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Part I   :   Synopsis

Biomass is a promising source of renewable energy that contributes to energy needs and is the best alternative for guaranteeing energy for the future. In Malaysia alone, oil palm industry producing over 83 million dry tonnes of solid biomass annually and by year 2020 the figure is expected to be between 85 and 110 million dry tonnes [1]. The solid biomass is a promising material for supporting catalyst due to high constituent of carbon. Over the recent years, research on the modification of carbon becomes interest. Carbon materials are relatively cheap, widely available and can be easily functionalized with SO_3H groups through simple treatment with concentrated sulfuric acid [2]. The use of heterogeneous acid catalyst in esterification is among the most promising of the solid acids developed for high FFA esterification. On the other hand, Malaysia annually generated palm fatty acid distillate (PFAD) almost 752,000 tonnes as a by-product of the refining process [3]. PFAD (72.7–92.6% FFA) is potentially a valuable, low-cost feedstock for the production of biodiesel. With high FFA content, acid catalyst is required. No one has reported the use of palm mill biomass-based carbon as solid acid catalyst for the esterification of PFAD. In this work, a novel approach is proposed where the palm mill biomass-based carbon will be functionalize with different acids (sulphonate and phosphoric) and treated under different functionalizing methods and used as a solid catalyst in the esterification of PFAD. The optimization of functionalized groups and the methods plays an important role in term of the catalytic stability and its activity towards esterifying low-cost PFAD into more usable product, methyl esters.

Biomas adalah sumber tenaga yang boleh diperbaharui yang menjanjikan kepada keperluan tenaga dan merupakan alternatif terbaik untuk menjamin tenaga untuk masa depan. Di Malaysia saja, industri kelapa sawit mengeluarkan lebih daripada 83 juta tan biomas pepejal setiap tahun dan menjelang tahun 2020 angka itu dijangka antara 85 dan 110 juta tan [1]. Biomas pepejal adalah bahan yang digunakan untuk emangkin kerana susunan karbon yang tinggi. Sejak beberapa tahun kebelakangan ini, penyelidikan mengenai pengubahsuaian karbon menjadi ikutan. Bahan-bahan karbon agak murah, tersedia secara meluas dan mudah berfungi dengan kumpulan SO_3H melalui kaedah mudah dengan asid sulfurik pekat [2]. Penggunaan pemangkin asid heterogen esterifikasi adalah antara yang paling menjanjikan asid pepejal yang dijalankan untuk pengelasan FFA yang tinggi. Setiap tahun Malaysia menghasilkan distilat asid lemak sawit (PFAD) hampir 752,000 tan sebagai hasil sampingan proses penapisan [3]. PFAD (72.7-92.6% FFA) berpotensi menjadi bahan makanan berharga murah untuk pengeluaran biodiesel. Dengan kandungan FFA yang tinggi, pemangkin asid diperlukan. Tidak ada yang melaporkan penggunaan karbon berasaskan biomas sawit sebagai pemangkin asid padu untuk pengesterilan PFAD. Dalam kerja ini, pendekatan baru dicadangkan di mana karbon berasaskan biomassa kilang kelapa sawit akan berfungi dengan asid yang berbeza (sulfonat dan fosforik) dan dirawat di bawah kaedah fungsi yang berlainan dan digunakan sebagai pemangkin padu dalam pengesterilan PFAD. Pengoptimuman kumpulan yang difungsikan dan kaedah memainkan peranan penting dari segi kestabilan pemangkin dan aktivitinya ke arah penggabungan PFAD kos rendah ke dalam produk yang lebih berguna, metil ester.

