



**Comparison between the Catalytic activity of water soluble and water insoluble parts of the Catalyst derived from trunk of *Musa balbisianacolla* for Transesterification**

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**Abstract**

Development of heterogeneous, non-toxic, eco-friendly and cost-effective catalyst is the need in the present scenario. This paper examines the catalytic activity of water soluble and water insoluble part of the ash derived from trunk of *Musa balbisianacolla* for transesterification of simple aromatic esters. The ash obtained from the trunk of *Musa balbisianacolla* is the combination of water soluble and water insoluble parts which can be easily separated. Water soluble part of the catalyst is found to be more efficient than the water insoluble part for the transesterification of simple aromatic esters like cinnamates and benzoates when going from higher to lower esters. This new catalytic system is non-toxic, heterogeneous, inexpensive and biodegradable.

Key-Words: *Musa balbisiana*, Transesterification, *Kolakhar*, Trunk

**Introduction** Transesterification is a very popular one pot equilibrium reaction having tremendous applications in industrial and academic research<sup>1, 2, 3, 4</sup>. Transesterification occurs by exchange of the alkoxy group of an ester with that of an alcohol. Transesterification is a very convenient way to prepare esters that can be carried out by simply mixing the reactants. However, the reaction gets accelerated in presence of a catalyst. Esterification is a two-step process for the synthesis of esters involving hydrolysis of the ester followed by re-esterification of the carboxylic acid. Esters are stable and soluble in most of the organic solvents whereas carboxylic acids have often low solubility in organic solvents. In this case, transesterification has received considerable attention and has emerged as a useful alternative to esterification<sup>5</sup>. Transesterification plays a vital role in biodiesel industries<sup>6, 7, 8, 9</sup>, paint industry<sup>10</sup> and is a useful tool in the synthesis of drugs<sup>11</sup>. Organic esters are widely used in a variety of industries including perfumery, flavor, plasticizer, solvents and pharmaceuticals<sup>12</sup>. Developing a new synthetic strategy for the construction of esters by a non-toxic, biodegradable catalyst is the need in the present scenario for green synthesis. Transesterification can be catalyzed by both basic and acidic, homogeneous and heterogeneous catalysts.

The base-catalyzed reaction is much faster than the acid catalyzed reaction<sup>13</sup>. A literature survey shows the transesterification reaction catalyzed by tin oxide-modified mesoporous SBA-15<sup>14</sup>, Li-CaO<sup>15</sup>, in situ generated lanthanum(III) nitrate alkoxide<sup>16</sup>, DMAP, metal alkoxides, metal carbonates, various efficient homogeneous catalysts such as Lewis acids including Zn clusters, Sn, Ti, Zr, Fe, Pd<sup>17</sup> have been developed. Due to the well-known drawbacks of homogeneous catalysts like short life span and difficult separation step, heterogeneous catalysts are always appealing amongst the researchers. A number of heterogeneous protocols have been developed for transesterification but most of them are toxic, hazardous and expensive. Economic and environmental factors limit the applicability of most of the catalysts in industrial field. In the search of an eco-friendly, heterogeneous and inexpensive catalyst, we have explored the use of the ash from the trunk of *Musa balbisianacolla* as an effective catalyst for transesterification. The present catalyst is locally known as *kolakhar*, which is a very popular food additive in the Assamese community of the North-Eastern region of India. The catalyst is combination of two fractions – water soluble and water insoluble. The two fractions were separated and their catalytic activities were compared for the transesterification of simple aromatic esters with methanol. Both the fractions are heterogeneous, non-toxic and biodegradable.

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### Material and Methods

All the chemicals were procured from commercial sources and were used without further purification. Reactants were prepared by Dean-Stark trap method for the removal of water using *p*-toluene sulfonic acid as catalyst and was chromatographed prior to use. Methanol was dried over Na<sub>2</sub>SO<sub>4</sub> prior to use.

