International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.12 No.06, pp 01-06, 2019

Water hyacinth ash: An ecofriendly heterogeneous reusable catalyst for the transesterification of soybean oil to biodiesel

Anjumani Talukdar

Department of Chemistry, Gauhati University, Guwahati-781014, Assam, India

Abstract : The catalytic activity of water hyacinth ash (WHA) has been evaluated for the transesterification reaction of soybean oil with methanol. The reaction was carried out under ambient temperature as well as reflux conditions. The yields of the corresponding fatty acid methyl esters were 95% under both experimental conditions. The catalyst loading was 20% by weight of the oil and the reaction time varied from 30 minutes under reflux condition to 2.5hours at ambient temperature. The catalyst is recyclable and could be reused for up-to 4 runs with marginal loss in catalytic activity.

Keywords : Water Hyacinth, Meteka, Biodiesel, ecofriendly, heterogeneous, transesterification.

Introduction:

The depletion of fossil fuel and to minimize the emission of Green House Gases are the two major concerns to develop the alternative fuels.[1-3] As a result,production of biodiesel and its application have gained considerable attention throughout the world as an alternative fuel owing to its renewable, and clean-burningfuel for diesel engines with less pollutant emissions properties.[4-8]Biodiesel is a mixture of fatty acid methyl esters (FAME) having similar chemical composition and fuel properties to that of petroleum based diesel.[9] It is generally prepared by transesterification of vegetable oils or animal fats with a low chain alcohol in presence of a catalyst. Many catalysts have been employed; however, in case of use of strong base and corrosive acids produces hazardous waste.[10-12]In recent years much of the biodiesel research has been focussed on development of efficient catalysts from biomass for transesterification reaction of oils and fats. Preparation of catalyst from waste biomass opens up novel avenues of lowering costs. Use of waste biomass not only lessens the cost but also helps easy disposal without compromising environmental benignity.[13]Combusted oyster shell[14], waste egg shell[15], biont shell[16], waste Rohu (*Labeorohita*) fish scale[17], waste mud crab shell[18] and waste cockle shell[19] *musa balbisiana* Colla[20,21] are some of the biomass-derived catalysts that have been successfully utilized so far for biodiesel production.

Anjumani Talukdar *et al* /International Journal of ChemTech Research, 2019,12(6): 01-06.

DOI= http://dx.doi.org/10.20902/IJCTR.2019.120601

Water hyacinth (*Eichhornia crassipes*), locally known as *meteka* in Assam[22], is an aquatic plant.Water hyacinth has been considered as one of the world's worst water weeds and has gained international attention in getting rid of its rapid growth and proliferation.[23,24]The International Union for Conservation of Nature (IUCN) has identified water hyacinth as one of the 100 most aggressive invasive species and recognized as one of the top 10 worst weeds in the world.[25,26]It isabundantly available in the North-Eastern region of India including Assam. It has only little commercial value.Recently, we have reported the use of water hyacinth ash as a heterogeneous catalyst in bis(indolyl)methanes and bis(pyrrolyl) methanes synthesis.[27]

In this study, water hyacinth ash (WHA) is reported as an eco-friendly and active heterogeneous catalyst for conversion of soybean oil to biodiesel.

Experimental Section:

Materials

The methanol (anhydrous, purity $\geq$ 99.8%) and other analytical reagents were of high grade and were supplied from Sigma Chemical Co. Commercial grade soybean oil was purchased from a local grocery store.

Catalyst preparation

Matured water hyacinth plants were collected from the ponds thoroughly washed to remove the undesired materials,stems were detachedfrom the roots and allowed to dry under sun for at least two weeks. The dried mass was then burnt in presence of air. The ash was allowed to cool down to ambient temperature. The ash was kept in an air tight container before use.

Composition of the catalyst

The chemical composition of the catalyst was estimated by chemical analysis, atomic absorption spectroscopy and flame photometry, EDX and XRF technique. Major components present are K^+, Ca^+, Mg^{2+}, CO_3^{2-} and Cl^- along with other metals viz.Na, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ti which are present only in trace amounts (ppm level). Metals are present as their carbonates, sulfates, phosphates, chlorides or oxides. Polycrystalline nano-sized particles are also present.