Part II: Introduction

The high production cost and the non-availability of proper raw materials, it has not yet attained the anticipated worldwide momentum. The main challenge in the development of a commercially viable technology lies in handling low quality feed stocks such as high free fatty acid (FFA) oils (example PFAD). The concept of environmentally friendly approaches to chemical processes has motivated the use of heterogeneous acids in place of homogeneous acid catalysts. Functionalize carbon-based acid catalysts from biomass revealed that these are promising materials for the production of biodiesel. How the effects of functionalize acid on surface of carbon by measuring the acidity and surface analysis by TPD, Hammett indicator test XRD, BET, FTIR and FE-SEM. In addition the catalytic activities of compound in esterification need to be evaluated. The various acid and different methods in the functionalize carbon including thermal treatment with concentrated acid, the thermal decomposition of ammonium sulphate, the *in situ* polymerization of acetic anhydride and sulphuric or phosphoric acid for the esterification of the low-value industrial by-product PFAD will effect on the stability, activity of catalyst and the ester content. Therefore, in this study, the first objective was to to prepare and characterize solid acid catalysts using biomass-based carbon treated with different acids and functionalizing methods (thermal treatment and polymerization) in esterification of PFAD. Then, the study was done to investigate the performance of the prepared catalyst in esterification of PFAD. Lastly, the study aim to investigate the reusability and the reproducibility of the spent catalyst in esterification of PFAD.

Part III : Methodology

Description of Methodology

1. **Preparation of Carbonaceous Material**

   Palm mill biomass (palm kernel shell and fiber) (10 g) was heated under N_2 flow for 1 h at various temperatures i.e. 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C in a tube reactor.

2. **Purification of Carbon**

   A mixture of pristine carbon (1 g) and HNO_3 (100 ml) was subjected to 1 h of ultrasonication treatment before heated to 80 °C for 8 h. The treated carbon was then filtered, washed with distilled water until the pH of the filtrate is same as the pH of the distilled water and then dried at 120 °C for 12 h to obtain carbon, which was then subjected to sulphonation and phosphorynation.

3. **Functionalize with concentrated acid**

   1 g of carbon was mixed with 50 ml concentrated H_2SO_4 and was sonicate for 30 min. Then, the mixture was stirred for 12 h at 250 °C under nitrogen flow (100 ml min^{-1}). After cooling to room temperature, filter the product was filtered, washed with distilled water until the pH of the filtrate is same as the pH of distilled water and then dried it at 120 °C for 12 h. The same procedure was used for phosphoric, hydrochloric and hy*drofluoric acids.*

4. Functionalize with polymerization

- **Sulphonation by *in situ* polymerization.**

  In this process, 0.4 g of carbon in a mixture of 0.8 g poly(sodium 4-styrenesulphonate) (PSS) and 100 ml deionized water (DI) was stirred vigorously at room temperature for 10 h. Subsequently, 1.6 g of $(NH_4)_2S_2O_8$ was added to the mixture. Then, stirred and heated the mixture at 65°C for 48 h to initiate polymerization. Cooled the mixture to room temperature, then, dilute the mixture with 100 ml of DI water and sonicate for 1 h to allow the polymer to coagulate. Repetitively the polymer was washed with water. The mixture was filter out, then, mixed and stirred it with 500 ml of 4 M H_2SO_4 at room temperature for 24 h. Filtered the mixture and washed the filtrate with DI water until the pH of the filtrate is same as that of the pH of distilled water. Finally, the filtrate was dried at 120°C for 12 h.

- **Phosphorination by *in situ* polymerization.**

  Initially, added polyphosphoric acid (PPA) to a flask and heated it up to 60 °C under dry nitrogen atmosphere. Then, added 1 wt.% carbon to the polyphosphoric acid and homogenize through stirring and heating up to 160 °C. After 0.5 to 48 h for carbon functionalization, added hydrazine sulfate salt (HS) to this mixture. After dissolving the HS, added 4,4'-dicarboxyphenyl-hexafluoropropane, HF, to the flask. The molar dilution rate (PPA/HS) and the molar monomer rate (HS/HF) must kept constant and equal to 10 and 1.2, respectively. After reacting the mixture for 3 to 48 h, poured the reaction medium into water containing 5% w/v of sodium hydroxide, for precipitation of the polymer composite. Finally, filtered the mixture, and washed it with DI water until the pH of the filtrate is same as that of the pH of distilled water and then dried the filtrate at 120 °C for 12 h.

