



PALM KERNEL SHELL-DERIVED BIOCHAR AND CATALYST FOR BIODIESEL PRODUCTION

(Biochar dan Pemangkin Berasaskan Tempurung Kelapa Sawit untuk Penghasilan Biodiesel)

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Abstract

A promising catalyst based on a biomass pyrolysis by-product, biochar, has been developed to produce biodiesel. A carbon-based solid acid catalysts were prepared by sulfonating pyrolysis char with concentrated sulfuric acids. The catalysts were characterized using thermogravimetric analyses (TGA), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and surface area analyzer. Prepared catalysts were studied for their ability to catalyze transesterification of vegetable oils. The catalyst sulfonated with the concentrated sulfuric acid demonstrated considerable conversion in free fatty acid esterification. Further investigation of the catalyst was conducted to determine the effect of sulfonation time (1 and 3 hours) and surface area on the transesterification reactions. The surface area of the biochar was increased by chemical treatment using 10M potassium hydroxide through porosity development. Results showed the catalyst with the highest surface area and acid density to have the highest catalytic activity to produce biodiesel from canola oil in the presence of methanol as the reagent. The effects of alcohol to oil (A:O) molar ratio, reaction time and catalyst loading on the esterification reaction catalyzed by the sulfonated biochar were also investigated. Results revealed that more than 90% biodiesel yield was achieved at 15 wt% of catalyst amount, methanol to oil molar ratio was 9:1 and the agitation rate was 700 rpm. As a conclusion, the prepared biochar-based catalyst has a tremendous potential to be used in a process converting a high Free Fatty Acids (FFA) feedstock to biodiesel.

Keywords: transesterification, vegetable oil, palm kernel shell, biochar-based catalyst

Abstrak

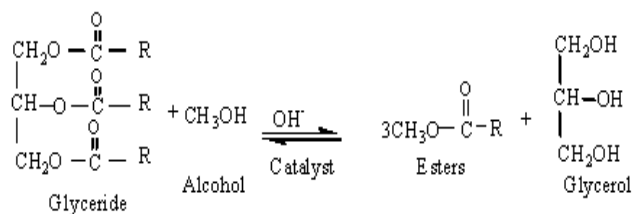
Pemangkin yang berasaskan pirolisis biomass produk sampingan, biochar, telah dibangunkan untuk penghasilan biodiesel. Pemangkin asid pepejal berasaskan karbon telah dihasilkan daripada sulfonasi pirolisis char dengan asid sulfurik pekat. Pemangkin telah dicirikan menggunakan analisis termogravimetri (TGA), mikroskop imbasan elektron (SEM), spektroskopi infra merah transformasi Fourier (FTIR) dan penganalisa luas permukaan. Pemangkin yang tersedia telah dikaji keupayaannya untuk menjadi pemangkin transesterifikasi minyak sayur-sayuran. Pemangkin sulfonat dengan asid sulfurik pekat menunjukkan penukaran ini boleh dipertimbangkan dalam pengesteran asid lemak bebas. Kajian lanjut terhadap pemangkin telah dijalankan untuk menentukan kesan masa sulfonasi (1 dan 3 jam) dan luas permukaan pada tindak balas transesterifikasi. Luas permukaan biochar telah meningkat melalui rawatan kimia menggunakan 10M kalium hidroksida melalui pembangunan liang. Hasil kajian telah menunjukkan pemangkin dengan luas permukaan dan ketumpatan asid yang paling tinggi mempunyai aktiviti pemangkinan tertinggi bagi pengeluaran biodiesel daripada minyak kanola dengan kehadiran metanol sebagai reagen. Nisbah molar kesan alkohol kepada minyak (A:O), masa tindak balas dan muatan pemangkin keatas tindak balas pengesteran yang dimungkinkan oleh biochar sulfonat turut disiasat. Hasil kajian menunjukkan bahawa lebih daripada 90% hasil biodiesel telah dicapai pada 15 wt% daripada jumlah pemangkin, nisbah molar metanol kepada minyak adalah 9:1 dan kadar pergolakan adalah 700 rpm.

Kesimpulannya, pemangkin berasaskan biochar yang dihasilkan mempunyai potensi yang amat besar untuk digunakan dalam proses penukaran bahan mentah asid lemak bebas tinggi (FFA) kepada biodiesel.

