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PHOTO-ESTERIFICATION OF WASTE COOKING OIL USING A NOVEL NANOCATALYST TiO_2 IMPREGNATED WITH EMPTY FRUIT BUNCHES ASH HETEROGENEOUS CATALYST

(Foto-Esterifikasi Sisa Minyak Masak Menggunakan Novel Nanocatalyst TiO_2 yang Diimpregnasi dengan Mangkin Heterogen Abu Tandan Buah Kelapa Sawit Kosong)

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Abstract

Photo-esterification of Waste Cooking Oil (WCO) with TiO_2/EFBA500 photocatalyst as heterogeneous photo-catalyst has been investigated in this study. WCO is nonedible oil with high free fatty acid (FFA) content which needs esterification to reduce its FFA content followed by transesterification to produce Fatty Acid Methyl Ester (FAME). WCO was esterified with methanol through photocatalytic process with UV light irradiation as the light source. TiO_2/EFBA500 photocatalyst was synthesized using simple wet impregnation method. The samples were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Ultraviolet Diffuse Reflectance Spectroscopy (UV-Vis DRS) analysis. Characterization results revealed that the bandgap energy of TiO_2/EFBA500 was successfully reduced from 3.0 eV to 2.88 eV which was suitable in UV light irradiation and needed low energy in the process. TiO_2 semiconductor composite doped with Empty Fruit Bunches Ash (EFBA) showed a very high catalytic activity for FFAs photo-esterification. Experimental results showed that the optimum condition of photo-esterification with catalyst loading to oil was 4 wt.%, 20:1 methanol to oil molar ratio and 2 h reaction time achieved the reduction of FFA content from 11.65% to 2.04% with FFA conversion of 83%. FFA content was successfully reduced indicating that photo-catalytic esterification is a viable option in order to produce FAME. Biodiesel analysis using Gas Chromatography Mass Spectrometry (GCMS) is used to calculate yield and methyl ester content according to international biodiesel standard European (EN14103).

Keywords: biodiesel, photo-esterification, transesterification, waste cooking oil, empty fruit bunches ash

Abstrak

Foto-esterifikasi sisa minyak masak (WCO) dengan foto-mangkin TiO_2/EFBA500 sebagai mangkin foto heterogen telah dikaji dalam kajian ini. WCO ialah minyak tidak boleh dimakan dengan kandungan asid lemak bebas (FFA) yang tinggi, memerlukan pengesteran untuk mengurang kandungan FFA diikuti dengan transesterifikasi untuk menghasilkan asid lemak metil ester (FAME). WCO telah diesterkan dengan metanol melalui proses fotokatalitik dan penyinaran cahaya UV sebagai sumber cahaya. Foto-pemangkin TiO_2/EFBA500 telah disintesis menggunakan kaedah impregnasi basah yang biasa. Sampel dicirikan dengan Pembelauan Sinar-X (XRD), Mikroskopi Imbasan Elektron (SEM), Serakan Tenaga Sinar (EDX) dan Spektroskopi Pemantulan Resap UV-vis (UV-Vis DRS) analisis. Keputusan perincian mendedahkan bahawa tenaga jurang jalur TiO_2/EFBA500 berjaya dikurangkan daripada 3.0 eV kepada 2.88 eV yang sesuai dalam penyinaran cahaya UV dan tenaga yang rendah diperlukan dalam proses tersebut. Komposit semikonduktor TiO_2 yang digabungkankan dengan abu tandan buah kelapa sawit kosong (EFBA) menunjukkan aktiviti pemangkinan yang sangat tinggi untuk pengesteran foto FFAs. Keputusan eksperimen menunjukkan keadaan optimum foto-esterifikasi dengan muatan mangkin nisbah kepada minyak ialah 4 wt.%, 20:1 metanol kepada nisbah molar minyak dan 2 jam masa tindak balas mencapai pengurangan kandungan FFA daripada 11.65% kepada 2.04% dengan penukaran FFA sebanyak 83%. Kandungan FFA telah berjaya dikurangkan menunjukkan bahawa pengesteran foto-mangkin adalah pilihan yang terbaik untuk menghasilkan FAME. Biodiesel dianalisis dengan Kromatografi Gas-Spektroskopi Jisim (GC-MS) analisis untuk mengira hasil dan kandungan metil ester mengikut piawaian biodiesel antarabangsa Eropah (EN14103).

Kata kunci: biodisel, foto-esterifikasi, transesterifikasi, sisa minyak masak, abu tandan buah kelapa sawit kosong

Introduction

The depletion of fossil fuels has brought about the development of a renewable and sustainable alternative energy which is environmentally friendly for the benefit of the future [1]. Fatty acid alkyl ester, also named as biodiesel, has almost the same properties as petroleum fuel which is a good replacement for conventional petroleum product especially in the transportation sector. Besides that, it produces low emission of carbon monoxide, sulfur dioxide and un-combusted hydrocarbon [2]. This alternative energy is claimed to be as clean as the biofuels produced via catalytic transesterification of triglycerides (TG) with alcohol e.g. methanol converted to fatty acid alkyl ester (biodiesel) and glycerol as by-product [3]. TG is the main component of fat and oil in vegetable oils and animal fats. Examples of vegetable oils are such as soybean oil, sunflower, cottonseed etc., [4]. Reported by Volli et al. in order to reduce the cost of biodiesel and to avoid ecological imbalance due to the use of this edible sources, non-edible sources have become a new target feedstock for the biodiesel production [5]. The examples of non-edible oil are waste cooking oil, jatropha curcas oil, greased oil and etc. [6]. The usage of non-edible oil can solve the waste management problem. It is also sustainable and is able to reduce the production cost. This type of non-edible feedstock consists of high FFA content (>1% FFA) and therefore requires a pretreatment step to reduce it [7].

Reported by Razak et al. the homogeneous catalyst has been widely used over generations [8]. However, this catalyst can harm our environment and there are many disadvantages in using this catalyst. Homogeneous catalyst cannot be reused because the reactant and the product are inseparable, and this process also triggers waste water problem during the purification process [9]. Moreover, it can reduce the yield of biodiesel production. Several types of heterogeneous catalysts have been introduced by many researchers that can solve the separation problem. The use of catalyst that can be recycled is an advantage and it will also reduce the operational cost. The example of heterogeneous catalyst includes sulfated zirconia [10], heteropoly acid [11], carbon nanotubes [12], biomass carbon based [13] and more. However, these types of thermal catalytic processes cannot outdo heterogeneous photocatalyst as it is performed at room temperature under either solar energy or artificial light sources, thus reducing the operation cost as it can save the energy [3]. As reported by Guo et al., using photocatalyst in the production of biodiesel can convert more than 90% of FFA [14]. Examples of nanomaterials are cerium oxide [15], zinc oxide [16], titanium dioxide [17], chromium (IV) [18] and metal oxide which are highly stable, very effective, and requires a low cost with high availability [19].

