

Biodiesel production from waste cooking oil using calcium oxide/nanocrystal cellulose/polyvinyl alcohol catalyst in a packed bed reactor

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ABSTRACT

In this study, biodiesel was synthesized from a reaction of waste cooking oil (WCO) and methanol in the presence of catalyst which was derived from chicken bone and coconut residue in a packed bed reactor. Calcium oxide (CaO) was extracted from calcined chicken bone and nano-crystal cellulose (NCC) was isolated from coconut residue by acid hydrolyzed and were supported with polyvinyl alcohol (PVA). The catalyst was analyzed using Fourier transform infrared (FTIR), Field emission scanning electron microscopy (FESEM), Thermogravimetric analysis (TGA) and X-ray diffraction (XRD) to study its elemental composition and surface morphology. The parameters used for the reaction were optimized by Design of Experiment (DOE) using Central Composite Design (CCD) to maximize the biodiesel yield. The maximum yield of 98.40% was obtained at optimum temperature, methanol to oil and catalyst loading of 65 °C, 6:1 and 0.5 wt%, respectively. Investigation on the kinetic of the reaction specified that the reaction followed pseudo first order reaction with k-value ranged from 0.0092 min⁻¹ to 0.0151 cm⁻¹ and Thiele modulus was less than 2. The activation energy E_a for the transesterification reaction was 45.72 kJ/mol.

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1. Introduction

In recent years, the environmental issues related to the releasing of the greenhouse gases and shortage in the conventional fossil fuel sources were caused by the global consumption of fossil fuel [1]. In fact, the available fossil fuel is expected to be used up in 2050 due to the consumption of fossil fuel is 10⁵ faster than its natural production [2,2,2,2]. In addition, based on Organization of the Petroleum Exporting Countries (OPEC), by 2040, the demand of fuel oil will keep increasing and it would be reached to 109.4 million barrel/day and the developed countries will be the highest. However, the demand of fuel diesel is expected to be in 2040 is 5.7 million barrel/day [3]. This is because, the most important element for growth and development of an economy is energy [4].

Biodiesel or also defines as biofuel is a source of energy that can be renewed and has the potential to replace fossil fuels [4]. Normally, biodiesel can be produced from transesterification reaction which is a chemical reaction between triglycerides and alcohol in the presence of a catalyst to produce methyl esters (biodiesel) and

glycerol [5]. For the source of triglycerides, vegetable oil or animal fat can be used. However, waste cooking oil (WCO) also can be used in biodiesel production in order to reduce the waste. For instance, European Union (EU) produces about 700,000 to 1,000,000 tonnes of WCO annually and it was estimated approximately 40,000 tonnes of WCO produced per year in Asia countries including Malaysia which can cause environmental problems [6].

In the production of biodiesel, catalyst was used to enhance the reaction rate and the yield of methyl ester. There are several types of catalyst that can be used in biodiesel production such as homogeneous, heterogeneous and enzymatic catalyst. However, catalyst must be separated at the end of the reaction and it is difficult to be done by using homogeneous catalyst and the process produced a lot of waste of water from the purification. Therefore, by using heterogeneous catalyst, it can be separated and reused which will decrease the production cost [5,7]. Recently, catalyst extracted from organic waste materials has gained much attention because they are safe to handle and store, non-toxic, abundantly available, low cost and it comes from renewable sources [8]. Usually, high amount of carbon (C), oxygen (O) and metal salt such as potassium (K), sodium (Na), magnesium (Mg) and calcium (Ca) can be found in the organic compound [9]. Moreover, animal bone and shell were

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the examples of organic waste that enriched with calcium carbonate and the most catalysts were derived from these sources such as bovine bone, seashells and eggshells [10]. In fact, among these types of solid wastes catalyst, animal bone act as best solid waste. This is because, the main component of bone is calcium phosphate and it can be transformed to hydroxyapatite which has a high catalytic activity, good thermal and chemical stability, can make the production of biodiesel environmentally friendly, non-toxic and hence safe to handle and store as well as potentially renewable [8,11].

Coconut tree is an important industrial crop in Malaysia after palm oil, rubber, and paddy in terms of total planted area [12]. The total crop area for coconut tree in Malaysia is 95,000 ha. However, approximately about 90,000,000 coconut was imported by Indonesia in 2017. Indirectly, this scenario has increased the production of coconut waste in Malaysia. Malaysia produces approximately 168 million tons of biomass annually including coconut waste [13]. Nano-cellulose is described as the products or extracts from native cellulose that can be found in animals, bacteria or plants and is composed of the nano-scaled structure material and it also can be extracted from coconut residue. Nano-crystal cellulose (NCC) exhibit impressive properties such as low-density, high mechanical strength, low thermal expansion, and excellent biocompatibility and renewability [14].

Furthermore, nano-sized catalyst has 30 times higher conversion rate compared to meso-sized of catalyst due to large pore size, larger surface area to volume ratio, high catalytic activity, shorter reaction time, less amount of catalyst required, easy separation, better recovery, recyclability and reusability [15].

In biodiesel production, packed-bed catalytic reactor can be used to reduce the mechanical damage of catalyst due to continuous stirring during the process [16]. The possibility of using a packed-bed reactor improves the reaction because the catalyst stays confined in the reactor bed and the reaction products can be easily separated, also the mechanical stability of the catalyst particles is achieved. In addition, it is also one of the most attractive reactor types for the continuous process due to its high production efficiency, simple and easy operation, and good mixing performance [17]. Therefore, in this study, novel catalyst, nano-sized of chicken bone and NCC (heterogeneous catalyst) was used in transesterification reaction in a packed bed reactor. The reaction conditions of the process were varied by using Response Surface Methodology (RSM) to optimize the reaction conditions.

2. Experimental

2.1. Materials

Coconut residue was collected from a small coconut milk shop whereas chicken bone and waste cooking oil (WCO) were collected in a night market Temerloh, Pahang, Malaysia. Coconut residue was dried in a dry oven for overnight and blended with a blender. Chicken bone was treated with boiled water and dried in a dry oven before crushed and blended. The chemicals that were used in this study were sulfuric acid (H_2SO_4), methanol, polyvinyl alcohol (PVA), sodium hydroxide (NaOH) which were purchased from R&M Chemicals, hydrogen peroxide (H_2O_2) from Progressive Scientific Sdn. Bhd., Batu Caves, Selangor, Malaysia and n-hexane as standard GC grades purchased from Merck.

