Synthesis of Oil Palm Empty Fruit Bunch Derived Magnetic Solid Acid Catalyst for Levulinate Production

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Abstract. Ethyl levulinate is widely known as a fuel additive, flavour, and fragrance components. In this study, the biomass-derived magnetic catalyst was synthesised, and its efficiency was evaluated in the esterification reaction. Oil palm empty fruit bunch (EFB) was used in the preparation of the solid magnetic catalyst. The synthesised catalyst was analysed by scanning electron microscope (SEM), electron dispersive X-ray spectroscopy (EDX), vibrating sample magnetometer (VSM) analyses, and acidic test. The magnetisation value of 24.97 emu/g for EFB fiber-MAC was reported that the catalyst has excellent magnetic properties and a strong acid density of 2.4 mmol/g. The catalytic performance was evaluated via the esterification of levulinic acid. The highest ethyl levulinate conversion of 66.78 mol% and yield of 84.87 mol% were recorded corresponding to 10 wt% catalyst loading and 10:1 ethanol to levulinic acid molar ratio with reaction temperature of 70 °C for 5 h. FTIR and GC-FID analysis confirmed the appearance of the ester group after the esterification reaction. Finally, the magnetically separable catalyst can be easily separated, and it shows a potential solution to the utilisation of heterogeneous catalysts in the esterification reaction.

Keywords: Levulinate; esterification; oil palm empty fruit bunch; magnetic; catalyst

1. Introduction
The global depletion fossil fuels have resulted in researching alternative energy sources with consideration given to the use of lignocellulosic biomass for the chemical production, fuel and energy sources [1]. Levulinic acid is a biomass-derived lignocellulosic chemical and one of the twelve chemicals in the building blocks [2]. The ester products of levulinic acid have been vastly used as flavours for fragrance, pharmaceutical intermediates and as an additive for transportation fuels. Interestingly, the esters which are known generally as alkyl levulinate have been an attractive product as the ester can be used up to 5 wt% as miscible diesel biofuel in regular diesel car engines [3,4]. Levulinate esters are generally produced from biomass with high reaction temperature and desired alcohol. Besides, levulinate esters can be synthesised via esterification reaction using a catalyst with alcohols such as methanol, ethanol and butanol [5]. Usually, the esterification reaction conducted by using a homogeneous catalyst such as sulfuric acid, phosphoric acid or hydrochloric acid, but the product requires further purification and difficulties in catalyst recovery [6].

Hence, the use of solid catalysts can be easier as it is easy to be recovered and further purification or neutralisation required, besides it can be reused several times [7]. Ramli et al. [8], prepared sulfated silica catalyst using silicon dioxide and different concentration of sulfuric acid, which has the highest yield of 53.6 % with catalyst acidity of 170.7 µmol/g. In another study, a conversion yield of 82 % methyl levulinate was exhibited by using Amberlyst-15 with 30 % catalyst loading. Zainol et al. [9], worked on the production of ethyl levulinate using calcined cryogel and reported with a yield of 86.5 % under an optimised condition of 25 wt% catalyst loading at the high reaction temperature, 150 °C. However, the esterification of levulinic acid was mostly conducted using acidic ion exchange resins, zeolites, sulfated silica and heteropolyacid-based catalyst [10]. As an
environmental concern, biomass-based solid catalysts can be a potential substitution to the existing solid catalyst.

Biomass has been widely used in many fields, such as the generation of biomass power, the preparation of biomass-based carbon nanomaterials and bio-oil and biofuel production [11]. Biomass was classified as agricultural waste, forest waste, industrial waste and municipal solid waste. Biomass, also known to be environmentally friendly and can be used to produce many value-added products [12]. Agricultural waste is known as lignocellulosic materials consisting of lignin, cellulose and hemicellulose. Oil palm is one of Malaysia's most abundant crops with oil palm empty fruit bunch (EFB) produced as waste following the process of oil extraction [13]. Traditionally, EFB was burned in the palm oil mill incinerator, and ashes were recycled as fertilizers into the plantation [14]. Because of the environmental issue, the process of incineration was discouraged. EFB waste must then be used for various uses to reduce the environmental issue. This waste was mainly used to produce renewable energy crudes [15]; however, only a few works on the use of EFB waste as carbon precursors are reported.