Photocatalyst is a light induced catalytic process that involves oxidization and/or reduction of organic molecules via redox reactions. This process generated electron-hole pair on the surface of semiconductors upon light irradiation [3]. This photocatalyst has been widely used in the applications of wastewater treatment [20], bacteria disinfection [21], hydrogen production [22] and carbon dioxide removal [23]. Photocatalyst in the photo-esterification reaction takes place when alcohol e.g., methanol reacts with positive holes (h^+), generating methanol radicals ($CH_3O^\cdot$) and releasing electron (e^-) which is generated under solar irradiation react with FFA formed radical of fatty acid ($R\text{-}COOH^\cdot$) on the surface of photocatalyst. From the intermediates of $CH_3O\cdot$, $R\text{-}COOH\cdot$ and H^+, then formed final products of methyl ester and water [5]. Reported by Citra Dewi & Slamet, they applied TiO_2P_{25} in the photo-esterification and successfully converted 45.2% of FFA in waste cooking oil [24]. Ghani et al., reported that they synthesized bismuth vanadate with reduced graphene oxide bismuth vanadate for photo-esterification of soap nut oil and achieved maximum conversion of FFA at 88% [6, 25]. Thus, photocatalyst is suitable and capable in the reaction process with methanol and FFA under light irradiation. Not only that, it is environmentally friendly, reusable, and produced high yield which assured the successfulness in the production for new alternative energy.

Titanium dioxide nanoparticles (TiO_2) is among high photocatalytic activity consisting of three main crystallographic phases, which are anatase, rutile and brookite [26]. It is nontoxic, easily available, superior redox ability, and photostability. It has become the main focus in bioenergy field as promising heterogeneous catalyst in the esterification process. The photocatalytic activity of TiO_2 depends on the recombination rate of the photogenerated electron hole pair (e^-/h^+). However, it is usually limited by its large bandgap (~ 3.2 eV for anatase) that increases the recombination rate [27]. In order to reduce the e^-/h^+ pair recombination rate, combining techniques with high surface area supported by materials such as zeolite [28], carbon nanotube [29], graphitic carbon nitride [30] and active carbon [31] is the best option. Besides that, it can improve reactivity and kinetic of the catalyst as they formed crystal with high specific surface area. In recent work by Corro et al. they used ZnO/SiO_2 in the photo-esterification of Jatropha Curcas Crude Oil (JCCO) which achieved 96% FFA conversion [32]. Redjeki et al. used CuO/TiO_2 by conversion FFA of Kemiri Sunan Oil around 59%. Therefore, by combining technique with other supported material can prevent the recombination rate of e^-/h^+ pair and enhanced the photocatalytic activity [33].

Recently, some researcher use ash as dopant with TiO_2 semiconductor. Ash is the industrial waste byproduct resulting from the burning of solid fuels. The constituents of ash are mostly unburned carbon, metal oxides (Si, Al, K, Fe, Ca) and other inorganic substances [34]. Reported by Suliman et al., they doped palm oil fiber ash (POFA) with TiO_2 and reduced almost 50% of chemical oxygen demand (COD) in wastewater [35]. Shi et al. also claimed that they had also doped fly ash (FA) with TiO_2 and successfully degraded 95% of phenol in aqueous solution. The concentration of metal oxide of ash materials might be an excellent opportunity when dope with TiO_2 that can enhanced the photocatalytic activity in the reaction [36]. Empty fruit bunches ash (EFBA) from palm oil mill has recently suggested as supported material in the synthesized of photocatalyst. EFBA does not only work to enhance the efficiency of the interfacial charge transfer in the photocatalytic process but also function as a major non-toxic waste sources which is low-cost adsorbent and easily available. It is safe to state that EFBA is the outcome of the thermal power generation plant. Besides that, EFBA can reduce the cost of waste management and environmental problem. In this study, the photocatalytic activity of TiO_2 alone and TiO_2 doped with EFBA is compared in removal of FFA in WCO and further utilized in transesterification for biodiesel production.

Materials and Methods

Materials

Empty fruit bunches ash (EFBA) was obtained from FTJ Bio Power Sdn. Bhd. The feedstock of waste cooking oil (WCO) was obtained from the local restaurant in Bandar Jengka Pusat, Pahang. 1.5 L of WCO is collected, filtered, and saved for analysis. Titanium Dioxide (Degussa P25), n-hexane, methanol, methyl heptadecanoate, sodium hydroxide, potassium hydroxide, phenolphthalein is all purity > 99%, hydrochloric acid (HCl, purity >32%) were obtained from QReC. All reagent will be directly purchased with analytical grade and used without further purification.

Preparation of catalyst

EFBA was dried in the oven at 120 ᵒC then sieved through 100 mesh screening. TiO_2-Degussa P25 (1.0 g) was mixed with EFBA (1.0 g) in 100 ml distilled water (1:1). The new nanocomposite photocatalyst was obtained from the slurry under stirring (300 rpm) for 1 h, at room temperature, on a thermoset heating plate. After filtration, the slurry was further washed with deionized water followed by drying in oven at 120 °C overnight. Finally, dried material was calcined at 500˚C for 3 h in a tube furnace with a heating rate of 5˚C/min. The sample obtained is 1.8 ± 0.3 g and denoted as TiO_2/EFBA500.

Characterization of catalyst

The catalysts were analyzed using X-Ray Diffraction (XRD) to identify the composition of samples. The diffractograms were measured in the 2θ mode, within the range of 20° to 90° at the speed of 6.0°/min. Scanning Electron Microscopy and Energy-Dispersive X-ray spectroscopy (SEM-EDX) is used to study the morphology of samples. It was done with a SEM JEOL JSM-7100F scanning electron microscope at 15.0 kV. UV-Vis Diffuse Reflectance Spectrometer (UV-Vis DRS) as to measure the bandgap of the samples.

