Oil palm trunk and sugarcane bagasse derived solid acid catalysts for rapid esterification of fatty acids and moisture-assisted transesterification of oils under pseudo-infinite methanol

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HIGHLIGHTS

- Biodiesel was produced using oil palm trunk and bagasse derived catalysts.
- Pseudo-infinite methanol promoted facile access of reactants to Bronsted acid sites.
- Rapid esterification of fatty acids under pseudo-infinite methanol.
- Prolonged moisture-induced violent bumping increased rate of transesterification.
- Two-folds FAME yields in the presence of 8.3% moisture compared to neat oil.

GRAPHICAL ABSTRACT
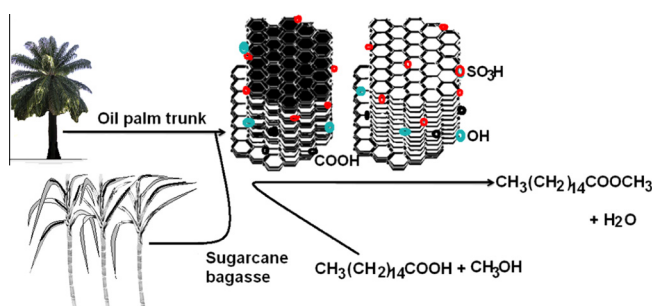
ABSTRACT

The use of pseudo-infinite methanol in increasing the rate of esterification and transesterification reactions was studied using oil palm trunk (OPT) and sugarcane bagasse (SCB) derived solid acid catalysts. The catalysts were prepared by incomplete carbonisation at 400 °C for 8 h, followed by sulfonation at 150 °C for 15 h and characterised using TGA/DTA, XRD, FT-IR, SEM–EDS, EA and titrimetric determinations of acid sites. Under optimal reaction conditions, the process demonstrated rapid esterification of palmitic acid, with FAME yields of 93% and 94% in 45 min for OPT and SCB catalysts, respectively. With the process, moisture levels up to 16.7% accelerated the conversion of low FFA oils by sulfonated carbon catalysts, through moisture-induced violent bumping. Moisture assisted transesterification of palm olein containing 1.78% FFA and 8.33% added water gave FAME yield of 90% in 10 h, which was two folds over neat oil.

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1. Introduction

Energy consumption is absolutely necessary in diverse aspects of human life and the natural hydrocarbon deposits have been exclusively exploited for over two centuries to cater to the ever-increasing demand for electricity, heating and transport fuels. The search for renewable alternative energy resources began in the past few decades because of the increasing prices of petroleum products, the diminishing global fossil fuel reserves and the untoward impacts of human activities on the environment and the biota (Motasemi and Ani, 2012). This led to the development of alternative fuels from renewable resources, amongst which biodiesel was considered as the best alternative

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fuel to petroleum-based diesel. Biodiesel can be used directly to operate normal diesel engines or as a blend with petroleum based diesel. It is biodegradable and contributes less toxic gaseous inputs into the atmosphere (Van Gerpen, 2005). It has no net carbon emission, and in comparison with petroleum based diesel, it reduces net carbon dioxide emissions by 78% on a life-cycle basis (Tyson, 2001). Besides, the emission profile of biodiesel has a reduction in the emissions of carbon monoxide (CO), particulate matter and unburned hydrocarbons in the magnitude of 46.7%, 66.7% and 45.2%, respectively (Shumaker et al., 2007). However, the unit cost of biodiesel is still higher than that of petroleum base diesel because of the higher cost of triglyceride feedstocks (Marchetti et al., 2008). This underscores the significance of feedstock cultivation and exploitation to the socio-economic stabilization of the biodiesel industry, especially, if biodiesel is to become a significant component of global energy resources.

The current global biodiesel market dependence on feedsocks cost does not undermine the importance of scientific and technological innovations to sustainable biodiesel development (Vasudevan and Briggs, 2008). In the future, the current market dependence on feedstocks cost could be annulled and bring to the fore the competitive advantage of production know-how (Sivasamy et al., 2009). The relevance of this to future biodiesel development has elicited a significant research interest in the biodiesel technologies and also in search of appropriate catalyst systems for alternative feedstocks. The low-cost feedstocks such as non-edible oils, waste frying oils and animal fat generally contain high water and free fatty acid contents (Knothe et al., 2005) which lead to soap formation during transesterification with alkali catalysts. Consequently, acid catalysts are used in converting such feedstocks into biodiesel, as acid catalysts can simultaneously catalyse esterification of the free fatty acids impurity and transesterification of the oils. The development of heterogeneous acid catalysts has attracted attention lately because of the corrosion of production facilities and the requirements for catalyst neutralisation and separation when the homogeneous Brønsted acid catalysts are used. Besides high FFA tolerance and simultaneous esterification and transesterification, the ease of catalyst separation (Sharma et al., 2011) and the potential for continuous biodiesel processing have endeared the heterogeneous acid catalysts to the biodiesel developers and researchers.

