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Synthesis of Oil Palm Empty Fruit Bunch (EFB) Derived Solid Acid Catalyst for Esterification of Waste Cooking Oils

(Sintesis Mangkin Asid Pepejal daripada Tandan Buah Kosong (EFB) Kelapa Sawit untuk Pengesteran Sisa Minyak Masak)

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ABSTRACT

Oil palm empty fruit bunch (EFB) contributes to a large quantity of lignocellulosic waste. It is an abundantly available waste biomass in Malaysia. This project was aimed to utilize the waste materials for a better benefit. EFB were used as raw material to prepare a new solid catalyst for biodiesel production. Solid acid catalyst derived from EFB was used to catalyze the esterification process in biodiesel production from waste cooking oil. Solid acid catalyst was prepared by direct impregnation with transition metal sulfides, $Fe_2(SO_4)_3$. This new catalyst was used to catalyze the esterification of high free fatty acid (FFA) value oil, e.g. waste cooking oils (WCOs) as pre-treatment step prior to biodiesel production. The highest catalytic activity with 90.95% esterification rate was achieved. The catalyst can be easily separated for reuse compared to homogenous catalyst which are used in biodiesel production. EFB has the potential to be converted into useful feedstock and the derived catalyst can replace the traditional liquid acid catalyst in biodiesel production especially for high acid value content feedstock.

Keywords: Acid value; catalyst; esterification; oil palm empty fruit bunch; solid acid catalyst

ABSTRAK

Tandan kosong kelapa sawit (EFB) telah menyumbang sisa lignosellulosik dalam kuantiti yang banyak di Malaysia. Objektif penyelidikan ini adalah untuk mempergunakan bahan buangan tersebut untuk faedah yang lebih baik. EFB telah digunakan sebagai bahan mentah untuk menyediakan mangkin pepejal baru dalam penghasilan biodiesel. Mangkin asid pepejal yang diperoleh daripada EFB telah digunakan untuk memangkinkan proses pengesteran dalam penghasilan biodiesel daripada sisa minyak masak. Mangkin asid pepejal telah disediakan melalui impregnasi terus dengan sulfida logam peralihan $Fe_2(SO_4)_3$. Mangkin baru ini telah digunakan untuk memangkinkan pengesteran minyak bebas asid lemak berkualiti tinggi seperti sisa minyak masak (WCO) sebagai langkah rawatan awal sebelum penghasilan biodiesel. Aktiviti mangkinan yang tinggi dengan 90.95% kadar pengesteran telah dicapai. Mangkin ini mudah dipisahkan untuk digunakan semula jika dibandingkan dengan mangkin homogen yang digunakan dalam penghasilan biodiesel. EFB berpotensi ditukar menjadi stok suapan dan mangkin yang diperoleh boleh menggantikan mangkin asid cecair tradisi dalam penghasilan biodiesel terutama untuk nilai asid tinggi kandungan stok suapan.

Kata kunci: Mangkin; mangkin asid pepejal; nilai asid; pengesteran; tandan kosong kelapa sawit

INTRODUCTION

Malaysia, being a country that actively promotes agricultural activities has abundant of biomass wastes. Oil palm is the most important agricultural crop in Malaysia, since Malaysia is one of the main palm oil producer and exporting country in the world. In year 2013, the oil palm planted area reached 5.23 million hectares of land in Malaysia (ETP 2013). Oil palm industries in Malaysia generate about 90 million tons of renewable biomass per year. Oil palm biomasses include oil palm trunks, pruned and felled fronds, shells, palm press fiber and empty fruit bunches (EFB). In 2012, Malaysia's palm oil industry produces over 83 million dry tons of solid biomass p.a. EFB as one of the biomass, is the bunch residue after removal of all the fruits and is produced as waste at the end of the palm oil extraction process. Every year, palm oil mills in Malaysia generates approximately 15 million tons of EFB. Indiscriminate disposal of these wastes will cause serious environmental problems. The traditional methods such as composting and incineration are not suitable to process these organic solid wastes, whereas the nitrogen content of EFB is too low for composting, incineration and the smoke evolved would cause serious environmental pollution by volatiles and dust particles. In contrast, EFB is a suitable and potential renewable biomass material for the conversion into other valuable product because it is locally abundant and rich in lignocellulosic components (Pua et al. 2013; Zakaria et al. 2013).

