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Biochar Supported Cao As Heterogeneous Catalyst For Biodiesel Production

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Abstract

In this paper we report an environmentally benign biodiesel production using biochar supported CaO as a heterogeneous catalyst. Both the active part as well as catalyst support reported in this work has been derived from waste materials (i.e. waste shells of Turbonillastriatula and deoiled cake of MesuaferreaLinnseeds). The catalyst was prepared by impregnation method and optimal reaction conditions for achieving maximum yield were investigated. Under optimal conditions biodiesel yields <90 was obtainedwith biochar supported CaO which was similar to the yield reported for shell derived CaO catalyst.

Keywords: *Biochar; CaO, Waste shell; Mesuaferrea; Pyrolysis;Biodiesel*

Introduction

Biodiesel is an alternative diesel fuel derived from vegetable oils or animal fats. Owing to its properties which are similar to petroleum-based diesel, it can be used either as a substitute for diesel fuel or more commonly in fuel blends [1-2]. It also presents an alternative to petroleum diesel for reducing emissions of gaseous pollutants such as CO, SOx, particulate matter and organic compounds [3]. Amongst the available methods, transesterification is the easiest and most cost effective way to produce biodiesel [1]. Transesterification also called alcoholysis is the reaction of a fat or oil with an alcohol to form esters and glycerol. In the reaction, 1 mol of triglyceride reacts with 3 mol of methanol in presence of catalysts. Usually transesterification of vegetable oil to biodiesel (fatty acid methyl ester, FAME) can be catalyzed by bases, acids and enzymes [5, 6]. The industrial synthesis of biodiesel uses homogeneous catalyst KOH, NaOH, in a liquid-phase reaction [7]. However, transesterification with these catalysts has disadvantages related with catalyst separation and reusability. To address these issues, heterogeneous catalyst have been considered a viable alternative since they eliminate the usual difficulties related to homogenous catalyst and can be reused several times [9-11].Due to the high cost and complex syntheis of existing heterogeneous base catalysts such as supported alkaline catalysts, alkali earth oxides, mixed metal oxides, dolomites, perovskite-type catalysts, and zeolites, hydrocalcites [12-13]; research for production of biodiesel has been focused towards renewable "green catalyst" prepared either from biomass or from waste generated in the households. Recently renewable heterogeneous catalysts such as carbon-based catalysts (activated carbon, biocharetc) [14-18] and metal oxides catalysts derived from shells: shrimp shell, eggshells [13,19,20] have gained much importance owing to their low material costs which could significantly bring down the biodiesel production cost. In our previous studies we reported biodiesel synthesis from vegetable oils using CaO derived from waste shells of Turbonillastriatulaas heterogeneous catalyst. [12]. Comparative studies with commercial grade CaO showed no difference in terms of activity for transesterification of soybean oil [21]. However, the catalyst was plagued by problems like very low surface area, sensitivity to the presence of water, leaching of active sites by polar species(e.g., glycerol) and competed with soap forming side reactions. To overcome such limitations CaO can be impregnated into supports such as silica and alumina or carbon materials such as activated carbon, nanoporous carbon, nanotubes etc[22]. Carbon materials have recently gained attention as catalyst supports, owing toproperties like: high stability in acidic, basic media and possibility of tailoring both their texture and surface chemistry. In this context biochar is also a potential candidate as it mirrors charcoal in all aspects. Surface chemistry of biochar may be modified to have very high area (by physical or chemical activation) similar to charcoal [23].In the present study we used activated biocahar as support and impregnated it with the CaO derived from waste shells obtained by calcination of waste Turbonillastriatulashells. The physical and chemical properties of this biochar-supported CaO material were evaluated and catalytic properties were studied in the transesterification of Mesua F. oil with methanol.

Materials And Methods

Waste shells of T. striatula were obtained from a local household of Chirang district of Assam, India. Synthesis-grade methanol (≥99% assay and ≤0.2% water content) and all necessary solvents were purchased from Merck Limited, Mumbai, India and were used as received. MesuaferreaLinn oil was extracted by soxhlet extraction from the powdered seeds. The raw oil was pretreated in order to reduce its acid value which was found to be 16mg/KOH.

