reactions occur rapidly than the acid catalysed reactions [14]–[20]. Transesterification can be accomplished using both homogeneous and heterogeneous catalysts. Homogeneous alkaline catalysts have expansive use because the reaction is completed in a short time under mild temperature and pressure but it is appreciably costlier to separate homogeneous catalysts from the reaction mixture [17], [19], [20]. Heterogeneous catalysts are more profitable than the homogeneous catalysts as they are non-corrosive, easily separable from the reaction mixture making purification step easier and reusable [21]–[26]. Here we have prepared an efficient and environmentally benign catalyst for transesterification reaction. The North-Eastern part of India is a hub of natural resources and they have not been exploited fully. Development of catalyst from the natural resource is a green and economic. We examined the catalytic activity of the ash derived from different parts of banana plant waste. The ash is traditionally being used as a source of alkali in the entire North Eastern region of India. The alkaline solution extracted from the ash is known as *kolakhar* among the people of Assamese community and is used as a food additive in Assamese cuisines. The post-harvest banana plants are agricultural waste and obtainable in plenty throughout India. This agricultural waste is an excellent raw material for the preparation of the catalyst due to its wide source, minimal cost and biodegradability. The catalyst derived from the trunk of *Musa balbisiana* has been successfully utilized in biodiesel production from yellow oleander (*Thevetia peruviana*) seed oil. Fuel properties conform to standards set for ASTM D6751, EN14214, BSII and BSIII, and in certain aspects it is found to be better [27]. The same catalyst have been successfully (utilised) exploited in the transesterification of seed oils with methanol producing fatty acid methyl esters with a very good yield [28]. The prominent advantages of this catalyst are: (a) low cost, (b) non-toxic in nature, (c) general applicability, (d) mild reaction conditions, (e) high yield, (f) heterogeneous and (g) easy separation. A wide range of structurally varied aromatic esters underwent transesterification with methanol by this catalyst. Reactions can be carried out effectively at ambient temperature. We believe our procedure will provide a better and more practical alternative to the existing methodologies and find useful applications both in laboratories and industries.

EXPERIMENTAL SECTION

Materials

All the esters used were prepared in the laboratory by Dean-Stark trap for the removal of water and used after purification and characterization by NMR and IR. All other chemicals were procured from commercial sources and used without further purification. Methanol (Merck Ltd.) was procured from commercial vendors. Methanol was dried over anhydrous Na_2SO_4 before use. Catalysts were dried in oven at 120 °C for 2h prior to use as they are hygroscopic in nature.

Preparation of the catalyst

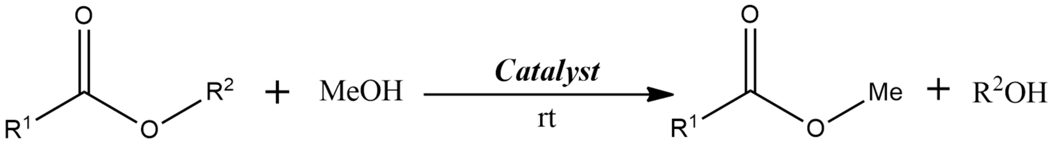
Traditional method was followed for the preparation of the catalyst. The trunk of the banana plant was sliced into thin pieces and air dried under sun for several days. Dry material was ignited, and allowed to burn and cool down to ambient temperature in its own. The ashes were then preserved in an air tight plastic container for use as and when necessary. Time required for burning and natural cooling down process depends on the quantity of material taken. Burning is usually expected to complete within half an hour, but cooling down process may take hours. Similar procedure was followed to prepare catalyst from the rhizome of *Musa balbisiana* and trunk of *Musa acuminata*. The chemical composition of the catalyst was estimated by chemical analysis, atomic absorption spectroscopy and flame photometry [29]. Major components present are K^+, Na^+, CO_3^{2-}, and Cl^- along with some other metals viz. Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb in trace amounts (ppm level). Metals are present as their carbonates, oxides or chlorides. Finely divided carbon particles are also found to be present. Nitrogen adsorption-desorption studies carried out using TriStar3000 V6.08A provided BET surface area as shown in Table 1. The decomposition temperature of the catalyst was found to be above 700 °C by Thermogravimetric Analysis.