Biomass supported solid catalysts have been extensively studied, and carbon materials can be easily activated by the sulfonation process. Filoklis et al. [16] synthesised sulfonated hydrothermal catalysts using glucose, cellulose and rye straw as carbon sources and reported that sulfonated hydrothermal glucose had exhibited the best ethyl levulinate result, 97 %. Meanwhile, Liu et al. [17] reported that esterification of levulinic acid using a sulfonated bagasse-carbonized solid acid catalyst exhibited the highest conversion of ethyl levulinate 88.2 % at 120 ºC after 9 h reaction. Sulfonated biomass materials can be inexpensive and reusable catalysts for esterification reaction; however, sulfated carbon catalysts exhibit limited acidity and have poor recyclability due to sulfate group leaching [18]. On the other hand, the separation process of heterogeneous catalyst still considered as the main drawback, which requires either filtration or centrifugation process. Therefore, magnetic particle infusion in the preparation of sulfated acid catalyst can be removed easily with a strong magnet than filtration or centrifugation process. [19]. Iron oxide was described as the Lewis acid that can induce catalytic activity besides the functionality of the sulfuric acid group [20]. To our knowledge, biomass-derived magnetic acid catalysts have not been used as solid catalysts in the esterification of levulinic acid.

In this study, empty fruit bunch (EFB) supported magnetic acid catalyst was prepared. Morphology, structural and elemental analysis were conducted to characterise the catalyst. The acidic of the catalyst was determined via titration method. The catalytic efficiency was evaluated in the esterification of levulinic acid.

2. Methodology

2.1 Materials
All chemicals used were analytical grade. Levulinic acid (99 %) and ethanol (95 %) purchased from Merck and Suria Pembebal Umum Sdn. Bhd (Malaysia), respectively, were used in the catalytic reaction.

2.2 Catalyst Preparation

2.2.1 Synthesis of EFB Fibre Magnetic Acid Catalyst
Firstly, the raw EFB fibres were pre-treated with 0.1 M sodium carbonate, Na2CO3 solution. Later, the treated EFB fibres were washed with distilled water to remove the excess Na2CO3 solution and dried at 105 ºC overnight. The treated EFB magnetic acid catalyst was synthesised using the one-step impregnation method. Treated EFB was mixed in FeSO4·7H2O and Fe2(SO4)3 solution stirred for 2 h at 60 ºC and after the reaction, the mixture in slurry form was oven-dried at 80 ºC overnight. The collected sample was calcined at 500 ºC for 2 h using a vacuum furnace. Meanwhile, the catalyst was denoted as EFB fiber-MAC.
2.3 Catalyst characterisation
The sample was analysed by scanning electron microscopy (SEM) with electron dispersive X-ray spectroscopy (EDS) (JSM-6010PLUS/LV, Universiti Tenaga Nasional) to examine the morphology and elemental compositions of the raw material and catalyst. The magnetisation value was determined by using vibrating sample magnetometer, VSM (Lake Shore 7400 Series) Nanocat Lab, Universiti Malaya. The acidic of the solid acid catalyst was measured by neutralisation titration method.

2.4 Esterification reaction – Ethyl Levulinate production
The batch catalytic esterification of Levulinic acid with ethanol using EFB derived magnetic acid catalysts was conducted in a 100 mL flat bottom flask with a reflux condenser, hotplate stirrer and thermocouple. 10 g levulinic acid and 10:1 molar ratio of ethanol to levulinic acid and heated at 70 °C. Then, 10 wt% of EFB fiber-MAC was added into the mixture. After the reaction completed, the catalyst was separated using a magnet. The unreacted ethanol was evaporated at 80 °C, and the esterified was cooled to room temperature.