2.2. Nano-catalyst preparation

NCC was isolated from coconut residue and it was dried in an oven at 55 °C for 24 h before grinding the material by using a blender. The powder of coconut residue was bleached with H_2O_2 in

the proportion 1:20 (w/v) under constant stirring for 2 h at 50 °C and was repeated three times to remove the lignin [18]. The residue was washed with distilled water until a neutral pH. 5% of sodium hydroxide (NaOH) aqueous solution was used to remove hemicellulose and other impurities as described by Yu et al.. Suspension of coconut residue was hydrolyzed by diluted H_2SO_4 (40%) with continuous stirring in the proportion 1:25 (w/v) at 45 °C for 45 min under vigorous and constant mechanical stirring. To remove the acidic solution the method described by Kumar et al. was used [18]. The collected suspension was then ultrasonicated for 10 min to homogenize the generated NCC [19]. Aqueous suspension was stored in a refrigerator at 4 °C for further use. Meanwhile, calcium oxide (CaO) was extracted from chicken bone and it was treated with boiled water for about 30 min and then was washed and dried in an oven for 48 h. After the chicken bone was fully dried, it was crushed and blended to a fine powder. The powder material was calcined in a furnace at 700 °C, 800 °C and 900 °C for 4, 5 and 6 h respectively. The produced white fine powder was sieved to a size of 100 μm [20].

2.3. Nano-catalyst characterization

The characterization of catalysts which are CaO and NCC were done by using Field Emission Scanning Electron Microscopy (FESEM), Fourier-transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) model Hitachi STA7300, X-ray diffraction (XRD) model Bruker D8 Advance and Gas Chromatography Mass Spectroscopy (GCMS) model Agilent Technologies 7890A. For NCC, the FTIR analysis was done with three different forms of NCC which were cellulose in suspension, NCC in solid and NCC/PVA in solid. Meanwhile, for the CaO, the FTIR analysis was done in two different forms; CaO in powder and CaO/PVA in solid. FESEM analysis was done to determine the surface morphology of NCC; coconut residue (before isolation of NCC), dry NCC suspension and NCC/PVA and for CaO; before calcination (chicken bone in powder), after calcination and CaO/PVA. For the crystallinity of catalysts produced were characterized by using XRD machine (Bruker D8 Advance).

2.4. Biodiesel production (Transesterification reaction)

In this work, biodiesel was produced using transesterification between waste cooking oil and methanol with the presence of a catalyst, NCC/CaO supported by PVA. The parameters of this method were methanol to oil molar ratio, temperature and catalyst loading. This process was done in a packed-bed reactor column and it was set up as shown in Fig. 1. The set-up includes a peristaltic pump, packed bed glass column, three-necked round bottle flask, and cooled water condenser. Mixing and heating were provided by a hotplate magnetic stirrer.

NCC/CaO supported by PVA was loaded into the packed bed reactor. Mixing was applied throughout the experiment to provide a continuous mixing. In the packed-bed process, the solvent mixture was added to a three-necked round bottom flask and then transferred into the packed-bed reactor for the reaction by a peristaltic pump. The magnetic stirrer was stirred at 600 rpm to form oil emulsion and the flow rate of the peristaltic pump was set to 5 ml/min [21]. After 4 h of reaction, the mixture was removed so that the concentration of fatty acid methyl ester (FAME) could be determined. Then, a new mixture was added to the reactor and the process continues.

2.5. Design of Experiment

The optimization of FAME was conducted using Design-Expert

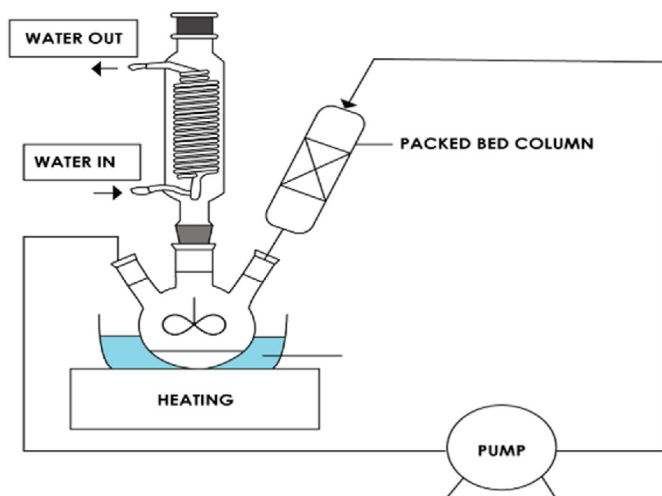


Fig. 1. Schematic figure of the experimental set up.

7.1.5 (Stat-Ease Inc., USA). Response Surface Methodology (RSM) using Central Composite Design (CCD) was used to study the effects of process variables on the reaction yield [22]. In this study, the independent variables were catalyst loading, the ratio of methanol to oil and temperature while the response was the yield of biodiesel. The responses variable, methanol to oil ratio, temperature and catalyst loading were varied from 6:1 to 20:1, 55–65 °C because methanol evaporates at temperature above 65 °C due to its boiling point (65 °C). The catalyst loading were varied from 0.5 to 10.0%. The analysis of biodiesel was performed using GCMS to identify the compositions of fatty acids as described by Nasaruddin et al. [23]. Then the yield of biodiesel was defined as the weight percentage of final product relative to the weight of waste cooking oil that was used at the beginning of the experiment. The quantitative yield of biodiesel was calculated by using Eq (1) as shown below:

$$\text{Yield (\%)} = \frac{\text{volume of biodiesel} \times 100}{\text{volume of waste cooking oil}} \quad (1)$$

2.6. Reusability of catalyst

The reusability of the CaO/NCC supported by PVA catalyst was examined by conducting a subsequent reaction cycle. The catalyst was separated from the liquid mixture and it was washed with methanol and hexane. Then, it was used again under the same reaction condition as before. The yield of biodiesel was measured after each cycle to determine the reusability of the catalyst.

2.7. Kinetic study

The transesterification reaction was assumed to follow the first order kinetics as a function of the concentration of biodiesel formed during the reaction. To determine the kinetics of the reaction, the effect of its reaction temperature was measured. Transesterification involves the conversion of triglycerides to mono-alkyl esters in the presence of methanol as one of the reactants [24]. In this study, the amount of FAME, i.e. the yield of methyl esters with respect to time was used to study the reaction kinetics. Besides, in the transesterification reaction, triglycerides were converted to glycerides, then to monoglycerides and to fatty acid methyl ester (FAME). For every step, a molecule of methanol was consumed to produce a

molecule of FAME. By considering only one reactant caused dramatic influence on the overall yield of reaction was expressed as:

$$-r_a = -\frac{d[\text{TG}]}{dt} = k [\text{TG}] \quad (2)$$

Where TG is triglycerides and k is reaction rate constant. At $t = 0$, it was assumed that total TG = 0, thus integration of Eq (2) at $t = 0$ gave to the following equation:

$$\ln[\text{TG}_0] - \ln[\text{TG}_t] = kt \quad (3)$$

Considering the product formation after sometimes, methyl ester formed in the reaction denotes as X_{ME} and the mass balance give the following equation:

$$X_{\text{ME}} = 1 - \left(\frac{[\text{TG}]}{[\text{TG}_0]} \right) \quad (4)$$

Rearranging Eq (4) resulted in

$$[\text{TG}] = [\text{TG}_0](1 - X_{\text{ME}}) \quad (5)$$

In terms of product formation, rate of reaction can be expressed as the following:

$$\left(\frac{d[X_{\text{ME}}]}{dt} \right) = k(1 - X_{\text{ME}}) \quad (6)$$

Integration of Eq (6) resulted in

$$-\ln(1 - X_{\text{ME}}) = kt \quad (7)$$

k -value of the overall reaction can be determined by plotting a graph of $-\ln(1 - X_{\text{ME}})$ vs t . The k -value of the overall reaction and at optimized condition was calculated by finding the slope of the graph.

