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To cite this article: J Janaun et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 206 012015

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Synthesis of Biodiesel in Batch and Packed-Bed Reactors **Using Powdered and Granular Sugar Catalyst**

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Abstract. Increasing world production of palm oil warrants effective utilization of its waste. In particular, conversion of waste cooking oil into biodiesel has obtained global interest because of renewable energy need and reduction of CO2 emission. In this study, oleic acid used as a model compound for waste cooking oil conversion using esterification reaction catalysed by sugar catalyst (SC) in powdered (P-SC) and granular (G-SC) forms. The catalysts were synthesized via incomplete carbonization of D-glucose followed by functionalization with concentrated sulphuric acid. Catalysts characterizations were done for their physical and chemical properties using modern tools. Batch and packed-bed reactor systems were used to evaluate the reactivity of the catalysts. The results showed that G-SC had slightly higher total acidity and more porous than P-SC. The experimental conditions for batch reaction were temperature of 60°C, molar ratio of 1:20 (Oleic Acid:Methanol) and 2 % wt. catalyst with respect to oleic acid. The results showed the maximum oleic acid conversion using G-SC and P-SC were 52 % and 48 %, respectively. Whereas, the continuous reaction with varying feed flow rate as a function of retention time was studied by using 3 g of P-SC in 60 °C and 1:20 molar ratio in a packed-bed reactor. The results showed that a longer retention time which was 6.48 min and feed flow rate 1.38 ml/min, achieved higher average conversion of 9.9 % and decreased with further increasing flow rate. G-SC showed a better average conversion of 10.8 % at lowest feed flow rate of 1.38 ml/min in continuous reaction experiments. In a broader perspective, large scale continuous biodiesel production is feasible using granular over powdered catalyst mainly due to it lower pressure drop.

1. Introduction

In the concern of the environment issues and limited fuel resources, the discovery of biodiesel is one of the viable solutions for the problems. Biodiesel is biodegradable, non-toxic and gives a lower emission profile [1]. It is environmentally friendly as well as beneficial [2]. Biodiesel can be produced by various types of feedstocks such as vegetable oil, animal oil, and waste cooking oil or any feedstock that contains free fatty acid (FFA) or triglycerides (TG) [3]. The most favoured reaction pathways are catalytic transesterification and esterification [3]. Both of the reactions required the presence of catalyst, either acid or base catalyst. Acid catalyst can simultaneously catalyse esterification and transesterification [3], [4]. Sugar catalyst is one of heterogeneous acid catalysts which had been reported to be successful in biodiesel production [5].

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29th Symposium of Malaysian Chemical Engineers (SOMChE) 2016IOP PublishingIOP Conf. Series: Materials Science and Engineering 206 (2017) 012015doi:10.1088/1757-899X/206/1/012015

Most of the reactions are carried out in a batch reactor in laboratory scale, in which the condition of the reaction is easier to be optimized in a long period of reaction, especially when using solid acid catalyst [4], [6]. For continuous production, packed bed reactor (PBR) is used. However, the pressure drop is the main concern on every continuous PBR. By then, catalyst preparation becomes a matter to reduce the resistance of the fluid flow by increasing the particle size [7].

The sugar catalyst exists fine in particle size, which is in the range of 65 μ m [8]. Powdered catalyst will be likely to encounter pressure drop in the large scale production which will likely affects equilibrium compositions and the maximum conversions that can be achieved for a given feed. However, catalytic performance was poorer for larger catalyst particles, most likely due to mass transfer limitations [9].

In the present study, the effect of catalyst particle size on converting of fatty acid into fatty acid methyl ester in both batch and PBR was determined. Sugar catalyst was prepared in powdered and granular forms and the reactivity of the catalysts was investigated.

2. Methodology

2.1. Preparation of G-SC and P-SC

Dried D-glucose was pyrolysed at temperature 400 °C for 4 h with continuous supply of nitrogen gas, N_2 in a rate of 100 mL/min. The resultant material was a dark char. The char was crushed into smaller pieces by rolling method using glass rod until the largest particle size was 5-8 mm. The crushed char was sulfonated with concentrated H₂SO₄ (95 %) for 12 h. The sulfonated char was washed repeatedly using hot distilled water until no sulfate ion was detected in the wash water. Then, the washed char was dried in oven for 3 h at temperature of 100 °C. The dried sulfonated char was sieved with two meshes with openings size of 0.5 mm and 1.4 mm. The sulfonated char was divided into two different sizes, (<0.5mm) and (>1.4 mm). Sulfonated char with smaller particle size was named P-SC and larger particle size was G-SC.