Table 1: Textural properties of the catalysts

Catalyst	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Catalyst from the trunk of *Musa balbisiana*	1.4870	0.019329	51.99612
Catalyst from the rhizome of *Musa balbisiana*	0.5790	0.010196	70.44064
Catalyst from the trunk of *Musa acuminata*	1.3349	0.022677	67.95042

Typical procedure for transesterification

A 1:100 molar ratio mixture of aromatic ester (5 mmol) and methanol (500 mmol) together with the catalyst (20% wt. of ester) was magnetically stirred in a two neck round bottom flask with a magnetic stirrer in nitrogen atmosphere. Reactions (Scheme 1) were carried out at ambient temperature.



Ester:alcohol=1:100
R^2 = *n*-Bu, *n*-Pr.

Scheme 1: Transesterification from higher to lower esters

The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated by filtration, and the reaction mixture was partitioned between petroleum ether and water. The organic layer was washed with brine solution (10%, 10 ml×2) and dried over anhydrous Na_2SO_4. Solvent was removed under vacuum and crude product was purified by column chromatography over silica gel (60 - 120 mesh size) using light petroleum ether (bp 40-60 °C) and ethyl acetate as the eluent. Products were identified by IR, NMR. ^1H and ^{13}C NMR were recorded in $CDCl_3$ at 300 and 75 MHz, respectively using Bruker Advance III 300MHz/54mm NMR spectrometer. FT-IR spectra were obtained on a Shimadzu IR Affinity-1 IR spectrometer.

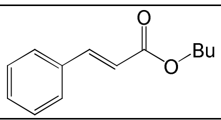
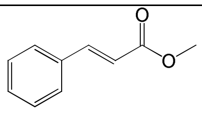
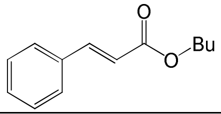
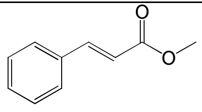
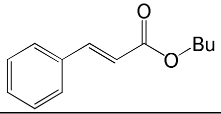
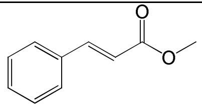
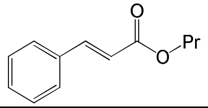
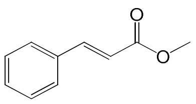
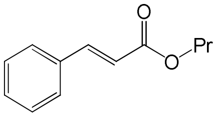
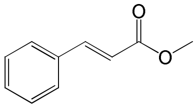
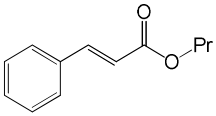
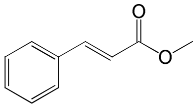
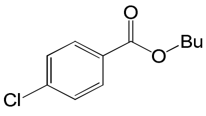
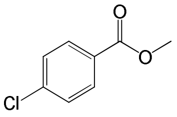
Recycling of the catalyst

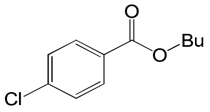
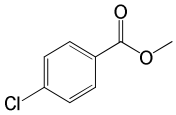
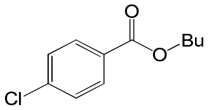
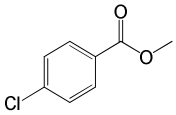
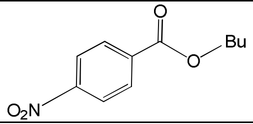
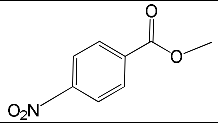
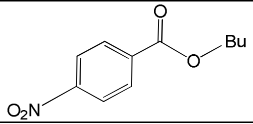
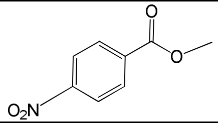
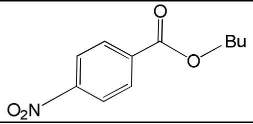
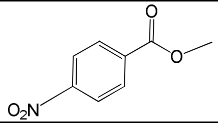
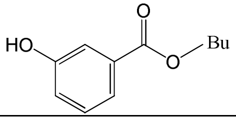
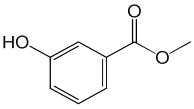
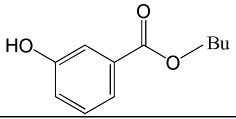
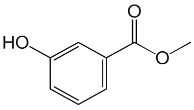
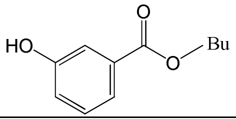
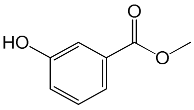
Before executing the reusability test, catalysts, after separation by filtration from the reaction mixture, were washed with DCM to remove any traces of organic compounds left and then dried in oven for 2h at 120 °C followed by cooling to ambient temperature inside a desiccator. The catalyst was then reused in transesterification experiments. The catalyst was recycled without loss in their activity upto three cycles.