Recently, attention has been drawn to produce solid catalyst for replacing liquid catalysts especially in the biodiesel industry. The solid acid catalyst derived from the abundant EFB fibers could be a potential application for

this industry. A good catalytic performance can promise for catalyst recyclability and reuse during the reaction. Synthesis and applications of solid acid catalysts to replace liquid acid catalysts has gained wide attention. In recent year, the sulfonation of incompletely carbonized polymer and carbon material to produce carbon-based solid acid catalysts has also been studied (Suganuma et al. 2008). A number of studies have investigated the uses of solid acid catalysts in biodiesel production. A good solid acid catalyst for biodiesel production should be low cost, high stability and larger pores (Deng et al. 2011; Guo et al. 2011). However, no report to our best knowledge was found for EFB derived mesoporous catalyst in biodiesel production. Only high cost carbohydrate-based biomass (e.g. starch & glucose) was used as raw material to make solid acid catalyst and showed high catalytic activity for biodiesel production from low-qualified oils with high FFAs (Chen & Fang 2011; Lou et al. 2008).

Traditionally, the production of biodiesel can be catalyzed by basic or acidic catalysts such as NaOH, KOH, $NaOCH_3$ or sulfuric acid, sulfonic acid or phosphoric acid (Lu et al. 2009; Tiwari et al. 2007; Yee et al. 2011). However, those liquid catalysts have been facing several problems at the end of reactions. First, the difficulty of removing catalyst from wastewater, corrosiveness of acidic catalysts, sulphur contamination in biodiesel product and the formation of soap (Guo et al. 2011; Shu et al. 2010). In contrast, a solid acid catalyst gives significant benefits on eliminating separation, reasonable and gets to possess a high activity for various reactions under mild conditions. Besides, they were able to replace homogeneous base catalysts in order to minimize the production of pollutants and overcome the disadvantages brought by conventional liquid acid catalysts (Deng et al. 2011).

In this paper, waste by product from palm oil industry, oil pam empty fruit bunch (EFB) was converted into a solid acid catalyst via a direct impregnation with transition metal sulfide, $Fe_2(SO_4)_3$ (20 wt. %). The morphology and surface chemistry for the solid acid catalyst were characterized by SEM-EDX and FTIR. Catalytic performance of the catalyst was studied via esterification of waste cooking oils. The new solid acid catalyst was used to esterify the high acid value waste cooking oils which were collected from a café in Universiti Tenaga Nasional (UNITEN). The results showed that 1% of the solid acid catalyst loading has achieved a good conversion rate which 90.95% at a reaction temperature of 65°C and reaction time of 60 min. The results and findings in the present work offer a potential alternative for environmentally friendly choice of catalyst in the biodiesel industry.

Experimental Details

Methods

Waste oil palm empty fruit bunch (EFB) fibers were pre-treated with sodium hydroxide to remove the wax layer and impurities on the surface of fibers. 10 g oven-dried EFB powder was directly impregnated with $Fe_2(SO_4)_3$ (20 wt. %). The impregnation reaction was carried out at room temperature for 60 min. The impregnated sample was then oven dried at 105°C for 24 h.

The derived solid acid catalyst was used for esterification of high acid value oil, e.g. waste cooking oils (WCOs). WCOs, methanol and catalyst were loaded together and the experiment was carried out at 65°C for 60 min. After the reaction, the catalyst was separated from the mixture and methanol was evaporated. The mixture was then cooled to room temperature. The solid acid catalyst was washed with n-butanol and oven-dried for recycling purpose.

KOH titration process was carried out to calculate the acid value of the esterified product. The acid value of WCO was calculated based on (1). The titration step was repeated thrice to obtain an average reading and was recorded. Acid value of the esterified products from waste cooking oils was measured using KOH titration method and the esterification rate was calculated as (2) (Pua et al. 2011; Wang et al. 2014).

$$\text{Acid value} = (56.1 \times \text{Concentration of KOH} \times \text{Volume used}) / (\text{Weight of sample}). \quad (1)$$

$$\text{Esterification rate} = ((AV_0 - AV_N) / AV0) \times 100\%, \quad (2)$$

where AV_0 is the initial acid value of waste cooking oils; and AV_N is the instant acid value for waste cooking oils.