Kata kunci: transesterifikasi, minyak sayuran, tempurung kelapa sawit, pemangkin berasaskan biochar

Introduction

Increasing environmental problems, global fuel consumptions and strike increase in fossil fuel price has led to production of renewable fuels such as biodiesel. Biodiesel, consisting of methyl esters of long chain fatty acids has become very attractive as a biofuel due to its environmental benefits, renewable and less polluting alternatives. Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The largest possible source of suitable oil comes from oil crops such as rapeseed, palm or soybean. Biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash. The biodiesel yields are estimated 90% to 40% more energy than the energy invested in producing it [1]. Biodiesel can be produced by the transesterification of vegetable oils with alcohol which involved the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol in the presence of a catalyst. The economy of the process depends on the type and quantity of catalyst used among other factors. Transesterification of vegetable oil as shown in Scheme 1.



Scheme 1. Transesterification of vegetable oil

The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion. The catalyst can be homogeneous or heterogeneous depending on whether it is in the same or different phase with reactants; oil and alcohols [2]. Homogeneous basic catalyst such as potassium hydroxide (KOH) is widely used in industrial processes. However, drawbacks such as difficulties in the recovery of the catalyst and the formation of abundant wastewater in the neutralizing and separating processes are the major disadvantages in alkali-catalyzed transesterification processes [3]. Therefore, heterogeneous catalyst is recommended due to easier operational processes, higher activity and selectivity and longer catalyst lifetimes [3]. Recently, sulfonated carbon precursors derived from the partial carbonization of sugar, starch, or cellulose for catalyzing the production of biodiesel is of great interest. Biochar as carbon based precursor is well established in recent literatures [4,5]. In this study, low cost and renewable carbon-based precursor (biochar) is investigated as a solid acid catalyst for the transesterification process of mixture of canola oil for biodiesel production. Surface chemistry and physical and structural changes biochar –based catalyst was also using Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), Bruner-Emmet-Teller (BET) surface area composition of methyl esters produced using Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

Materials and Methods

Catalyst preparation

Palm kernel shells (PKS) biochar was used as carbon precursor. The as-received biochar was ground and sieved between 300 – 500 µm and then dried in an oven at 110 °C for 2 hours. The carbonized biochar mixed and stirred with 0.1 molL⁻¹ HCl for 1 hour. The activated biochar samples were then sulfonated using sulfuric acid for 15 hours at 150 °C and ambient pressure [6]. Subsequently, the sulfonated biochar was washed with excessive distilled water and dried in an oven at 110 °C overnight.

Characterization study

The BET surface area of the prepared catalyst was measured with surface area analyzer (Quantachrome AS1Win). Morphological study was carried out with a scanning electron microscopy (SEM) (HITACHI model, S-3400N, Japan). A Perkin-Elmer pyris diamond thermogravimetry (TG/DTG) was used for TGA. The presence of functional group on the surface of the PKS biochar and catalyst (after the sulfonation process) was analyzed by using Fourier Transform Infrared (FTIR) spectroscopy (model Perkin-Elmer 100 series, USA at the frequency ranges of 600 cm^{-1} to 4000 cm^{-1}). Composition of the methyl ester was analyzed with gas chromatography-mass spectrometry (GC-MS) (QP2010 Plus SHIMADZU).

Transesterification procedures

Transesterification was carried out in a 250 ml 3 neck round bottom flask equipped with a reflux condenser and a magnetic stirrer. PKS-based biochar was used as catalyst with the amount varied from 5 to 15wt% and the methanol ratio was kept constant 9:1. Catalysts were first suspended in a methanol at 65 °C under vigorous mixing for 2 hours. Later, the catalyst was separated by centrifuge, and the reaction mixture was loaded into rotary evaporator to remove excess methanol. Methyl-ester phase was then obtained in a separating funnel. The obtained methyl ester was then washed and dried in the oven. Products in the biodiesel consist of methyl esters, monoglycerides, diglycerides and triglycerides. Composition of the methyl ester was analyzed using GC method. The experiments were repeated for other parameters includes molar ratio alcohol to oil (3:1, 6:1 and 9:1), catalyst loading (5 wt%, 10 wt% and 15 wt%) and agitation rate (350 rpm, 700 rpm and 1100 rpm).

Results and Discussion

Catalyst characterizations

The measured BET surface areas are shown in Table 1. There was pronounced increases in micro pore surface area when the raw biochar was activated and treated with strong sulfuric acid. This is likely due to the nature of the biochar substrate, which were all forms of woody biomass. Visual observation of the catalyst samples via SEM was performed to gain insight into catalyst morphology and pores size. As shown in Fig. 1(a) and (b), the catalyst samples have a highly irregular, convoluted fibrous surface structure, with little regular texturing. The structure of the biochar had a highly complex network of pores, channels and otherwise fibrous ridged surfaces, as opposed to the planar structure of sugar-derived biochar.