For confirmation, Thiele modulus of the reaction was determined for reaction at 55 °C, 60 °C and 65 °C according to the following equation. Equation (8) also was used in previous study that was conducted by Sulaiman et al., in 2016 which it was calculated by assuming D_{eff} is constant with the Y , yield at time, t and initial yield of the oil based on Fick's second law [25]. Based on the value of Thiele modulus, it may be concluded on the catalyst surface utilization during a catalytic reaction, particularly, the lower is the value of the Thiele modulus, the higher is the degree of a catalyst utilization and vice versa [26].

$$\ln Y = \ln \left(\frac{6}{\pi^2} \right) - \frac{\pi D_{\text{eff}}}{r^2} t \quad (8)$$

Where Y is biodiesel yield, r^2 ratio of reactant size, and D_{eff} was determined from graph of $\ln Y$ versus time. Once D_{eff} value was computed, Thiele modulus was determined using Eq (9). Where ϕ is the Thiele modulus. R refers to radius of catalyst. Since this study uses catalyst supported on PVA which is in thin sheet R represents half of thickness of the catalyst slab. k is the reaction constants at respective temperature. If the value of Thiele modulus is not more than 2, thus, the system is expected to have no internal mass transfer [25].

$$\phi^2 = \left(\frac{R^2 k}{D_{\text{eff}}} \right) \quad (9)$$

The calculation to determine the activation energy, E_a required for the reaction, was done according to Arrhenius equation as described by Harsha et al. [15].

3. Result and discussion

3.1. Synthesis of heterogenous nano-catalyst

NCC was isolated from coconut residue after the milk was extracted. The residue was bleached three times with H_2O_2 and treated with NaOH in order to remove lignin and hemicellulose aimed to purify the cellulose. Meanwhile, CaO was derived from chicken bone via calcination at 700–900 °C for 4–6 h. The temperature and time varies because calcination temperature mostly influences the catalytic properties of the CaO that was produced. During the calcination process, calcium carbonate, CaCO_3 decomposed to CaO and carbon dioxide, CO_2 leaving a white powder of CaO. Screening of NCC was conducted with seven different catalyst loading and according to the result, 0.2 wt% of NCC was chosen in order to increase the yield of biodiesel instead of using CaO only as the catalyst for biodiesel production. This is due to the significant interest in the synthesis of more than one type of catalyst which can vary the characteristics that may arise from the combination of two or more constituents.

3.2. Characterization of nano-catalyst

3.2.1. FTIR

FTIR was used to identify the functional groups and feature of NCC, CaO, NCC/CaO/PVA. Fig. 2 (a) shows the spectra of NCC that was isolated by acid hydrolysis of 40% of H_2SO_4 . The spectra band at 3375.97 cm^{-1} which was in between 3175 and 3490 cm^{-1} indicates the presence of O–H stretching intramolecular hydrogen bonds for cellulose I. Besides, the peak at 2922.39 and 2852.42 cm^{-1} shows the stretching of C–H bond (alkane/alkyl group). Meanwhile, for the 1742.41 cm^{-1} stretch, it shows alkyl carbonate which ascribes the presence of carbonyl compound. According to Kumar et al. [26], the

presence of spectral bands of 1250 cm^{-1} indicates the lignin compound presence in the sample due to ary group of C–O out of plane stretching. However, for the FTIR analysis of NCC, there was absence of this stretch thus proves that the lignin was completely removed.

Fig. 2(b) demonstrates the characteristic absorption bands of CaO nano-particles recorded within the range 700 – 4000 cm^{-1} . The FTIR spectrum showed a strong peak at 1032.68 cm^{-1} which was in between of 1000 and 1320 cm^{-1} and it was attributed to the stretching vibration of C–O group which was similar to the study that conducted by Anr et al. [27].

Meanwhile, Fig. 2(c) shows the spectrum peaks of NCC/CaO supported by PVA. In the spectra region of 3600 – 300 cm^{-1} shows a broad band of stretching vibrations of O–H and C–H groups. It was observed at 3317.13 cm^{-1} the presence of the functional group of cellulose. However, for C–O bond, it was slightly shifted to 1095.04 cm^{-1} compared to the peaks in Fig. 2(b). Therefore, it can be proved that, the prepared nano-catalyst consists of cellulose and CaO compound.

3.2.2. FESEM

Fig. 3 shows the FESEM micrographs of NCC and CaO which was isolated from coconut residue and extracted from chicken bone waste respectively. Fig. 3 (a) shows the morphology of NCC which was isolated by acid hydrolysis technique. Fig. 3 (a) shows the rod-like NCC that was isolated from coconut residue. In a study conducted by Kumar et al. [18] also found a rod-like NCC which was isolated from sugarcane bagasse by acid hydrolysis. Besides, Yu et al. [29] reported in their study, crystallites cellulose had a rod-like structure which can be seen from its morphology studies.

Fig. 3(b) and (c) show the surface morphology of chicken bone before calcination and after calcination at 800 °C in 5 h, respectively. From Fig. 3(b), it can be seen that low surface area of particle

