Investigation of carbon-based solid acid catalyst from *Jatropha curcas* biomass in biodiesel production

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ARTICLE INFO

ABSTRACT

In this study, a carbon-based solid acid catalyst was prepared using the de-oiled *Jatropha curcas* (JC) seed cake waste. The catalyst was consequently used to esterify the JC oil in order to lower the high free fatty acid content (FFA) to an acceptable level (<4 mg KOH g^{-1}) for biodiesel production. The chemical and physical properties of the catalyst were characterized using a variety of techniques. The conversion of FFA reached 99.13% under optimum conditions of 12:1 methanol/oil molar ratio, 7.5 wt% catalyst loading, 60 min reaction time and 60 °C reaction temperature at 350 rpm. The catalyst was also determined to outperform the conventionally used sulfuric acid catalyst in terms of reaction time needed to achieve the highest conversion yield. The high catalytic ability of the catalyst was associated with the high acid site density formed in the catalyst which was due to the high porosity and large pore size of the carbon framework of the catalyst. The hydrophobic nature of the catalyst also contributed to the stability of the catalyst in which it can be re-used up until the 4th cycle. The recyclability of the catalyst and its cheap feedstock makes the overall process much simpler, cost-efficient and environment-friendly.

1. Introduction

Over the years, instabilities in fuel prices, depleting fuel reserves and increase in environmental concerns brought upon by usage of fossil based fuel has increased the urgency of finding a new energy source that is not only more sustainable, but also safer for the environment [1]. In response, biodiesel has been recommended as the best replacement for diesel fuel. Biodiesel is a mixture of long-chain alkyl esters produced from organic materials (edible, non-edible, waste frying oil, animal fats and algae biomass) via transesterification reaction in the presence of a catalyst (acidic, basic or enzymatic) [2]. Biodiesel has a cleaner production process, sustainable, biodegradable and can be readily utilized in engines without any alterations. Exhaust fumes from biodiesel is also less toxic and thus results in less pollutants released into the environment [3,4].

Besides several other factors affecting the sustainability of the biodiesel production process, choice of feedstock and catalyst used play the most prominent role to the whole process. Currently, more than 95% of feedstock used for biodiesel production is from edible agricultural crops that lead to increased production cost and negatively affect the food supply market [5]. With that, a non-agricultural, inedible and sustainable feedstock such as *Jatropha curcas* (JC) seed oil was proposed in order to curb this problem. The JC plant is drought resistant and can be grown under harsh conditions. It has high seed productivity that is toxic for human consumption and the seeds has high oil content that is deemed highly suitable as feedstock for biodiesel production [6,7]. The oil content used to produce biodiesel generally makes up 40 wt% of the JC seeds [8], and given the high volume of JC crude oil extracted for biodiesel production process, a substantial amount of seed cake waste is generated. Hence, an effective use of the JC seed cake is due in order to expand the value of JC in biodiesel production [9], also to reduce biomass waste and to facilitate energy security by renewable resources [10]. Therefore in this study, the JC seed cake is projected to be converted into a carbon-based acid catalyst used in the esterification of JC oil.

For the case of JC oil that has a high free fatty acid content (FFA) that exceeds the acceptable value (<4 mg KOH g^{-1}) for direct transesterification into biodiesel, a carbon-based acid catalyst can aid in the esterification of the oil prior to transesterification into biodiesel [11].

Compared to the usage of conventional acid catalyst such as sulfuric acid and hydrochloric acid, the carbon-based acid catalyst does not incur formation of emulsions or saponification [12] that

subsequently lead to a complicated, costly and energy consuming product separation and purification process that also produces high chemical waste that is detrimental to the environment [13]. All of these complications can be overcome by the usage of a solid carbon-based acid catalyst instead that requires no extensive washing step, simplifying the overall process and reduces the chemical waste production while maintaining the production of high quality biodiesel. Cost of production is further reduced as the catalyst can be reused for multiple cycles [14,15]. Although there had been other heterogeneous acid catalysts developed to overcome these problems, most of them had centred around costly, metal-based catalysts such as sulphated zirconia, zeolites, ion-exchange resins and mixed oxides that require more intensive reaction conditions [16], showed poor reusability and were non-decomposable, all of which resulted in a more complicated and higher cost of biodiesel production [17,18].

Hence, the carbon-based catalyst is gaining attention owing to its low material cost, high sustainability, high surface area, high porosity and thermal stability, all of which attributes to an effective heterogeneous catalyst [19]. With the increased recognition of JC oil as a feasible biodiesel feedstock, a research into the utilization of the resulting seed cake as a carbon-based acid catalyst can be beneficial as it makes the whole process more "green", addresses the waste discarding concerns [4] and allows for maximum utilization of the JC feedstock potential, indirectly increasing the sustainability of JC as biodiesel feedstock itself.