Table 1. BET Surface area of raw biochar and biochar-based catalyzed

Sample	BET surface area (m^2/g)
Biochar	0.02
Biochar-based catalyst	290.44

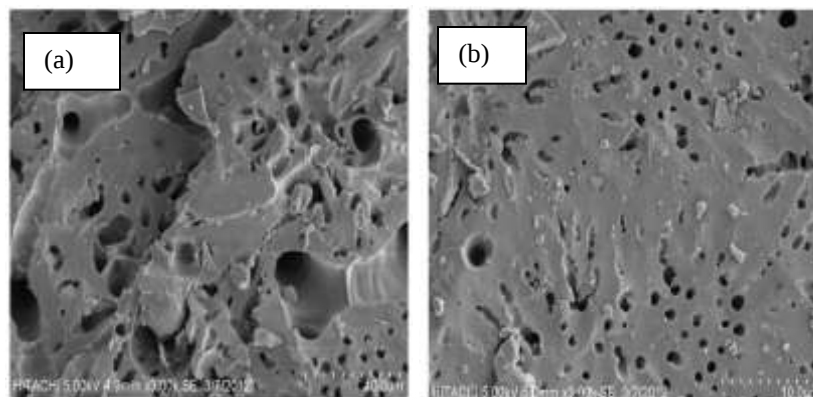


Figure 1. SEM images of (a) PKS biochar and (b) PKS-biochar based catalyst

Fig. 2 compares surface functional groups between raw biochar and biochar based catalyst. The IR spectrum of raw biochar shows a peak 724 cm^{-1} and 830 cm^{-1} for sulfonated char attributed to the ring C-H bonds of aromatic and heteroatomic compounds [11]. In addition, peaks attributable to aromatic ring modes can be found at peaks 1498 cm^{-1} for PKS biochar and 1495 and 1577 cm^{-1} for sulfonated biochar. Peaks attributable to C-O-C asymmetric stretching are presented in both PKS biochar at 1170 cm^{-1} , and sulfonated biochar at 1119 and 1158 cm^{-1} .

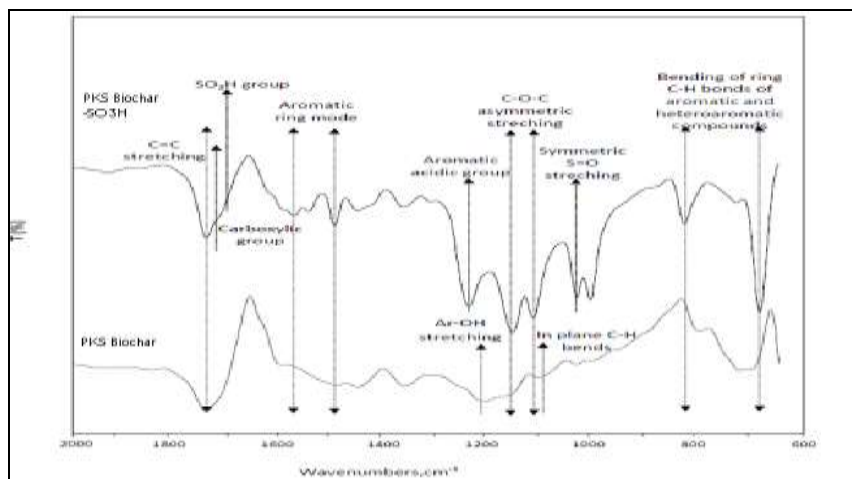


Figure 2. FTIR for PKS biochar before and after sulfonation

The PKS biochar also has peaks at 1107 cm^{-1} which corresponding to in-plane C-H bends while at 1214 cm^{-1} attributable to Ar-OH stretching. At peak 1745 cm^{-1} , both samples attributable to C=C stretching. The peaks attributed to aromatic acidic groups and carboxylic groups can be found at spectrum 1242 and 1730 cm^{-1} for sulfonated char. Besides, the spectrum for sulfonated biochar exhibits a peak at 1035 cm^{-1} which can be attributed to the symmetric S=O stretching and a peak at 1710 cm^{-1} attributable to the presence of SO_3H groups thereby confirming the incorporation of sulfonic groups onto the carbon matrix.

