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Room temperature production of jatropha biodiesel over coconut husk ash

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ABSTRACT

A cost effective and efficient method for the preparation of fuel grade biodiesel by the transesterification of jatropha oil at room temperature over a coconut husk derived catalyst under mild reaction conditions without the use of any cosolvent is reported here. Catalyst is prepared by means of controlled heating of coconut husk, without any chemical treatment. The main active component over the catalyst was found to be potassium. When the reaction temperature was increased to 45 °C, the catalyst showed excellent performance on the transesterification of Jatropha oil in a range of methanol/oil molar ratios. The important speciality for the present catalytic systems is the comparatively low reaction temperature requirement for effective reaction. For the optimization of different reaction variables including molar ratio of the reactants, reaction time, the catalyst calcination temperatures and the catalyst/oil weight percentage, a series of transesterification reactions were conducted and the results obtained are presented here.

1. Introduction

The increasing global concern about the depleting petroleum resources leading to uncontrollable escalation in petroleum prices resulted in a concerted effort worldwide in order to find out suitable alternatives as energy sources. Biodiesel is one of the proposed alternatives which has several advantages like its renewability, non-hazardous nature and high flash point which enable easy handling and transport [1]. Apart from all these, one of the added advantages which make biodiesel as one of the best alternative fuels which we can think of is the fact that it can be used in the existing diesel engines without much engine modifications [2]. The air pollution from automobile exhaust also can be substantially reduced by the use of biodiesel [3,4]. Biodiesel is basically the transesterified oil or fat in which lower alcohols, especially methanol is incorporated, replacing the branched chain glycerol moiety in the molecule of oil or fat [5,6]. This transesterification process reduces the viscosity and related problems of oils and fats making them more compatible as alternative vehicle fuels [7].

The starting materials for biodiesel preparation are vegetable oils and animal fats. The edible oils are generally excluded in order to avoid their scarcity in the future for edible purposes [8]. Among the plant sources for non-edible oils, the use of *Jatropha curcas* is more popular because of several reasons [9]. The ability of this plant to grow in dry climate conditions and in areas which are not so suitable for normal cultivation is remarkable. Thus, cultivation of jatropha in barren lands can be considered as an easy way of converting such areas into agricultural areas for future plantation. This is important especially for highly populated countries like India where economy depends mainly on agriculture. It can also be argued that in the entire process of biodiesel production in this manner, the total CO_2 generation is comparatively very less if we also account the intake of CO_2 by the plant for its growth [10].

The common strategy for transesterification of oils is by employing homogeneous base catalysts such as NaOH, KOH, etc [11]. Even though there are many reports in literature using the heterogeneous catalyzed route for the transesterification of oil [12], only a few of them report more than 96.5% fatty acid methyl ester (FAME) yield, matching with the ASTM and EN standard specifications for biodiesel [13–20]. The room temperature production of

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fuel grade biodiesel, which meets international standards was mainly achieved by employing microwave radiations [21], UV irradiation [22], ultrasonication [23–27], electrolysis [28], enzyme catalyzed reaction [29–32] or by means of cosolvents/ionic liquids [33–36]. However, since most of the above methods involve additional energy consumptions, the overall cost of the production will be more. In addition, Gökhan and Selim [37] had reported a two-step NaOH mediated process for the production of biodiesel with 97% yield. But the process is tedious and time consuming when compared to the normal biodiesel production processes.

In the present work, we report the use of coconut husk for the preparation of a base catalyst for the first time. We selected coconut husk as the raw material for the catalyst production since it is naturally available in plenty and inexpensive. The catalyst preparation is done by a simple procedure, by means of controlled heat treatment (combustion) alone without any chemical processing and the ash obtained is used as such for the biodiesel preparation. Recently there are a few reports on ash-based catalysts for the biodiesel production. However, either the amount of catalyst needed was high (around 20 wt% of the oil) or high calcination temperature was required for the catalyst development [20,38]. The catalytic performance was further improved by chemical treatment with K or Ca containing compounds [20,38]. The advantage of coconut husk derived catalyst is that the presence of high K content inherently present is sufficient for giving excellent catalytic activity, producing biodiesel meeting international standards even by room temperature reaction.

The most promising feature of the present catalytic systems is the low reaction temperature for effective reaction. Usually higher reaction temperatures of at least 60 °C were preferred for oil transesterification reaction in order to decrease the viscosity of oil to enhance the mass transfer effects. As far as we know, there are no such cost effective catalysts available that can yield biodiesel which meets international standards at temperatures lower than 60 °C (which is near to the reflux temperature of methanol) and at lower methanol:oil molar ratios (15:1) without the use of any high energy options such as ultrasonication, UV irradiation, microwave irradiation or by the use of cosolvents/ionic liquids.

