



Contents lists available at ScienceDirect

Energy

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

Oil palm trunk and sugarcane bagasse derived heterogeneous acid catalysts for production of fatty acid methyl esters

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ARTICLE INFO

Article history:

Received 20 August 2013

Received in revised form

2 April 2014

Accepted 9 April 2014

Available online xxx

Keywords:

Oil palm trunk

Sugarcane bagasse

Heterogeneous acid catalysts

Phosphotungstic acid impregnation

Completely randomized design

Biodiesel

ABSTRACT

In this study, new catalysts were prepared from oil palm trunk (OPT) and sugarcane bagasse (SCB), which are available in enormous quantities. Effect of carbonization time with statistical validation, effect of reaction variables such as catalyst loading, methanol molar ratio, reaction time, alcohol selectivity, effect of grafting Keggin anions onto the multifunctional catalyst and composition of the biomasses were investigated. Under optimum conditions, the OPT and SCB catalysts afforded 88.8% and 96% yield of methyl palmitate, respectively. From statistical analysis, *P*-value (prob. > *F*) for OPT indicates that difference between the means of different carbonizations is not significant, but it is significant for SCB 4 h and 8 h carbonizations. In synthesis of ethyl palmitate and butyl palmitate, OPT catalyst gave FAME yield of 86.7% and 88% respectively, while SCB catalyst gave 90.7% and 91.6%, respectively. Grafting of Keggin anions by incipient wetness impregnation resulted in 3.6% increase in FAME yield, which shows that very few active sites consisting of Keggin anions and lacunary Keggin anions have been introduced. The catalysts are recyclable, and showed only 10.5–12.5% loss in activity after six cycles of repeated use. The catalysts are highly suitable for biodiesel production.

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1. Introduction

In recent years, there has been an enormous increase in global demand for energy due to industrial development and population growth. Fossil fuels are non-renewable and are limited in supply, thus could be depleted. The rates of production and consumption point to a future energy crisis. Combustion of fossil fuels releases carbon dioxide, the number one greenhouse gas contributing to global warming. This has become the driver of the search for renewable and environmental-friendly alternative energy resources [1]. Biodiesel has received greatest attention due to its special qualities- it is renewable, biodegradable and non-toxic with favourable energy balance, cleaner combustion emission profile, higher flash point and reduced fire-risk [2]. In spite of the advantages over the conventional diesel, the high cost of biodiesel production is a major challenge [3]. The use of alternative low-cost feedstocks such as inedible oils, waste oils, animal fat and restaurant grease is also limited by their high water and free fatty acid

contents which are inappropriate for alkali catalyzed conversion of these feedstocks to biodiesel [4].

In general, unrefined feedstocks require pre-esterification of free fatty acids contaminant prior to the base-catalyzed transesterification process and sulphuric acid has been widely used for this purpose. However, its use is limited by the downstream catalyst neutralization and separation processes which add to production costs [5] and also generates large sulphate waste [6]. The search for more appropriate catalysts that can replace the homogeneous Bronsted acids resulted in the development of a number of heterogeneous acid catalysts that are either limited by their cost or activity. The low activity and stability of commercial solid acid catalysts such as the strong solid acids (Niobic acid and H-mordenite) [7] and the strong ion-exchange resins (Amberlyst-15 and Nafion-NR50) [8] are constraints to their industrial application.

The amorphous carbon catalyst reported by Hara et al. [9] displayed high sulfonic acid density and catalytic activity, but the process has shortcomings in relation to large scale production and safety [10]. Toda et al. [11] prepared catalysts through incomplete carbonization of D-glucose or sucrose powder which exhibited efficiency and robustness in esterification of fatty acids to methyl esters, but the SO₃H density of the catalyst was lower than that of the former. Several studies on carbon catalysts were subsequently

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reported, involving incomplete carbonization and sulfonation of sugars, starch and cellulose [5,12,13], activated carbon [14] and H₃PO₄-impregnated pulp fibres [15]. However, the catalytic activity and processing are still not sufficient to replace homogeneous Brønsted acid catalysts [10].

As used (waste) oil is increasingly becoming a significant part of biodiesel feedstock globally, development of efficient heterogeneous acid catalysts is imperative. Here in, the preparation of new catalysts from oil palm trunk and sugarcane bagasse for biodiesel production, effect of carbonization time and statistical validation, physico-chemical properties, effect of reaction variables and effect of grafting Keggin anions onto the SO₃H, COOH and OH bearing catalysts, are described.

2. Experimental

2.1. Materials

Palmitic acid was supplied by Natural Oleochemicals Ltd., Johor. Methanol (99.8%), *n*-hexane (grade GR, 99%), diethyl ether (AR 98%), acetic acid (AR, 99.8%), absolute ethanol, nitric acid and sodium hydroxide were supplied by OREC (Asia) Ltd. Heptane (99%) was supplied by R and M Chemicals, Essex, UK, sulphuric acid (96%) was purchased from J. T. Baker, USA. Methyl heptadecanoate (Fluka) and KBr (FT-IR grade) were supplied by Sigma–Aldrich. Other chemicals such as sodium carbonate, sodium hydrogen carbonate, sodium chloride, sodium chlorite (technical grade, 80%), barium chloride, phenolphthalein and phosphotungstic acid were supplied by Sigma–Aldrich.

