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Esterification of free fatty acid in used cooking oil using gelular exchange resin as catalysts

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Abstract

The esterification of free fatty acids (FFA) in used cooking oil was investigated using gelular ion exchange resins, SK104H and SK1BH catalysts. Characterization methods such as Fourier transform-infra red (FT-IR) spectroscopy, particle size distribution (PSD), scanning electron microscopy (SEM), elemental analysis (CHNS) and acid capacity analysis were conducted to determine the physicochemical properties of the catalysts. These catalysts were then subjected to a screening study to select the best performance catalyst, which further subjected to esterification reaction using one-variable-at-a-time (OVAAT) method. Using OVAAT method, the effect of mass transfer resistance, catalyst loading, reaction temperature and methanol to oil mass ratio were studied to optimize esterification reaction conditions. The conversion of FFA in the used cooking oil was successfully achieved 88% under optimal conditions of 18:1 methanol to oil mass ratio, reaction temperature of 60°C, catalyst loading of 3.0 wt. % and 300 rpm of stirring speed. Excellence catalytic performance may attributed to the smallest average particle size, high sulfur content and high acid capacity value of SK104H, resulting high conversion of FFA.

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1. Introduction

Nowadays, there are significant interests towards utilization of waste raw materials (i.e. vegetable, animal oils and fats) to increase the competiveness of biodiesel processing cost. At present, the major feedstock employed in biodiesel production is the high quality of edible vegetable oils (e.g. soybean, sunflower and palm oil). However, due to the high cost of virgin vegetable oil, it has escalated the interest among researchers and industrialist towards the utilization of less expensive feedstock. Furthermore, the rapid growth of world population increases the demand on both food and fuel and significantly contributes to the food versus fuel issues. As a result, cheap and non-edible feedstocks such as waste cooking oil (WCO) has attracted considerable attention to overcome these problems. However, high level of free fatty acid (FFA) content in the feedstock such as WCO cannot be directly used in base-catalysed transesterification as the presence of high levels of FFA may cause saponification thus reduces the yield of fatty acid methyl ester (FAME). These contribute to the difficulties in products separation and catalyst reutilization. Therefore, the recommended percentage of FFA must be between 0.5 % - 1.0 % by weight to avoid the saponification process.

A two-stage esterification-transesterification has been investigated by many researchers to achieve high yield of FAME [1,2]. Esterification acts as a pre-treatment step to reduce the FFA content in the raw material and has been widely studied at different operational conditions using various types of catalysts such as homogenous acid catalysts (i.e. sulfuric acid or hydrochloric acid), heterogeneous acid catalysts (i.e. heteropolyacids, zeolites, sulphated metal oxides and ion exchange resins) and enzyme catalysts. Homogeneous acid catalysts such as sulfuric acid is commonly used in esterification reaction. However, the use of this type of catalyst causes problems such as corrosion of equipment, existence of side reactions, generate high amount of wastewater, difficulties in process separation and reutilisation of catalyst and high production cost due to additional equipment for separation and neutralization processes [2].

Recently, the ion exchange resins have showed a good performance in the esterification and transesterification reaction. Ion exchange resin owns the advantages of having high catalytic activities under mild reaction, easily recovered from the reaction mixture and can be operated at mild condition. The most popular exchange resin used in esterification reaction is the cation exchange resins. Cation exchange resins can be categorized into two types of matrix nature; gelular and macro-reticular. Kouzu *et al*. [3] tested the activity of gelular (Amberlyst-31) and macroeticular (Amberlyst-15) in the esterification of soybean oil. It was found that gelular resin has a higher catalytic activity as compared to macro-reticular resin. Additionally, gelular resin is more active in catalyzing the esterification than macro-reticular one and greatly depends on swelling properties as its controls the reactants movement to the acid sites and their overall reactivity [4].