RESULTS AND DISCUSSION

In this investigation, the catalytic performance of the new catalyst was studied with a number of structurally varied carboxylic esters (Scheme 1). The corresponding transesterified products were obtained in good yields. The results of transesterification are summarized in Table 2. These results strongly suggest that the new catalytic system is highly active towards transesterification. *n*-Propyl and *n*-butyl esters of cinnamic acid are efficiently transesterified to methyl cinnamate by all the three varieties of catalysts (Table 2, entries 1 to 6). However, the catalyst derived from the trunk of *Musa acuminata* requires longer time (entry 6) as compared to that needed by the catalysts derived from *Musa balbisiana.* Both the catalysts derived from the trunk and rhizome of *Musa balbisiana* appear equally efficient. Esters of substituted benzoic acid are less efficiently transesterified by all the three varieties of catalysts. The reactions demand much longer time (8 to 10 times) as compared to that involving cinnamic acid esters. As expected, substituent effects are visible on the transesterification reactions. Presence of electron withdrawing group such as $-NO_2$ group in the benzene ring accelerates the transesterification of benzoic acid esters to some extent (Table 2, entries 10 to 12). Electron releasing groups such as -Cl (entries 7 to 9) and -OH (entries 13 to 15) appear to have retarding effect on the transesterification reactions.

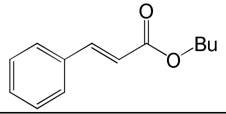
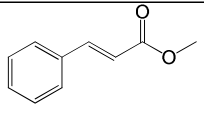
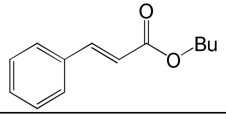
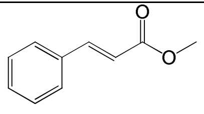
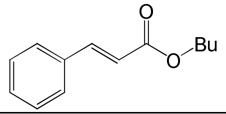
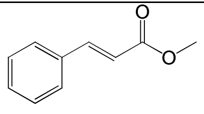
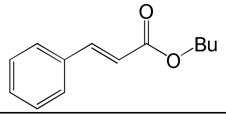
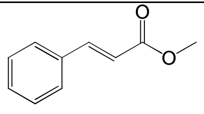
Table 2. Transesterification at ambient temperature with the banana plant derived catalysts

Entry	Ester	Product	Time (h)	Plant variety (part)	Temp (°C)	Isolated yield (mol%)
1			6	*M. balbisiana* (Trunk)	29	80
2			6	*M. balbisiana* (Rhizome)	29	80
3			6	*M. acuminata* (Trunk)	29	76
4			6	*M. balbisiana* *(* Trunk)	25	85
5			6	*M. balbisiana* (Rhizome)	30	83
6			9	*M. acuminata* (Trunk)	30	82
7			72	*M. balbisiana* (Trunk)	31	79

Entry	Ester	Product	Time (h)	Plant variety (part)	Temp (°C)	Isolated yield (mol%)
8			72	*M. balbisiana* (Rhizome)	35	80
9			72	*M. acuminata* (Trunk)	35	73
10			48	*M. balbisiana* (Trunk)	30	80
11			48	*M. balbisiana* (Rhizome)	30	78
12			48	*M. acuminata* (Trunk)	30	76
13			60	*M. balbisiana* (Trunk)	32	53
14			60	*M. balbisiana* (Rhizome)	32	51
15			67	*M. acuminata* (Trunk)	32	45

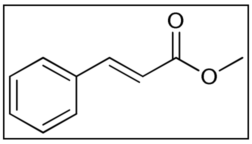
To compare the catalytic performance of the new catalytic system with commercially available catalysts, we carried out experiments using K_2CO_3, Na_2CO_3 and NaOEt. To make direct comparisons, all the experiments were carried out in the same molar ratio 1:100(ester: methanol) at room temperature. Results of these reactions are summarized in Table 3.