Preparation Of Biochar Supported Cao Catalysts

The active phase of the catalyst, CaO was produced by the high temperature calcination of Waste shells of T. striatulaas described elsewhere [12]. For preparing support biochar produced from MesuaferreaLinn deoiled cakes were used,since biochar produced by fast pyrolysis have very low surface area, [23, 24] it was than subjected to chemical activation (with 7 M KOH) in order to increase the surface area. The biochar-supported CaO (BCh-CaO) catalystwas prepared by the wet impregnation method. Typically, a Ca-containing solution was prepared by dissolving 20 g CaO produced earlier in minimum amount of dilute HNO_3(aq). To this solution, a 20 g of dried and powdered support was added and the resultant mixture was stirred for about 2 h at room temperature. Thereafter, it was heat treated at a calcination temperature of 600 °C under atmospheric pressure. The resulting material from hereafter was treated as catalyst.

Catalyst Characterization And Testing

The powder X-ray diffractograms of catalyst samples were recorded on a Rigakuminiflexdiffractometer (Cu-Kα radiation, λ=1.5406 Å) in 2θ range 10–70° at a scanning rate of 2 °C min−1. The Brunauer–Emmett– Teller (BET) surface area and pore size were measured by the multipoint N_2 adsorption–desorption method with ASAP® 2020 Accelerated Surface Area and PorosimetryAnalyzer, USA at liquid nitrogen temperature (-196 ºC). SEM and EDX were performed on a Jeol, JSM-6290LV instrument. IR spectra were recorded in KBr pallets on a Nicolet (Impact 410) FT-IR spectrophotometer. The chemical composition of the catalyst was estimated by Energy-dispersive X-ray spectroscopy (EDX). The basic strength (H_) and basicity were determined according to the methods based on the colour change of Hammet indicators. The catalytic performance of biochar supported-CaO (BCh-CaO) catalystwas evaluated in the transesterification of pretreated*Mesuaferrea*Linnoil with methanol. The transesterification reactions were performed in a 100 ml three-neck round-bottom flask equipped with magnetic stirring, thermometer and a reflux condenser. Oil conversions were determined from the ^1H NMR. Sample aliquots were drawn periodically from the reactor and analyzedby ^1H NMR on a Jeol JNM-ECS400 NMR spectrometer at 25.5 °C with $CDCl_3$ and TMS as solvent and internal standard respectively [25]. The yield ofmethyl esters was calculated as follow:

$$\text{Yield} = \frac{2A_{Me}}{3A_{CH_2}} X\ 100$$

Where,A_{Me} = integration value of the methoxy protons of the methyl esters and

A_{CH_2}= integration value of α-methylene protons.

Results And Discussion

The catalyst changed the colour of phenolphthalein (H_ = 8.2) from colorless to pink, the colour of indigo carmine (H_=12.2) from blue to green and the colour of 2,4-dinitroaniline (H_ = 15) from yellow to mauve but failed to change the colour of 4-nitroaniline (H_ = 18.4). As such, the catalyst's basic strength was designated as 15 < H_ < 18.4, and it was considered as a strong base for the transesterification reaction. Fig. 1 shows the XRD patterns of shell-CaOand BCh-CaO respectively. New peaks corresponding to the graphite carbon appeared in the XRD pattern of the prepared catalyst (BCh-CaO) along with the peaks of CaO. It was observed that major peaks corresponding to 2θ=32.14, 37.22, 53.57, 64.24 and 67.49 are identified as the fundamental peaks for calcium oxide corresponding to JCPDS file no. 00-003-1123. The presence of carbon is indicated by the peak for 2= 29.26 which corresponds to JCPDS file no.01-074-2328. This indicates that the activated supported carbon catalyst consists of calcium oxide and carbon. Both shell-CaO and BCh-CaO shows peaks at 2θ=32.14, 37.22, 53.57, 64.24 and 67.49, which were the characteristic peaks for calcium oxide (JCPDS file no. 48-1467). The Diffractograms of produced biochar was quite similar to biochars as per literature [24,26], while the graphitic basal planes peaks at 2θ=32.14, 37.22, 53.57, 64.24 and 67.49, which were the characteristic peaks in the activated samples.