Transesterification procedure

Prior to transesterification the oil was purified by column chromatography. The purified oil was transesterified to fatty acid methyl esters (biodiesel) using the heterogeneous catalyst WHA. A mixture of oil in methanol (10 mL/g of oil) and the catalyst (20 wt.% of oil) at ambient temperature (34°C). The reaction progress was monitored by TLC. The reaction mixture was filtered under vacuum pump and the residue was washed with petroleum ether and the combined filtrate was extracted with water and petroleum ether. The organic phase was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed using a rotary evaporator and the crude product was obtained. It was further purified by column chromatography over silica gel using petroleum ether and ethyl acetate as the eluent.

Analysis of FAME

All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz respectively using BrukerAvance III 300 MHz/54 mm NMR spectrometer. IR spectra were recorded with a Perkin Elmer RX I FT-IR spectrometer as a thin film on KBr plate.

Results and Discussion:

Primarily, the transesterification reaction of soybean oil with methanol was first attempted at ambient temperature. The catalyst found to be quite efficient at this temperature (34°C) yielding 96% of the desired products in 3 hours with 20 wt% (w.r.t wt of the oil) catalyst loading(Table 1).

Study of catalytic activity for transesterification reaction at ambient temperature

Table 1. Amount of catalyst at ambient temperature

Entry	Catalyst wt% [b]	Reaction time (h)	Yield (wt%)
1	5	9	25
2	10	8	43
3	15	6	82
4	20	2.5	95
5	25	2	95

[a]1 g oil taken in 10 mL methanol and stirred with the required amount of catalyst at 34°C. [b]Wt% with respect to wt. of oil.

Study of catalytic activity for transesterification reaction under reflux

Table 2.Amount of catalyst at 65 °C[a]

Entry	Catalyst wt% [b]	Reaction time (min)	Yield (wt%)
1	1	90	16
2	5	90	41
3	10	40	81
4	15	25	93
5	20	20	95
6	25	20	95

[a]1 g oil taken in 10 mL methanol and stirred with the required amount of catalyst at 65 °C.[b]Wt% with respect to wt. of oil.

The catalyst efficacy was studied for the transesterification of soybean oil with methanol under refluxcondition. It was observed that the reaction time was drastically reduced to 20 minutes on increasing the temperature from ambient to 65 °C.The catalyst amount was also optimised at this temperature and it was found that 20 wt% (w.r.t wt of the oil) gave the best result with 95% yield in 20 minutes (Table 2). However, increase amount of catalyst has no effect in increase in yield nor decrease in reaction time.

