Fuel Processing Technology 114 (2013) 12–20

Contents lists available at SciVerse ScienceDirect

Fuel Processing Technology

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

Single-step esterification of crude karanj (*Pongamia pinnata*) oil to fatty acid methyl esters over mesostructured SBA-16 supported 12-molybdophosphoric acid catalyst

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ARTICLE INFO

Article history:
Received 13 December 2012
Received in revised form 11 March 2013
Accepted 12 March 2013
Available online 13 April 2013

Keywords:
SBA-16
Biodiesel
Karanj oil
FAME
TOF

ABSTRACT

Fatty acid methyl esters (FAME) are synthesized via the single step esterification of non-edible feedstock, crude karanj oil (CKO), of high level of free fatty acids (FFAs about 20%) with methanol over series of solid acid catalysts prepared by anchoring molybdophosphoric acid (MP, 5 to 25 wt.%) onto SBA-16 support. The prepared catalysts were intensively characterized for their intrinsic physicochemical and textural properties using BET surface area, NH_3-TPD, XRD, SAXS, FT-IR, SEM and EDX. Characterization results revealed that the intact MP Keggin structure was preserved in the final catalyst after the thermal treatment at 220 °C. The catalyst with 15 wt.% MP (MP-S-16(15)) exhibited a peerless catalytic activity achieving 82% of FAME yield using a molar ratio of methanol to CKO of 1:8 at 140 °C and after 5 h. The effect of different operational parameters such as MP concentration in the final catalysts, reaction temperature, molar ratio of methanol to CKO, catalyst wt.% and reaction time were investigated over the MP-S-16(15) catalyst toward the maximum FAME yield. The stability of the catalytic activity was examined through leaching and reusability tests. As such, the MP-S-16(15) catalyst was recycled through four consecutive batch runs to understand its stability.

1. Introduction

The immense increase of the world energy demands, the foreseen depletion of the fossil energy sources and the growing environmental concerns to limit exhaust emissions had motivated the quest for alternative fuels that are not only cleaner, sustainable and efficient but also more affordable [1,2]. Recently, biodiesel has been categorized as a "green fuel", being the most attractive substitute to the conventional petro-diesel. It is a non-petroleum based fuel that composes of fatty acid alkyl esters synthesized through the transesterification and/or esterification reactions of triglycerides (TGs) of fatty acids (C_{12}–C_{22}) with short chain alky source (methanol, ethanol, propanol or recently dimethyl carbonate) [3,4]. The term "FAME" that refers to fatty acid methyl esters, is commonly used to describe the biodiesel produced by methanol [5,6]. Biodiesel combustion is environmentally benign, offers good storage properties, biorenewable in nature, has a higher flash point and cetane number than petro-diesel, non-aromatic and completely biodegradable (capable of being broken down into harmless products) [7–11]. These characteristics of biodiesel reduce the noxious emissions in the exhaust gas compared to petro-diesel; carbon monoxide (CO) by 46.7%, unburned hydrocarbons (UHC) by 45.2% and particulate matter (PM) by 66.7%. While, NO_x emissions have been reported to increase due to the high oxygen content of biodiesel [12,13].

Biodiesel produced from either vegetable feedstock (edible or non-edible oils) or algal oils is environmentally more benign than those obtained from exhaustible platforms, since its combustion yields an eco-friendly CO_2 to the atmosphere that can contribute to the plant photosynthesis process and result in a carbon neutral environ. Despite its desirable properties as petro-diesel alternative, the commercial scale production of biodiesel is still infeasible due to such issues as the high prices of food-grade oils, which represent more than 70% of the whole biodiesel production cost, and the processing conditions [14,15]. In addition, employing edible virgin oils such as palm, sunflower, canola, rapeseed and soybean oil in biodiesel industry can affect the world food market. Thence, utilizing such oils for biodiesel production in some developing countries with limited arable land per capita is not economic and even prohibited [15]. Recently, research interests have been expanded toward the exploration of worthy alternatives, apart from edible vegetable oils, to address the shortages of feedstock for biodiesel production and to minimize the concern of food versus fuel argumentation [8,16]. For instance, crude karanj (*Pongamia pinnata*) oil (CKO) is a high fatty acid non-edible oil that can be effectively utilized for biodiesel production [8,13].