5. Catalysts characterization

The catalysts were identified by X-ray diffraction (Rigaku) with Cu Kα X-ray as a source. A FTIR (PerkinElmer Spectrum 100) spectrophotometer was used to characterize the chemical structure of alkali metal silicate at 400-4000 cm^{-1} range. Surface analysis of the catalyst was examined by using Micromeritics ASAP 2000. Prior to the analysis, all the samples were degassed at 105 °C and N_2 adsorption was measured at −196 °C. The size and morphology of catalyst were observed by using FE-SEM (JSM-7800F). X-ray fluorescence (XRF) analysis was performed employing Bruker S8 Tiger using the pressed-pellet (pressure at 8.0 Pa) method. The base strengths of the catalysts were determined by using TPD analysis and Hammett indicators.

6. Esterification

The esterification of PFAD was carried out in a pressurized reactor under the following conditions: reaction temperature of 110 °C, reaction period of 4 h, methanol-to-PFAD ratio of 15 and catalyst loading of 3 wt%. These reaction conditions was selected based on the trial and error experimentation conducted prior to this study. Upon completion of the reaction period, cooled the mixture to room temperature and filtered. The excess methanol was removed by using a rotary evaporator. Two layers of liquids will form after the evaporation of methanol; the upper layer (dark yellow) is crude fatty acid methyl esters, whereas the bottom layer is water. The concentration of ME in the sample was determined by following the European regulation procedure EN 14103. In this study, GC-MS (Agilent Technologies, 7890A GC-System) with capillary column DB-wax (length 30 x diameter 0.25 mm x film thickness 0.25 μm) using methyl heptadecanoate as an internal standard will be employed. Helium was used as the carrier gas with a linear velocity of 40 cm/s. The oven temperature is programmed at 190 °C, held for

2 min, then ramped at 10 °C per min until it reached 230 °C, and with a last hold time of 8 min. The sample volume of 0.6 µL will be injected into GC.

Part IV   :   Background and site of research

Palm fatty acid distillate (PFAD) is by-products resulting from the extraction and refining of palm oil. Oil palm cultivation in Malaysia (in 2012) takes up a total land area of 5 million hectares in 2012 and yielded 18.8 million tonnes of crude palm oil (CPO), furthermore almost 752.000 tonnes of PFAD will generated in Malaysia as a by-product of the refining process [3]. PFAD is potentially a valuable, low-cost feedstock for the production of biodiesel. Unfortunately, PFAD contains 72.7–92.6% FFA and with a small amount of unsaponifiable components (1–2.5%) [4]. The esterification of high free fatty acid is difficult to get the high of conversion methyl ester. The two-step (esterification-transesterification) adopted to increase the conversion of methyl ester. Boey et al. [5] successfully to convert high free fatty acid oil into biodiesel with almost 100% conversion. The sequential esterification and transesterification method was used. The esterification system was catalysed by ferric-alginate beads (0.16:1 ferric-alginate beads to lauric acid mass ratio, 15:1 methanol to lauric acid molar ratio, methanol refluxing temperature (65 °C), reaction time of 3 h) and transesterification was catalysed by boiler ash-calcium oxide mix (3 wt.% boiler ash, calcium oxide according to the stoichiometric amount of water produced in esterification, 15:1 methanol to oil molar ratio, methanol refluxing temperature (65 °C), reaction time of (0.5 h). However, this type of oil has high FFA and water content that present some drawbacks when base catalysts are considered for biodiesel production process. Therefore, possibility for the application of highly active solid acid catalysts should be explored to convert this oil to biodiesel. Solid acid catalysts such as zirconia, sulfonic acid-functionalized silica and tungstophosphoric acid (TPA) as excellent catalyst in esterification oil with high FFA content [6-8]. Furthermore, a solid acid catalyst, prepared by sulfonating carbonized corn straw, was proved to be an efficient and environmental benign catalyst for the esterification of oleic acid and methanol [9]. In this respect, solid acid catalyzed systems seem to be an interesting research field to be investigated to improve the biodiesel production from low

quality oil sources. Similarly, by utilizing the different groups and functionalizing methods, PFAD could be converted to methyl esters with much higher conversion.