Study of recyclability and reusability of the catalyst

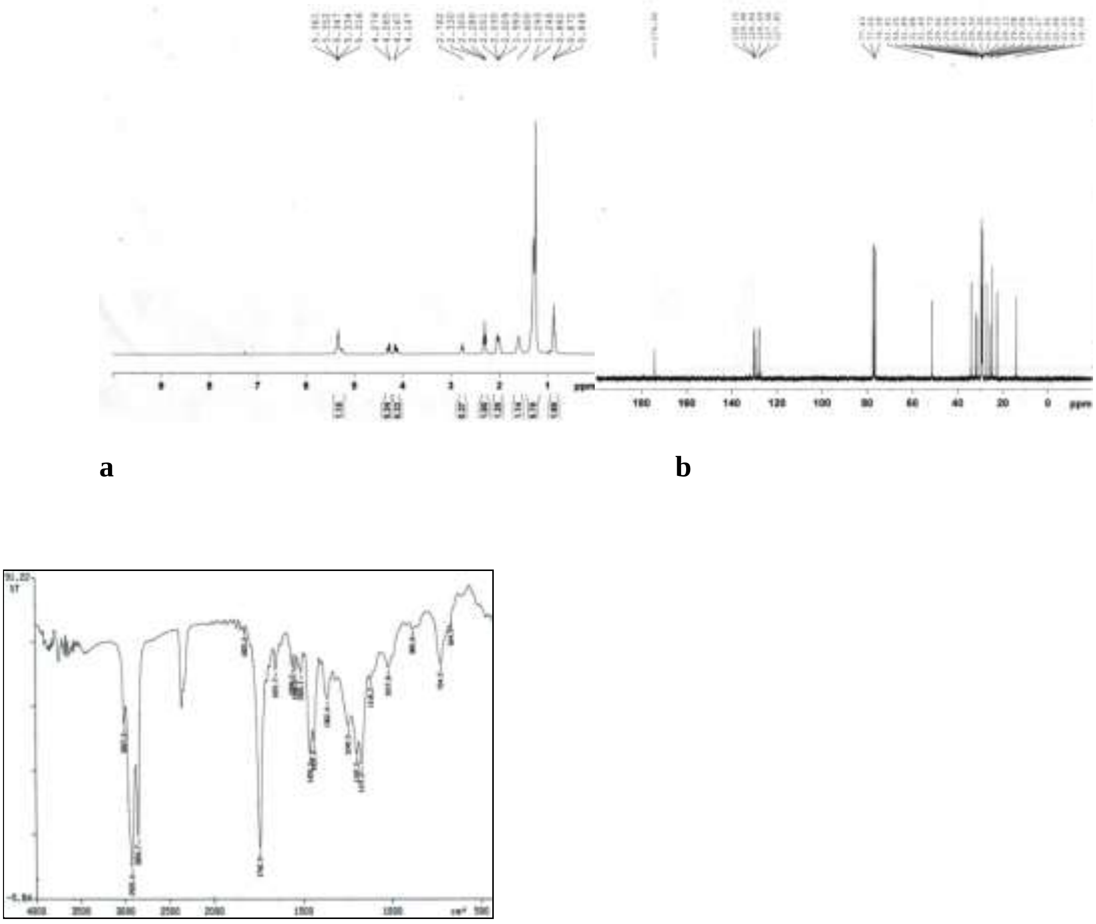
Reusability of the catalyst is examined after removing the catalyst from the reaction mixture by simple filtration. The used catalyst was dried in a hot air oven at 110-120 ºC for 2-3 h followed by cooling to ambient temperature inside a desiccator. The recovered catalyst could be reused for three catalytic cycles without any significant decrease in activity (Table 3). However, during the fourth run decrease in yield is observed. This may be due to sequential leaching of the catalytic species into methanol during consecutive runs.

Table 3. Recyclability of the Catalyst

Entry	Run	Time (min)	Yield (wt%)
1	1st	20	95
2	2nd	20	93
3	3rd	30	92

The ^{1}H, ^{13}C NMR and IR spectra of soybean seed oil are shown in Figs. 1 (a,b,c) and that of biodiesel in Figs. 2(a,b,c). The major difference between the ^{1}H NMR spectra of the oil (Fig. 3) and the biodiesel (Fig. 4) is the appearance of a singlet signal at δ 3.65 ppm representing methoxy protons ($-CO-OCH_3$) of the ester functionality and the disappearance of the signals representing protons of the glycerol moiety of the glyceride at δ 4.15 (dd), 4.31 (dd) and 5.27 (m) and on conversion of the oil to biodiesel. In the the^{13}C NMR spectrum of soybean oil, signals at δ 62.07 and 68.88 ppm depicted in Fig. 5 revealed the presence of methylene ($-CH_2-CO_2R$) and methine ($-CHCO_2R$) carbons of glycerine moiety in the triglyceride molecules. However, these two signals (δ 62.07 & 68.88) disappears in the ^{13}C NMR spectrum of biodiesel (Fig. 6) and a new signal at δ 51.40