2.2. Characterization of catalyst

The total acid density test was conducted by using back titration with 0.008 M NaOH and 0.02 M of HCl. Particle Size Distribution (PSD) analysis was carried out using Malvern Zetasizer series with water as dispersant for the machine refractive index of 1.330. 1.0 g of P-SC was diluted with 20 ml of distilled water and then pipetted the clear water after few hours of settling for measurement. This test was only suitable for P-SC due to its smaller particle size. Scanning Electron Microscopy (SEM) was used to analyze the surface morphology of the catalysts. It can also observe the microstructural scale which can inspect the capillary porosity and determine the particle size of G-SC as well. Energy-dispersive X-ray microanalysis (EDX) is a complementary technique to SEM and was used to determine the composition of the features. The pore size and surface area of catalyst were determined by using Automated Mercury Porosimeter, Pascal 440 series. Approximately 0.2 g of each sample was used for the analysis with the pressure of blank sample at 200 MPa and lowest increment of pressure. The functional group of catalyst was determined by using Fourier Transform Infrared (FTIR) Spectrometer, Perkin Elmer.

2.3. Catalytic Esterification Reaction

For batch system, esterification was performed in a STEM Reacto as shown in Figure 1(a) and continuous reaction was performed in PBR as shown in Figure 1(b). Figure 2 shows the apparatus setup for PBR. For laboratory scale, condenser was used as PBR. The inner column of the condenser was packed with catalyst.

29th Symposium of Malaysian Chemical Engineers (SOMChE) 2016

IOP Conf. Series: Materials Science and Engineering 206 (2017) 012015 doi:10.1088/1757-899X/206/1/012015



Figure 1(a). Image of STEM Reacto. Reactants and catalyst were placed in the vials.





In both systems, a molar ratio of oleic acid to methanol used was 1:20 at reaction temperature of 60 °C. For batch system, 2 wt.% of catalyst with respect to oleic acid was added and the reactants were stirred at stirring rate of 800 rpm. For every 2 hours, 100 μ L of sample was pipetted from the reactor using micro pipette and placed into a clean and dry conical flask for product analysis. In continuous system, the inner column of a condenser was packed with 3 g of P-SC with and secured with glass wool. Hot thermostat water bath (60 ± 3 °C) was pumped continuously to the outer column of the condenser to heat up the reactant up to 60 °C. Reactants mixture was pumped to the reactor with a peristaltic pump with different flow rates of 1.38 ml/min, 2.64 ml/min and 3.9 ml/min. The retention times for three different flow rates were 6.48, 3.38 and 2.29 min, respectively. Reaction time for each flow rate was 1 h. The experiment was repeated with G-SC using the same conditions. The product was collected at the top of the reactor at every 15 min.

2.4. Acid value analysis

The conversion of oleic acid into methyl oleate was determined using titration method. The reduction of acid value showed the conversion of FFA into Fatty Acid Methyl Ester (FAME). A calibration curve of concentration of oleic acid against acid value was plotted. 100 μ L of sample taken and diluted in 20 ml of diethyl-ether solvent and titrated with 0.1 M Potassium Hydroxide, KOH. The acid value of the sample was calculated using equation (1).

$$Acid \ value = \frac{56.1 \ g}{mol} \times Normality \ of \ KOH \ \times \ \frac{Volume \ of \ titrant \ (L)}{Mass \ of \ sample \ (g)}$$
(1)

A blank titration is performed to determine the initial and final volume of oleic acid by using potassium hydroxide solution. The conversion of the oleic acid was calculated by using equation (2), where initial volume of oleic acid is denoted by v_i and v_f for final volume of oleic acid.

$$Conversion (\%) = \frac{v_i - v_f}{v_i} \times 100$$
⁽²⁾

3. Results and Discussion

3.1. Characteristic of G-SC and P-SC

3.1.1. Total Acidity

G-SC was found to have slightly higher total acidity value than P-SC which is 1.778 mmol/g and 1.612 mmol/g, respectively. The results obtained are comparable to acidity of carbon catalyst reported by Zong et.al. (2007).

