PEANUT SHELLS DERIVED SOLID ACID CATALYST FOR BIODIESEL PRODUCTION

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ABSTRACT

Waste peanut shells are contributed to a large quantity of lignocellulosic waste. This project was aimed to utilize the waste materials for a better benefit. Waste peanut shells, were used as raw material to prepare a new solid catalyst for biodiesel production. Solid acid catalyst derived from waste peanut shells was used to catalyze the esterification process in biodiesel production from waste cooking oil. Solid acid catalyst was prepared by in-situ impregnation with sulfuric acid. This new catalyst was used to catalyze the esterification of high free fatty acid (FFA) value waste cooking oils as pre-treatment step prior biodiesel production. The effects of catalyst loading, oil-to-methanol molar ratio and catalyst reusability on the catalytic activity were investigated. The highest catalytic activity with 71.58% esterification rate was achieved and it can be reused for three times under optimized condition. The catalyst can be easily separated for reuse compared with homogenous catalyst which used in biodiesel production. Waste peanut shells are potential to be converted into useful feedstock and the derived catalyst can replace traditional liquid acid catalyst in biodiesel production especially for high acid value content feedstock.

Keywords: peanut shells, acid, catalyst, biodiesel, esterification.

INTRODUCTION

The demand of renewable energy had increased globally as there are credible speculations that supply of oil and gas are going to run out one day. Biodiesel, derived from vegetable oil or animal fats, is an attractive alternative fuel source and gained attention recently due to its non-polluted and environmental friendly [1-6]. Biodiesel obtained from energy crops produces positive impacts on the surroundings environment, such as reduction of the carbon emission and the greenhouse effect caused by combustion [7-12]. Unfortunately, the commercialization of biodiesel is yet to be surfaced all over the world due to its high cost of feedstock production cost. As a result, researches have been done using non-edible biomass oils such as Jatropha oil or fats, and other waste oils in order to help reduce the material cost [13]. Conventional way of production of biodiesel is catalyzed by homogeneous acid or base such as sulfuric acid or sodium hydroxide. However, use of homogenous liquid catalyst creates several problems in the end of reaction such as difficulty of catalyst separation, reactor corrosion, contamination of sulfur in biodiesel and soap formation when in high free fatty acid environment [13]. Peanut shells or called as peanut hulls considered as kind of agriculture waste that are low cost production, and abundance in nature. Waste peanuts shells, generated in large volume annually, considered as lignocellulosic biomass waste. According to Wilson *et al.* [14], peanut shells are classified as a biomass which has the characteristics of low in density and high in volume. They are used in animal feed or burned to obtain energy. It is also studied that waste peanut shells are agricultural by-products which contributed to the large amount of ligno-cellulosic waste dumped to the surrounding. This posed a problem to the environment that might lead to possible pollution.

In this study, we prepared a solid acid catalyst from peanut shells by single step sulfonation, and subsequently it was used as catalyst to esterify the high acid value waste cooking oils. The esterification of oleic acid was studied to optimize reaction variables. Various reaction parameters, such as catalyst loading, and oil-to-methanol ratio on the esterification rate were optimized. Under these optimized conditions, untreated waste cooking oils with high FFAs was underwent esterification and converted to ester with the solid acid catalyst.

EXPERIMENTAL

The waste peanut shells was sponsored by Ngan Yin Sdn, Bhd. Sulfonation was carried out at 150°C for 60 minutes with 5-g sample stirred in 50ml concentrated sulfuric acid. The sulfonated sample was washed with hot and cold distilled water to remove any adsorbed substance until free of sulfate ion. The sample was oven dried at 105°C for 24 hours. The derived solid acid catalyst was first used for esterification of oleic acid. Oleic acid, methanol and catalyst were loaded together and experiment was carried out at 65°C for 90 minutes. After the reaction, the catalyst was separated from the mixture and methanol was evaporated. Similar to the previous step, non-pretreated waste cooking oil with methanol and the catalyst were loaded into an autoclave (reaction temperature: 65°C) for esterification reaction. After the reaction, the mixture was cooled to room temperature. The solid acid catalyst was then filtered out from mixture. The solid acid catalyst was washed with n-butanol and oven-dried for recycle purpose.