Crude karanj oil (CKO) is extracted from the seeds of the matured pongam flowers, and has found different biocompatible applications with no adverse effects [9]. This evergreen tree is commonly available in many countries like Malaysia, India, Vietnam, Thailand, The

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http://dx.doi.org/10.1016/j.fuproc.2013.03.014

Philippines, Australia, The Seychelles, Oceania, and the USA (Florida and Hawaii) [17]. CKO is considered to be less toxic, cheaper and higher in free fatty acid (FFA) content than jatropha oil, so that it is recently introduced to the biodiesel research arena. CKO comprises more than 23% and not less than 73% of saturated and unsaturated fatty acids, respectively [13,18].

According to the literature, biodiesel production from karanj oil is performed by two approaches; first is the two-step process that involves the esterification of the FFAs via acid-catalyzed esterification followed by a base-catalyzed transesterification of TGs [19–21]; and the second is the single step esterification by strong acid catalyst that promotes both reactions at once [3,22]. Recently, Thiruvengadaravi and coworkers reported the two-step process to synthesize FAME using 1% sulfated zirconia as an acid catalyst to reduce the FFA content of karanj oil, followed by homogeneously catalyzed transesterification using KOH [21]. In general, homogeneous catalysts showed several demerits compared to the heterogeneous ones such as the difficulty of separating the catalyst from the product, cannot be regenerated and reutilized, and cannot be employed into packed bed reactor (continuous process).

Heterogeneous alkaline catalysts like zinc oxide (ZnO) [23], calcium oxide (CaO) [24], and mixed oxides ($K_y(MgCa)_{2x}O_3$) [25], have presented promising performance in FAME production via transesterification under mild reaction temperature of 65 °C [26]. However, the use of these catalysts for high FFA oils involves several drawbacks such as the soap formation as a consequence of the reaction of FFAs with the basic catalyst [27]. On the contrary, heterogeneous acid catalysts are not sensitive to FFA and capable to facilitate esterification and transesterification reactions at once [26]. It is an established fact that the esterification reaction of carboxylic acids with alcohol is an exothermic acid catalyzed process. As such, conventional acids like H_2SO_4, H_3PO_4, HCl and BF_3 have been reported to catalyze the simultaneous esterification of FFAs and transesterification of TGs in a single catalytic step, and thereby avoiding the pre-treatment step when using low cost feedstock with high FFA content [28].

It is worthy to note that none of the reported studies emphasized on developing a heterogeneously catalyzed single step process for the synthesis of FAME using the crude oil of karanj tree. Due to their strong Brönsted acidity, Keggin type heteropolyacids (HPAs) can be effectively employed instead of conventional acid catalysts, as sulfuric acid [3,29]. Up to date, the use of HPAs functionalized on an ordered silica as efficient super acid catalysts for CKO esterification had never been reported in literature. Therefore, we report in this contribution the single step esterification of CKO with methanol over the reusable SBA-16 supported molybdophosphoric acid catalyst for the synthesis of fatty acid methyl esters (FAME).

2. Materials and methods

2.1. Materials

Crude karanj oil (CKO) was purchased from Telaga Madu Resources Ltd., Malaysia. Hydrochloric acid (~37%) was obtained from Mallinckrodt. Molybdophosphoric acid $H_3PMo_{12}O_{40}$ (MP, 99.99% purity), Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) and tetraethylorthosilicate (TEOS, 98% purity) were purchased from Sigma-Aldrich, Malaysia. HPLC grade methanol and GC-grade hexane were supplied by Merck, Germany. Except CKO, which was filtered to remove the suspended impurities, all received chemicals were used without further treatment.