#### Preparation of the catalyst

We have followed the traditional procedure for the preparation of the catalyst known as *kolakhar*. Parts of banana plant are cut into pieces and air dried under sun for several weeks. The dry material is burnt into ashes. Chemical and spectroscopic investigation of the catalyst shows the presence of chlorides and carbonates. Major components present are K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, Na<sup>+</sup>, Cl<sup>-</sup> along with other metals viz., Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, in trace amount (ppm level)<sup>18</sup>. The ashes are then extracted with distilled water. Weighed quantity of ash is suspended in distilled water in a glass beaker and then stirred continuously with a mechanical stirrer for 45 minutes<sup>18</sup>. The mixture is then filtered through a sintered glass crucible under suction. The solid residue is collected and dried in oven at 120°C for 2 hours. The filtrate containing the water soluble part of the catalyst is then placed on a hot plate to evaporate the water content from it and the solid residue was collected and dried in oven at 120°C for 1 hour to remove any traces of water left. After drying, the catalysts are ready to use. Both parts of the catalyst are heterogeneous and can be separated from the reaction mixture and found to be non-toxic and biodegradable.

#### Typical procedure for transesterification

A 1:100 molar ratio mixture of ester and methanol together with the catalyst derived from trunk of banana plant (20% wt. of ester) without a co-solvent were stirred in a two neck round bottomed flask with a magnetic stirrer. Reactions were carried out at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was partitioned between petroleum ether and water. The organic layer was washed with 10% brine solution and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed under vacuum and crude product was chromatographed on silica gel using light petroleum ether (bp. 40°-60°C) and ethyl acetate as the eluent. Products were identified by IR, NMR and GC-MS. <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> at 300 and 75 MHz, respectively using Bruker Advance III 300MHz/54mm NMR spectrometer. FT-IR spectra were obtained on a Perkin Elmer RX I FT-IR spectrometer. Gas chromatographic analyses were

performed using Perkin Elmer Clarus 600 GC-MS. The column used was Elite 5MS with dimension 30.0m × 250µm.

### Results and Discussion

To compare the catalytic activity of the two parts of the catalyst, all transesterification reactions were carried out with the same reactants in the same ester:methanol molar ratio and with the same amount of the catalyst. Transesterification reactions were carried out with butyl cinnamate, propyl cinnamate and butyl benzoate using methanol at room temperature. From results summarized in *Table 1*, we have found the water soluble part of the catalyst to be more efficient for transesterification of cinnamate and benzoate ester. In terms of productivity, the soluble fraction is better than the insoluble fraction and that too with shorter reaction time.

**Methyl benzoate:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.912 (3H, s), 7.4-8.05 (m, 5H). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 52.07, 128.30, 129.50, 130.04, 132.87, 167.08. FT-IR (thin film/cm<sup>-1</sup>): 713.66, 964.41, 1026.13, 1111, 1180.44, 1280.73, 1446.61, 1600.92, 1724.36. EI-MS: m/z 105 (100%), 136 (M<sup>+</sup>).

**Methyl cinnamate (Methyl 3-phenylprop-2-enoate):** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.78 (s, 1H), 6.41-6.46 (d, 1H, <sup>3</sup>J<sub>HH</sub>=16.2 Hz), 7.35-7.50 (m, 5H), 7.6-7.7 (d, 1H). <sup>13</sup>C NMR (75MHz, CDCl<sub>3</sub>): δ 51.67, 117.77, 128-130.30, 134.35, 144.85, 167.38. FT-IR (thin film/ cm<sup>-1</sup>): 1585.49, 1639.49, 1716.65, 2951, 3020.53. EI-MS: m/z 131 (100%), 162 (M<sup>+</sup>).

### Conclusion

Among the two fractions of the catalyst, water soluble part of the catalyst is more suitable for the transesterification of simple aromatic esters into its methyl esters. Water insoluble part also shows catalytic activity towards transesterification but at the compensation of lots of time. The catalyst is edible, non-toxic, biodegradable, heterogeneous and cheap. We hope this novel catalyst will find widespread application in the field of organic synthesis.

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Fig. 1: Transesterification reaction with methanol

Table 1: Transesterification of aromatic esters with the two fractions of the catalyst

Entry	Substrate	Product	Catalyst	Time(h)	Temp.(°C)	Yield (%)
1				5.5	33	66
2			Water soluble part	7	33	86
3				17	29	60
4				190	32	49
5			Water insoluble part	68	33	68
6				78	26	18

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