Part V   :   Result(s)

Catalyst characterization

The acidic strength of the palm mill biomass-based carbon -SO$_3$H (PMB- SO$_3$H) catalyst, tested by Hammett indicators (bromophenol blue and methyl red) shows that the colors of indicators lie in the acidic form. However, the color of the crystal violet indicator lies in the basic form. Therefore, the acidic strength of the catalyst is in the range between pH 0.0 to pH 1.8 (Table 1). The TGA/DTA curve of the catalyst showed about 6% weight loss occurred from room temperature to 130 °C which indicates the evaporation of water. The second weight loss about 20% around 130 to 300 °C showed that the -SO$_3$H groups had decomposed to SO$_2$. This shows that the methanol refluxing temperature for the esterification and transesterification reaction is acceptable as the catalyst remains stable without losing the -SO$_3$H groups below 130°C. In PMB-SO$_3$H spectrum, the broader peak appeared around 3427.63 cm^{-1} due to –OH stretching absorption of -SO$_3$H groups. The S-O stretching in –SO$_3$H group mode did appear in the catalyst spectra at 885.64 cm^{-1} and 578.26 cm^{-1}, thus confirming the existence of the sulfonic group in the prepared catalyst. The existence of sulfonic group also been proven by the elemental analysis, EDX as depicted in Figure 1which showed the existence of sulfur group (S) in the catalyst. The average pore size of the PMB-SO$_3$H catalyst is 10.7nm (mesoporous) which suit best as a catalyst for preparation of biodiesel.

Table 1: Acid strength determination of PMB-SO$_3$H catalyst

Indicators	pH range	Acidic form (<pH)	Colour change
Methyl red	4.4 – 6.2 Red – Yellow	Red (<4.4)	Remain Red
Bromophenol blue	3.0 – 4.6 Yellow – Purple	Yellow (<3.0)	Remain Yellow
Crystal violet	0.0 – 1.8 Yellow – Purple	Yellow (0.0) Purple (<1.8)	Yellow to Purple

Part VI   :   Interpretation

The ideal solid acid catalysts for esterification and transesterification process should have characteristic of strong Brønsted and/or Lewis acid properties, hydrophobic surface and unique porosity properties (morphology of the support). However, leaching of acid site, deactivation and poisoning during the reaction process should be avoided. The Brønsted acid sites act as the H$^+$ donor, highly polarized hydroxyl groups at the surface of the catalyst while the Lewis acid sites serve as the electron-pair acceptor are coordinately unsaturated cationic sites, which leave the exposed M$^+$ ion to interact with guest molecules. The best choice of solid acid catalyst for biodiesel production would be having both Brønsted and Lewis acid site (bifunctional) with a hydrophobic environment protecting the Lewis site from the poisoning effect of water. Most of the solid acid-catalysed esterification or transesterification reactions usually perform under higher temperature and higher pressure due to their lower catalytic activity compared with solid bases [10].

Esterification of PFAD with prepared catalyst

Statistical Analysis

Catalyst amount (A), methanol /PFAD molar ratio (B) and reaction time (C) were the selected manipulate variables observed over the methyl esters conversion (Table 2).