Photocatalytic esterification of WCO

The photocatalytic esterification process was conducted in a reactor assisted by a 6 W UV lamp (λ = 365 nm) as the light source. The reaction mixture catalysed by TiO_2 and TiO_2/EFBA500 photocatalyst, stirred continuously under stirring rate of 400 rpm by using an internal magnetic stirrer which generated a strong liquid rotation leading to homogeneous irradiation of the whole reacting mixture. A 10 g of WCO was used with varies parameter of methanol to WCO molar ratio in the range of 12:1, 16:1, 20:1, 24:1, the amount of catalyst is 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, 5 wt.%, UV irradiation time is 1 h, 2 h, 3 h, 4 h, 5 h. After esterification, the mixture was centrifuged at 5000 rpm for 15 min. The lower layer consists of unreacted triglycerides (further trans-esterification), and insoluble catalysts. The upper layer consists of unreacted methanol and water from reaction process. The catalyst was first filtered and separated, and the excess methanol was removed by drying in the oven for 15 min at 60 ᵒC to obtain the esterified WCO for use in transesterification reaction. Acid value of the WCO was determined by titration method (in triplicates) using standard isopropanol potassium hydroxide (0.1 N) according to AOCS; Cd 3a-63. The conversion was calculated using equation 2.

Trans-esterification of WCO

Trans-esterification of WCO was performed in a 100 mL three necked flask in an oil bath equipped with magnetic stirring for temperatures up to 65 ˚C using reflux method. 1 wt.% of NaOH catalyst was added to methanol 12:1 methanol to WCO molar ratio, stirred, and addition of 5 g esterified WCO. Transesterification product was separated into two layers using separating funnel. The upper layer is Fatty Acid Methyl Ester (FAME) and the lower layer is glycerol. FAME is the main product or called biodiesel, meanwhile glycerol is the by-product in this experiment. FAME was then washed with hot water (< 90 ᵒC). Biodiesel produced was going through yield calculation and methyl ester content by Gas Chromatography Mass Spectrometry (GCMS) analysis (GC-7860B Agilent). The temperature at injector and detector were programmed at 240 ᵒC. The flow rate of Helium as carrier gas at 19.2 mL min $^{-1}$ and the column temperature was set at 150 ᵒC with ramping rate of 15 ᵒC min $^{-1}$. Table 1 showed the formula to calculate biodiesel conversion, ester content and biodiesel yield according to international standard European EN14103.

Table 1. Equation to calculate the biodiesel conversion, ester content and biodiesel yield [37]

Formula	Equation
Conversion (%)	$d = \frac{A}{Mass\ of\ WCO} \times 100$
Ester content (%) from EN14103	$c = \frac{TA - AEI}{AEI} \times \frac{CEI \times VEI}{m} \times 100$
Mass of pure biodiesel from biodiesel conversion (g)	$Y = c \times A$
Pure biodiesel yield (%)	$FAME\ yield, \% = \frac{Y\ (g)}{mass\ WCO\ (g)} \times 100$

A = Mass of biodiesel collected (g), TA =Total area, AEI = Area of internal standard, CEI = Concentration (mg/mL) of methyl heptadecanoate solution, VEI = Volume of (mL) methyl heptadecanoate solution, and m = Mass of sample

Determination of acid value and FFA conversion

250 ml conical flask was prepared and 0.2 g of WCO. 10 mL toluene: isopropanol KOH (1:1) was added in the conical flask with a few drops of phenolphthalein indicator in the sample solution, titrated with 0.1 mol/L isopropanol KOH standard solution. The solution was observed from colorless to slightly red until it remained unchanged for 30 s, which meant that the titration endpoint was reached. The acid value (AV) was calculated by the following formula Eq. (1):

$$A = \frac{V \times C \times 56.11}{m} \quad (1)$$

where AV is the acid value of the sample, V is the volume of isopropanol KOH standard solution consumed to reach the titration end point, C is the concentration of KOH standard solution, 56.11 is the molecular weight of KOH, m is the weight of the test sample. The conversion rate of FFA (FFA conversion%) is considered as the fraction of the esterification reaction of FFA and methanol, and the conversion rate of FFA (FFA conversion%) was determined according to the acid value ratio using Eq. (2):

$$FFA\ conversion\ \% = \frac{A_a - A_b}{A_a} \times 100 \quad (2)$$

where Aa is the acid value of the WCO. Ab is the acid value of WCO after esterification.

Results and Discussion

Properties of waste cooking oil

The FFA chemical composition analysis was performed physiochemically using titration method. The results shown in Table 2 indicated that WCO has 11.65 % content of FFA with 23.30 mg KOH g^{-1} of acid value.

Table 2. The properties of waste cooking oil

Properties	Waste Cooking Oil
Acid value (mg KOH g^{-1})	23.30
Free Fatty Acid (%)	11.65
Saponification value (mg KOH g^{-1})	184
Molecular weight ($gmol^{-1}$)	915

Characterization of photo-catalyst

The diffraction pattern of raw EFBA, dry EFBA and TiO_2/EFBA500, are presented in the Figure 1. The peaks of the raw and dry EFBA showed all the cellulose materials from 2θ = 29˚ to 90˚. Dry materials that had been dried in the oven at 120 ˚C showed graphite structure at $2\theta = 27^\circ$, 80° and 88°. Also, the intensity of dry EFBA was a bit higher than raw EFBA. This was due to the drying process of EFBA at 120 °C which developed the crystallite size and produced the graphite structure [38]. As for TiO_2/EFBA500, it showed that dry EFBA had well embedded to the anatase and rutile phase of TiO_2. The peaks of rutile, anatase and cellulose of the EFBA were dispersed throughout the surface of the catalyst. This promoted active photocatalytic activity in the esterification. As reported by Berrones-Hernández et al. the impregnation technique promoted a deposition element of one element on another [36]. Therefore, the catalyst will have improvement in stability and efficiency in the photo esterification process due to deposition of TiO_2 on EFBA. As proven, the conversion of FFA catalyzed by TiO_2EFBA500 achieved 83% after 2 h reaction time under UV light irradiation.