2. Experimental

2.1. Materials

Oil is expelled from *Jatropha curcas* seeds which were purchased from a local Indian firm. The cleaned seeds were subjected for oil expelling using a hand operated oil expeller. The oil is made gum free following a reported procedure [39]. First jatropha oil is heated to a temperature of 60 °C. Phosphoric acid (0.01 weight percentage of oil) is added to the jatropha oil with stirring and stirring is continued for 30 min. Then, 2% water is added to the oil followed by heating at 70–80 °C for about 15 min. Gums present settle in the bottom and is drained from the jatropha oil. The degummed oil obtained was stored in the dark room. Before transesterification reaction, the free fatty acids (FFAs) present in the jatropha oil are reduced (to <1%) by pretreatment using HCl [40–42]. Oil is pretreated with 6 wt% of concentrated HCl and methanol at a methanol/oil molar ratio of 6:1 at 50 °C for 1 h [43]. The contents were separated and the esterified oil is washed with distilled water to remove the acid. Since the presence of water is detrimental to biodiesel production [44,45], oil is then dried over anhydrous sodium sulphate before the transesterification reactions [46–48]. Coconut husk was collected from a local coconut oil mill. *N*-methyl-*N*-trimethylsilyltrifluoro-acetamide (MSTFA) and the biodiesel standards were obtained from Sigma Aldrich Chemicals Pvt. India Ltd. Methanol, anhydrous sodium sulphate, phosphoric acid and HCl were purchased from Nice Chemicals, India. Solvents (Nice Chemicals, India) used in this experiment were of analytical reagent grade.

2.2. Preparation of coconut husk ash

Coconut husks were washed with deionized water and dried under sun for about 5 h. Then the husks were subjected to calcination at different temperatures starting from 250 °C to 500 °C. The calcination (combustion of coconut husk) was performed by placing the dried coconut husk as such into a cleaned muffle furnace (Hexatech Instruments Pvt. Ltd, Model No. HIPL-022 A, with Microprocessor based Programmable PID Controller). During the combustion, the set temperature was slightly increased (~10 °C). The time of combustion was fixed as 1 h except in the case of system treated at 250 °C, where the time needed to develop coke free catalyst was 3 h. The different catalytic systems thus prepared were designated as CH*n*, where *n* indicates the catalyst treatment temperature in °C. The catalyst treated at 350 °C (CH350) is used to optimize the reaction parameters. The ash content of coconut husk is found to be 5%.

2.3. Catalyst characterization

The coconut husks treated at different temperatures were characterized using various techniques. Powder XRD analyses of the coconut husk based catalysts were recorded on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) as the X-ray source. The FTIR spectral analyses were done in NICOLET6700 FTIR Thermoscientific in the region 400–4000 cm^{-1}. SEM analyses of the systems were done on a JEOL Model JSM − 6390LV Scanning Electron Microscope and EDS elemental analysis on JEOL Model JED − 2300 energy dispersive spectrometer.

2.4. Optimization of reaction variables on the transesterification reaction of jatropha oil

Different reaction conditions such as molar ratio of the reactants, reaction time, the catalyst calcination temperatures and the catalyst/oil weight percentage were varied so as to carry out a sequence of oil transesterification reactions. Typically, jatropha oil (10 g) with FFAs less than 1 was subjected for transesterification reaction with methanol in the presence of the coconut husk derived catalyst in a 50 ml RB flask fitted with reflux condenser. The RB flask was kept in an oil bath and the reaction temperature was varied up to the reflux temperature of methanol. Thorough mixing of the reactants and the catalyst in the RB flask was achieved using a magnetic stirrer. Product separation after the reaction was done by centrifugation and the top biodiesel layer was washed with deionized water thrice, in order to remove any extra catalyst present in the mixture. Then water is removed from the biodiesel by the addition of anhydrous sodium sulphate [47,48].

2.5. Biodiesel analysis

ASTM D6584 is employed for the analysis of the biodiesel samples [20,49]. The FAME content (wt%) of biodiesel samples was analysed using a Thermofisher Trace GC 700 Gas Chromatograph equipped with MXT® biodiesel TG column and flame ionization detector. The column had an internal coating with 5% phenyl-polydimethylsiloxane and cross-linked upper phase. The GC had a temperature limit of 400 °C. The carrier gas used was nitrogen which was fed at a flow rate of 3 ml/min. Oven temperature program was started at 50 °C and heated to 180 °C with a heating rate of 15 °C/min and heated to 230 °C with a rate of 7 °C/min, then

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