Table 2   Experimental designs matrix and their corresponding FAME conversion results

Point type	Catalyst amount (wt.%), A	MeOH:Dc-oil (molar ratio), B	Reaction time (h), C	X_A	X_B	X_C	FAME conversion (%)
Center	3	4	5	0	0	0	90.2
Center	3	4	5	0	0	0	92.2
Center	3	4	5	0	0	0	92.2
Center	3	4	5	0	0	0	92.2
Center	3	4	5	0	0	0	91.3
Center	3	4	5	0	0	0	90.4
Axial	1.59	4	5	-1.41	0	0	88.2
Axial	4.41	4	5	1.41	0	0	83.2
Axial	3	1.17	5	0	-1.41	0	84.1
Axial	3	6.83	5	0	1.41	0	93.4
Axial	3	4	2.17	0	0	–	90.0
Axial	3	4	7.83	0	0	1.41	94.5
Fact	4	6	3	1	1	-1	87.3
Fact	4	2	7	1	-1	1	88.0
Fact	2	6	7	-1	1	1	90.3
Fact	2	2	3	-1	-1	-1	80.8

X: coded of variable levels.

The statistical Model Fit Summary suggested the quadratic model looks as the best fit-model. The quadratic model comes out best as it exhibits low standard deviation, high 'R-Squared' value and low 'PRESS' (a measure of how good a particular model fits each point in the design). Although, the cubic model showed the lowest standard deviation, the model comes

with many of aliased terms. Meanwhile, the analysis of variance (ANOVA) in Table 3 confirms the adequacy of quadratic model as the model 'Prob > F' is 0.0009 which is less than 0.05 ("Prob > F" less than 0.05 indicate model terms are significance). In addition, the model proposes an adequate signal of more than 17. The signal to noise ratio (adequate precision) should be greater than 4 to confirm its ability to navigate the design space. Moreover, the high regression, $R^2 = 0.98$ (about 98% of variability of the data fitted to the model), and low coefficient of variance (CV, 1.03) which indicates a high degree of precision and a good deal of reliability of the experimental values have proved that the suggested model was well validated. The predicted and observed values of fatty acids methyl esters conversion were in reasonable agreement (R^2 value closed to unity), thus given convincingly good estimate of response for the system. As suggested, the following regression analysis equation was generated (in term of coded factor) as in Equation 1. Furthermore, the model comes out with good reproducibility of the data as it has low value of pure error (3.58). The lack of fit test is not significant with p-value of 0.4404 which is good and indicates the model equation was adequate for predicting the conversion of methyl esters under any combination of values of the variables. The term 'lack of fit' is used to measure the failure of the model to represent data in the experimental domain at points which are not included in the regression. In other words, it can say that strong lack of fit ($p<0.05$) is an undesirable property, because it indicates that the model does not fit the data well and it is desirable to have an insignificant lack of fit ($P>0.1$). According to the analysis of variance, the model clearly identified that methanol/PFAD molar ratio (p-value of 0.0009) have strongly significance effect on methyl esters conversion followed by catalyst amount (p-value of 0.0122) and reaction time (p-value of 0.0187) respectively. The lowest the p-value, the most significance the response is. In addition, the dominancy characteristic of methanol/PFAD molar ratio also shown by the highest magnitude value (3.27) it has in the regression analysis in Equation 1. The methanol to PFAD molar ratio and reaction time exhibit synergistic effect in increase methyl esters yield as indicate by positive sign of the terms. In contrary, the catalyst amount shows antagonistic effect as it possesses a negative sign.

Final Regression Model (Coded Factors)

$$\text{FAME conversion, (\%)} = 91.56 - 1.76A + 3.27B + 1.58C - 0.99AB + 1.09AC \qquad (1)$$