2.2. Sampling and preparation of OPT and SCB samples for analysis

Fresh samples of oil palm trunk were collected within 48 h after the trees were felled from a private oil palm estate in Malaysia. Samples of sugarcane bagasse were collected from a restaurant that sells fresh sugarcane juice in Penang, Malaysia. Bagasse samples were collected the same day after juice extraction. Sampling and sample preparation were done according to TAPPI standard method T 257 cm-12 (TAPPI, 2012). Engineered sampling plan was adopted for samples collection. Oil palm trees were divided into subdivisions, from which four subdivisions were selected using random number table and samples were taken at random from two logs per subdivision. Sugarcane bagasse sampling was done accordingly, except that each delivery to the processor was treated as a subdivision, from which two samples were selected at random. Samples were cleaned, chipped, air-dried, milled and stored in plastic airtight containers.

Holocellulose (chlorite holocellulose) was determined by acetic acid–sodium chlorite method [16]. Cellulose was determined by nitric acid–ethanol method [17,18]. Acid insoluble lignin (Klason lignin) was determined using TAPPI standard method T 222 om-02 (2002). Determination of ash content was done by combustion at 600 °C for 5 h using ASTM D1102-84(2013) Standard Test Method for ash in wood. Moisture content was determined according to TAPPI standard method T 550 om-08, while extractives were determined as described by Rowell [16]. Some samples were also cleaned, dried in the oven at 105 °C for 18 h, milled using Panasonic MX-799S blender and stored in plastic airtight containers.

2.3. Catalyst preparation

The preparation was carried out using a modification of the method described by Toda et al. [17]. Ground biomass (25 g) was subjected to incomplete carbonization in a pyrolysis machine at 400 °C under nitrogen flow, with carbonization time varied from

30 min to 8 h. The brown carbon mass obtained was ground to fine powder, mixed with 200 mL of concentrated sulphuric acid (96%) in a round bottomed flask fitted with a condenser and then heated at 150 °C for 15 h. The sulfonated carbon catalyst was precipitated in 1500 mL of deionised water and then washed several times with 100 mL of hot deionised water (preheated to 80 °C) until there was no sulphate impurity. This was monitored by adding drops of BaCl₂ solution to the filtrate. The catalyst was then filtered and dried in an oven at 105 °C for 18 h.

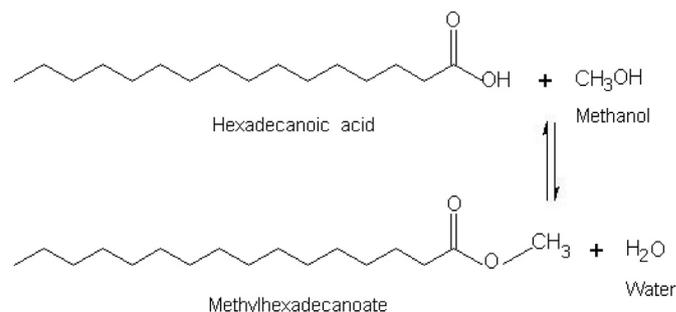
Another catalyst was prepared by supporting different amounts of Phosphotungstic acid (HPW) on sulfonated carbon using a modification of the incipient wetness impregnation described by Haber [19]. Sulfonated SCB (0.5 g) was dried in an oven at 110 °C for 6 h, added to 15 mL solutions containing 0.3, 0.5, 1.0 and 1.5 g of tungstophosphoric acid and then heated at 80 °C with stirring for 1 h. After cooling, the supported catalyst was washed with deionised water until the filtrate was neutral. It was then dried in an oven at 105 °C for 8 h and thereafter calcined at 170 °C for 30 min.

2.4. Catalyst characterization

Thermal analysis of the catalysts was performed using a Perkin Elmer thermogravimetric analyzer (TGA)/differential thermal analyzer (DTA) under nitrogen flow at a heating rate of 20 °C/min. FT-IR analysis was performed using Perkin Elmer System 2000 FT-IR, in the wavelength range of 4000–400 cm⁻¹. The XRD (X-ray diffraction) analysis was conducted with Bruker D8 Advance powder X-ray Diffractometer. Scanning electron microscopy was performed with FESEM (Carl Zeiss Leo Supra 50 VP Field Emission equipped with an Oxford INCA-X energy dispersive microanalysis system). The surface acidity of the catalysts was determined using titration method as described by Fu et al. and Wu et al. [15,20].

2.5. Catalyst evaluation in esterification reaction

Catalyst evaluation was performed by esterification of palmitic acid (hexadecanoic acid) with methanol, as illustrated in Scheme 1. Catalysts were dried at 105 °C for 1 h prior to each esterification reaction. The reaction mixture consisted of 8 mmol of palmitic acid, 144 mmol of methanol and 7 w/w % catalysts (based on the weight of palmitic acid). The esterification reactions were conducted under reflux with stirring speed of 500 rpm. Palmitic acid conversion was monitored with thin layer chromatography (TLC). Thereafter, methyl ester in aliquots withdrawn at suitable time intervals was extracted with 2 mL *n*-hexane and subsequently centrifuged to separate catalyst particles and water from the methyl ester layer. The prepared methyl ester was then dried, transferred into vials and stored in the refrigerator for GC analysis. A series of esterification reactions were performed with varying catalyst loading and



Scheme 1. Esterification of hexadecanoic (palmitic) acid with methanol.

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