The objective of this research is to investigate the esterification of FFA in acidified oil using gelular ion exchange resins namely SK1BH and SK104H as catalyst. SK1BH and SK104H are the strongly acidic low crosslinked resins (<10%) with polystyrene matrix incorporated with sulfonic groups. Different types of characterization method such as Fourier transform-infra red (FT-IR) spectroscopy, particle size distribution (PSD), scanning electron microscopy (SEM), elemental analysis (CHNS) and acid capacity analysis were conducted to determine the physicochemical properties of the catalysts. These catalysts were then subjected to a screening study to select the best performance catalyst, which further subjected to esterification reaction using one-variable-at-a-time (OVAAT) method. The relationship between the FFA conversion with different operating variables such as the mass transfer resistance, catalyst loading, reaction temperature, and methanol to oil ratio will be investigated.

2. Materials and Methods

2.1. Chemicals

The used cooking oil (UCO) was prepared by mixing the cooking oil (Saji brand) with the oleic acid (95% purity) purchased from Sigma Aldrich (Malaysia) to produce a simulated used cooking oil (SUCO) with an acid value of 11.5 mg of KOH/g and 6 % FFA content. Methanol (99% purity), 2-propanol (99.5% purity), toluene (95% purity), 0.1 M volumetric standard hydrochloric acid, 0.1 M of volumetric standard sodium hydroxide, potassium hydroxide, *p*-naphtholbenzein and methyl red (≥99% purity) were purchased from Sigma Aldrich (Malaysia) and Merck

(Malaysia). Diaion catalyst of SK104H and SK1BH resins were supplied by Mitsubishi Corporation Sdn. Bhd. in wet form of spherical beads. These catalysts were pre-treated before being used in the esterification reaction.

2.2. Catalyst characterization

Fourier transform-infra red (FT-IR) spectroscopy analysis using PerkinElmer Spectrum 100 FT-IR was performed to determine the functional groups of the catalysts. Infrared spectra for each catalyst were measured at wavelength range from 400 to 4000 cm-1. The particle size distribution (PSD) was performed to measure the distribution pattern of the catalysts. The Malvern Mastersizer 2000 was used for measurement and the average particle size distribution was taken as the final results. The surface morphology of the resins were captured by using CARL ZEISS scanning electron microscopy (SEM). Elemental analysis was carried out using vario MACRO cube to investigate the percentage of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) elements in the resins. Acid capacity determination was conducted using a conventional titration method with methyl orange as an indicator.

2.3. Experimental method

The esterification process was being carried out in a batch reactor consist of 0.5L of round bottom flask reactor equipped with a condenser to prevent loss of reactant due to vaporization, thermocouple to control the temperature and sampling port via fabricated syringe for the product collector. The effect of stirring was achieved via the usage of magnetic stirrer. A specified amount of SUCO and methanol were added into the reactor. The reactants were stirred and pre-heated until it reached the designated temperature. After that, an amount of catalyst was added and the time taken was started to be counted as zero. Approximately 2 grams of sample was periodically taken from the reactor to determine the conversion of FFA. In this study, a few variables such as external and internal mass transfer resistance, catalyst loading, reaction temperature and oil to methanol mass ratio were investigated.

2.4. Analysis method

2.4.1. Acid value and FFA content analysis

Determination of acidic or basic constituents in the sample was determined using ASTM D974. An amount of sample from the reactor was weighted and mixed with the titration solution containing toluene, isopropanol and a small amount of water, forming a single phase solution. The sample mixture was then titrated at ambient condition with an alcoholic base solution; 0.1M solution of potassium hydroxide (KOH) and alpha-naphtolbenzein as the indicator. The end point was detected as the colour of indicator changes; from orange to green. FFA analysis concentration of weight percent and conversion can be calculated using the following equation:

$$\text{FFA conversion, } \% = \frac{C_{AO} - C_A}{C_{AO}} \times 100 \tag{1}$$

where:

C_{AO} = Initial concentration of FFA of the mixture (i.e. at time t = 0)
C_A = Concentration of FFA at any time t

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Particle Size Distribution (PSD) analysis

   The information on particle size distribution of gelular ion exchange resins catalysts was presented in Table 1 and Fig. 1. The results (Table 1) shows that SK104H resin has smallest average particle size distribution as compared to SK1BH resins. Abidin *et al.* [1] found that that small average particle size may attributed to the large external surface area of the resins. Thus, it can be concluded that the large external surface area of SK104H resin may lead to faster rate of reaction, hence increase the conversion of FFA.