$$-2.82BC - 3.13A^2 - 1.6B^2 + 0.14C^2$$

Table 3	Analysis of variance (ANOVA)					
Source	**Sum of squares**	**df**	**Mean square**	**F value**	**Prob>F**	
Model	212.59	9	23.62	27.92	0.0009	significant
A	12.45	1	12.45	14.71	0.0122	
B	42.69	1	42.69	50.45	0.0009	
C	9.95	1	9.95	11.75	0.0187	
AB	1.97	1	1.97	2.33	0.1873	
AC	2.38	1	2.38	2.82	0.1541	
BC	15.90	1	15.90	18.79	0.0075	
A^2	77.81	1	77.81	91.96	0.0002	
B^2	20.28	1	20.28	23.97	0.0045	
C^2	0.16	1	0.16	0.19	0.6834	
Residual	4.23	5	0.85			
Lack of fit	0.65	1	0.65	0.73	0.4404	Not significant
Pure error	3.58	4	0.89			
Cor total	221.01	15				
Std. dev[a]	0.92		R-squared	0.9805		
Mean	89.29		Adeq precision[c]	17.505		
C.V %[b]	1.03					
PRESS	185.95					

[a] standard deviation; [b] coefficient of variation; [c] adequate precision

[4] Cheah, K.Y., Toh, T.S., Koh, P.M., 2010. Palm fatty acid distillate biodiesel: Next-generation palm biodiesel. <http://www.aocs.org/Membership/FreeCover.cfm?itemnumber=3504> [accessed June 2014].

[5] Boey, P.L., Ganesan, S., Maniam, G.P, Khairuddean, M., 2012. Sequential conversion of high free fatty acid oils into biodiesel using a new catalyst system, Energy 46, 132-139.

[6] Jitputti, J., Kitiyanan, B., Rangsunvigit, P., Bunyakiat, K., Attanatho, L., Jenvanitpanjakul, P., 2006. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. *Chemical Engineering Journal* 116, 61-66.

[7] Melero, J.A., Bautista, L.F., Morales, G., Iglesias, J., Sánchez-Vázquez, R., 2010. Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts. *Chemical Engineering Journal* 161, 323-331.

[8] Badday, A.S., Abdullah, A.Z., Lee, K.T., 2014. Transesterification of crude Jatropha oil by activated carbon-supported heteropolyacid catalyst in an ultrasound-assisted reactor system. Renewable Energy. 62, 10-17.

[9] Liu, T., Li, Z., Li, W., Shi, C., Wang, Y., 2013. Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol. Bioresource Technology 133, 618-621.

[10] Su, F. and Guo, Y., 2014. Advancements in solid acid catalysts for biodiesel production. Green Chemistry, 16(6), 2934-2957.

Part VII : **Conclusion and Suggestion**

A one-step process converting palm fatty acid distillate into methyl ester by functionalizing the catalyst with desired functional groups. Conventionally a two-step method is adopted which has drawbacks in term of product yield, material and energy used.

To understand the behaviour and explore the application of the carbon-based catalysts further investigations are recommended, such as:

• Boehm titration of the catalyst following (Fictorie et al. 2011), procedure would help quantify the amount of each functional group on the catalyst.

• Determining the strength of the different active sites would create a better understanding of the functional groups and their effect on catalytic activity.

• Further studies could be performed on the development of the catalyst. Using different functionalizing reagents such as fuming acids with a higher percentage of free SO3, other strong acids, or super acids as suggested by Dehkhoda (2010).

• Study of reusability and regeneration of carbon-based catalysts.

• Examining the changes in composition and structure of the biochar following the chemical activation or functionalization steps would be useful.

Part VIII : **References**

[1] The Star Online. Lahad Datu oil palm biomass pact seen to draw 12 to 15 companies, 2013 <http://bizthestarcommy/news/storyasp?file=/2013/6/22/business/13274514&sec=business> [accessed June 2014].

[2] Dora, S., Bhaskar, T., Singh, R., Naik, D.V., Adhikari, D.K., 2012. Effective catalytic conversion of cellulose into high yields of methyl glucosides over sulfonated carbon based catalyst. Bioresource Technology 120, 318–321.

[3] Malaysian Palm Oil Board, 2014. <www.mpob.gov.my> [accessed May 2014]