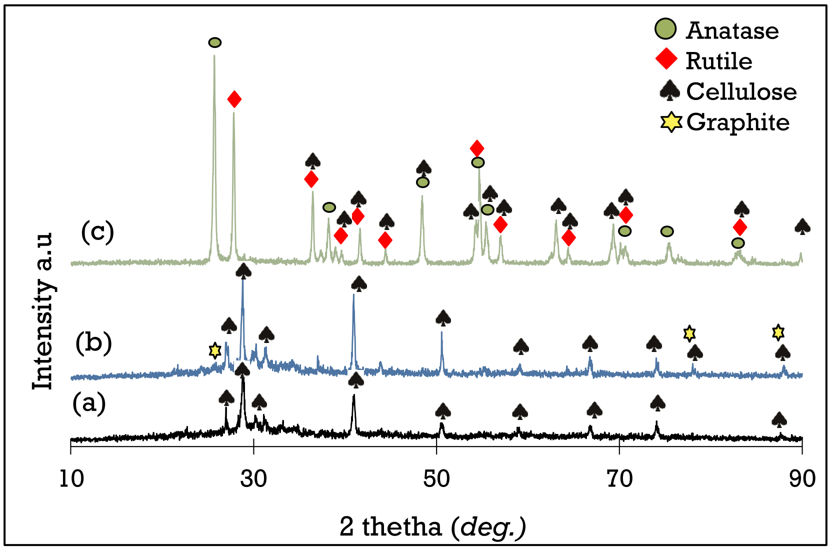

Figure 1. The XRD pattern of (a) Raw EFBA, (b) Dry EFBA and (c) TIO_2/EFBA500

Figure 2 showed SEM image of the dry EFBA, TiO_2, TIO_2/EFBA before and after being calcined at 500°C. A micrograph showed rough appearance for all the catalyst. Raw and Dry EFBA appeared granular and spherical in shape whereas TiO_2 exhibited agglomerated nanoparticles, spherical and irregular shapes [38]. Naeem et al., reported that doping technique can prevent the agglomeration of TiO_2 nanoparticles during the reaction process [40]. From the micrograph, it showed that TiO_2 was well deposited on the surface of EFBA which successfully doped between TiO_2 and EFBA. The effect of calcination temperature at 500°C showed ordered and homogeneous distribution of the TiO_2 nanoparticles on the EFBA composite [36]. The result from experimental data of XRD confirmed that EFBA was successfully coordinated with TiO_2 metal as TiO_2 has cubic and spherical crystal that can promote larger cluster formation on the EFBA particles [41]. The reactive species suggested favorable reduction of FFA content and active photocatalytic esterification of WCO. Furthermore, the presence of elemental composition of this catalyst was confirmed by EDX analysis in the Table 3.

Figure 3 showed the UV–vis diffuse reflectance spectra of Dry EFBA, TiO_2, TiO_2/EFBA and TiO_2/EFBA500 respectively, and the band gap energy was estimated to be about 4.0, 3.0, 2.95 and 2.88 eV, respectively using Tauc plot equation. This showed that the band gap energy of the EFBA-doped TiO_2 samples monotonically became narrower after doping and calcination at 500°C.

Catalytic activity of the TiO_2 and TiO_2/EFBA photocatalyst

To determine the optimal conditions of FFA esterification reaction photocatalyzed by TiO_2 and TiO_2/EFBA500, we examined the effects of the reaction time under UV irradiation, methanol to WCO molar ratio and photocatalyst/WCO mass ratio. Figure 4 and Figure 5 show the FFA content after photo esterification process using TiO_2 and TiO_2/EFBA500 respectively. There is a comparison of FFA reduction using TiO_2 and TiO_2/EFBA500 photocatalyst as TiO_2/EFBA500 photocatalyst reduced more FFA content than TiO_2 photocatalyst. As reported by Klubnuan et al. ash can modify the semiconductor material and control the bandgap energy [42]. Therefore, doping EFBA with TiO_2 can increase the crystallite size and reduce the bandgap energy from 3.0 eV to 2.88 eV confirmed by XRD and UV-Vis-DRS results which improve the photocatalytic reaction. From the results, the optimized value reduction of FFA content using TiO_2 catalyst only achieved 4.88% from 11.65% FFA content with 4 h reaction time under UV light, 20:1 methanol to WCO molar ratio and 4 wt.% TiO_2 catalyst. Same condition with different optimized parameter for TiO_2/EFBA500 photocatalyst achieved 2.04% of FFA reduction from 11.65% FFA content by 2 h reaction time, 20:1 molar ratio and 4 wt.% catalyst loading. These results suggested that TiO_2/EFBA500 photocatalyst was more active and efficient during the photo-esterification compared to TiO_2. TiO_2/EFBA500 only needed 2 h reaction time to convert 83% FFA rather than using TiO_2 that needed 4 h reaction time to convert only 58% FFA.

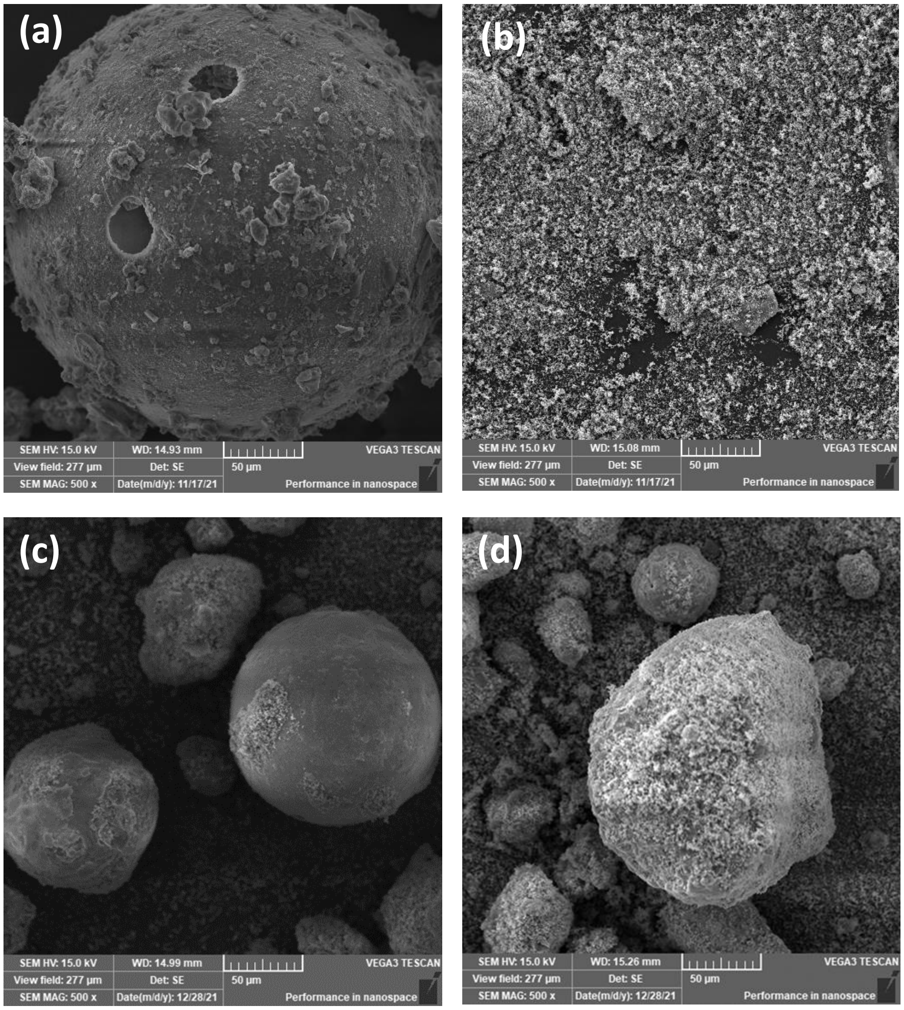

Figure 2. SEM image of the (a) Dry EFBA, (b) TiO_2, (c) TIO_2/EFBA and (d) TIO_2/EFBA500