Amongst several heterogeneous acid catalysts developed, the amorphous carbon catalyst derived from inexpensive raw materials has been seen as one of the promising catalysts due to its high activity in esterification reaction, reusability and good thermal and mechanical stabilities. In efforts to improve its performance, several studies have been conducted on its preparation from sugars, starch and cellulose (Zhang et al., 2010; Hara, 2010; Chen and Fang, 2011; Jiang et al., 2011), activated carbon (Liu et al., 2010), H_3PO_4–impregnated pulp fibres (Fu et al., 2012), bio-char (Dora et al., 2012) and on structure–activity correlations (Lou et al., 2012). In all, the performance and processing of the amorphous carbon catalyst have not been sufficiently improved for it to replace the homogeneous Brønsted acid catalysts (Nakajima and Hara, 2012).

The effects of reaction variables such catalyst amount, reaction time, temperature and methanol: oil ratios have been generally studied, and found to affect the yield of methyl esters (Liu et al., 2007). While excess methanol has been exploited to optimise both esterification and transesterification reaction, as increase in methanol: oil/fatty acid ratios increases the yield of methyl esters, the use of large excess dilutes reaction mixtures thereby causing no further increases (Shu et al., 2010). In this study, further inherent properties of the amorphous carbon catalyst developed from oil palm trunk (OPT) and sugarcane bagasse (SCB) were investigated. This novel catalytic process employed infinite methanol concentration with limited contact with the reaction mixture at any given time, thereby creating a pseudo-infinite methanol condition. The methanol vapour was expected to continuously alter the reaction milieu and the effects of the recalcitrant moisture in esterification and transesterification reactions.

2. Methods

2.1. Materials

Oil palm trunk (OPT) sample was sourced from Perak Oil Palm Estate, Malaysia, while sugarcane bagasse (SCB) was sourced from a local sugarcane processor in Sungai Dua, Penang. Palmitic acid as the limiting reactant was supplied by Natural Oleochemicals Ltd., Johor, while sulphuric acid (95–97%), methanol (99.8%), n-hexane (grade GR, 99%), diethyl ether (AR 98%), acetic acid (AR, 99.8%) and sodium hydroxide were purchased from OREC (Asia) Ltd. Heptane (99%) was purchased from R and M Chemicals, Essex, UK. Methyl heptadecanoate (Fluka), KBr (FT-IR grade) and other chemicals including sodium carbonate, sodium hydrogen carbonate, sodium chloride, barium chloride, methyl orange and phenolphthalein were supplied by Sigma Aldrich.

2.2. Catalyst preparation

Catalyst was prepared by modifying the method described by Toda et al. (2005). Ground biomass (25 g) was partially carbonized at 400 °C under a continuous flow of purified nitrogen for 8 h in a pyrolysis machine and at a heating rate of 20 °C/min. The brown incompletely carbonized biomass generated was then ground in a laboratory mortar to form fine powder, which was mixed with 200 mL of concentrated sulphuric acid (95–97%) in a round bottomed flask fitted with a condenser and subsequently heated at 150 °C for 15 h under nitrogen. The sulfonated mass of carbon was poured into a 1500 mL of deionised water, stirred and allowed to settle. After settling, excess water was decanted and the precipitated catalyst was filtered and washed several times with 100 mL portions of deionised water preheated to 80 °C. Washing was monitored by the addition of drops of $BaCl_2$ solution to the filtrate until no sulphate impurity was detected. The catalyst was then filtered and dried in an oven at 105 °C for 18 h.

2.3. Catalyst characterisation

The thermal degradation profiles of the catalysts were determined using Perkin Elmer thermogravimetric analyzer (TGA)/differential thermal analyzer (DTA), under nitrogen flow and a heating rate of 20 °C/min. The FT-IR spectra of the catalysts were obtained using Perkin Elmer FT-NIR Spectrometer Frontier/Perkin Elmer System 2000 FT-IR in the wavelength range of 4000–650 and 4000–400 cm^{-1}, respectively. The XRD analysis was performed with Bruker D8 advance powder X-ray diffractometer. Scanning electron microscopy was conducted using FESEM (Carl Zeiss Leo Supra 50 VP Field Emission) attached to an Oxford INCA-X energy dispersive microanalysis system. The Brauner–Emmet–Teller (BET) specific surface area and Barrett–Joyner–Halenda (BJH) pore size distribution of the catalysts were determined by N_2 adsorption using Micromeritics ASAP 2020. Elemental analysis was performed using Perkin Elmer 2400 CHNS analyzer (EA). As every sulfur atom present in the catalyst exists as $-SO_3H$, the sulfur content obtained from the analysis was used for calculating the sulfonic acid density as done in all studies. The total acid density was determined by ion exchange of the catalyst proton by Na$^+$ in aqueous NaOH solution as described in literature (Liu et al., 2010). The details of total acid density determination are described below. A known mass of catalyst (0.0500 g) was added to 50 mL of standardised 0.01 M NaOH