3.1.2. Surface Area and Porosity

Table 1 shows the properties of the granular and powdered sugar catalyst by using the mercury porosimeter. The results show that the catalysts are mesoporous with an average pore size of 1300-2300 nm (1.3 μ m-2.3 μ m), while the surface area is between 2.9 m²/g to 4.0 m²/g.

	G-SC	P-SC
Total cumulative volume (mm ³ /g)	46.4	29.9
Total specific surface area (m^2/g)	4.0	2.9
Average pore diameter (Nanometer)	2272.1	1326.6
Total porosity (%)	1.58	1.04
Total acidity (mmol/g)	1.78	1.61

Table 1. Properties of G-SC and P-SC Obtained from Porosimeter.

Different particle size of catalysts does show some difference on the total porosity with a difference of 0.535 %. G-SC has a higher surface area and so does its total cumulative volume, these facts suggested that there are many layers of surface underneath the outer surface area. Therefore when mercury intrudes deep into the catalyst, there are more empty spaces and pores to be filled up, thus its total specific surface area is 1.4 times greater than P-SC. The heterogeneous catalyst activity is mainly depends on its surface area, porosity and acid group [10]. This is because the bigger the surface area, the higher the chances of attaching the acid group, so more reaction can be catalyzed, glycerol or water could block the pores which contain acid groups, thus preventing more reactions to occur [8]. G-SC has higher surface area which might also explain higher total acidity of the catalyst that P-SC.

3.1.3. Surface Morphology and Particle Size

3.1.3.1 Granular Sugar Catalyst

The size of the catalyst sample measured is approximately 3.0×2.7 mm. The average particle size of G-SC is 3.0 mm. In Figure 2, it can be clearly seen that glucose synthesized char is very porous, hundreds of pores can be seen on the surface of the catalyst. Pores are clearly visible under the magnification of 190. The diameter size of the pores is ranged from $4.57 \mu m$ to $119 \mu m$.

3.1.3.2 Powdered Sugar Catalyst

Figure 3 shows the image of P-SC under SEM. The pores are not clearly seen as G-SC. Particle size of P-SC was measured by using Particle Size Distributor (PSD). The PSD result gave a range of 18.92 nm to 3219 nm in radius, thus the calculated average diameter is 843.8 nm. However, the detection scale of PSD is limited from 0.4 nm to 10000 nm in diameter. Some P-SC particle could be larger than 10000 nm (10μ m). To reconfirm the analysis on the particle size, P-SC was also measured using SEM.

The result shows the particle size is in range of 100-500 μ m. The smallest diameter of the visible pore determined is 2.22 μ m and biggest pore size is 53 μ m.

Both catalysts, G-SC and P-SC, have the smallest visible pore size of 4.57 μ m and 2.22 μ m, respectively under SEM analysis. The determination of pore size using porosimeter shows that the average pore size of G-SC and P-SC are 2.27 μ m and 1.33 μ m respectively. The results was comparable with the pore size detected using SEM.



Figure 2. Granular Sugar Catalyst under SEM with magnification of 35.



Figure 3. Powdered Sugar Catalyst under SEM with magnification of 47.

3.1.4. Surface Element Analysis

The compositions of the catalysts were determined by using Energy-Dispersive X-Ray Spectroscopy (EDX) analysis. For EDX analysis, it analyzed the composition of the elements presence on the surface of the catalyst. Table 2 shows the elemental compositions on G-SC and P-SC. Assuming all sulfurs in the catalysts are in the form of SO₃H, [4], [11] the estimated density of SO₃H is as shown in Table 2. The SO₃H density of the synthesized G-SC and P-SC are 1.380 mmol/g and 0.929 mmol/g, respectively. The SO₃H density of fresh G-SC is comparable with the result reported by Zong *et al.* (2007) P-SC shows a slightly lower SO₃H density. Reductions of sulphur content are 7.06 % and 1.82 % in mole for G-SC and P-SC, respectively.

Cat	alyst		Mol		SO_3H
		С	0	S	(mmol/g)
Fresh	G-SC	6.395	1.174	0.138	1.380
	P-SC	6.672	1.078	0.082	0.820
Used	G-SC	5.943	1.603	0.093	0.929
	P-SC	6.551	1.176	0.078	0.780

Table 2. Composition of elements on different particle size of fresh and used sugar catalyst.

3.1.5. Functional Group

Figure 4 shows the FT-IR spectrum of P-SC. Since the two different particle sizes show almost similar spectra, therefore the spectrum below infer the FT-IR result of both P-SC and G-SC as well.