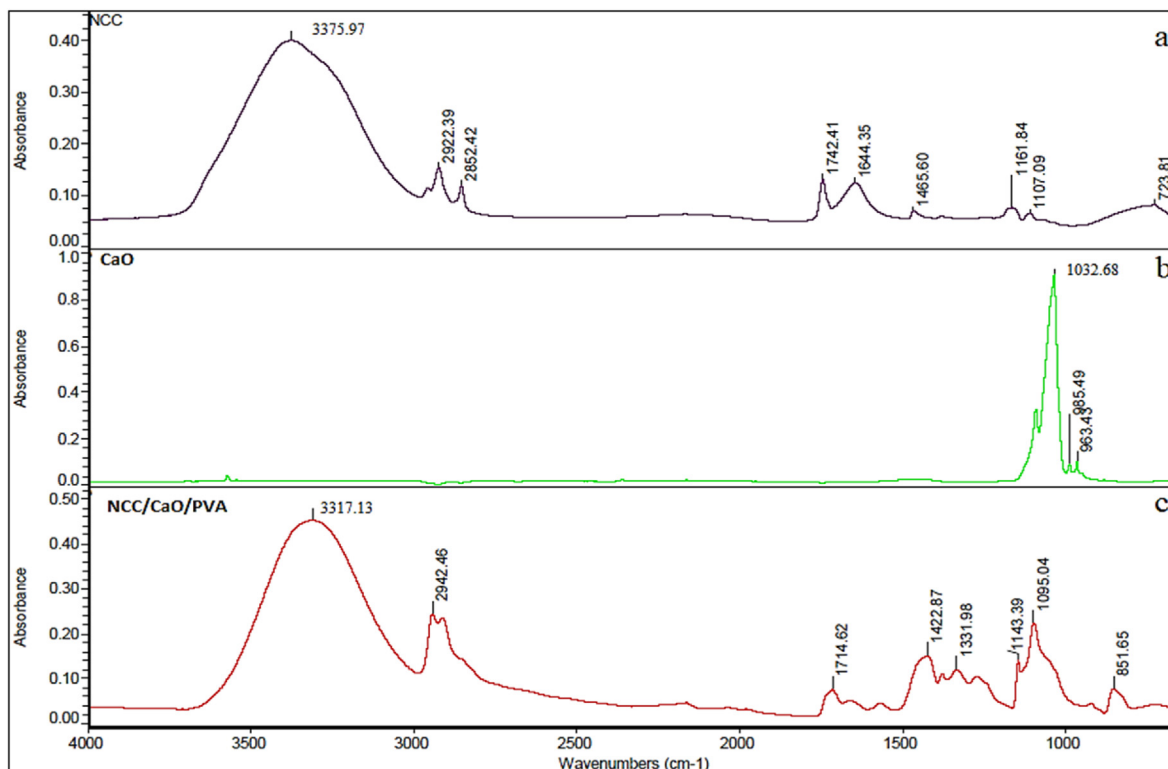


Fig. 2. FTIR spectrum of (a) NCC (b) FTIR spectrum of CaO (c) FTIR spectrum of NCC/CaO/PVA.

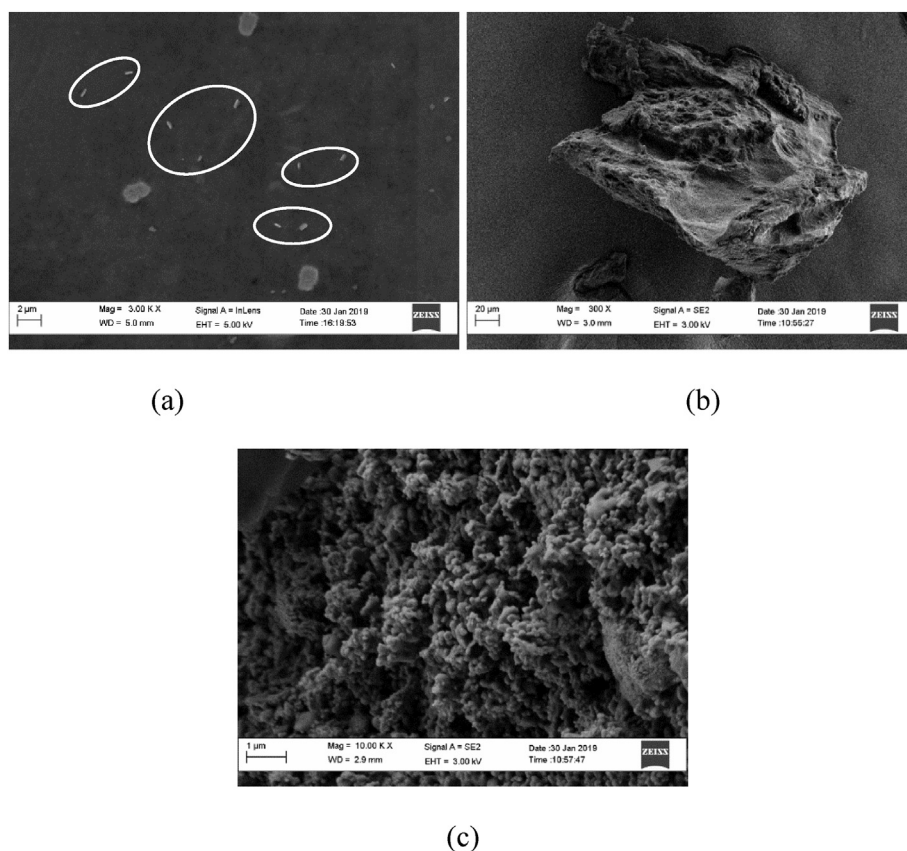


Fig. 3. FESEM images of (a) NCC (b) chicken bone (c) calcine chicken bone.

due to large particle size of chicken bone and irregular shape with aggregations of particle. After calcination as shown in Fig. 3(c), the morphological properties was changed and exhibits particles with lower particle and agglomerate size compared to raw chicken bone. The same morphology structure was reported in a study conducted by Niju et al. [30] of CaO from calcination treatment of egg shells which was spherical shape morphology. Smaller particles could provide higher specific surface areas [30]. The surface area increases with the small particle size which also increases the active

site of the catalyst and the reaction rate during transesterification.

Meanwhile, Fig. 4 shows the surface area FESEM image of NCC/CaO/PVA membranes. As can be observed in the image, the morphology of the catalyst was there was no agglomeration of CaO and NCC particles, thus suggesting that the particles were well dispersed in PVA matrix. The morphological properties was also reported in a study by N. C. Mat and A. Liong in 2009 where PVA were mixed with CaO [31]. Besides, Bilal et al. also reported that after the adding of CaO and NCC, the surface of PVA became more rough and the aggregates of NCC showed a wide size and even distribution [32]. Thus, during transesterification reaction, the active site of the catalyst reacted evenly.

3.2.3. XRD

For NCC, fully dried NCC was used for XRD analysis and the peaks were exhibited around $2\theta = 16.59^\circ$ and $2\theta = 22.18^\circ$ as shown in Fig. 5 (a). Wulandari et al. [19] also found a peak around $2\theta = 22^\circ$ and they reported that the peaks are typical for cellulose II which has antiparallel structure. Besides, the same peaks of cellulose II also found at $2\theta = 22.1^\circ$ as mentioned in a study by Ilyas et al. [33]. In this study, the sharpest peak was found at $2\theta = 22.18^\circ$. The sharper the diffraction peak, the higher crystallinity degree of the fibers [34]. In addition, to identify the crystallite size of the sample, Scherrer equation was used. By using the equation, the crystallite size of NCC was identified to be 84.25 nm.