Table 3. Elemental composition of photo-catalyst

	Elemental Composition (%)									
	C	**O**	**Ti**	**Si**	**K**	**Ca**	**Mg**	**S**	**P**	**Al**
Dry EFBA		53.86		10.85	23.80	5.39	0.71	2.50	2.45	0.16
TiO_2		48.39	51.61							
TiO_2EFBA	28.54	65.96	1.59	2.19	0.53	0.33	0.34			
TiO_2EFBA500	24.21	65.75	5.37	2.51	1.17	0.48	0.52			

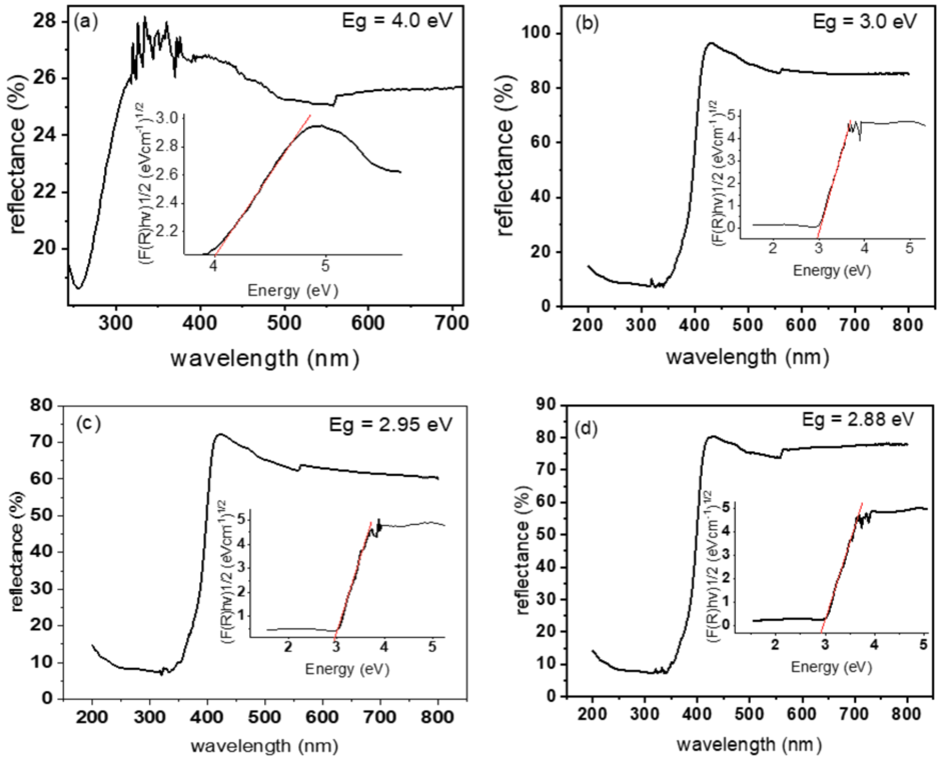

Figure 3. UV Vis DRS of (a) Dry EFBA, (b) TiO_2, (c) TiO_2/EFBA and (d) TiO_2/EFBA500

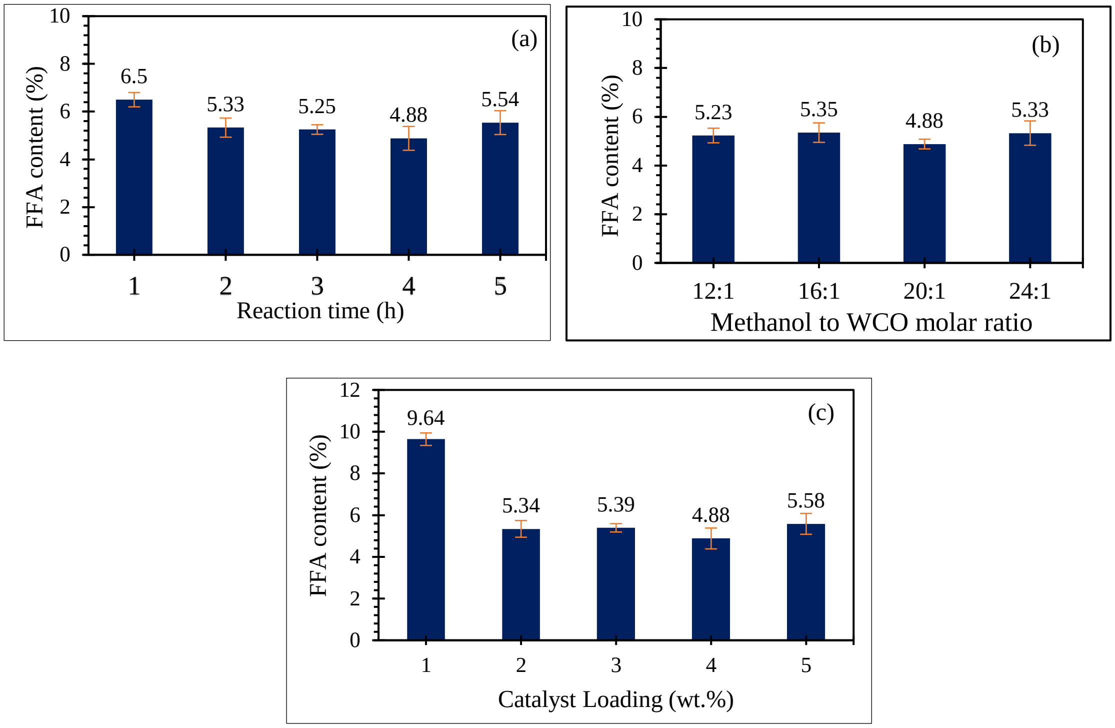

Figure 4. Photocatalytic esterification of WCO using TiO_2 photocatalyst (a) reaction time with (4 wt.% catalyst loading and 20:1 methanol to WCO ratio), (b) methanol to WCO molar ratio with (4 wt.% catalyst loading and 2 h reaction time) and (c) catalyst loading with (20:1 methanol to WCO molar ratio and 2 h reaction time).