RESULTS AND DISCUSSION

Morphology analysis

The surface morphology of the peanut shells and solid acid catalyst were studied by scanning electron microscope (SEM) analysis. Figure-1 shows the morphology for waste peanut shells powder. They have many open volumes on the rough surface. Figure-2 shows the morphology of solid acid catalyst. The open volumes reduced after sulfonation. According to Janaun *et al.* [15], the physical changes in structure of the peanut shells powder is caused by the harsh sulfonation reaction. It caused the porosity and the wall of the peanut shells powder structure to be destroyed [15]. The energy-dispersive x-ray spectrometry (EDX) result and it can be attributed to the impregnation of SO_3H groups on the surface of catalyst.

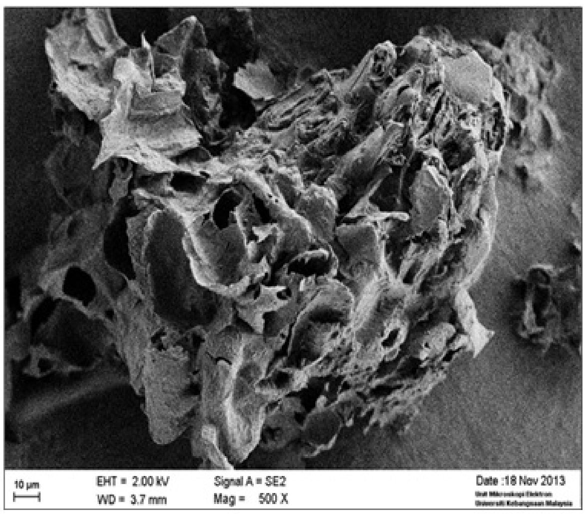

Figure-1. SEM image for peanut shells powder.

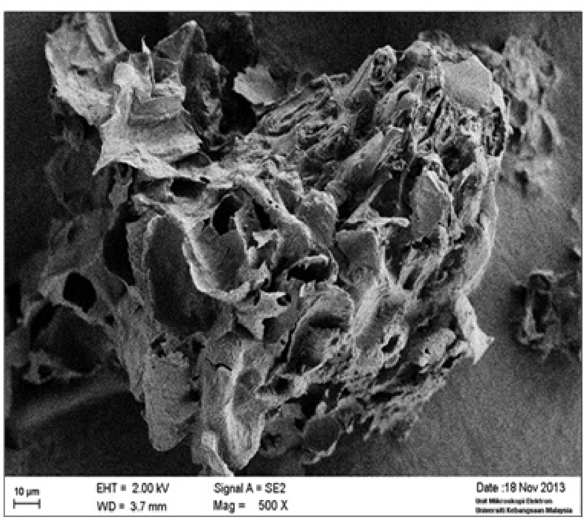

Figure-2. SEM image for solid acid catalyst.

FT –IT analysis

Table-1 shows the FTIR result for the solid acid catalyst. The characteristic peak in the frequency region of 900 – 1300 cm^{-1}, 500 – 680 cm^{-1} and peak centered at 885 cm^{-1} corresponded to the characteristics peaks of $H_2SO_4$and H_2SO_4 ions, such as SO_4^{-2} and other sulfate ions. The bands found at 1295 cm^{-1} for sulfonated peanut shells powder can be assigned to asymmetric SO_2 stretching. It indicated the presence of SO_3H group in the solid acid catalyst produced from peanut shells. Furthermore, the SO_3H from the concentrated sulfuric acid has been proven to be successfully loaded into the porous peanut shell structure [16]. Based on the esterification results obtained, the catalytic loading of 5 wt % achieved the highest esterification rate which was 85.32 %. This parameter was brought forward to the esterification of waste cooking oil. The experiment successfully reduced the acid value of waste cooking oil by 71.58 %. This indicates that the FFA content of the waste cooking oils was reduced.

Table-1. FTIR result of solid acid catalyst.

Bond	Functional Group	Frequency (cm^{-1})
O–H(stretch)	Alcohols, Phenols	3357
N–H (bend)	Primary amines	1618
CH_2 (benching)	Lignin, Polyxylose	1410
SO_2 (stretch)	Sulfur dioxide	1295
S-O (stretch)	Sulfoxide	1170
SO_4^{2-}1,HSO^{2-} ions	Sulfate ions	885
C – X (stretch)	Alkyl halides	589

CONCLUSIONS

In this study, a solid acid catalyst was successfully produced from waste peanut shells via direct sulfonation and it was shown to be useful for esterification of high acid value oils such as waste cooking oils. The result shows it was highly effective in converting oleic acid and other free fatty acid to ester. This solid acid catalyst is potential to find other applications as a heterogeneous green catalyst.