Table 1. Particle size distribution of gelular ion exchange resins.

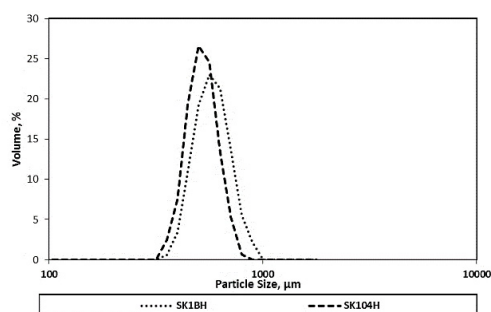| Particle size distribution (µm)	SK1BH	SK104H
10% >	482.3	447.4
50% >	610.3	549.3
90% >	775.7	673.9

Fig. 1. Particle size distribution of catalysts.

3.1.2. Fourier transform-infra red (FT-IR) spectroscopy analysis

   Fig. 2 shows the FT-IR spectrums of both gelular resins, SK104H and SK1BH catalyst. The FT-IR spectra for both resins were similar as presented in Fig. 2. A sharp peak around 1000-1500 cm^{-1} were identified for both resins as the $-SO_3H$ functional group demonstrating the presence of sulfonic acid group. The band of 2000-2500 cm^{-1} was assigned to C=O functional group (CO_2 in the air) and the peaks around 1650 cm^{-1} is associated to benzene ring (double bond) stretching vibration. On the other hands, the peaks from 3000-3700 cm^{-1} is assigned to O-H stretching vibration which commonly resulted from the absorption of hydroscopic water during the KBr sampling preparation.
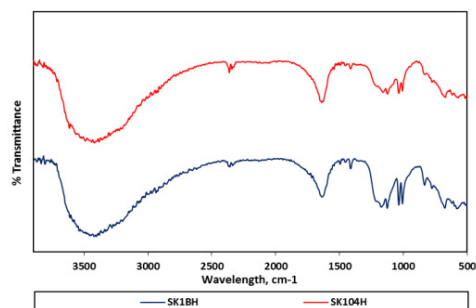

Fig. 2. FT-IR spectra for catalysts.

3.1.3. Surface morphology analysis (SEM)

Fig. 3 shows the surface morphology of fresh gelular ion exchange resins, SK1BH and SK104H. The SEM images shows a rough surface of both resins which taken at high magnification of 2.00 kX. It can be seen both resins portrayed quite similar surfaces, indicating that both catalyst were categorized as the same type of gelular resin.
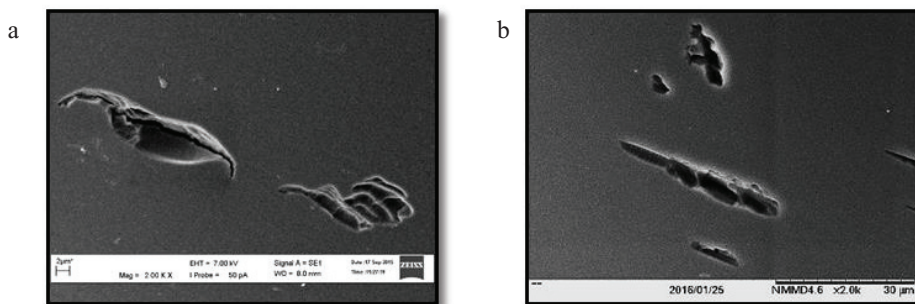

Fig. 3. SEM analysis of a) SK1BH; b) SK104H.

3.1.4. Elemental analysis (CHNS)

Table 2 demonstrated the results of elemental analysis for fresh gelular resins, SK1BH and SK104H. In this analysis, oxygen cannot be measured, thus the oxygen element was determined by the difference from the total weight percentage of other elements which are carbon, hydrogen and nitrogen [1]. Carbon was the most abundant element observed in both resins. The level of carbon detected in SK1BH resin was ~43.85% and ~42.29% in SK104H resin. According to the manufacturer of these gelular resins, the structure of the resins was only consists of carbon, hydrogen, sulfur and oxygen. However, from Table 2, it can be seen that the presence of nitrogen element in SK1BH resin was ~3.04% and SK104H resin was ~2.83%. It might due to contamination of N compounds during the analysis. On the other hand, it can be observed that, SK104H has the highest level of sulfur as compared to SK1BH resin. Sulfur element was important for esterification reaction which provide strong acidity of the catalyst. High level sulfur in the catalyst resulting high catalytic activity of SK104H, thus increases FFA conversion.