Meanwhile, Fig. 5 (b) shows the XRD pattern of chicken bone that was calcined at 800°C in 5 h. The data of XRD showed that CaO was detected at $2\theta = 23.11^\circ, 32.02^\circ, 36.12^\circ, 39.43^\circ, 40.04^\circ, 43.08^\circ, 48.31^\circ, 53.73^\circ, 57.35^\circ, 60.64^\circ, 63.20^\circ, 64.19^\circ, 65.23^\circ$ and 76.31° . The peaks were similar to the study reported by Kirubakaran & Selvan [35]. Kirubakaran & Selvan found that the peaks of CaO were at

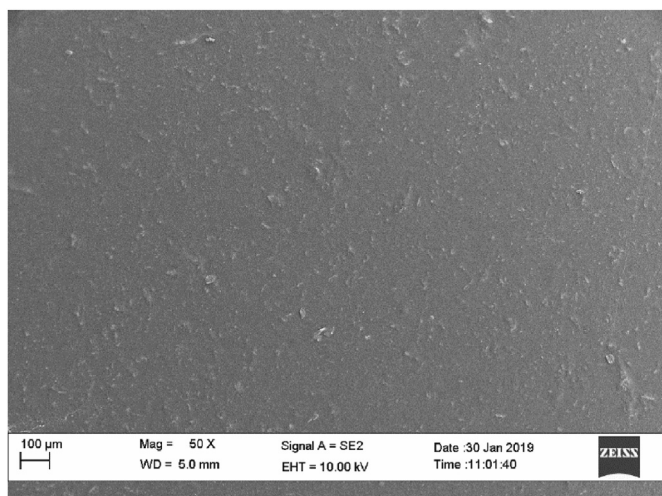


Fig. 4. FESEM image of a surface of NCC/CaO/PVA.

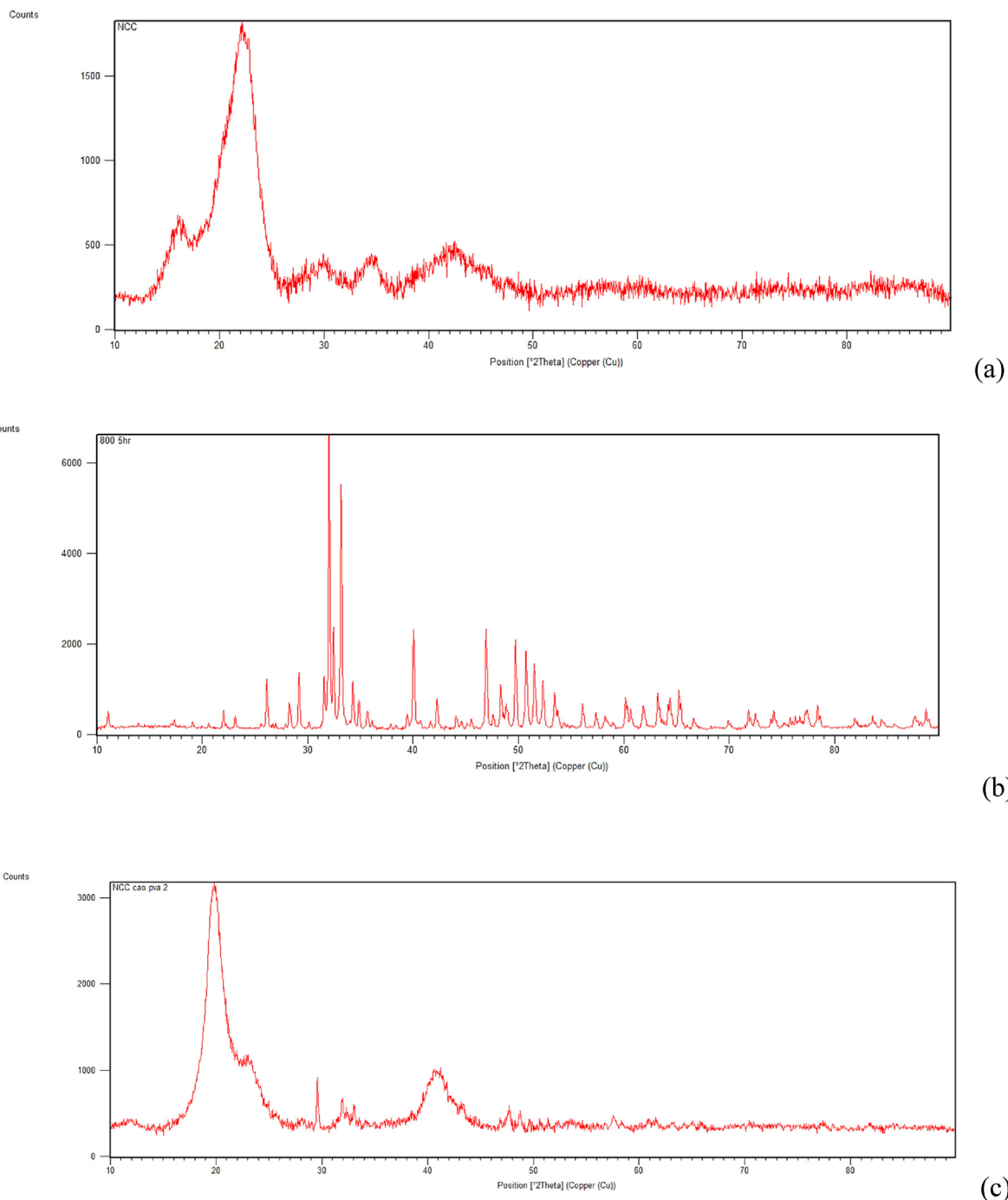


Fig. 5. X-ray diffraction pattern of a) NCC b) CaO c) NCC/CaO/PVA.

$2\theta = 34.12^\circ$, 53.52° and 64.21° . Furthermore, the crystallite size of CaO also calculated by using Scherrer equation and it was found to be 64.54 nm.

Fig. 5 (c) shows the XRD pattern of NCC/CaO/PVA which was prepared through mixing process. Fig. 5 (c) shows a peak at $2\theta = 20.18^\circ$ and 21.97° which indicates cellulose II. Besides, the peaks for CaO were found at $2\theta = 36.12^\circ$, 39.57° , 40.02° , 48.24° , 57.43° , 63.27° and 64.19° . Moreover, the size of NCC/CaO/PVA sample was calculated by using Scherrer equation and the result was 50.34 nm. The size was smaller compared to NCC and CaO itself due to the preparation of the nano-catalyst, CaO and NCC. The sample were mixed with PVA by continuous stirring for hours and

the size become smaller due to the mechanical effect.

3.2.4. TGA

Fig. 6 shows three major stages of degradation process. In the first stage (100.0 – 230.0°C), during the thermal degradation the nano-catalyst that was supported by PVA experienced a very small weight loss. However, in the second stage (230.0 – 400.0°C), the NCC/CaO/PVA experienced a higher weight loss. This is because, incorporation of nano-catalyst in PVA matrix slightly reduced the thermal stability of nanocomposites membranes [32]. Nevertheless, at the last stage of degradation, the weight loss was gradually decreased. For the first stage of the weight loss, it was caused by

