Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Sucrose-derived catalytic biodiesel synthesis from low cost palm fatty acid distillate

Kok Leong Theam[a,b], Aminul Islam[a,b], Hwei Voon Lee[a], Yun Hin Taufiq-Yap[a,b,*]

[a] Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

ARTICLE INFO

Article history:
Received 5 January 2015
Received in revised form 20 February 2015
Accepted 23 February 2015
Available online 1 March 2015

Keywords:
Biodiesel
Palm fatty acid distillate
Solid acid carbon
TPD-NH_3
Response surface methodology
Ball milling

ABSTRACT

The current homogeneous acid catalyst for biodiesel product however, would lead to formation of many undesirable by-products that make the post treatment of the biodiesel to be difficult and costly. Thus, sucrose-derived solid acid catalyst was developed in the present study which aims to improve the esterification process and reduce the generation of waste. The physicochemical properties of the synthesized catalysts were studied by various techniques such as, BET surface area, X-ray diffraction (XRD), temperature programmed desorption of NH_3 (TPD-NH_3), scanning electron microscopy (SEM). Response surface methodology (RSM) with central composite design (CCD) is used to determine the optimum parameters for the catalytic reaction. The experimental results showed that the catalyst exhibited good catalytic activity in the transesterification of PFAD, providing maximum biodiesel yield of 94% at optimum parameters. The better catalytic activity of the aforementioned catalyst in the biodiesel reaction could be attributed to the presence of optimal number of catalytically active acid site density on its surface.

1. Introduction

The increasing awareness of the depletion of fossil fuel resources and greenhouse gas emissions of fossil fuel combustion have become the main concern of many countries all around the world. Many researchers have started to utilize lipids from biomass to supply power usage as the gradual increases in the price of petroleum, limited resources of fossil oils and environmental concerns (Islam et al., 2013a). Biodiesel is defined as non-petroleum-based diesel fuel which is derived from the fats and oils of biomass and used as combusting fuel to generate power in ordinary diesel engines (Islam et al., 2014). The animal fats and vegetable oils belong to lipids which are the essential products of metabolism of living things, functioning as energy storage. Yet, there are many problems dealt with using the creature lipids in diesel engines, such as the large molecular size of triglycerides, high viscosity and low combustion efficiency. All of these can be solved if the oils and fats are chemically modified to biodiesel which has the similar properties with petroleum-based diesel (Shajaratun Nur et al., 2014). Many refined virgin vegetable oils, such as palm, canola, soybean and corn, have been used to produce biodiesel in industries to be petroleum diesel substitute. Due to the high cost of the refined oils, non-edible oils also become a promising alternative of biodiesel production feedstock. Palm fatty acid distillate (PFAD) is an inedible side product from physical refining of crude palm oil, and it can be a good alternative feedstock for biodiesel production.

The main fatty acid components in PFAD included palmitic acid (C16:0), oleic acid (C18:1), linoleic acid (C18:2), lauric acid

* Corresponding author at: Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia. Tel.: +60 3 89466809; fax: +60 3 89466758.
E-mail address: taufiq@upm.edu.my (Y.H. Taufiq-Yap).
http://dx.doi.org/10.1016/j.psep.2015.02.017

Table 1 – Fatty acid composition of PFAD.

Fatty acid	Composition (%)
Myristic acid (C14:0)	1.06
Palmitic acid (C16:0)	47.78
Palmitoleic acid (C16:1)	0.27
Stearic acid (C18:0)	4.10
Oleic acid (C18:1)	36.67
Linoleic acid (C18:2)	9.03
Arachidic acid (C20:0)	0.28
Nervonic acid (C24:1)	0.81

(C12:0), and myristic acid (C14:0) (Aranda et al., 2008). Esterification of fatty acid with methanol or ethanol with the addition of catalyst will produce fatty acid methyl ester (FAME) and water (Aranda et al., 2008). The reaction can be described as following equation:

$$\underset{\text{Fatty Acid}}{R_1-COOH} + \underset{\text{Alcohol}}{ROH} \rightleftarrows \underset{\text{Ester}}{R_1-COOR} + \underset{\text{Water}}{H_2O} \quad (1)$$

