Magnetic nanobiochar as an efficient heterogeneous acid catalyst for esterification reaction

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Abstract:
In this work, magnetic nanobiochar were prepared through the pyrolysis-carbonization of biomass, oil palm empty fruit bunches, following the pretreatment with $FeCl_3$. The magnetic nanobiochar were sulfonated by sulfuric acid to increase their acidity, MBC-SO_3H. The properties of MBC-SO_3H were characterized by Surface Area Analyzer, XRD, SEM, FTIR and NH_3-TPD. The catalytic activity of MBC-SO_3H was evaluated via esterification reaction of oleic acid at 393 K for 2 h. The optimum ester yield of 96% was obtained at catalyst loading of 5.0 % (w/w), confirming that the magnetic nanobiochar may be applied as an efficient heterogenous acid catalyst from biomass waste.
Keywords: magnetic nanobiochar, heterogeneous acid catalyst, esterification**.**

1. Introduction

Targeting biomass as the natural precursor for carbon based nanostructured materials is advantageous due to its high carbon content and purity. Biomass are also well known to be environmentally friendly as renewable resources [1]. Pyrolysis has been the current method of choice to engineer such nanomaterials from biomass waste. Recent reports have showed the application of amorphous carbon encapsulated with Fe nanoparticles as catalyst. Compared with convensional heterogenous catalysts, these Fe-contained carbon nanomaterials could be easily separated in the presence of external magnetic fields from the reaction mixture. Mun, *et al*. (2013) has reported the synthesis of biochar-encapsulated Fe nanoparticles from wood char. The results showed that the Fe-contained biochar were completely separated from the carbonized char after the pyrolysis treatment [2, 3]. Another study by Liu, *et al*. (2013) reported using sawdust as the biomass to generate magnetic porous carbon nanomaterials as solid acid catalyst [4].

Herein, we investigate the catalytic performance of the magnetic nanobiochar samples based on the pyrolysis of oil palm empty fruit bunch, as heterogenous acid catalyst *via* esterification of oleic acid.

2. Experimental

2.1. Preparation and characterization of Magnetic Heterogeneous Acid Catalyst from Biomass

The magnetic carbon-based nanostructures were prepared using Fe-loaded biomass as the precursor. Briefly, 10.0 g of oil palm EFB and 1,000 mL of $FeCl_3$ solution with a concentration of 10 mmol/L were mixed in a flask and stirred in room temperature for 300 min. The magnetic carbon nanomaterials were synthesized by controlled pyrolysis of the Fe-loaded biomass in a vertical drop fixed bed stainless steel flow reactor.

The solid acid catalyst were prepared by sulfonation, in which the MBC samples were mixed with concentrated sulfuric acid (10 mL per 1 g of MBC) at 423 K for 10 h. Characterization of the magnetic solid acid catalyst was conducted through Surface Area Analyzer, XRD, SEM, FTIR and NH_3-TPD.

2.2. Catalytic Esterification of Oleic Acid

The catalytic activity of the sulfonated biochar (MBC-SO_3H) sample were evaluated through a typical esterification reaction. The reaction was performed as follows: 0.03 g of MBC sample was added to a mixture of 3 mL of oleic acid and 24 mL of methanol (p.a.) in a round bottom flask at 393 K. The catalyst loading were varied from 2.5, 5.0, 7.5, 10.0, 25.0 and 50.0% (w/w). The reaction was completed after 2 h, and the catalyst was removed from the product mixture for further GC-MS analysis.

3. Results and discussion

The magnetic nanobiochar samples obtained from carbonization at 773 K, MBC-SO_3H, was proven to have higher surface area, crystallinity properties and surface chemical composition after sulfonation process, which were confirmed by the Surface Area Analyzer and XRD analysis. The acidity of the magnetic nanobiochar samples were evaluated through FTIR and NH_3-TPD analysis. Given the previous results, the catalytic performance of the samples were evaluated for esterification of oleic acid as the model reaction. This reaction was conducted at 393 K for 2 h and the catalyst loading was varied. Figure 1 shows the yield of the ester (methyl oleate) against the catalytic loading in the reaction. It is shown that the optimum catalyst loading was obtained at loading of 5.0% (w/w) giving 96% of ester yield. Moreover, the presence of MBC-SO_3H as the acid catalyst in the reaction showed significant increase of ester yield compared to that without catalyst, which gives the yield of only 4%. This proved that the magnetic nanobiochar, MBC-SO_3H, may be applied as an efficient heterogenous acid catalyst for the production of methyl oleate.

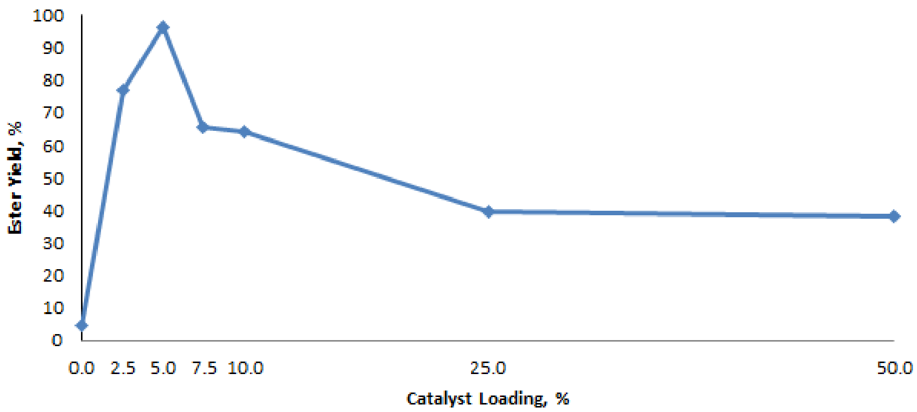

Figure 1. Evaluation of catalytic performance of MBC-SO_3H through variation of catalyst loading in the esterification of oleic acid

4. Conclusions

In summary, we have synthesized and characterized magnetic nanobiochar through pyrolysis-carbonization of biomass, the oil palm empty fruit bunches. The sulfonation of these nanomaterials resulted in the formation of an efficient heterogenous acid catalyst in which the performance was evaluated through the esterification of oleic acid. The results from this work open new opportunities for the development of magnetic heterogenous acid catalyst from biomass waste.

References

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