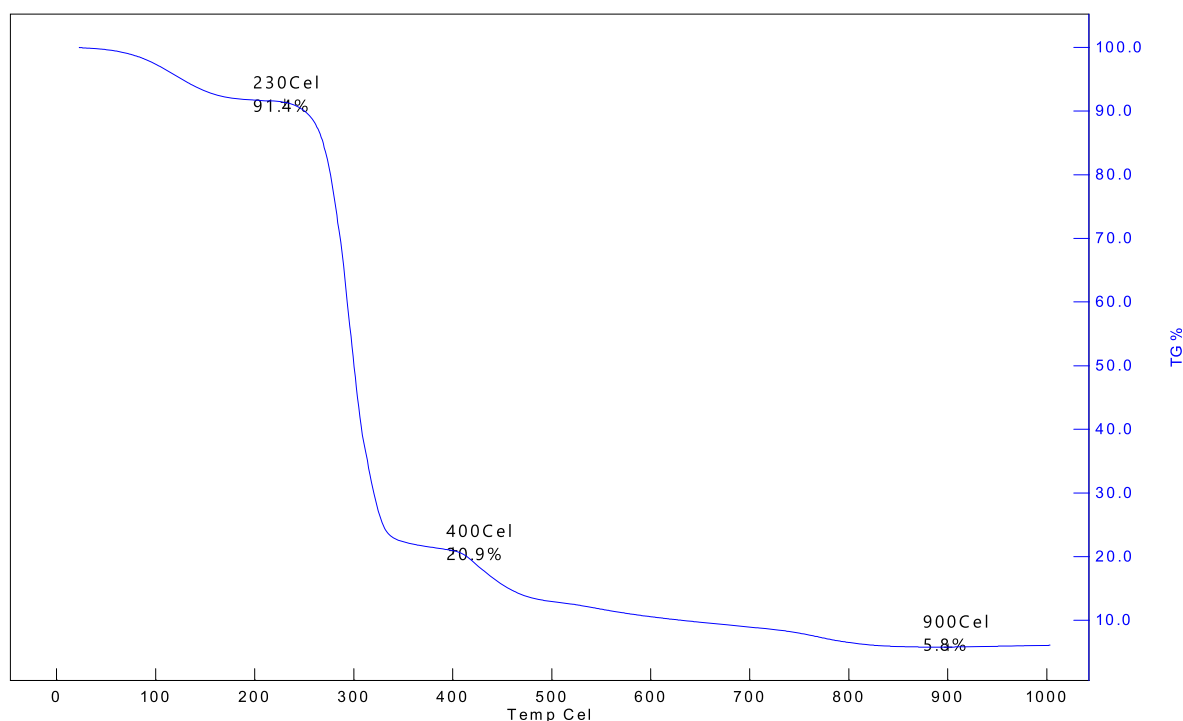


Fig. 6. TGA curves of NCC/CaO/PVA nano-catalyst.

water evaporation of the sample which was also reported by Bilal et al. [32] and Ilyas et al. [33]. In a study that was conducted by Bilal et al. [32], the nanocellulose/PVA sample started to degrade at 70 °C which was lower than the current study. This may be due to the greater number of free end chain of NCC particles caused by their smaller particle size [36]. However, CaO started to degrade at 370 °C, which was at a high temperature [15]. In this study, the weight loss was observed to start at a lower temperature due to the presence of NCC and PVA in the sample.

3.3. Biodiesel production

3.3.1. Optimization of reaction conditions

Three independent variables such as methanol to oil molar ratio, temperature (°C) and catalyst loading (wt%) were optimized while the dependent variable was the yield of biodiesel (%). For this optimization, CCD was used and the parameters of methanol to oil molar ratio, temperature and catalyst loading were varied between 6:1 to 20:1, 55–65 °C and 0.5 to 10.0 wt%, respectively. 17 runs were conducted to analyze the effect of the transesterification parameters as shown in Table 1.

Significance and suitability of the regression model was proved by ANOVA as shown in Table 2. Based on the results, the quadratic regression model of the experiment data was developed as given in Eq (10) with the coded factor, A, B and C which indicated methanol to oil molar ratio, temperature and catalyst loading, respectively while Y is the yield of biodiesel. The model identified catalyst loading as the most important factor in determining high yield of biodiesel. Table 1. Central composite design from response surface methodology for reaction conditions for optimization in biodiesel production.

$$Y = 94.14 - 3.24A + 1.68B - 3.47C - 1.34AB - 1.51AC - 0.88B^2 - 1.88C^2 \quad (10)$$

Table 2 shows a statistical analysis of ANOVA for the quadratic model which was carried out to evaluate the significance and fitness of the model as well as the effects of significant individual terms and their interactions with the chosen responses using the probability value (*p*-value). For the *p*-value below than 0.05, the model and its terms were considered as significant. Table 2 shows that the coefficient for overall effect of variables was highly significant because the *p*-value for the model was $p < 0.0001$. The smaller the *p*-value, higher significant is the corresponding coefficient [37]. It was observed that the yield of biodiesel, methanol to oil molar ratio, and catalyst loading were highly significant ($p < 0.0001$). The temperature was also significant ($p = 0.0011$) which was less than 0.05. AB and AC were observed to be significant. The *F*-value of 4.20 implies the lack of fit was not significant relative to the pure error. An insignificant of *F*-value was good and the model was statistically significant. Thus, the regression model given in Equation (10) shows a good prediction of experimental results.

The predicted values obtained were quite close to the experimental values, indicating that the model developed was successful in capturing the correlation between the transesterification condition parameters to the yield of biodiesel [38]. The value of adjusted- R^2 (0.9537) indicates that the model has 95.37% of variability.

Fig. 7(a) represents the influence of temperature and methanol to oil molar ratio on the biodiesel yield. The yield increases with the temperature when a lower methanol to oil molar ratio was used at 4 h of reaction time. The biodiesel yield of 98.35% was achieved when the optimum condition was fixed at 65 °C, 6:1 of methanol to oil molar ratio and 0.5 wt% of catalyst loading. The yield of biodiesel declines when the methanol to oil molar ratio increases and reaction temperature decreases. The reaction temperature influences both the reaction rate and the yield of biodiesel because the intrinsic rate constants are strong functions of temperature [38]. The stoichiometric molar ratio of methanol to oil is 3:1 [39].

Table 1

Standard	Run	Factor 1: Methanol to Oil Ratio (v/m)	Factor 2: Temperature (°C)	Factor 3: Catalyst Loading (wt%)	Response: 1 Yield (%)
1	15	6.00	55.00	0.50	94.70
2	13	20.00	55.00	0.50	93.00
3	14	6.00	65.00	0.50	98.35
4	17	20.00	65.00	0.50	93.50
5	16	6.00	55.00	10.00	88.75
6	2	20.00	55.00	10.00	82.65
7	11	6.00	65.00	10.00	96.05
8	1	20.00	65.00	10.00	82.95
9	3	6.00	60.00	5.25	97.80
10	7	20.00	60.00	5.25	91.75
11	10	13.00	55.00	5.25	91.25
12	12	13.00	65.00	5.25	95.70
13	4	13.00	60.00	0.50	94.95
14	9	13.00	60.00	10.00	90.01
15	6	13.00	60.00	5.25	93.50
16	8	13.00	60.00	5.25	93.05
17	5	13.00	60.00	5.25	94.15

Table 2

Statistical analysis of variance for biodiesel yield.