Table 2. Elemental analysis for fresh gelular resins.

Sample	N [%]	C [%]	H [%]	S [%]	O [%]
SK1BH	3.04	43.85	6.59	13.26	33.27
SK104H	2.83	42.29	6.45	13.46	34.68

3.1.5. Acid capacity analysis

Table 3 illustrated the results of acid capacity of both resins, SK1BH and SK104H. From Table 3 it can be observed that the acid capacity of SK104H was higher than SK1BH resin. This indicates that SK104H has high acidity level as compared to SK1BH resin. Strong acidity level in catalyst would favour the forward reaction of the esterification process, resulting faster reaction rate and high FFA conversions.

Table 3. Acid capacity of fresh gelular resins.

Sample	Acid capacity, mmol/g
SK1BH	5.0
SK104H	5.2

3.2. Screening of different type of gelular ion exchange resins

Screening of the catalytic activity of two types of gelular resins, SK1BH and SK104H were conducted to choose the best performance catalyst. Both gelular resins, SK1BH and SK104H were analysed under same reaction conditions of 6:1 methanol to SUCO mass ratio, 3.0 wt. % amount of catalyst, 60°C reaction temperature and 300 rpm of stirring speed. Fig. 4 shows the effect of each catalyst on the esterification reaction of SUCO with methanol. According to the results, it can be observed that, SK104 demonstrated the best catalytic performance with ~78% FFA conversion while SK1BH was only able to achieve ~66% of FFA conversion. The outcome was closely related to the differences on the physical and chemical properties of both resins. Based on the particle distribution results (Table 1), SK104H resin exhibits the smallest average particle size as compared to SK1BH resins. This contributed to a wider external surface area of the resin, resulting faster reaction rate and higher FFA conversion. It was also supported by the elemental analysis (Table 2) results where SK104H was found to have higher amount of sulfur content as compared to SK1BH catalyst, contributing to higher acidity and catalytic activity of SK104H. The elemental analysis results was supported by acid capacity analysis where SK104H shows the highest acid capacity value (Table 3) as compared to SK1BH catalyst. As a result, higher FFA conversion was achieved when SK104H was used as catalyst. Hence, SK104H has been selected for a detail study which was carried out using OVAAT method.
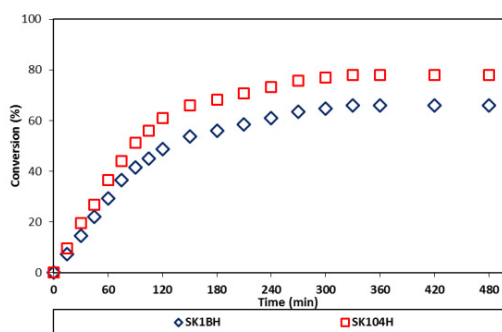

Fig. 4. Effect of different gelular ion exchange resins on FFA conversion.

3.3. Studies on the effect of reaction variables using OVAAT method

OVAAT method was applied to investigate the effect of reaction variables on the esterification of FFA using selected gelular resin, SK104H. Mass transfer resistances (i.e. internal and external), catalyst loading (1.0 - 5.0 wt. %), reaction temperature (40 - 60°C) and methanol to oil mass ratio (6:1 - 24:1) were the independent variables selected to optimize the FFA conversions of SUCO. The reaction time of 8 h was used in this experimental work.

3.3.1. Effect of mass transfer resistance and catalyst loading on FFA conversion

Mass transfer resistance is one of an important factor that affect the rate of reaction, product formation and the rate of conversion. Mass transfer resistance involved in heterogeneous catalytic esterification are divided into two types; the external mass transfer and internal mass transfer resistance. In this study, internal mass transfer can be neglected because the catalysts are in the form of gelular type thus impossible to be sieved due to the high temperature constraint.