2.2. Synthesis of support (SBA-16)

The synthesis of SBA-16 material was performed according to standard literature procedure [30]. The synthesis used F127 as a structure directing agent and TEOS as the silica source. In a typical preparation, 3.85 g of F127 was dissolved into 120 mL (0.2 M) HCl solution under vigorous stirring at 10 °C over controlled water bath until homogeneous. Then 9.21 mL of TEOS was added to the former gently and stirred for 20 h at the same temperature. Subsequently, the synthesis gel was aged in Teflon-flask at 100 °C for 24 h under static hydrothermal condition. The precipitated product was recovered, thoroughly washed with double distilled water, air dried at ambient temperature for 4 h and then dried in vacuum oven at 105 °C for 12 h. Finally, the solid powder was calcined (using open cup crucible) in air at 520 °C with heating rate of 1 °C/min for 6 h.

2.3. Synthesis of MP loaded onto SBA-16 catalysts

A series of catalysts with variant amounts of molybdophosphoric acid (MP, 5–25%) immobilized onto SBA-16 support was synthesized by incipient wet impregnation method. Briefly, 1 g of support was dispersed in 10 mL of ethanol/water solution (1:1) and then added to an aqueous solution of MP (1 g/100 mL of deionized water). The resulting suspension was aged at room temperature for 12 h and then evaporated at reduced pressure. The as obtained material was calcined in static air atmosphere at 220 °C for 2 h. The final catalysts were denoted as MP-S-16(x) where x refers to the theoretical MP loading percent. To this end, 1 g of SBA-16 was loaded with 0.176 g of MP to achieve 15 wt.% theoretical loading of MP and thus, 0.93 wt.% of Mo. The theoretical MP and Mo loading were calculated from the following formulae:

$$\%\mathrm{MP} = \frac{\mathrm{MPmass}}{\mathrm{MPmass} + \mathrm{SBA} - 16\mathrm{mass}} \times 100 \tag{1}$$

$$\%\mathrm{Mo} = \frac{\mathrm{MPmass} \times \mathrm{Moat.wt}}{\mathrm{MPM.wt}} \times 100 \tag{2}$$

2.4. Characterization of the catalysts

The determination of surface areas and textural characteristics of the prepared catalysts were carried out using Brunauer Emmett Teller (BET) method over Micromeritics ASAP 2020 surface area and porosity analyzer (Micromeritics Instruments Corporation, USA). X-ray diffraction (XRD) patterns of the pristine SBA-16 support and the MP-S-16(15) catalyst were acquired on Bruker D8 Focus X-ray diffractometer (Bruker, Germany) over $10° \le 2\theta \le 90°$ using Cu K_α radiation ($\lambda = 1.5406°$). Small angle X-ray scattering (SAXS) diffractograms over $0.5° \le 2\theta \le 5°$ were used to determine the structural arrangement of the synthesized materials.

FTIR spectra of the support and catalyst samples were acquired on Perkin-Elmer System 2000 spectrometer by using the standard KBr technique over the range of 1500–400 cm^{-1}. Typically, the sample (ca. 100 mg) grinded with 1 g of KBr into fine powder and loaded in stainless steel cylindrical mold was gradually pressed to 8 MPa to form the transparent disc.

The morphologies of the synthesized materials were studied by scanning electron microscopy (SEM) using a Zeiss Supra TM 35 VP scanning electron microscope (Zeiss, Jena, Germany) coupled with FEI as a source of electrons and accelerated at 300 kV. Energy-dispersive X-ray spectroscopy (EDX) was performed in conjunction with SEM to determine the catalyst surface composition.

The total amount of acidic sites of the pristine support and the so-developed MP-S-16(15) catalyst was carried out via the temperature-programmed desorption of ammonia (NH_3-TPD) using Micromeritics AutoChem 2920 II instrument. The analysis was performed by loading 50 mg of the sample into quartz reactor and drying it with continuous He flow at 400 °C for 1 h followed by a pure He purge at the same temperature for 1 h. After the sample was cooled to 100 °C by He gas flow, NH_3 adsorption was carried out by exposing the sample to NH_3–He gas mixture (90 vol.% He) and then keeping it at 100 °C for 1 h. The reactor was then degassed from the gaseous NH_3 using pure He purge allowing the accurate detection of the desorbed NH_3. The NH_3-TPD