Energy Conversion and Management 100 (2015) 277–287

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Central composite design approach towards optimization of flamboyant pods derived steam activated carbon for its use as heterogeneous catalyst in transesterification of *Hevea brasiliensis* oil

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ARTICLE INFO

Article history:
Received 2 February 2015
Accepted 30 April 2015
Available online 20 May 2015

Keywords:
Biodiesel
CCD
Flamboyant pods
Hevea brasiliensis oil
RSM

ABSTRACT

The present investigation emphasises the preparation of carbon based KOH impregnated heterogeneous catalyst from flamboyant pods (*Delonix regia*) for the production of biodiesel from novel feedstock *Hevea brasiliensis* oil (HBO). Initially, carbonized char was physically activated by superheated steam and the process was optimized to study the effects of activation time and temperature by central composite design approach (CCD) using response surface methodology (RSM). Activated carbon was impregnated with KOH at four different ratios. Biodiesel production process was carried out at constant temperature 60 °C, reaction time 1 h, and 5 g of carbon based catalyst at varying quantities of catalyst loading (0.5, 2, 3.5, 5 wt%) and methanol to oil ratio (5:1–20:1). The influence of parameters on the biodiesel yield at varied condition was studied. Maximum yield of 89.3% was obtained at methanol to oil ratio 15:1 and catalyst loading 3.5 wt% and corresponding yield at same process parameters was observed to be 88.7% implying the significant activity of catalyst in reutilization. Produced biodiesel was characterized following ASTM standards. The experimental analysis confirmed that the carbonaceous catalyst developed from flamboyant pods under optimized condition is capable of transesterifying HBO into biodiesel.

1. Introduction

The ever-increasing energy demand and gradual depletion of conventional energy reserves have been the matter of significant research for exploration of alternative sources of energy to replace the diminishing petro-fuels from the earth's crust [1]. In order to mitigate the energy demand and supply as well as the negative impacts of fossil fuels onto the environment, researchers are paying wide attention to the sustainable approaches for generation of clean and promising alternative fuels from the feedstock available abundantly in the nature. In this alarming situation, biodiesel could be a promising alternative toward the replacement of a conventional petro-diesel as it has been receiving a major boost over the past few decades due to its environment-friendly properties like biodegradability, renewability and ease of combustion. One of the major advantages of biodiesel is that its properties stand acceptable in comparison to the conventional diesel [2–4], and can be used directly or in blending with diesel in an unmodified engine [5].

In the current scenario biodiesel production potentially involves homogeneous transesterification of vegetable oils or animal fats with strong alkali (NaOH, KOH) as catalysts [6]. However, profuse energy consumption for separation and purification of product alongwith loss in catalytic activity after separation thereby rendering catalyst unusable are some of the limitations associated with the process. This leads to significant wastage of energy and the problem of producing chemical waste disposal. Transesterification of oils can also be catalyzed by strong acids like H_2SO_4, HCl; but its lower rate of reaction limits commercialization of the process at industrial level [7]. Few works have been reported on the use of lipase enzyme as catalyst since the process is free of soap formation and further product purification cost is less. But again the rate of reaction and cost of enzyme required are of primary concern. Hence the transesterification process employing homogeneous acids, alkali and enzyme as catalyst is not economically feasible [8].

Heterogeneous catalysis can overcome the limitations of homogeneous catalysis through easy separation and reuse of catalyst. But mass transfer diffusional resistance becomes prominent in heterogeneous catalysis and thus lowers the rate of reaction. To minimize this resistance, structure promoter or catalyst support plays a vital role because it can provide maximum surface area

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http://dx.doi.org/10.1016/j.enconman.2015.04.083
0196-8904/

for reaction or sufficient number of active sites where triglyceride can react with catalyst [9]. Many researchers have worked in the direction of utilization of different catalyst supports in heterogeneous transesterification reaction and it has been reported that zinc oxide and aluminum oxide are potential candidates owing to their desirable properties to be used as catalyst support [9,10]. A considerable amount of research have also been carried out toward exploitation of several heterogeneous catalysts such as alkali metal catalysts, alkali and alkaline earth oxides, mixed metal oxides, dolomite sperovskite-type catalysts and zeolites, heteropoly acids, Amberlyst-15, hydrotalcite, and zirconia [11–18]. However, none of the catalysts were reported to be efficient in comparison to alkali metal hydroxides for biodiesel production [19]. In the recent years glycerol enriched heterogeneous catalyst is also used for biodiesel production.

In order to produce efficient alternative to the conventional petro-diesel through energy efficient, environmentally benign and cost effective process, the development of low cost renewable heterogeneous green catalyst support is the need of the hour. Such a novel catalyst support can either be prepared from biomass or waste generated in households. Activated carbon can meet the desirable properties of green catalysts as it is highly effective as catalyst support in liquid and vapor phase reactions. The appreciable micro-porous surface of activated carbon makes it suitable to be used as catalyst support in transesterification reaction. Hence, catalyst like KOH/NaOH can easily be dispersed onto the surface of activated carbon possessing high surface area and low ash content leading to the enhancement of the reaction.