From the FFA content results in Figure 4 and Figure 5, different parameters were studied to determine the optimized parameter for reduction of FFA content in WCO which were reaction time from 1 to 5 h, methanol to WCO molar ratio from 12:1 to 24:1 and catalyst loading from 1 wt.% until 5 wt.%. The reaction was conducted for three replications in each level. Photo-esterification of WCO contained 11.65% FFA catalyzed by TiO_2 photocatalyst showed in Figure 4 from 1 to 4 h, the FFA content decreased slowly from 6.5% until 4.88 %. Then the FFA increased again at 5 h as it faced reversible esterification reaction due to longer reaction time. Guo et al., reported that, reaction time under UV light more than 3 h will inhibit the reaction process [14]. The reason is because increasing reaction time will also increase the temperature of UV irradiation in the reactor that can cause saponification reaction. For the methanol to WCO molar ratio, the best ratio was at 20:1 as it achieved the maximum reduction of FFA content. It was the same for catalyst dosage, as the catalyst increased from 1 wt.% to 4 wt.%, the percentage of FFA content decreased from 9.64% to 4.88%. When exceeding 4 wt.%, the FFA content increased again which reduced the conversion of FFA. Adequate catalyst dosage can reduce the FFA content. However, excessive catalyst dosage can inhibit the reaction due to high viscosity in the reaction process. The maximum conversion of FFA catalyzed by TiO_2 photocatalyst reached only 58% under 4h reaction time, 20:1 methanol to WCO molar ratio and 4wt.% catalyst loading. This basis was also applied for photo-esterification in Figure 5. Photo-esterification reaction catalyzed by TiO_2EFBA500 in Figure 5 showed that the optimized parameter at 2 h reaction time, 20:1 methanol to WCO molar ratio and 4 wt.% catalyst loading reduced the FFA content from 11.65% to 2.04% in which the conversion of FFA was up to 83%.

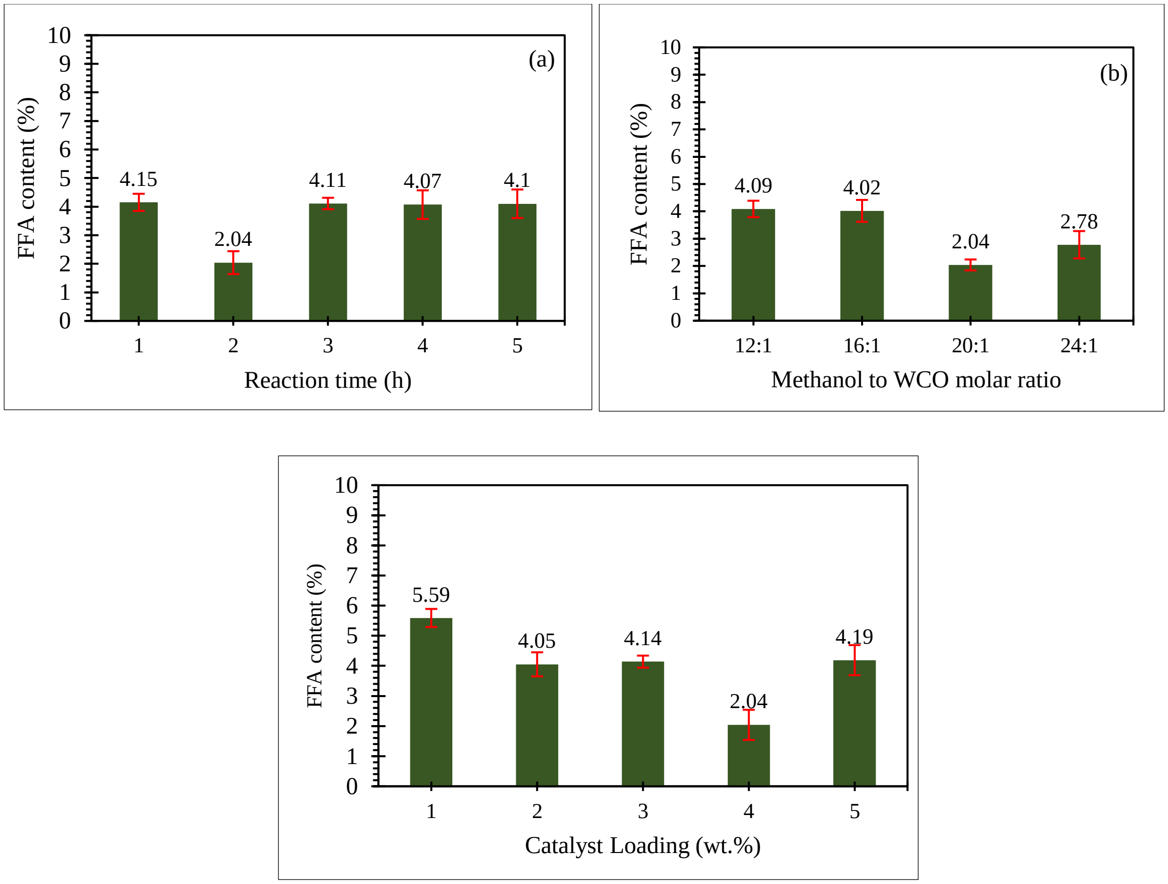

Figure 5. Photocatalytic esterification of WCO using TiO_2/EFBA500 photocatalyst (a) reaction time with (4 wt.% catalyst loading and 20:1 methanol to WCO ratio), (b) methanol to WCO molar ratio with (4 wt.% catalyst loading and 2 h reaction time) and (c) catalyst loading with (20:1 methanol to WCO molar ratio and 2 h reaction time)

After the photo-esterification process, the esterified WCO will be trans esterify for a second step reaction. The process conducted using reflux method and catalyzed by NaOH under 1 h reaction time; 12:1 methanol to oil molar ratio, 1 wt.% catalyst loading and 65 °C. The WCO Biodiesel was analyzed using the GC-MS analysis to determine the chemical composition of the product. Each peak of the WCO Biodiesel product chromatogram was identified by comparing to published data and GC libraries. The largest peak in Figure 6 and detailed compound of fatty acid in Table 4 showed the presence of high amount of esters of oleic acid 34.84% followed by palmitic acid 29.01%, linoleic acid 9.99% along with stearic acid 4.86%, linolenic acid 1.74%, palmitoleic acid 1.42% and myristic acid 1.11% in alkali catalyzed process. As reported by Mekonnen & Sendekie, homogenous base catalyst using non-edible feedstock oil produces high yield of biodiesel that can achieve the limit set by international standard D6751 [43]. From the results, triglycerides of esterified WCO oil were successfully converted to FAME product only using a minimum range reaction parameter producing 65.5% FAME product and calculated using the equation in Table 1 [44].