There are many problems associated with the use of H_2SO_4 due to its corrosive properties, consumed as unrecyclable catalyst and post treatment (neutralization) (Shu et al., 2010). Recently, starch-derived solid acid catalysts have gained focus from many researchers as it would be a suitable catalyst for esterification or biodiesel production from oil-based feedstocks due to its comparable catalytic activity with the homogeneous catalyst (Nakajima et al., 2008). Partial carbonation of starch and sugar yields in a rigid carbon material comprised of polycyclic aromatic carbon sheets. The amorphous carbon material can incorporate many hydrophilic groups (COOH, OH) which enable the good entry of reactants to the active sites *i.e.* SO_3H in the sugar-derived solid acid catalyst (Nakajima et al., 2008). However, the small surface area (<2 $m^2\,g^{-1}$) of the catalysts might influence its catalytic performance. Mechanochemical treatment is an effective method for the modification of the defect structure and the electronic properties of catalytic materials (Su et al., 2001). Furthermore, most efficient mechanochemistry of solid materials can be achieved in planetary ball mills. The advantage of this type of ball mill is not only that high impact energy can be obtained but also high impact frequency, which shortens the duration of the mechanochemical process. The mechanochemical treatment initially leads repeated fracture of the solid, reducing its particles' size and corresponding increase of the specific surface area. Moreover, improvements in the catalytic performance of ball-milled catalysts have been reported (Zazhigalov et al., 1997). Hence, the aim of this research is to investigate the physicochemical properties of sucrose-derived carbon solid acid catalyst and its catalytic performance.

2. Experimental

2.1. *Chemicals*

The PFAD feedstock was obtained from PGEO Edible Oils Sdn. Bhd. Its composition was determined by using Gas Chromatography technique (GC-FID) in order to obtain appropriate molecular weight of the feedstock. As the feedstock, palm fatty acid distillate (PFAD) will have various fatty acid compositions. There are several main components of PFAD as shown in Table 1. Methyl ester standards were purchased from Supelco, USA. Analytical grade methanol and HPLC grade hexane (99.9%) were purchased from Fisher scientific, UK.

2.2. *Preparation of ball-milled sucrose-derived carbon solid acid catalyst*

Sucrose was used as the starting material to prepare the incomplete carbonized material (*i.e.* the precursor of the carbon solid acid catalyst). The starting material was carbonized in the flow of nitrogen gas at 673 K for 2 h. The resultant baked solid was ground into fine powder before the mechanochemical treatment. Mechanochemical treatments of the precursor were carried out by using a *vario-planetary* ball mill (model Pulverisette 4 from Fritsch) with an agate bowl having 250 mL volume together with 50 agate balls (diameter = 10 mm). About 20 g of the precursor and 120 mL of ethanol as milling medium were put together inside the bowl. The ball milling process was performed at the speed of 1400 rpm for 1 h. Once the milling procedure was completed, the milled precursor was recovered by oven-dried at 373 K to remove the solvent. The ball-milled precursor was mixed with concentrated sulphuric acid (98%) in a ratio of 10 mL H_2SO_4/1 g of precursor. The mixture was then heated to 423 K and the sulfonation was performed for 15 h in the flow of nitrogen gas. The reaction mixture was diluted, filtered and washed with hot water until the pH of filtrate was close to pH 7 [20–24, 28, 34, 35]. The solid was dried at 393 K for 12 h and the catalyst was denoted as S400 M. Besides, the non-ball-milled catalyst was denoted as S400.

2.3. *Catalysts characterization*

The X-ray diffraction (XRD) analyses were carried out using Shimadzu diffractometer model XRD-6000 employing CuKα radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. Scanning electron microscopy (SEM) analyses were carried out using a JSM-6701F Field Emission electron microscope. The total surface area of the catalyst was measured by Brunauer–Emmett–Teller (BET) method and pore size distribution was calculated *via* Barrett–Joyner–Halenda (BJH) method by using nitrogen adsorption–desorption at 77 K. This was done by using a Quantachrome AS1Win instrument. Acidity of the solid acid catalyst was determined by temperature programmed desorption of ammonia (TPD-NH_3) using a ThermoFinnigan TPD/R/O 1100 apparatus utilising a thermal conductivity detector (TCD) coupled with mass spectrometer.

2.4. *Trends study of synthesis of biodiesel*

The variables used for reaction temperature were 50, 60, 70, 80 and 90 °C. The studied points for reaction duration were 30, 60, 90, 120, 150 and 180 min. The investigation for the effect of catalyst concentration was started from 0.5% until 6%. For molar ratio, the methanol to PFAD ratio were 2.5:1, 5:1, 10:1, 15:1 and 20:1.

2.5. *Response surface methodology (RSM)*

After various sets of parameters were done and tested, a suitable range of parameters were introduced into Design Expert 8.0.7 software which RSM with Central Composite Design (CCD) were utilized to obtain the optimized conditions.