To investigate the external mass transfer resistance, three runs were conducted at different stirrer speed of 150, 300 and 450 rpm. The reaction condition was fixed at 60°C reaction temperature, 3.0 wt. % of catalyst loading and 6:1 methanol to SUCO mass ratio. The results of the effect of external mass transfer resistance was illustrated in Fig. 5. From Fig. 5, it can be seen that the trends was almost the same when the agitation speed increases from 150 rpm to 450 rpm. This findings suggested that the external mass transfer resistance in the reaction can be neglected. To enhance the solubility between the oil and methanol and to avoid the breakage of catalyst at higher stirring speed, 300 rpm of stirring speed was chosen for subsequent experimental work.

To investigate the effect of catalyst loading on the FFA conversion, different amount of catalyst were introduced to the reaction which are 1.0, 1.5, 3.0 and 5.0 wt. % respectively. In this study, other variables such as methanol to SUCO mass ratio, reaction temperature and stirrer speed was fixed at 6:1, 60°C and 300rpm. Fig. 6 presented the effect of different catalyst loading on the FFA conversion. From the figure, 76% of FFA conversion was achieved with 1.0 wt. % catalyst loading. As the catalyst loading increases, the FFA conversion increased to 79% for 1.5wt. % and 87% for 3.0 - 5.0 wt. % respectively. Thus, it can be concluded that higher the catalyst loading resulted in higher the FFA conversion due to the increase in the number of active catalytic sites. The conversion pattern in 8 hours reaction also revealed that the higher catalyst loading help to fasten the reaction, and simultaneously shorten the time to reach equilibrium. This result is qualitatively in agreement with the findings from a few researchers [1,2]. In addition, it can be observed that there was no significant improvement in the FFA conversion with the further increment of catalyst loading from 3.0 wt. % to 5.0 wt. %. Turapan *et al*. [5] noted that large numbers of active catalytic sites may not contributes to higher FFA conversion and faster reaction rate if the reactants experiencing difficulties in accessing the active sites. Therefore, the optimum catalyst loading was selected as 3.0 wt. %.
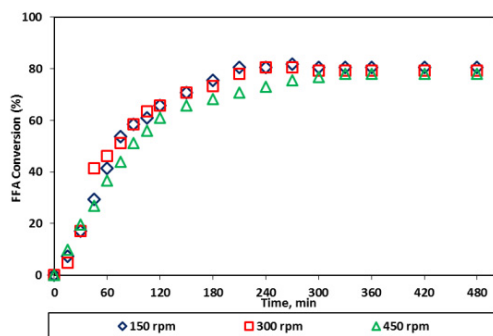

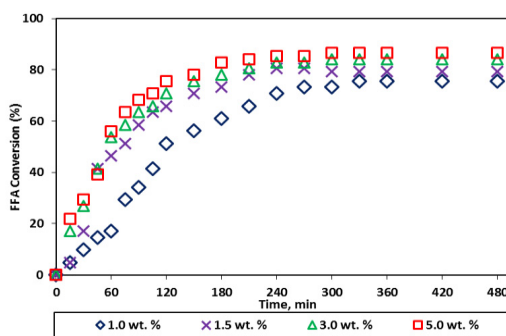Fig. 5. Effect of different stirring speed on FFA conversion.

Fig. 6. Effect of different catalyst loading on FFA conversion.

3.3.2. Effect of reaction temperature and methanol to oil mass ratio on FFA conversion

Fig. 7 shows the effect of reaction temperature (40, 50, 55 and 60°C) on FFA conversion. For this study, the reaction variables was fixed as follows: 6:1 mass ratio of methanol to SUCO, 3.0 wt% catalyst loading and 300 rpm stirrer speed. It was found that the rate of reaction increases with an increase of reaction temperature. The difference between each range of conversions also were very small (±2), and the final conversions were approximately the same. On the other hand, there was also no improvement observed with further increase of temperature, which means that the reaction attends the equilibrium at 60°C. In addition, there was no losses of methanol during the reaction as the reaction temperature did not exceeded the boiling point of methanol. Therefore, the optimum reaction temperature was taken at 60°C to shorten the reaction time while maintaining the FFA conversion.