Source	<i>p</i> -Value, Prob.>F
Model	<0.0001
A: Methanol:Oil	<0.0001
B: Temperature	0.0004
C: Catalyst loading	<0.0001
AB	0.0033
AC	0.0016
B ²	0.1436
C ²	0.0078
Lack of fit	0.2347
R-squared	0.9740
Adj. R-squared	0.9537
Pred. R-squared	0.9537
Adeq. precision	25.450

Transesterification reaction is a reversible reaction therefore, the transesterification could be accelerated by increasing the amounts of methanol [20]. However, the excess amount of methanol can promote the transesterification reaction forward and also extract product, such a glycerin and methyl esters, from the system to

renew the surface of the catalyst [38]. Therefore, in this study 6:1 of methanol to oil ratio was found to be the optimum amount to maximize the yield of biodiesel.

Fig. 7(b) shows the effect of catalyst loading and methanol to oil molar ratio on the yield of biodiesel. The catalyst loading, methanol to oil molar ratio and temperature were varied between 0.5 and 10.0 wt%, 6:1 to 20:1 and 55–65 °C respectively. The result shows that, when the molar ratio of methanol to oil and catalyst loading was increased, the yield of biodiesel decreases. The highest yield of biodiesel (98.35%) was achieved at 6:1 of methanol to oil molar ratio and 0.5 wt% of catalyst loading. The lowest yield of biodiesel was observed when the highest amount of methanol and catalyst loading was used for the transesterification reaction. Increasing the amount of catalyst beyond the optimum amount (0.5 wt%) causes the yield of biodiesel to decrease. This is due to the saturation of catalyst particles inside the reaction mixture which decreased the contact area between methanol and oil molecules [36]. Moreover, from the study by Sivakumar et al. [40], a successful conversion of oils and fats to FAME was observed at 1% of base catalyst concentration [40]. Hence, in the current study the maximum yield of biodiesel was obtained at catalyst loading of 0.5 wt% thus, the same amount was further used in the production of biodiesel.

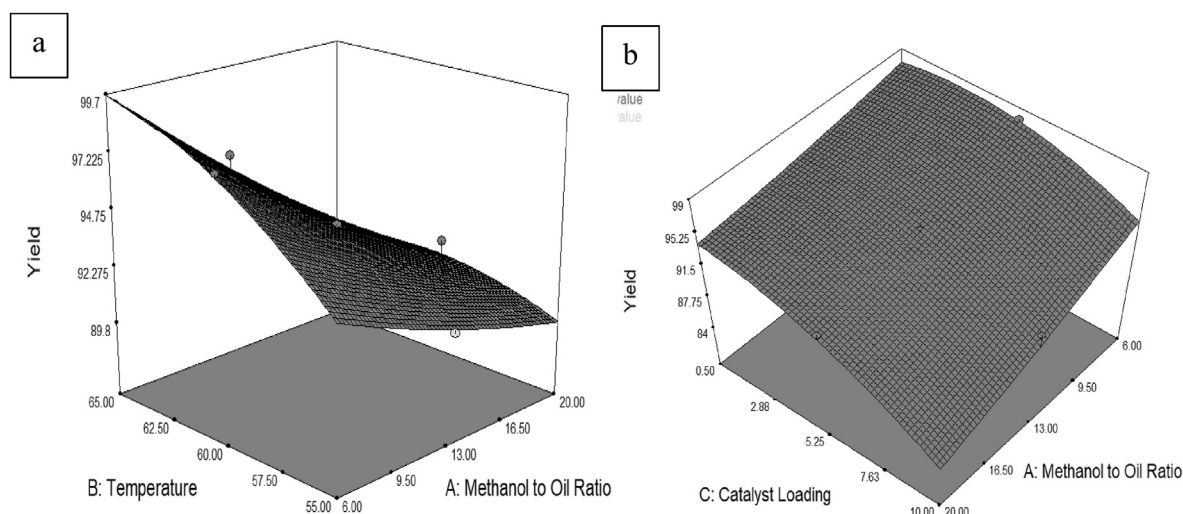


Fig. 7. 3D response of biodiesel yield based on interaction between two independent variables of (a) temperature vs methanol:oil (b) catalyst loading vs methanol:oil.

3.3.2. Catalyst reusability

The reusability of the prepared nano-catalyst NCC/CaO/PVA was studied in order to evaluate the stability of the nano-catalyst in the production of biodiesel in optimum reaction conditions; methanol to oil molar ratio (6:1), reaction temperature (65 °C) and catalyst loading (0.5 wt%) within 4 h. For the first four cycles, the yield of biodiesel slightly decreased which was 98.40% for the first cycle, 95.45, 93.62 and 92.55% for second, third and fourth cycles, respectively. However, for the fifth cycle the yield of biodiesel was only decreased to 89.25% and after the fifth cycle the yield started to decrease dramatically to 84.30%, 73.18% and 67.67%. The yield decreased due to the leaching effect of active species in the reaction medium after repeated use. In addition, CaO particles that contained in the nano-catalyst can be solubilized in the glycerol obtained as by-product, calcium diglyceroxide species, which is the active phase in biodiesel production [41]. Moreover, PVA membrane that was soaked in methanol and oil swelled with time led to increment in its hydrophobicity property and reduced contact with methanol. However, the potentiality of prepared nano-catalyst to be reused in biodiesel production can reduce the raw material cost for the overall production [35]. In a study conducted by Talha & Sulaiman [42], after five cycles, the yield of biodiesel was reduced from 94.55% to 67.07% and the pattern in terms of catalyst reusability was similar to current study where the yield of biodiesel was decreased slightly at the early cycle.

3.4. Biodiesel properties

The physicochemical properties of the synthesized biodiesel were analyzed. The analysis was conducted to determine the density of biodiesel at 15 °C, viscosity at 40 °C and acid value. Based on the value of biodiesel properties, it was found that all values were within the limit of ASTM standard. In this study, the density was reported to be 0.878 g/cm³ which were in the range of the international standards. As compared to other studies, the density of WCO biodiesel by using calcined ripe banana was 0.89 g/cm³ which was higher than the current study [43].

Kinematic viscosity is defined as the resistance to flow of certain liquid. The international standard has specified the required kinematic viscosity of biodiesel is to be between 3.5 and 5.0 mm²/s (EN 14214) and 1.9–6.0 mm²/s (ASTM D 6751). The kinematic viscosity of the biodiesel produced from WCO in current study was 4.61 mm²/s which fulfilled the standards. In a study conducted by Borah et al. [44], the kinematic viscosity of biodiesel that produced from WCO with the presence of TiO₂/RGO composites was 4.57 mm²/s which was lower than current study. In addition, the methyl ester content in the biodiesel has been correlated with viscosity and the biodiesel produced from WCO have higher viscosity due to oxidation reactions that alter their composition [45]. Acid value is defined as the amount of potassium hydroxide needed to neutralize the biodiesel acid moieties [46]. Based on EN 14214 and ASTM D 6751 standard, the acid should be below than 0.5 mg KOH g⁻¹. In the current study, the acid value of biodiesel produced was 0.42 mg KOH g⁻¹. The acid value of biodiesel is important to be considered in production of biodiesel because it could affect the stability of biodiesel [45]. In a separate study using chicken bone catalyst, Farooq & Ramli [20] revealed a lower acid value of 0.35 mg KOH g⁻¹ using low FFA of WCO. In addition, 0.41 mg KOH g⁻¹ of acid value was reported in a study conducted by Joshi et al. [23]. The acid value of the final product in biodiesel production is really important because the high levels of free fatty acid influence biodiesel aging [47]. Besides, high acid value in biodiesel production leads to saponification which could hinder the transesterification reaction. Thus, feedstock with low acid value has to be used in order to ensure the acid value of biodiesel produced does not exceeds the

limit given by the international standards.