2.5 Characterisations of the products
The functional group of levulinate ester was determined using Fourier transform infrared spectroscopy (FT-IR), and the percentage of levulinate ester conversion (ELC) was calculated using Eq. 1.

\[
EL_C = \left( \frac{EL_n}{LA_n} \right) \times 100
\]

(1)

ELn: moles of ethyl levulinate formed
LAN: initial moles of levulinic acid

The yield of ethyl levulinate was determined using gas chromatography-flame ionisation detector (GC-FID), Agilent Technology, 7890A. The percentage of yield was obtained based on the standard concentration of ethyl levulinate by using the prepared calibration curve and calculated using the following equation (Eq. 2).

\[
EL_Y = \left( \frac{C_E \times V_P}{1000 \times \frac{M_E}{M_L}} \right) \times \frac{W_F}{W_I} \times 100
\]

(2)

ELy: Ethyl levulinate yield (mol.%)
CE: Concentration of levulinate ester (mg/mL)
ME and ML: Molecular mass of levulinate ester and levulinic acid (g/mol), respectively
Vp: Final volume of the product (mL)
WF: Mass of levulinic acid (g)

3. Results and discussion

3.1 Acid density test
Table 1 shows the acidic strength of EFB fiber-MAC was determined using a neutralisation titration method. The EFB fiber-MAC catalyst had an acidic acidity of 2.4 mmol/g. The strong acidic was considered to the presence of sulfonic acid (−SO3H) groups in the catalyst [21]. Hence, the catalyst acidic can enhance catalytic activity in the esterification reaction.
3.2 Morphology analysis
Figure 1 shows the SEM images of raw EFB fibre and EFB fiber-MAC using a scanning electron microscope (SEM). Based on the SEM image in Fig. 1(a), the raw EFB fibre surface was embedded with granules known as silica bodies and impurities. The impurities and silica bodies on EFB fibre surface can be detached by alkaline treatment using sodium carbonate solution. Rosli et al. stated that the silica bodies are phytoliths that could lead to poor particle absorption at fibre's surface [22]. The removal of the granules with alkaline treatment can increase the appearance of small pores which allows the accessibility of the particles during the impregnation process [23]. The SEM image of EFB fiber-MAC shows the catalyst was impregnated with sulphates (SO$_4^{2-}$) and iron (Fe) particles (Fig. 1(b)). The treated EFB fibre exhibited rough surface with sulphated magnetic particles embedded on the surface after calcined at 500 °C for 2 h.

![Figure 1. SEM image of Raw EFB fibre and EFB fiber-MAC.](image)

3.3 Elemental analysis
Table 1 shows the composition of EFB fiber-MAC and consisted of carbon, oxygen, sulphur and iron. The EDS results illustrated that the impregnated EFB fiber-MAC has loaded with 21.82 wt% iron, 34.78 wt% oxygen and 5.52 wt% sulphur groups. These results proved that the existence of oxygen and sulphur in the catalyst indicated the presence of a sulfonic group (-SO$_3^-$) in the catalyst [24]. The content of iron and oxygen on the catalyst indicates the magnetic property of the catalyst and it can be easily recovered by using an external magnet.

| Catalyst     | Element Composition (%) |
|--------------|-------------------------|
|              | Carbon  | Oxygen  | Sulphur | Iron   |
| EFB-MAC      | 37.88   | 34.78   | 5.52    | 21.82  |

3.4 VSM analysis
The magnetisation value of EFB fiber-MAC was determined using vibrating sample magnetometry, and the catalyst had a high saturation magnetisation value of 24.97 emu/g. It proved that EFB fiber-MAC has the strongest magnetism which corresponded to the highest composition of Fe in EDX analysis. However, the catalyst was able to be recovered from the reaction mixture by using a magnet. According to Wang et al. [25], the magnetism of FCHC-SO$_3$H catalyst derived from chitosan recorded as 18.9 emu/g, which was comparatively low with EFB derived magnetic catalyst. Moreover, the saturation magnetisation of zirconia/titanium coated magnetic catalyst was about 21 emu/g [26] and shows that biomass-derived magnetic catalysts have greater magnetisation value. The EFB fiber-MAC has lower retentive magnetism (7.91 emu/g) compared to the saturation value. The high saturation
value and low retentive magnetism demonstrate the catalyst has good magnetic dispersibility and magnetically sensitive [27]. This characteristic is known as superparamagnetic, and it allows a better catalytic performance [28]. Thus, biomass-derived magnetic catalysts potential to exhibit good magnetisation value compared to commercially derived magnetic catalysts.