In this study, a carbon-based acid catalyst was prepared from the de-oiled seed cake waste of JC to be used as catalyst in the esterification of crude *Jatropha curcas* oil in order to lower the high FFA content (25.4 mg KOH g^{-1}) to acceptable levels (<4 mg KOH g^{-1}) for biodiesel production. The main objective of this study is to determine the characteristics of the prepared catalyst and to evaluate its effectiveness and stability as a catalyst in the esterification process.

2. Experimental

2.1. Materials

Jaropha curcas (JC) seeds were purchased from Indonesia. JC oil was extracted using soxhlet extraction method with hexane (500 mL) as solvent. The JC cake was then dried overnight. Other chemicals and solvents including hexane, sulfuric acid and methanol were of analytical grade and purchased from Merck Sdn. Bhd., a local supplier in Malaysia.

2.2. Catalyst preparation

De-oiled JC seeds were collected and dried for 24 h to remove all traces of moisture before being crushed into powder form. Weight changes of the carbon precursor was determined by Thermo Gravimetric Differential Thermal Analyzer (TGA/SDTA851^e), heated from 30 to 630 °C at a rate of 10 °C/min under a flow of N$_2$ (flow rate 40 mL/min) to determine the suitable carbonization temperature. The powdered JC seed cake was then carbonized at the designated temperature for 4 h. The product carbon powder was then characterized and analyzed.

10 g of the carbon produced was then sulphated with concentrated sulfuric acid (H$_2$SO$_4$) (80 mL, 99%), heated at 90 °C for 5 h under constant stirring [20]. The sulphated mixture was then filtered and washed with 2 L distilled water and 200 mL of hexane. The catalyst was then dried overnight to allow excess chemical to evaporate before being dried in the furnace again at 110 °C for 3 h to remove any remaining moisture.

2.3. Catalyst characterization

In order to investigate the physical and chemical properties of the catalyst, the carbon precursor and the prepared catalyst were characterized using a number of varying methods. The structure of the carbon precursor and the prepared carbon-based solid acid catalyst were evaluated and characterized by Surface Area Analysis (BET) via the nitrogen adsorption-desorption instrument, Micrometrics Tristar II 3020 instrument. Prior to analysis, the samples were desorbed in vacuum at 150 °C until static pressure remained less 6.6 × 10 Pa before carrying out the N$_2$ adsorption at −196 °C. Then, surface area, average pore diameter and pore volume were calculated by Brunauer-Emmet-Teller (BET) equation and Barrett-Joyner-Halenda (BJH) model respectively [21]. The Field Emission Scanning Electron Microscopy (FESEM) was conducted simultaneously with the Energy-Dispersive X-ray Spectrometry (EDX) testing to determine the components of the catalyst using FESEM/EDS system PEGASUS APEX 4 (Ametek/EDAX), Electron Optics.

The presence and types of acid sites in the catalyst was determined by observing the catalyst framework vibration through Fourier Transform Infrared Spectroscopy (FTIR) with spectrum of 400–3900 cm^{-1} with resolution of 4 cm^{-1} and 16 scans per spectrum and Temperature Programmed Desorption (TPD-NH$_3$) respectively using Quantachrome equipment (Model ChemBET 3000, Quantachrome Corporation). The sample was activated at 400 °C in H$_2$ flow for 2 h (heating rate 10 °C/min). The sample was then cooled to 100 °C in He flow. At this point, 0.1% NH$_3$ in N$_2$ was passed through the sample for 1 h followed by cooling to room temperature in He flow. TPD was carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} with He flow rate of 35 mL min^{-1}.

Total acidity of the catalyst was determined using the titration method [22], whereby 0.1 g of sample was added to 20 mL of sodium bicarbonate solution (0.05 M) and stirred for 24 h at room temperature. Subsequently the mixture was filtered and each 5 mL of the filtrate was titrated using hydrochloric acid (0.1 M).

2.4. Reaction study

Esterification of JC oil was conducted using a 500 mL three-necked round bottomed flask with attached refluxing condenser, thermometer and a magnetic stirrer. The flask was immersed in an oil bath heated to a stable temperature. The esterification process used 2.5–10 wt% catalyst loading while the methanol to oil molar ratio was varied from 6:1 to 18:1. The reaction time was also monitored from 30 to 120 min and the reaction was carried out at varying temperature from 45 to 70 °C. After each reaction, the samples were filtered using a vacuum pump to separate the catalyst, methanol evaporated and the product analyzed for acid value (A. V.) [23]. The conversion rate was calculated using the following formula:

$$\text{Conversion rate} (\%) : \ (\text{Initial A.V.} - \text{Final A.V.})/\text{Initial A.V.} \times 100\% \tag{1}$$

2.5. Leaching and reusability study

After esterification, the catalyst was collected and thoroughly washed with hot distilled water (80 °C) and hexane before being dried at 110 °C for 3 h. The catalyst was then re-used to catalyze the esterification process on multiple cycles under the optimum parameters obtained from the study (12:1 methanol/oil ratio, 7.5 wt% catalyst, 60 °C, 60 min, 350 rpm). After each cycle, the esterified oil was tested for acid value and ester conversion yield was calculated to determine the catalyst effectiveness. The filtered