FFA conversion is also influenced by the mass ratio of methanol to oil. Experiments on variations of methanol to SUCO mass ratios were carried out and the results was illustrated in Fig. 8. The mass ratio of methanol to SUCO was varied from 6:1, 12:1, 18:1 and 24:1 at a reaction temperature of 60°C, catalyst loading of 3.0 wt. % and stirrer speed of 300 rpm. According to Fig. 8, the results indicates that the FFA conversion increases with the increase of methanol to SUCO mass ratio. It can be seen that about 82% conversion of FFA was achieved with 6:1, 84% for 12:1, 88% for 18:1 and 91% for 24:1 mass ratio of methanol to oil. Since this process are known to be a reversible process, the presence of excess methanol in the reaction will lead to a forward reaction; contributing to the formation of fatty acid methyl ester (FAME). On the other hand, inadequate amount of methanol introduced to the mixture will cause a reverse reaction, resulting lower reaction conversion [2]. Nevertheless, too much of methanol may cause slower reaction activity due to the dilution of reaction mixture within the system. This situation may also contributed to saturation of catalyst surface, which simultaneously affecting the catalytic activity of the reaction [6]. Thus, 6:1 mass ratio was not suitable to be selected as the optimal mass ratio for this reaction process. Although the 24:1 of mass ratio of methanol to SUCO gave the highest FFA conversions, high methanol consumption is not

advisable for industrial production because it may contribute to the high cost and high energy consumption. Therefore, the optimal methanol to SUCO mass ratio was determined to be at 18:1 methanol to SUCO mass ratio.
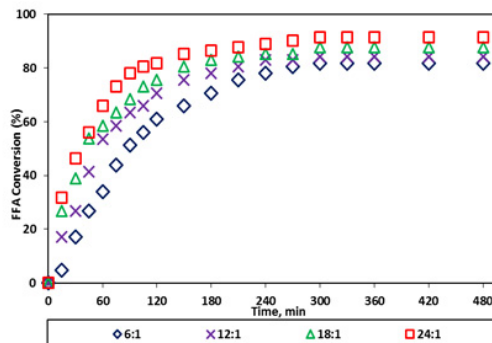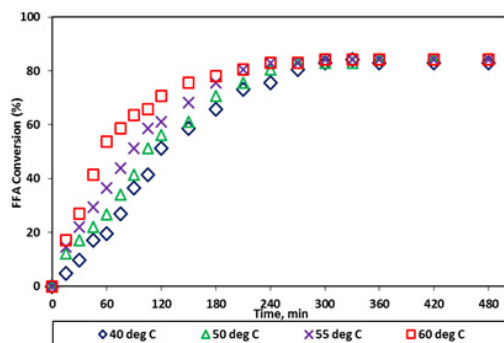

Fig. 7. Effect of different reaction temperature on FFA conversion   Fig. 8. Effect of different methanol to oil mass ratio on FFAs conversion.

4. Conclusion

The performance of gelular ion exchange resins, SK1BH and SK104H was successfully investigated in the esterification of FFA using used cooking oil as the feedstock. In the preliminary study, SK104H was found to give better FFA conversion as compared SK1BH resin. This may attributed to the excellence physicochemical properties owned by SK104H resin where this catalyst was found to have the smallest average particle size, highest sulfur content and highest acid capacity value. This properties contributes to faster rate of reaction, leading to higher FFA conversions. SK104H was further investigated by varying the effect of mass transfer resistance, catalyst loading, reaction temperature and methanol to SUCO mass ratio using OVAAT method. Maximum FFA conversion of 88% was achieved using optimized esterification conditions of 18:1 methanol to SUCO mass ratio, 60°C reaction temperature, 3.0 wt. % catalyst loading and 300 rpm stirrer speed. Therefore, it was proven that SK104H is a potential catalyst in esterification reaction as it was found to give the highest FFA conversion at faster reaction rate.

Acknowledgements

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