Fig. 3(a) and (b) shows TGA patterns for raw biochar and biochar based catalyst. The results indicated that the raw biochar has two distinctive peaks at 100°C and 600°C which corresponds to moisture content and lignin content respectively. While for sulfonated PKS biochar (catalyst demonstrated that desorption was occurring at 350°C . The event can be attributed to desorption from a weak Brønsted acid site, which corresponds to the presence of COOH-groups as determined by FTIR. The event correlates with the sulfonic groups observed in the FTIR spectra for each catalyst. The TGA results were also analyzed to determine the approximate distribution of the type of acid sites.

Effect of reaction conditions

The effect of catalysts amount on the methyl ester content in the transesterification are showed in Fig. 4. The results showed that the use of 15wt% catalyst s, oil to molar ratio (9:1) and reaction times 3 hrs gave more than 90% methyl ester yield. However, when reducing the catalyst amount to 5 wt%, the methyl ester content decreased remarkably to below than 30%. This could be due to the fact that greater catalyst had increased the catalyst activity or transesterification due to high acidity [7]. This was verified with results shown in FTIR (see Fig. 2). Furthermore, as shown in Fig. 5 methyl ester yield about 90% after 2 hours reaction and there was no significant increase when the reaction time was prolonged. This is in accordance with which indicates that the reaction is completed [7].

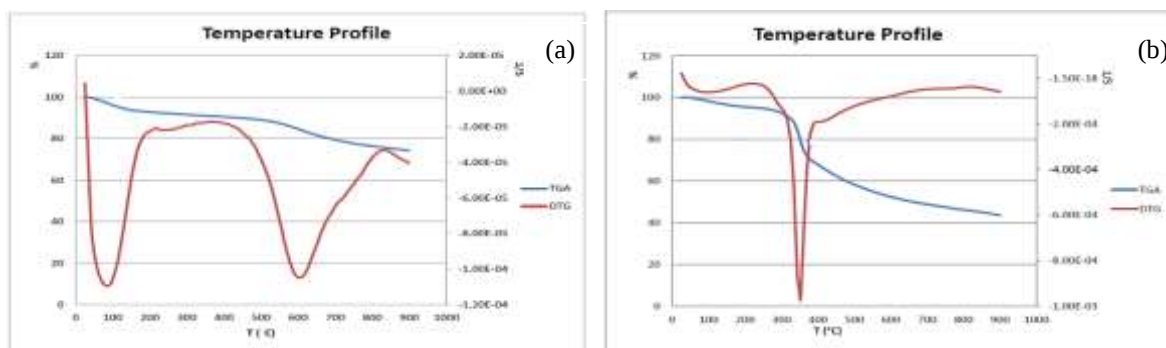


Figure 3. TGA patterns for (a) raw biochar and (b) biochar-based catalyst

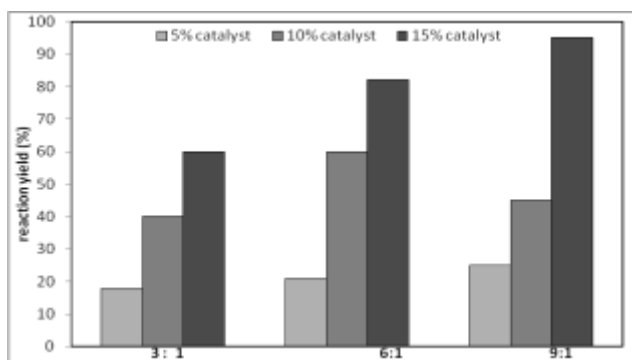


Figure 4. Reaction yields of methyl ester (ME) for various oil to methanol ratio and catalyst loading at constant speed (350 rpm)

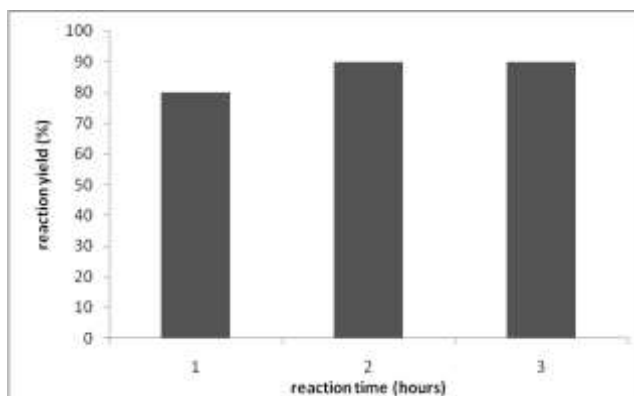


Figure 5. Reaction yields of methyl ester (ME) for different reaction time

Table 3 summarizes the chemical composition of the synthesized biodiesel of canola oil obtained in this study. It was observed that the fatty acid found in the biodiesel sample range from C6 until C22 FAME. The methyl ester compounds found in the sample are derived from the usage of methanol in the transesterification reaction. The main FAME in the biodiesel sample were oleic acid (C18:1), palmitic acid (C16:0), stearic acid (C18:0) and linolenic acid (C18:3). The cetane number (quality of the diesel fuel) of biodiesel depends on the distribution of fatty acid in