Table 3: Comparison of the banana plant derived catalyst with commercially available catalysts

Entry	Ester	Product	Catalyst	Temp. (°C)	Time (h)	Isolated yield (mol%)
1			K_2CO_3	30	6	79
2			Na_2CO_3	31	6	76
3			NaOEt	34	6	83
4			Trunk of *M. balbisiana*	29	6	80

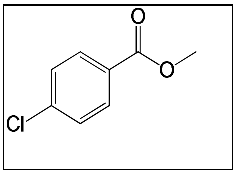
These results demonstrate that the efficiency of the new catalytic system towards transesterification is similar to that of commercially available K$_2$CO$_3$. However, it is found to be better than Na$_2$CO$_3$ and NaOEt. We examined the reusability of the three varieties of the catalysts and it is quite appealing that we have successfully reused the catalysts up to three cycles without significant loss in their activity.

Methyl cinnamate (Table 2, entry 1 - 6)



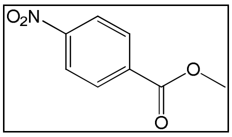
^{1}H NMR (300 MHz, CDCl$_3$): δ 3.809 (s, 3H), 6.45 (d, ^3J = 16.2 Hz, 1H, olefinic), 7.376-7.395 (m, 3H, aromatic), 7.51-7.53 (m, 2H, aromatic), 7.70 (d, ^3J = 15.9 Hz, 1H, olefinic). ^{13}C NMR (75 MHz, CDCl$_3$): δ 51.65, 117.70, 128.01, 128.82, 130.24, 134.28, 144.82, 167.38. FT-IR (thin film/cm^{-1}): 1176, 1442, 1585, 1639, 1716, 2951, 3020.

Methyl 4-chlorobenzoate (Table 2, entry 7 - 9)



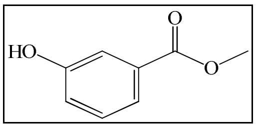
^{1}H NMR (300 MHz, CDCl$_3$): δ 3.9 (s, 3H), 7.40 (d, 3J = 8.4 Hz, 2H, aromatic), 7.96 (d, 3J = 8.4 Hz, 2H, aromatic). ^{13}C NMR (75 MHz, CDCl$_3$): δ 52.23, 128.47, 128.64, 130.86, 139.29, 166.17. FT-IR (thin film/cm^{-1}): 520, 852, 1103, 1280, 1442, 1593, 1724, 2951, 3047.

Methyl *p*-nitrobenzoate (Table 2, entry 10 - 12)



^{1}H NMR (300 MHz, CDCl$_3$): δ 3.983 (s, 3H), 8.198-8.309 (m, 4H, aromatic), ^{13}C NMR (75 MHz, CDCl$_3$): δ 52.81, 123.51, 130.68, 135.43, 150.48, 165.14. FT-IR (thin film/cm^{-1}): 717, 806, 1276, 1346, 1523, 1597, 1716, 2951, 3097.

Methyl *m*-hydroxybenzoate (Table 2, entry 13 - 15)



^{1}H NMR (300 MHz, CDCl$_3$): δ 3.922 (s, 3H), 6.537 (bs, 1H, phenolic), 7.069-7.093 (m, 3H, aromatic), 7.588 (s, 1H, aromatic). ^{13}C NMR (75 MHz, CDCl$_3$): δ 52.34, 116.28, 120.35, 121.71, 129.68, 131.19, 155.97, 167.44. FT-IR (thin film/cm^{-1}): 759, 879, 1234, 1068, 1315, 1442, 1593, 1685, 2966, 3039, 3398.

CONCLUSION

In conclusion, the present procedure using banana catalyst provides a very efficient method for transesterification. Using the catalyst a couple of structurally different *n*-butyl and *n*-propyl esters have been successfully transesterified to methyl esters in moderate to high yield (Table 2). The catalyst shows similar activity irrespective of the parts (trunk vs rhizome) used. The catalyst from the banana plant variety *Musa balbisiana* appears to have higher activity as compared to that from the banana plant variety *Musa acuminata*. The catalysts are, however, not much different in chemical composition or in activity. Work up is simple and the products can be easily isolated by column chromatography. The catalytic performance of this new catalytic system (obtained from banana plant) has been compared to those of three widely reported transesterification catalyst viz., K$_2$CO$_3$, Na$_2$CO$_3$ and NaOEt (Table 3). Results revealed that the performance of the banana plant (derived) extracted catalyst is at par with K$_2$CO$_3$ but superior to both Na$_2$CO$_3$ and NaOEt. The naturally obtained catalyst is environmentally acceptable, non-toxic, and more economical with higher efficacy which come at almost zero cost. We believe this protocol will find widespread applications in the field of modern organic synthesis.

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