Alkaline treated EFB fibres were analyzed using *FT-IR/FT-NIR MSM-FTI-005* in CRIM, Universiti Kebangsaan Malaysia. KBr pellets were used to obtain the FTIR spectra. Scanning Electron Microscope (SEM) analysis, was performed using *Hitachi SU1510* (Figure 4) at QUASI, (UKM) to examine the surface morphology of EFB and catalyst. Energy dispersive X-ray (EDX) was used to examine the elements on the surface of catalyst.

Results and Discussion

Catalyst Characterization

The surface morphology of the EFBs and solid acid catalyst were studied by scanning electron microscope (SEM-Hitachi SU1510). Figure 1 shows the morphology of treated EFB powder and solid acid catalyst. According to Baharuddin et al. (2013), the white granules are silica bodies which are known as phytoliths and they are embedded on the surface of EFB fibres. Figure 2 shows the morphology of solid acid catalyst under a magnification of 8000× and it shows that the shape structure of $Fe_2(SO_4)_3$ particles appeared in cubic shape and is arranged vertically on the EFB porous surface.

The energy-dispersive x-ray spectrometry (EDX) result attribute to the impregnation of sulfur groups on the surface of catalyst. Sulfur element on EFB fibre surface

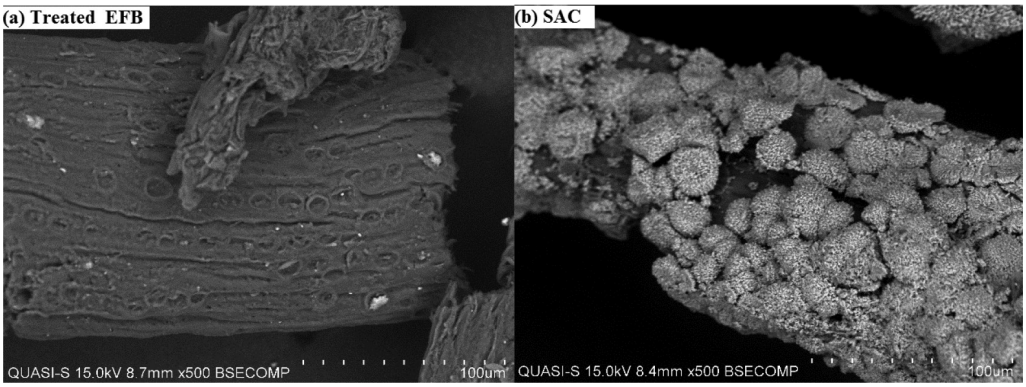

FIGURE 1. SEM images of (a) SAC and (b) treated EFB under magnification of 500×

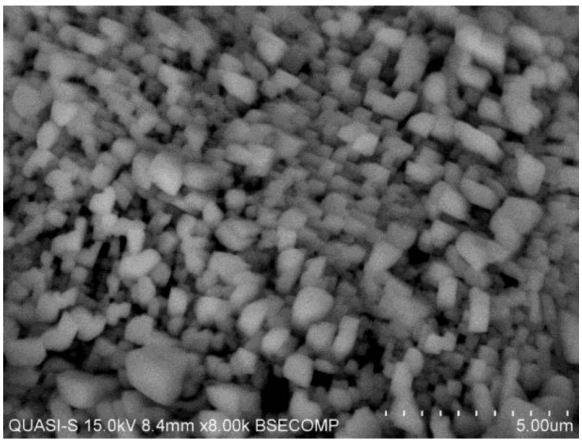

FIGURE 2. SEM image of SAC under magnification of 8000×

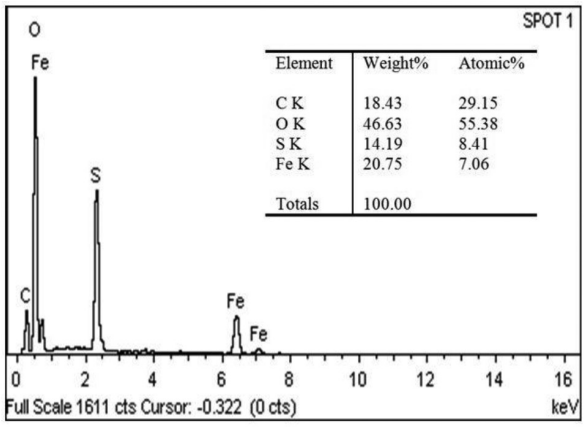

FIGURE 3. EDX analysis of SAC

is at a weight percentage and atomic percentage of 14.19 and 8.41, respectively, as well as iron (Fe) at a weight percentage and atomic percentage of 20.75 and 7.06, respectively, as shown in Figure 3.