3.5 Catalytic conversion of levulinic acid to ethyl levulinate

The efficiency of the EFB fiber-MAC catalyst in the esterification of levulinic acid was tested by employing ethanol as alcohol. Fig. 2 illustrates the catalytic conversion of levulinic acid to ethyl levulinate, and it also showed that a low conversion was attained in the absence of a catalyst (control experiment). The catalyst tested in this study resulted in higher ethyl levulinate yield than the control experiment, which explains the essential of an acid catalyst [29]. The highest conversion was achieved with 66.78 mol% in the presence of EFB fiber-MAC. The high acid density of catalyst contributed to the ethyl levulinate conversion. Meanwhile, it was mentioned that sulfonated carbon catalyst with a high amount of oxygen-containing functional groups performs better than other sulfonated catalysts which contain only sulfonic groups [30,31]. Thus, the high acidic content in the EFB fiber-MAC is also indicated the existence of other acidic sites such as carboxylic (-COOH) and phenolic (-OH) which could aid in the conversion process.

![Figure 2](image-url) Levulinic ester conversion with EFB derived magnetic catalyst and control experiment (Temperature = 70 °C; EtOH:LA molar ratio = 10:1; 10 wt% catalyst; 5 h).

3.5.1 GC-FID Analysis

To further investigate the catalytic activity, the ethyl levulinate samples were examined by gas chromatograph-flame ionisation detector (GC-FID). Fig.3 shows the yield of ethyl levulinate using GC-FID to determine the performance of EFB fiber-MAC catalyst in the esterification of levulinic acid. Based on the result in Fig.3, the highest ethyl levulinate yield was achieved with 84.87 mol% using EFB fiber-MAC catalyst followed by 0.95 mol% yield in the control experiment. The high yield could be attributed to the high acidic as high Brønsted acid sites content catalyst is required for the conversion of levulinic acid to ethyl levulinate through esterification process [32]. Hence, the high acidic of EFB fiber-MAC was favourable for the ethyl levulinate production. Compared to other researchers' results on ethyl levulinate production using solid acid catalysts, it is noticed that EFB...
fiber-MAC can achieve higher ethyl levulinate yield. Zainol et al. [33] studied ionic acid acidified carbon cryogel for esterification of levulinic acid, and the highest yield of 66.9 mol% was obtained. Li et al. [34] have also obtained an excellent catalytic activity for the production of ethyl levulinate over loofah sponge-derived carbon acid with the highest yield of 91% but, after a longer catalytic reaction time of 12 h.

**Figure 3.** Ethyl levulinate yield with EFB derived magnetic catalyst and control experiment (Temperature = 70 °C; EtOH:LA molar ratio = 10:1; 10 wt% catalyst; 5 h).

### 3.5.2 FT-IR Analysis

The presence of ester groups in the esterified products was determined by using FT-IR analysis. Fig. 4 illustrated the FT-IR spectra of esterified products and labelled as blank, and levulinate ester produced using EFB fiber-MAC (LE-EBF-FIB). Based on the results, the sharp absorption bands at 1697 and 1703 cm⁻¹ illustrate the stretching vibration of C=O groups. Thus, it characterises the presence of esters in the samples [35]. Meanwhile, the absorption bands at 1362 cm⁻¹ were assigned to the alkyl group, C-H stretching vibration, which indicates the presence of ethyl in the esterified samples. Besides, the absorbances at 1161 and 1155 cm⁻¹ were from the C–O stretching vibration in the carbonyl group, which can be referred to as aldehyde and ketone groups in esterified samples.
4. Conclusion
In this study, EFB derived magnetic catalysts, EFB fiber-MAC was successfully prepared. The magnetic solid acid catalyst demonstrated to be highly active in converting levulinic acid into ethyl levulinate. The highest conversion rate of 66.78 mol% and 84.87 mol% (by GC-FID) was obtained using EFB fiber-MAC, and the catalyst also had a high acidic and strong magnetism. The biomass-derived magnetic catalysts showed advantageous on its extensive usage in multiple application such as biodiesel and fuel additives production. Moreover, the synthesised biomass-derived magnetic catalysts had a simple recovery and potential to enhance the conversion rate.

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