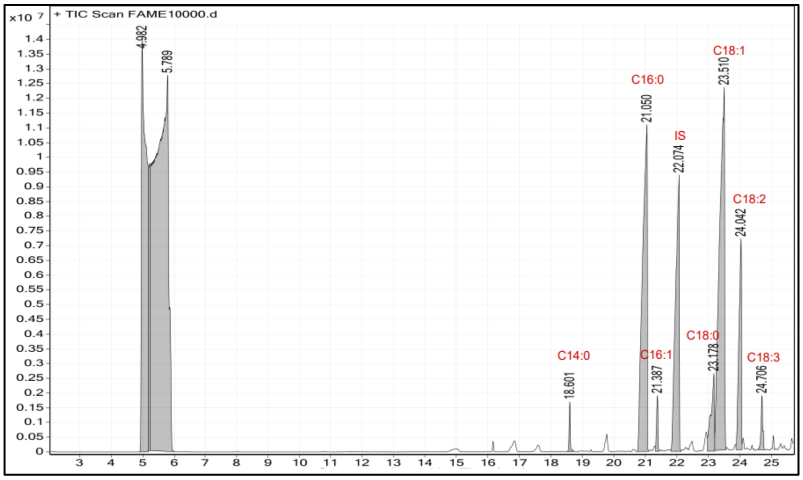

Figure 6. GCMS chromatogram of WCO Biodiesel produced by transesterification in the presence of 1 wt.% NaOH catalyst, 12:1 methanol, 65 ˚C at 1 h reaction time

Table 4. Composition of Fatty acid methyl ester in the WCO Biodiesel

Fatty Acid Compound	**Retention Time (min)**	**C N:U**	**Composition (wt.%)**
Myristic acid	18.60	C14:0	1.11
Palmitic acid	21.05	C16:0	29.01
Palmitoleic acid	21.39	C16:1	1.42
Stearic acid	23.18	C18:0	4.86
Oleic acid	23.51	C18:1	34.84
Linoleic acid	24.04	C18:2	9.99
Linolenic acid	24.71	C18:3	1.74

Conclusion

TiO_2/EFBA500 photocatalyst was prepared via simple impregnation method and used in the photo-esterification of waste cooking oil for biodiesel synthesis. Under optimum reaction conditions of 2 h reaction time with UV light irradiation, 20:1 methanol to WCO molar ratio and 4 wt.% catalyst loading achieved 83% FFA conversion and reduced from 11.65% to 2.04 FFA% content. Thus, TiO_2/EFBA500 photocatalyst is a promising catalyst for photo-esterification of waste cooking oil. TiO_2 alone can convert FFA up to 58% and doping with metal oxide compound from EFBA can enhance the effectiveness of photocatalytic activity which successfully achieved 83% FFA conversion. Therefore, photo-esterification process can increase the yield of biodiesel using high catalytic activity of semiconductor nanomaterial. It also has a low production cost as it can be carried out at room temperature and uses low quality feedstock oil. For future study, TiO_2 will be compared with other type of nanomaterials to determine the properties and mechanism of semiconductor nanomaterials doped with EFBA and also using different doping techniques.

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References

1. Hazmi, B., Rashid, U., Taufiq-Yap, Y. H., Ibrahim, M. L. and Nehdi, I. A. (2020). Supermagnetic nano-bifunctional catalyst from rice husk: Synthesis, characterization and application for conversion of used cooking oil to biodiesel. *Catalysts*, 10(2): 1-21.
2. Kefas, H. M., Yunus, R., Rashid, U. and Taufiq-

Yap, Y. H. (2018). Modified sulfonation method for converting carbonized glucose into solid acid catalyst for the esterification of palm fatty acid distillate. *Fuel*, 229: 68-78.

3. Oloruntoba, O. and Hamza, A. (2019). Photochemical and photocatalytic esterification of waste cooking oil under visible light irradiation using mechanochemically synthesized ZnO/silica. *Journal of Faculty of Food Engineering, University Zaria, Nigeria.*, 18(2): 89-96.
4. Singh, D., Sharma, D., Soni, S. L., Sharma, S., Sharma, P. K. and Jhalani, A. (2020). A review on feedstocks, production processes, and yield for different generations of biodiesel. *Fuel*, 262: 116553.
5. Volli, V., Purkait, K. M. and Shu, C. (2019). Preparation and characterization of animal bone powder impregnated fly ash catalyst for transesterification. *Science of the Total Environment*, 669*:* 314-321.
6. Lim, S. and Teong, L. K. (2010). Recent trends, opportunities and challenges of biodiesel in Malaysia: An overview. *Renewable and Sustainable Energy Reviews*, 14: 938-954.
7. Khalit, W. N. A. W., Asikin-mijan, N., Marliza, T. S., Gamal, M. S., Shamsuddin, M. R., Saiman, M. I., and Taufiq-Yap, Y. H. (2021). Catalytic deoxygenation of waste cooking oil utilizing nickel oxide catalysts over various supports to produce renewable diesel fuel. *Biomass and Bioenergy*, 154: 106248.
8. Razak, Z. K. A., Kamarullah, Shahida. H, Shohaimi, N. A. M., Kamalluddin, N. A. I. M. and Teh, W. N. S. W. (2020). Transesterification of palm oil for biodiesel production using Ni/Cao supported with alumina beads. *GADING Journal of Science and Technology*, 3(1): 100-106.
9. Ibrahim, S. F., Asikin-mijan, N., Ibrahim, M. L., Abdulkareem-alsultan, G., Izham, S. M. and Taufiq-Yap, Y. H. (2020). Sulfonated functionalization of carbon derived corncob residue via hydrothermal synthesis route for esterification of palm fatty acid distillate. *Energy Conversion and Management*, 210(3): 112698.
10. Zhang, Y., Wong, W.-T. and Yung, K.-F. (2014). Biodiesel production via esterification of oleic acid catalyzed by chlorosulfonic acid modified zirconia. *Applied Energy*, 116: 191-198.
11. Shin, H.-Y., An, S.-H., Sheikh, R., Park, Y. H. and Bae, S.-Y. (2012). Transesterification of used vegetable oils with a Cs-doped heteropolyacid catalyst in supercritical methanol. *Fuel*, 96: 572-578.
12. Lokman-Ibrahim, M., Khalil, N. N. A. N. A., Islam, A., Rashid, U., Fadhilah-Ibrahim, S., Mashuri, S. I. S. and Taufiq-Yap, Y. H. (2020). Preparation of Na_2O supported CNTs nanocatalyst for efficient biodiesel production from waste-oil. *Energy Conversion and Management Journal*, 205: 112445.
13. Naihi, H., Baini, R. and Yakub, I. (2021). Oil palm biomass-based activated carbons for the removal of cadmium—a review. *AIMS Materials Science*, 8(3): 453-468.
14. Guo, M., Jiang, W., Chen, C., Qu, S., Lu, J., Yi, W. and Ding, J. (2021). Process optimization of biodiesel production from waste cooking oil by esterification of free fatty acids using La^{3+}/ZnO-TiO_2 photocatalyst. *Energy Conversion and Management*, 229: 113745.
15. Mokhtar, W. N. A. W., Ramli, M. R., Jamaluddin, M. A. and Ramli, S. (2019). Rare earth metal doped CaO as catalyst for the transesterification reaction of cooking oil. *Malaysian Journal of Analytical Sciences*, 23(4): 660-666.
16. Zhu, X., Kavitha, P., and Hwang, H.-M. (2019). Green synthesis of titanium dioxide and zinc oxide nanoparticles and their usage for antimicrobial applications and environmental remediation. In *Green Synthesis, Characterization and Applications of Nanoparticles*. Elsevier Inc.
17. Manique, M. C., Silva, A. P., Alves, A. K. and Bergmann, C. P. (2016). Application of hydrothermally produced TiO_2 nanotubes in photocatalytic esterification of oleic acid. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, 206: 17-21.
18. Corro, G., Sánchez, N., Pal, U., Cebada, S. and Fierro, J. L. G. (2017). Solar-irradiation driven biodiesel production using Cr/SiO_2 photocatalyst exploiting cooperative interaction between Cr^{6+} and Cr^{3+} moieties. *Applied Catalysis B: Environmental*,