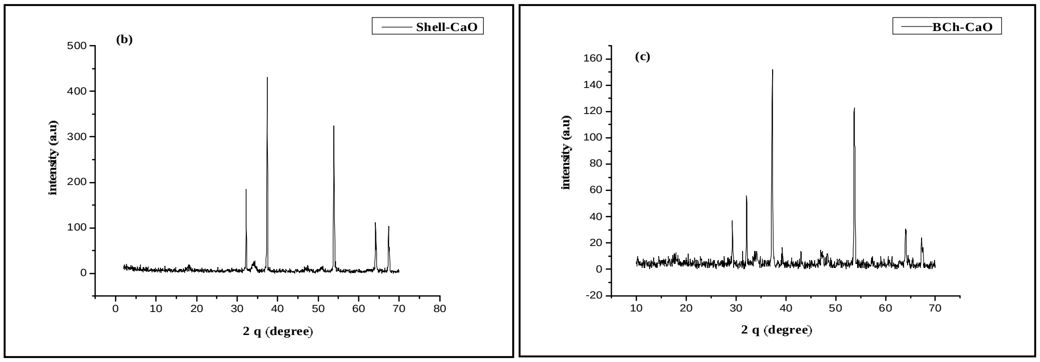

Figure 1: XRD patterns of Active phase and Supported Catalyst

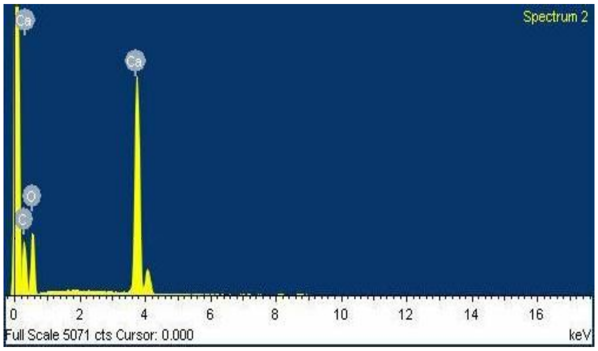

Figure 2: EDX spectra of BCh-CaO catalyst

The morphology of the catalyst (BCh-CaO) was observed by scanning electron micrographs (not shown here). The SEM images of the samples showed a good dispersion of CaO on the surface of activated biochar. It was observed that although biochar could retain its initial structure (which is supported by XRD pattern also) the CaO species were highly distributed on the surface of the support. It could be seen that the particles distinctly filled up all the pores of the support indicating that the resulting sample may have high activity.This conclusion is also supported by the surface area measurements. It was observed that there was a significant reduction in

BET surface area of activated biochar from (456 m^2/g) to the BCh-CaO catalyst (57.7 m^2/g) which indicates that the CaO molecules were successively impregnated into the pores of the activated carbon.The chemical composition of the catalyst was estimated by Energy-dispersive X-ray spectroscopy and the findings are shown in Fig. 2. It was observed that the major constituent elements present in the BCh-CaO catalyst were calcium, carbon and oxygen having weight % of 27.78, 17.66 and 54.55 respectively. This result supports the finding in XRD analysis and hence establishes that the catalyst proposed in this study is mainly composed of CaO particles dispersed on activated carbon.Biochar supported CaO (BCh-CaO) was found to be active in transesterification of MesuaferreaL.oil.To study the influence of different parameters on activity (FAME yield), reactions were carried out at different temperatures with varying methanol to oil molar ratio and catalyst amounts. The results are presented in Table 1. From the results it was observed that the catalytic activity of developed BCh-CaO catalyst was almost similar to the shell-CaO catalysts [13, 21] which could be attributed to the very high loading (50% w/w of support) of active CaO particles. The key parameters affecting biodiesel yield were temperature and catalyst loading.In our study, use of 3 (Wt. %) catalyst loading produced the best results yield of 96% with 12:1 alcohol to oil ratio at 65 °C (Entry 6).

Entry no	**Temperature (□C)**	**Catalyst (Wt. %)**	**Methanol/oil (molar ratio)**	**Time**	**Biodiesel Yield**
1	65	1	6/1	6	61
2	65	2	6/1	6	88
3	65	3	6/1	6	92.4
4	65	3	6/1	6	94.3
5	80	3	9/1	6	95.7
6	65	3	9/1	6	96
7	95	3	12/1	6	85.6
8	70	3	6/1	6	93
9	33	1	6/1	6	20
10	33	2	9/1	6	25.9
11	33	3	6/1	6	27.2
12	65	3	12/1	6	56
13	70	2	3/1	6	91
14	70	2	9/1	6	91.4

Table 1: Influence of different parameters on yield (Temperatures, methanol to oil molar ratio and catalyst loading)

Conclusion

In this work we successfully employed biochar supported CaO (BCh-CaO) as a heterogeneous catalyst in theproduction of biodiesel from MesuaferreaL.oil. The catalyst reported was synthesized entirely by processing waste materials. The active part of the catalyst (i.e. CaO) was derived from waste shells of Turbonillastriatula andthe support (i.e. activated biochar) was prepared from deoiled cake of Mesuaferrea Linn seeds. Use of this novel approach makes thebiodiesel synthesis process environmentally benign. It showed high activity and very high yield upto96% was achieved in 6 h using 3 Wt. % catalyst 12/1 (methanol/oil molar ratio) at reaction temperature of 65 °C.

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