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REFERENCES

[1] M. Mathiyazhagan, A. Ganapathi, B. Jaganath, N. Renganayaki and N. Sasireka. 2011. Production of biodiesel from non-edible plant oils having high FFA content. International Journal of Chemical and Environmental Engineering. Vol. 2, pp. 119-122.

[2] M. Kamil, M.M. Rahman and R.A. Bakar. 2011. Performance evaluation of external mixture formation

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strategy in hydrogen fueled engine. Journal of Mechanical Engineering and Sciences. Vol. 1, pp. 87-98.

[3] A. Gharehghani, R. Hosseini and T. Yusaf. 2013. Investigation of the effect of additives to natural gas on heavy-duty si engine combustion characteristics. Journal of Mechanical Engineering and Sciences. Vol. 5, pp. 677-687.

[4] B. Ghobadian, G. Najafi, M. Nayebi. 2013. A semi-empirical model to predict diesel engine combustion parameters. Journal of Mechanical Engineering and Sciences. Vol. 4, pp. 373-382.

[5] R. Rahim, R. Mamat, M.Y. Taib and A.A. Abdullah. 2012. Influence of fuel temperature on a diesel engine performance operating with biodiesel blended. Journal of Mechanical Engineering and Sciences. Vol. 2, pp. 226-236.

[6] A.F. Yusop, R. Mamat, M.H. Mat Yasin and O.M. Ali. 2014. Effects of particulate matter emissions of diesel engine using diesel–methanol blends. Journal of Mechanical Engineering and Sciences. Vol. 6, pp. 959-967.

[7] G. Antolın, F. Tinaut, Y. Briceno, V. Castano, C. Perez and A. Ramırez. 2002. Optimisation of biodiesel production by sunflower oil transesterification. Bioresource technology. Vol. 83, pp. 111-114.

[8] M. Kamil, M.M. Rahman and R.A. Bakar. 2013. Integrated simulation model for composition and properties of gases in hydrogen fueled engine. International Journal of Automotive and Mechanical Engineering. Vol. 8, pp. 1242-1155.

[9] M. Kamil, M.M. Rahman and R.A. Bakar. 2014. An integrated model for predicting engine friction losses in internal combustion engines. International Journal of Automotive and Mechanical Engineering, Vol. 9, pp. 1695-1708.

[10] A. Abbaszadeh, B. Ghobadian, G. Najafi and T. Yusaf. 2014. An experimental investigation of the effective parameters on wet washing of biodiesel purification. International Journal of Automotive and Mechanical Engineering, Vol. 9, pp. 1525-1537.

[11] M.M. Noor, A.P. Wandel and T. Yusaf. 2012. A review of MILD combustion and open furnace design consideration. International Journal of Automotive and Mechanical Engineering. Vol. 6, pp. 730-754.

[12] L.B. Soon, A.Z. M. Rus and S. Hasan. 2013. Continuous biodiesel production using ultrasound clamp on tubular reactor. International Journal of Automotive and Mechanical Engineering. Vol. 8, pp. 1396-1405.

[13] F.-l. Pua, Z. Fang, S. Zakaria, F. Guo and C.-h. Chia. 2011. Direct production of biodiesel from high-acid value Jatropha oil with solid acid catalyst derived from lignin. Biotechnology for biofuels, Vol. 4, pp. 1-8.

[14] K. Wilson, H. Yang, C.W. Seo and W.E. Marshall. 2006. Select metal adsorption by activated carbon made from peanut shells. Bioresource technology. Vol. 97, pp. 2266-2270.

[15] J. Janaun and N. Ellis. 2011. Role of silica template in the preparation of sulfonated mesoporous carbon catalysts. Applied Catalysis A: General. Vol. 394, pp. 25-31.

[16] M.J. Ariza, D.J. Jones and J. Rozière. 2002. Role of post-sulfonation thermal treatment in conducting and thermal properties of sulfuric acid sulfonated poly (benzimidazole) membranes. Desalination. Vol. 147, pp. 183-189.