Figure 4. FT-IR spectra of powdered sugar catalyst.

Both of the catalysts were undergoing similar preparation step, therefore they have the same functional groups. The spectrum contain peak around 1000-1030 cm⁻¹, which attributes to the existence of S=O stretching [12], as well as peak at 1154 cm⁻¹ attributable to the presence of SO₃H groups [13], thereby reassuring the sulfonic group existing on the carbon-based char after sulphonation. At wavenumber of 1620-1680 cm⁻¹, there is aromatic ring modes indicates C=C stretching [14]. Besides, the O-H stretching band appears at wavelength of 3200 cm⁻¹, and the band at 1702 cm⁻¹ was assigned to the C=O stretching mode of the COOH group [15]. Thus, the overall FTIR analysis proven that the sulphonated char consists of polycyclic aromatic carbon sheets containing SO₃H, COOH and OH groups.

3.1.6. Thermal Stability

Based on the TGA analysis, the weight of both catalysts started to drop at 100 °C as this could due to the moisture content of the sample which the vaporization of water causes the decrease in the weight percent [8]. The final %weight for G-SC and P-SC are 86.21 % and 87.03 %, respectively. The different final weight% for both sugar catalysts might due to different initial moisture content as weight% of G-SC starts to decrease more than that of P-SC from 30 °C to 80 °C and the rate of decreasing %weight for both catalysts were the same after 80 °C until the end of analysis. Thus, the carbon-based catalysts showed almost similar thermal stability. As for DTA result, there are two significant weight loss peaks for each sample. They occurred in a range of 69-79 °C and 246-249 °C for G-SC and P-SC which can be explained by the decomposition of the functional groups. From the TGA data, it can be conclude that the G-SC and P-SC are thermally stable until 246 °C and 249 °C, respectively.

3.2. Batch Esterification Reaction

3.2.1. Effect of Particle Size of Sugar Catalyst

Figure shows the reactivity of both catalysts. From the curve fitting in Figure 5, it concluded that both catalysts have similar initial rate of reaction. However, the maximum conversion of G-SC (52 %) is higher than P-SC (48 %). The conversion values of both catalysts were supported by the findings of two journals that use sugar catalyst. The conversion values obtained was 45 % and 61 %, respectively [13]. This proves that higher total acidity of enhance the conversion rate of esterification reaction. Sugar catalyst with high SO₃H density and larger surface area is likely to have more active sites attach on it, thus G-SC had higher rate of reaction after 10 h of reaction [8]. If the heterogeneous reaction only occurs on the outer surface of the catalyst, the rate of reaction will increase substantially with decrease in particle size, since larger surface area will be obtained with decreasing particle size [16]. However, it is an interesting finding since the total specific surface area per unit volume of G-SC

appears to be larger than P-SC. In this case, explanation of larger specific surface area can be incorporate with the assumption of more surface area within the granular catalyst in which there are layers of porous surface areas in G-SC catalyst.

3.2.2. Analysis of Rate Data (Kinetic Data)

Figure shows the order of reaction is second order and the k value for G-SC and P-SC are 8.0×10^{-7} and 7.0×10^{-7} mmol⁻¹.L.min⁻¹, respectively. The acid sites (SO₃H group) will speed up the reaction by decreasing the activation energy and increase the rate of effective collision, thus with higher total acidity value, the rate of reaction will be higher. The regressions of both lines were also in agreement with Janaun (2012) where the order of the reaction was two.



Figure 5. Conversion of oleic acid by G-SC and P-SC.



Figure 6. Concentration Differential Relationship with Concentration for k and α for G-SC and P-SC at 60°C and 1:20 Molar Ratio.

3.3. Continuous Esterification Reaction

3.3.1. Effect of Retention Time / Feed Flow Rate

Figure 7 shows the conversion of oleic acid against time in continuous reaction at different feed flow rates (Q1=1.38 ml/min, X_{ave} =9.9 %, Q2=2.64 ml/min, X_{ave} =5.1 %, and Q3=3.90 ml/min, Xave=0.4 %,). From Figure 7, the FFA conversion of three different feed flow rates catalyzed by P-SC with a condition of 60°C, 1:20 (OA:MeOH) molar ratio and 3g of P-SC. The maximum average FFA conversion of 9.9 % was achieved at lowest feed flow rate around 1.38 ml/min. This finding is in

agreement with the result obtained by Ren *et al.* (2012). It was reported that highest FAME conversion was obtained at lowest flow rate of 1.27 ml/min [17].