FT-IR ANALYSIS

Figure 4 shows the FT-IR spectra for treated EFB and solid acid catalyst. A significant peak in SAC sample at 808 cm^{-1} indicates the strong presence of sulfonates group with the bond of S-O stretch. The strong presence of sulfonates group in SAC was due to impregnation of $Fe_2(SO_4)_3$. According to previous study (Ariza et al. 2002), the characteristics peak in the region 900-1300 cm^{-1}, 500-680 cm^{-1} and peak centered at 885 cm^{-1} are the characteristic peaks of H_2SO_4 and H_2O_4 ions, such as SO_4^{2-} and other sulfate ions.

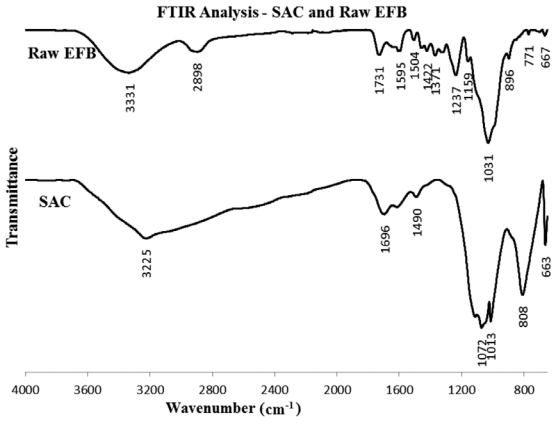

FIGURE 4. FTIR analysis graph of SAC and raw EFB

ESTERIFICATION OF WASTE COOKING OILS

The efficiency of the catalyst on acid value reduction was examined by esterification reaction on high acid value oils. Based on literature review, waste cooking oils are one of the high acid value feedstock in the biodiesel industry (Amin et al. 2013; Veera & Georgene 2013). Effect of catalyst loading was studied and 1% catalyst loading shows the highest esterification rate. The esterification rate of esterification reaction with the presence of catalyst was significantly higher compared to the esterification reaction without catalyst loading. Figure 5 illustrates the effect of SAC loading on esterification of waste cooking oils. The mechanism of acid catalyzed esterification was shown in Figure 6. A conclusion could be drawn by stated that the EFB derived solid acid catalyst has the potential to reduce free fatty acid (FFA) in oils.

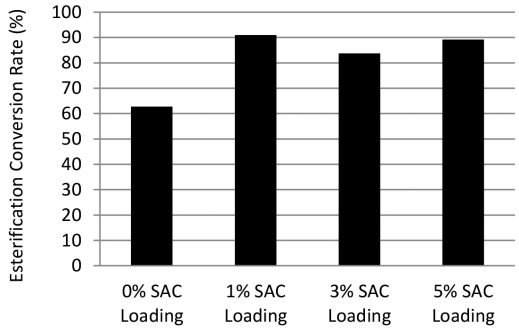

FIGURE 5. Effect of catalyst loading on esterification rate of WCO

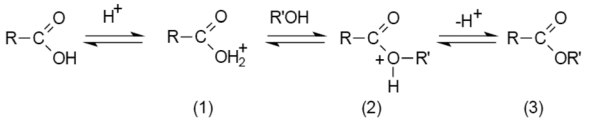

FIGURE 6. Mechanism of acid catalyzed esterification reaction (Christie 1993)

CONCLUSION

In this paper, preparation and characterization of a new EFB derived solid acid catalyst were reported. The characterization analysis showed that a solid acid catalyst was successfully produced from oil palm empty fruit bunch via direct impregnation with transition metal sulfides and it was shown to be useful for esterification of high acid value oils such as waste cooking oils. The result showed that it was potentially effective in converting free fatty acid to ester prior to transesterification reaction to produce biodiesel. This solid acid catalyst has the potential to find other applications as a heterogeneous green catalyst.

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