3.5. Kinetic heterogeneous catalyst

The performance of catalyst respects to time and temperature was further evaluated by its kinetics. The study of kinetics was performed with different reaction temperatures (55 °C, 60 °C, 65 °C). A set of experiments was carried out using the optimized conditions for the conversion: 0.5 wt% catalyst loading, methanol to oil molar ratio of 6:1 and reaction time from 5 min to 240 min. At the early stage of transesterification reaction, the reaction was at faster rate, however after 180 min, the reaction started to stabilize until the end of the reaction at 240 min. The optimal temperature of 65 °C was used for all experiments in this study.

3.5.1. Rate of reaction, *k*

A pseudo-first-order reaction model was applied in calculating the reaction of rate constant (*k*) on the performance of NCC/CaO catalyst that supported by PVA. From the slope of linear plot of Fig. 8, the values of *k* were obtained. Besides, the rate constant with respect to temperature was used in determining the activation energy through Arrhenius equation.

Fig. 8 shows a graph of $-\ln(1-X_{ME})$ versus time. The rate constant obtained was 0.0092, 0.012 and 0.0151 min⁻¹ at 55 °C, 60 °C and 65 °C, respectively. Harsha et al. [15] reported the value of *k* by using nanoparticles of CaO was 0.031 min⁻¹ under optimized operating condition. Compared to the current study, under optimized reaction condition, the value of *k* was calculated to be 0.0161 min⁻¹ which was lower than the study reported by Harsha et al. The smaller *k*-value indicates slower rate of reaction. Meanwhile, Bazargan et al., in 2016 reported that the *k*-value of the reaction varies from 0.003 to 0.014 min⁻¹ for the transesterification of *Nannochloropsis* microalgae oil at temperatures of 45–65 °C [48]. The range of *k*-value was lower than the current study. Thus, the value of *k* obtained in this study was consistent with the values reported in the literature.

Thiele modulus was calculated to prove the transesterification reaction was not affected by the internal mass transfer diffusion [25] as shown in Equations (8) and (9). The Thiele modulus were 0.37, 0.40 and 0.44, at temperature 55, 60 and 65 °C respectively. The value of Thiele modulus increased with increment of temperature and the rate constant. Since the values of Thiele modulus were less than 2, this indicated the overall transesterification reaction was not limited by internal mass transfer which could be neglected completely.

3.5.2. Activation energy, *E_a*

The value of *E_a*, was obtained from a plot of $\ln k$ versus $1/T$ which yields a straight line and the slope this plot, $-E_a/R$ which is *R* is the universal gas constant (8.314 kJ mol/K) and *T* is the absolute temperature in Kelvin. From the slope of Arrhenius plot, the value of *E_a* was 45.72 kJ/mol. Thus, 45.72 kJ/mol of energy required for the transesterification of WCO and methanol in the presence of NCC/CaO/PVA catalyst in the production of biodiesel.

Compared to other study, the *E_a* were 35.99, 34.12, 58.62 and 108.80 kJ/mol for CaO, fish bone, nano Ca(OCH₃)₂ and CaO-based palm kernel shell biochar respectively in biodiesel production [15,25,48,49]. The lowest energy needed in the production of biodiesel was from a reaction between WCO and methanol with fish bone as the catalyst was 34.12 kJ/mol with the optimum conditions of 6 wt%, 18:1, 65 °C and 2 h of catalyst loading, methanol to oil molar ratio, reaction temperature and reaction time. From this reaction, biodiesel yield was 86% [25]. Moreover, the lower value of *E_a* leads to faster reaction and the reaction would be more efficient [25]. Thus, for the current study, the value of *E_a* was considered as

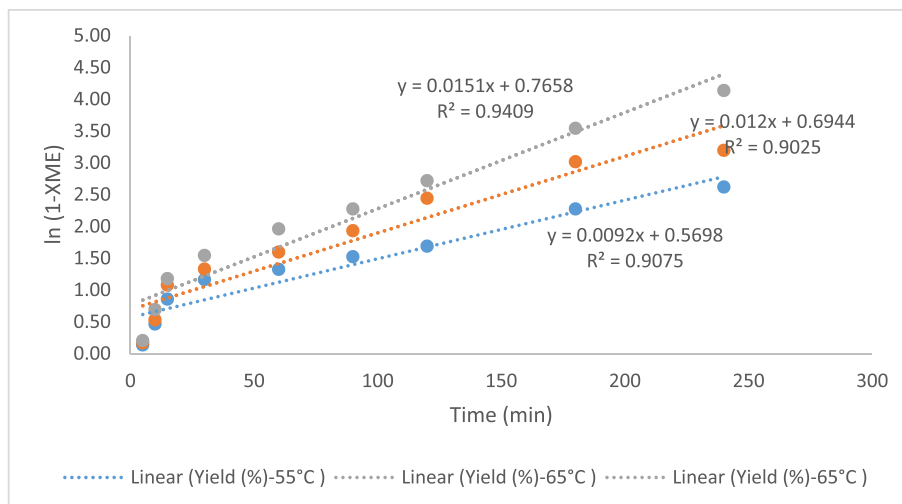


Fig. 8. A linear graph of $-\ln(1-X_{ME})$ versus time on different temperature.

efficient for transesterification reaction.

4. Conclusion

In this study, nano-catalyst of CaO and NCC for biodiesel production was successfully synthesized from chicken bone and coconut residue. Transesterification reaction was carried out in a packed bed reactor in the presence of CaO/NCC/PVA. Highest yield of 98.4% of biodiesel were obtained at the optimize conditions of 65 °C, 6:1 and 0.5 wt% of temperature, methanol to oil ratio and catalyst loading respectively. CaO/NCC/PVA catalyst showed a good catalytic activity as it can be reused up to 4th cycles while maintaining the yield of biodiesel above 90%. This is due to its larger surface area, higher active site of catalyst and the system used for transesterification could reduce the mechanical damage of the catalyst. Thus, the findings of this study provided another method in biodiesel production which is low cost and environmentally friendly that produced high yield of biodiesel.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

N.A.F.A. Zik: Writing - original draft, Investigation. **S. Sulaiman:** Supervision, Conceptualization, Writing - review & editing. **P. Jamal:** Writing - review & editing.

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