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Carica papaya stem: A source of versatile heterogeneous catalyst for biodiesel production and C–C bond formation

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ABSTRACT

Development of solid mixed oxide catalyst from waste biomass is a scarcely studied area. Thus, present protocol aims to prepare an environmentally friendly, efficient, renewable and recyclable heterogeneous base catalyst from *Carica papaya* stem. The chemical and structural properties of the catalyst were examined by Fourier-transform infrared spectroscopy (FTIR), X-ray diffractograms (XRD), Scanning electron microscopy (SEM), Energy Dispersive X-ray spectrometry (EDX), Transmission Electron Microscopy (TEM) and Brunauer-Emmett-Teller (BET) analysis. The CO_2-TPD and Hammett indicator test was conducted to determine the basicity of the prepared catalyst. The study revealed the presence of alkali and alkaline earth metals that provide the basic sites to facilitate transesterification reaction for biodiesel production and formation of benzylidenemalononitrile (BMN). The conversion of the waste cooking oil (WO) and *Scenedesmus obliquus* (SO) lipid to biodiesel was confirmed by the NMR and Gas chromatography Mass Spectroscopy (GC-MS) technique. Biodiesel conversions of 95.23% and 93.33% were achieved using 2 wt % catalyst loading under optimized reaction conditions for WO and SO respectively. Reusing the catalyst showed a slight drop in activity after 6 repeated uses. The reported catalyst has shown its potential as an alternative and cheaper green solid catalyst for biodiesel production and Knoevenagel reaction.

1. Introduction

The world has witnessed much of the emphasis on energy and related issues in the last few decades. The issue of continuous depletion of fossil fuel reserve along with the increase in fuel prices has drawn global attention towards the development of alternatives that would be renewable, sustainable, efficient and cost-effective [1,2]. Different countries have set goals to replace a part of their energy requirement from renewable sources; biodiesel being considered as a frontrunner to be taken up as an automobile fuel substitute [3]. Biodiesel is produced by transesterification of triglycerides of oils or fats with alcohol (methyl or ethyl) in the presence of a suitable catalyst [4,5].

Researchers have reported biodiesel as an oxygenated, biodegradable and non-toxic fuel [6,7] Although biodiesel has been reported as a potential substitute for petroleum diesel, much of the works involve homogeneous catalyst for its synthesis which is chemically synthesized and is toxic as well as corrosive in nature [8]. Use of homogeneous catalyst leads to additional cost in wastewater disposal generated during its separation from the reaction mixture [9]. On the other hand, the heterogeneous solid catalyst has been reported to be advantageous due to its insolubility in solvent or esters and hence can easily be recovered and reused [10].

In recent years, the utilization of eco-friendly and reusable

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heterogeneous catalyst has emerged as a major constituent of green chemistry [11]. Solid acids such as sulfated zirconia [12,13], sulfonated carbons [14–16], Amberlyst-15 [17] have attracted a lot of attention as an effective catalyst for biodiesel production. But, in the context of sustainability, economy and ecofriendly, the use of renewable catalysts prepared from biomass have been increasingly targeted. Waste biomass has been fabricated to prepare acid and alkali catalysts using activated carbon [18,19] as catalyst support. A number of works on the preparation of heterogeneous catalyst from waste biomass viz. coconut shell [20], palm shell [21], wood ash [22], deoiled cake waste [23] etc., have been reported. Activated carbon support based catalyst provides more specific surface area and pores for active species which results in excellent catalytic ability. But, the cost of production of such catalyst must be factored in catalyst fabrication such as high carbonization temperature and wasteful chemical reaction during functionalization of the activated carbon. However, CaO based heterogeneous catalysts have been extensively synthesized without any chemical functionalization from renewable sources like an eggshell [24], waste crab shell [25], etc. In this context, mixed oxide catalysts from waste biomass have drawn little attention.

The main problem associated with transesterification reaction using heterogeneous catalyst is the deactivation of the catalyst with time generally encountered when used oils are involved which may be due to poisoning, coking, sintering, and leaching [26,27]. Heterogeneous catalyst should possess some hydrophobic character to support triglycerides adsorption and to avoid deactivation of catalytic sites by strong adsorption of polar byproducts such as glycerol and water [28,29]. Reported literature suggests that the addition of metals onto the catalyst surface can improve its hydrophobicity [30–33]. To enhance the catalytic efficacy biomass containing metals can be exploited as a forth runner to prepare such catalyst without any chemical fabrication as a part of sustainable development.