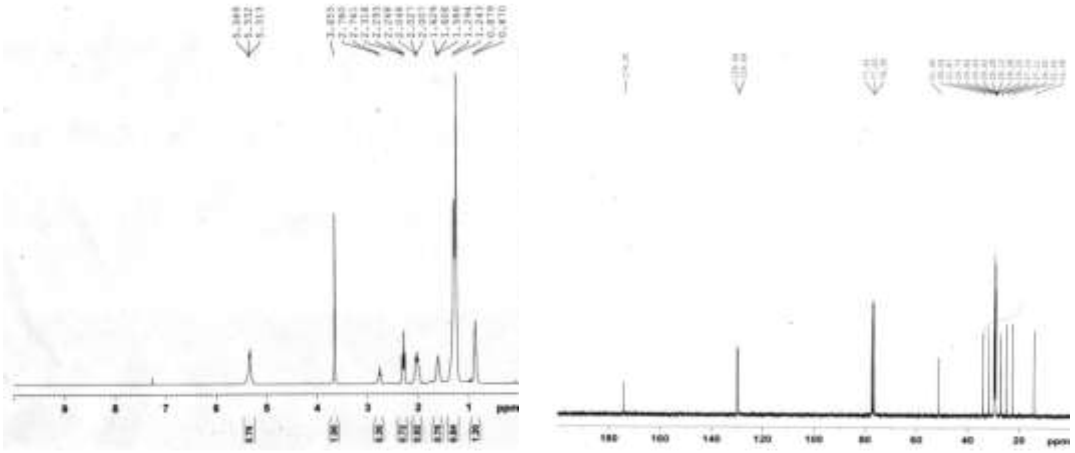
ppm appears due to methoxy carbon (-OCH_3) are again supports the formation of the desired products.



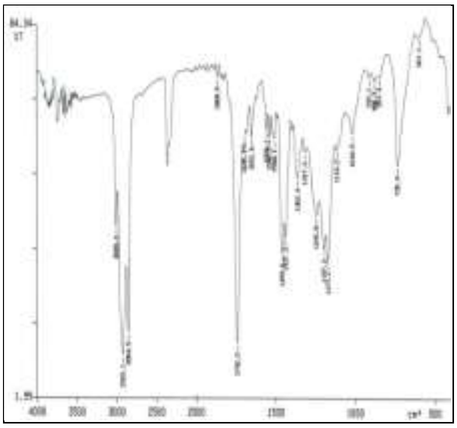
a **b**

c

Fig. 1. (a) ^{1}H (b) ^{13}C NMR (c) FT-IR spectrum of soybeanoil



a **b**



c

Fig. 2. (a) ^{1}H (b) ^{13}C NMR (c) FT-IR spectrum of FAME mixture of soybean oil

Conclusion:

In this study, water hyacinth ash (WHA) is used as aninexpensive heterogeneous catalyst for the conversion of soybean oil to fatty acid methyl esters (biodiesel). The transesterification reaction of soybean oil with methanol is efficiently catalysed by this catalyst to give 95-96 % yield under two reaction condition viz., ambient and reflux. The catalyst can be recycled and reused for the reaction for 3-4 times without much loss of activity. Thus, with the results a new biomass-derived catalyst for the production of biodiesel has been reported which is not only of academic interest but also has huge potential to be used on industrial scale. The catalyst is also a step towards sustainable chemistry with minimization and generation of hazardous substances by utilizing a low-cost biomass-derived feedstock for the production of a new catalyst for biodiesel production.

Spectral data of theFAME:

^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si) δ= 0.87 (m, 3H), 1.24 (m, $-(CH_2)n-$), 1.60 (m, 2H), 2.00 (m, , 2.26 (t, 2H, ^{3}J = 7.5 Hz), 2.76 (t, 2H, ^{3}J = 5.7 Hz), 3.65 (s, 3H: - $CO-OCH_3$), 5.31 (m, 2H). ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ= 14.04–34.04, 51.40, 129.69–129.94, 174.30 ($-CO-OCH_3$). FT-IR (thin film): 722, 870, 1023, 1116, 1172, 1248, 1366, 1451, 1528, 1597, 1660, 1743, 2842, 2926, 3018 cm^{-1}.

Acknowledgement:

Financial assistance received from the UGC-New Delhi during the tenure of the work is highly acknowledged.

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