the original oil or fat from which it was produced. The major factor affecting FAME yields was the plant itself and variation will occur depending on climate and processing methods [8].

Table 3. Composition of FAME in canola oil biodiesel sample

Peak	Retention Time (min)	Identity	% Area	Acid
1	9.325	C10	0.4492	Decanoic acid (capric)
2	12.019	C12	7.9655	Dodecanoic acid (lauric)
3	12.868	C22	0.0472	Docosanoic acid (behenic)
4	13.190	C6	0.0838	2,4-hexadienedioic acid (sorbic)
5	16.300	C20	0.0657	11,14,17 eicosatrienoic acid (linolenic)
6	16.341	C18	0.1645	9-octadecenoic acid (oleic)
7	16.533	C16	6.7855	Hexadecanoic acid (palmitic)
8	16.689	C10	1.9735	Benzenepropanoic acid
9	17.527	C13	0.0624	Tridecanoic acid
10	18.258	C18	78.049	9-octadecenoic acid (oleic)
11	18.410	C18	0.9745	9,12,15-octadecatrienoic acid (linolenic)
12	18.475	C18	2.7400	Octadecanoic acid (stearic)
13	20.056	C20	0.4923	cis-11-eicosenoic acid
14	21.883	C11	0.1460	Undecanoic acid

Conclusion

Transesterification of vegetable oil was studied using biochar-derived catalyst to produce biodiesel with high methyl ester content under different conditions. It was found that biochar-based catalyst was successfully produced through sulfonation with sulfuric acid. The optimum conditions (with 90% conversion) for this reaction is suggested at 15wt% catalyst loading, oil to molar ratio (9:1) and 2 hrs reaction time and at moderate temperature 65°C. Thus, it proved that sulfonated PKS biochar shows considerable potential for use as a catalyst in biodiesel production.

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References

1. Di Serio, M., Tesser, R., Pengmei, L. and Santacesaria, E. (2008). Heterogeneous catalysts for biodiesel production. *Energy & Fuels*, 22(1): 207 – 217.
2. Ejikeme, P. M., Anyaogu, I. D., Ejikeme, C. L., Nwafor, N. P., Egbuonu, C. A. C., Ukogu, K. and Ibemesi, J. A. (2010). Catalysis in biodiesel production by transesterification processes-An insight. *Journal of Chemistry*, 7(4): 1120 – 1132.
3. Hara, M. (2009). Environmentally benign production of biodiesel using heterogeneous catalysts. *ChemSusChem*, 2(2): 129 – 135.
4. Rebitanim, N. Z., Ghani, W. A. W. A. K., Rebitanim, N. A. and Salleh, M. A. M. (2013). Potential applications of wastes from energy generation particularly biochar in Malaysia. *Renewable and Sustainable Energy Reviews*, 21: 694 – 702.
5. Mahmoud, D. K., Salleh, M. A. M. and Karim, W. A. (2012). Characterization and evaluation of agricultural solid wastes as adsorbents: A review. *Journal of Purity, Utility Reaction and Environment* 1(9): 451 – 459.

6. Srilatha, K., Issariyakul, T., Lingaiah, N., Sai Prasad, P. S., Kozinski, J. and Dalai, A. K. (2010). Efficient esterification and transesterification of used cooking oil using 12-tungstophosphoric acid (TPA)/Nb₂O₅ Catalyst. *Energy & Fuels*, 24(9): 4748 – 4755.
7. Lien, Y. S., Hsieh, L. S. and Wu, J. C. (2010). Biodiesel synthesis by simultaneous esterification and transesterification using oleophilic acid catalyst. *Industrial & Engineering Chemistry Research*, 49(5): 2118 – 2121.
8. Bamgboye, A. I. and Hansen, A. C. (2008). Prediction of cetane number of biodiesel fuel from the fatty acid methyl ester (FAME) composition. *International Agrophysics*, 22(1): 21 – 29.