The average FFA conversion increased from 0.4 % to 9.9 % when the feed flow rate decreased from 3.90 ml/min to 1.38 ml/min (Table 3). This can be explained that the reactants have less contact time with the active sites of the catalyst when passing through the sugar catalyst column and resulting the low FFA conversion [8]. Thus, longer contact time between the reactants and the catalyst gives higher conversion.

Table 3. Summary of three different flow rates with their average conversions.

Flow rate (ml/min)	1.38	2.64	3.90
Retention time (min)	6.48	3.38	2.29
Average FFA conversion (%)	9.9	5.1	0.4

3.3.2. Effect of Particle Size of Sugar Catalyst

As expected, G-SC performed well in the continuous reaction with a slightly higher conversion of 10.8% than P-SC which convert 9.9 % of oleic acid for the same condition (feed flow rate=1.38 ml/min, temperature = 60° C, molar ratio of OA:MeOH=1:20, catalyst loading = 3 g).

In laboratory scale, pressure drop is not significant. The measurement of both inlet and outlet flow rate of the reactor, are almost similar which implies insignificant pressure drop. However, for large scale such as in industrial, P-SC is expected to encounter more pressure drop than G-SC if the length of bed catalyst is the same due to its fine particles that create more resistance to the fluid flow.



Figure 7. Conversion of oleic acid against time in continuous reaction with 3 different feed flow rates (Q1=1.38ml/min, X_{ave}=9.9%, Q2=2.64ml/min, X_{ave}=5.1%, Q3=3.90ml/min, X_{ave}=0.4%,).

3.4. Comparison Of Batch And Continuous Reactions

The esterification reaction is mostly carried out in batch condition as it is more stable and has a better control on temperature and the reactant mixtures is well-mixed throughout the entire process. Besides, the vaporization of methanol can be minimized due to the close system in batch reactor and a proper handling when pipetting the sample. Thus, the FFA conversion obtained shows a smooth curve throughout a long period of reaction. However, continuous reaction shows an undesired result data as the conversion values fluctuated during the experiment. Furthermore, difficulty to minimize the vaporization of the methanol and detection of well-mixed condition in the reactor are the factor

affecting the result. Therefore, the rate of reaction is hard to determine due to the inconsistency of data.

However, continuous esterification reaction is advantageous in term of shorter reaction time. The weight percentage of catalyst used is approximately 60 times more than that in batch condition. Therefore, average FFA conversion of 9.9 % and 10.8 % were obtained in continuous reaction in a retention time of 6.48 min only, while this conversion for batch reaction shows the similar result in 2.5 h. The esterification reaction time of continuous reaction was almost 96 % faster than batch reaction in this case. Esterification reaction has a higher rate when the catalyst to reactants ratio is higher, and reaction time is shorter.

Both P-SC and G-SC catalyst works well in the continuous system as the structure of catalyst retained after 6 hours of operation as shown in Figure 8. It did not break into fine particle size due of vigorous stirring as in batch reaction shown in Figure 9. Thus, it indicates that continuous reaction is likely to create no damage to the catalyst and more preferable when it comes to time saving and more production purposes.



Figure 8. Condition of the G-SC (left) and P-SC (right) after continuous reaction and washing



Figure 9. Condition of the P-SC and G-SC Before and After Batch Reaction

4. Conclusions

In this research, P-SC and G-SC were successfully synthesized with the particle size ranged from 100-300 μ m and 1.0-5.0 mm, respectively. The characterization of G-SC and P-SC showed that they had similarity with sugar catalyst. G-SC exhibited higher total acidity compared to P-SC. G-SC also showed better oleic acid conversion in batch and continuous reaction compared to P-SC. In short, the catalytic performance of G-SC was slightly better than P-SC. In continuous reaction, the results showed the conversion got higher as the feed flow rate got lower, this was due to the contact time of reactants with catalyst was longer.

In this research, G-SC and P-SC could be used in continuous reaction. The esterification reaction time of continuous reaction achieved 96% faster than the batch reaction. Therefore, bigger scale continuous biodiesel production by using G-SC is reasonable to perform in future for the purpose of time-saving and minimal pressure drop.

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