With the advancement in medicinal and pharmaceutical chemistry, higher attention has also been paid towards the development of environment-friendly processes that employ nontoxic reagents, solvents and catalysts [34]. The Knoevenagel condensation is one of the most efficient and widely used methods for C–C bond formation. Over the past years, various heterogeneous catalysts have been developed for Knoevenagel condensation including ion exchange resins, mesoporous zirconia [35], chitosan biohydrogel [36] etc. Several studies [37] suggest the formation of BMN and widespread applications of such moiety inspire for the development of a newer protocol.

Papaya plant has been grown extensively in most of the countries including tropical and subtropical regions of the world. Papaya fruit has high energy value as well as it contains a lot of vitamins and minerals. Papaya plant has been extensively used for the biochemical synthesis of different pharmaceutical compounds [38,39]. In 2017, the total world production of papaya was 13,016,281tonnes. India is leading in papaya production with 45.64% of the world total [40]. With such a large amount of papaya produced, and an estimated 30–50% cull rate, there is a large amount of agricultural waste produced [41]. The area under papaya cultivation in India increased from 63% i.e. 45.2 thousand hectares in 1991–1992 to 73.7 thousand hectares in 2001–2002 [42]. There are around 1700 papaya plants per acre [42], where stems are generally 5–10 m long. Cultivators discard the stem of papaya plant after they find it of no use for productivity and then, the stem becomes waste.

Owing to this, present work emphasizes utilization of waste (discarded papaya stem) as a source for the synthesis of the biocatalyst. To the best of our knowledge, it is the first study to explore *Carica papaya* stem as a source of heterogeneous biocatalyst which would be non-toxic, cost effective, renewable, recyclable and environmentally friendly in nature having widespread application i.e. for transesterification as well as Knoevenagel condensation reaction. Thus, a newer approach for the preparation of green heterogeneous solid base catalyst under the protocol of bio-waste utilization has effectively been investigated which meets the widespread scope of chemical transformation.

2. Experimental

2.1. Materials

Carica Papaya stem and WO were collected from the nearby locality. The SO was obtained from Gauhati University, India. Chemicals of analytical grades used in the present work were purchased from Sigma Aldrich and used without further purification.

2.2. Extraction of lipid

The extraction of lipid from SO dried biomass was carried out followed by Bligh and Dyer method [43]. Dried biomass sample was weighed and homogenized in a mortar and pestle using 0.1–0.5 g of anhydrous Na_2SO_4 and 1–2 mL of 2% butylated hydroxytoluene (BHT) (2.04 g of BHT in 100 mL $CHCl_3$). Total lipid was extracted from the homogenized powder with 5–10 mL mixture of $CHCl_3$: MeOH (2:1). The residue was extracted with chloroform until it became colorless. The extracts were mixed together, filtered and then transferred to a separating funnel. Then 0.9% NaCl solution (1/3 of the volume) and excess $CHCl_3$ was added to the separating funnel, mixed thoroughly and kept undisturbed overnight at room temperature. A clear biphasic layer was observed. The lower layer ($CHCl_3$) containing the lipid component was collected in a clean glass vial. The upper layer containing the methanol-water layer was washed twice with chloroform and collected similarly. All the collected chloroform layers were mixed together and were evaporated in a water bath at 60 °C and finally dried in desiccator in presence of anhydrous Na_2SO_4.

2.3. Catalyst preparation and its characterization

Carica Papaya stem was cut into small pieces to speed up the drying process, washed thoroughly using double distilled water and then dried in an oven at 80 °C for 48 h till constant weight. The dried *Carica Papaya* stem (CPS) pieces were ground and sieved to a fine powder. The sieved powdered stem was calcined in a porcelain crucible placed in a muffle furnace for 4 h at a temperature of 700 °C. The calcinated *Carica Papaya* stem (CCPS) was stored properly for further use.

The FTIR spectra were measured using Nicolet (Impact 410) on KBr pellets in 4000-500 cm^{-1} wavenumber range. The XRD of CPS and CCPS was analyzed by a Rigaku miniflex diffractometer in 2θ range 10–80° (CuKα radiation, λ = 1.5406 Å) at 2° scanning rate. The BET sorption isotherm method (NOVA 1000E, NOVA WIN, QUANTACHROME) was used to determine the surface area of the catalyst. The SEM and EDX study was performed using Jeol, JSM-6290 LV. The TEM study was analyzed using JEOL, JEM-2100 Plus Electron Microscope, Japan. The Hammett indicator method was used to determine the basicity. The basicity was also measured by temperature programmed desorption of CO_2 (Autochem 2920, micrometrics). To remove adsorbed water molecules and other impurities the sample was pre-treated with Helium gas at 350 °C for 1 h, followed by cooling to room temperature. The CO_2 desorption was monitored in the temperature range of 50 °C–670 °C. The static contact angle of the catalyst pellet with