Potassium hydroxide is extensively used as catalyst in the transesterification of vegetable oils and its applicability is favorable at industrial level due to high activity and low cost. It has been found that nearly 90% conversion can be achieved using potassium hydroxide impregnated palm shell carbon as catalyst in the transesterification of palm oil [20]. Very few researchers have worked on activated carbon as catalyst support in biodiesel production. Several researchers used carbon based solid acid catalyst for the preparation of biodiesel from vegetable oils containing high free fatty acids and obtained 80.5–90.4% of yield at temperature 220 °C, alcohol to oil ratio 16.8:1 and reaction time 4.5 h [21]. While Dehkhoda et al. used biochar based solid acid catalyst for conversion of canola oil into biodiesel and reported 92% of yield at 60 °C temperature, alcohol to oil ratio 15:1, catalyst loading 5 wt% and reaction time 15 h [22]. Most of the papers have focused on the use of carbon based acid catalyst for biodiesel production from cottonseed oil, waste oil, etc. using vegetable oil asphalt based catalyst, wood based carbon catalyst, carbon and biochar based catalyst. These researches highlighted that process requires high reaction time at larger molar ratio of oil to alcohol [23–26]. Sulphonated carbon nanotubes was also reported to be an efficient catalyst for biodiesel production but requires very high temperatures [27]. Among various carbonaceous supports flamboyant pods have been chosen as precursor in this work to develop catalyst support due to its easy availability, zero cost, high surface area and impressive micro pore volume. A single work has been reported on the preparation of activated carbon from the flamboyant pods which were chemically activated using sodium hydroxide. Generation of toxic waste water and high processing cost are the demerits of chemical activation process. Hence, in the present work superheated steam has been used as an activating agent to overcome this predicament which in turn makes this process cost effective [28].

The objective of present study is to develop a novel carbon based catalyst from waste material flamboyant pods for the production of biodiesel from HBO. Carbonized char from the flamboyant pods was physically activated with superheated steam. The activation process was optimized using the central composite design approach in response surface methodology [29]. The whole quantity of char was activated at the optimized condition and it was then impregnated with potassium hydroxide at four different ratios of KOH to activated carbon (AC). It was directly used in the transesterification reaction of HBO at different catalyst loadings and oil to methanol ratios keeping other parameters constant. Influence of catalyst loading and methanol to oil ratio on the yield of biodiesel from novel HBO was meticulously studied. Hence, flamboyant pods could be an eminent precursor for the development of catalyst support to be used efficiently in the transesterification of HBO into biodiesel to meet the growing energy demand.

2. Experimental work

2.1. Materials

Activated carbon used for the development of catalyst support was prepared in the laboratory from waste biomass flamboyant pods. The precursor was collected from a rural area of Wardha, India. Vegetable oil (Rubber seed oil/HBO) used as the raw material for production of biodiesel was purchased from the local market of Burdwan, West Bengal, India. Methanol (99.5%) was purchased from RANKEM RFCL Limited, India. Pure potassium hydroxide (98%) used as catalyst in the process was obtained from MERCK, India. Methyl ester reference standard 37% FAME mixture containing methyl oleate, methyl linoleate, methyl palmitate, methyl stearate of purity > 99% was purchased from SUPELCO, India. Deionized water was obtained from the Arium 611 DI ultra-pure water system (Sartorius A.G., Gottingen, Germany).

2.2. Precursor analysis

Proximate analysis estimates the moisture content, volatile matter, ash content and fixed carbon (weight%) either on dry or wet basis. Proximate analysis of flamboyant pods was conducted following standard biomass analytical procedures suggested by the National Renewable Energy Laboratory (NREL) [30]. Thermo gravimetric analysis (TGA) of biomass was also carried out to study mass loss of biomass with respect to time and temperature. From the results of TGA analysis carbonization temperature of chosen biomass was estimated and further carbonization had been carried out at the same temperature [28]. The pH of raw biomass and carbonized char was also estimated to check if it will alter the pH of the solution in which it is added. Several other properties like water soluble and methanol solubles were also estimated.

2.3. Catalyst preparation

Initially, collected flamboyant pods were sun dried for 10 days. It was then properly cleaned with distilled water to remove fines and dirt and dried in hot air oven at 105 °C for 24 h. Dried sample was ground to reduce the size in the range of 300–450 μm. Sized particles were put into a horizontal cylindrical shelled muffle furnace (CSMF136Z, N.R. Enterprise, Kolkata, India) and heated at the rate of 10 °C min^{-1} from ambient temperature to 500 °C in the inert environment created by continuous of flow of nitrogen gas to maintain the homogeneity in the furnace. Then it was kept at this temperature for 1.5 h. After carbonization char was exposed to superheated steam at pressure of 1.5–2.0 kg/cm^2 for surface modification and activation purpose. Physical activation process was optimized using the central composite design approach in response surface methodology to study the effect of activation time and activation temperature on surface area and pore volume. 10 g of carbonized char was taken for each run to study the activation process with the continuous supply of superheated steam for