203: 43-52.

19. Gardy, J., Hassanpour, A., Lai, X., Ahmed, M. H. and Rehan, M. (2017). Biodiesel production from used cooking oil using a novel surface functionalised TiO_2 nano-catalyst. *Applied Catalysis B: Environmental*, 207: 297-310.
20. Mashuri, S. I. S., Ibrahim, M. L., Kasim, M. F., Mastuli, M. S., Rashid, U., Abdullah, A. H., Islam, A., Asikin-Mijan, N., Tan, Y. H., Mansir, N., Kaus, N. H. M. and Hin, T. Y. Y. (2020). Photocatalysis for organic wastewater treatment: From the basis to current challenges for society. *Catalysts*, 10: 1-29.
21. Zhang, X., Sun, G., Jia, S., Xie, H., Kang, Z., Chen, W., Cui, M., Wang, B., Wang, B., Chen, X. and Yang, D. (2022). Intrinsic carbon defects induced nickel phosphate/carbon photocatalyst for high performance bacterial disinfection. *Chemical Engineering Journal*, 438: 135624.
22. Pellegrino, F., Sordello, F., Minella, M., Minero, C. and Maurino, V. (2019). The role of surface texture on the photocatalytic H_2 production on TiO_2. *Catalysts*, 9: 1-28.
23. Wang, J., Wang, Y., Yu, M., Li, G., Zhang, S. and Zhong, Q. (2022). Formation of flaky carbon nitride and beta-Indium sulfide heterojunction with efficient separation of charge carriers for enhanced photocatalytic carbon dioxide reduction. *Journal of Colloid And Interface Science*, 611: 71-81.
24. Citra Dewi, A. S. and Slamet. (2019). Novel approach of esterification process using heterogeneous catalyst in biodiesel synthesis from waste cooking oil. *IOP Conference Series: Materials Science and Engineering*, 509: 1-6.
25. Ghani, N., Iqbal, J., Sadaf, S., Nawaz Bhatti, H. and Asgher, M. (2020). comparison of photo-esterification capability of bismuth vanadate with reduced graphene oxide bismuth vanadate (RGO/$BiVO_4$) composite for biodiesel production from high free fatty acid containing non-edible oil. *Chemistry Select*, 5: 9245-9253.
26. Li, W., Liang, R., Zhou, N. Y. and Pan, Z. (2020). Carbon black-doped anatase TiO_2 nanorods for solar light-induced photocatalytic degradation of methylene blue. *ACS Omega*, 5: 10042-10051.
27. Lau, P. L. and Affam, A. C. (2019). Visible light driven photocatalyst for degradation of organophosphate pesticides: A review. *Borneo Journal of Sciences and Technology*, 1(2): 1-8.
28. Rathi, A., Barman, S., Basu, S. and Kumar, R. (2022). Post-fabrication structural changes and enhanced photodegradation activity of semiconductors@zeolite composites towards noxious contaminants. *Chemosphere*, 288: 132609.
29. Sawant, S. V, Patwardhan, A. W., Joshi, J. B. and Dasgupta, K. (2022). Boron doped carbon nanotubes: Synthesis, characterization and emerging applications – A review. *Chemical Engineering Journal*, 427: 131616.
30. Kondo, K., Murakami, N., Ye, C., Tsubota, T. and Ohno, T. (2013). Development of highly efficient sulfur-doped TiO2 photocatalysts hybridized with graphitic carbon nitride. *Applied Catalysis B: Environmental*, 142: 362-367.
31. Suliman, A., Isha, R. and Roslan, J. (2020). Effect of mass ratio of titanium dioxide and oil palm fiber ash (TiO_2 : Ash) in hybrid photocatalyst on photocatalytic seawater pretreatment. *National Conference for Postgraduate Research*: 124–132.
32. Corro, G., Pal, U. and Tellez, N. (2013). Biodiesel production from Jatropha curcas crude oil using ZnO/SiO_2 photocatalyst for free fatty acids esterification. *Applied Catalysis B: Environmental*, 129(7): 39-47.
33. Redjeki, A. S., Sukirno, S. and Slamet, S. (2021). Simultaneous photocatalytic esterification and addition reaction of fatty acids in kemiri sunan (*Reutealis trisperma* sp.) oil over CuO/TiO_2 catalyst - A novel approach. *Bulletin of Chemical Reaction Engineering* and *Catalysis*, 16(4): 816-830.
34. Alterary, S. S. and Marei, N. H. (2021). Fly ash properties, characterization, and applications: A review. *Journal of King Saud University - Science*, 33(6): 101536.
35. Shi, Z., Yao, S. and Sui, C. (2011). Application of fly ash supported titanium dioxide for phenol photodegradation in aqueous solution. *Catalysis Science and Technology*, 1: 817-822.
36. Berrones-Hernández, R., del Carmen Pérez-Luna, Y., Sánchez-Roque, Y., Pantoja-Enríquez, J., Grajales-Penagos, A. L., López-Cruz, C. F., Longoria, A., Eapen, D. and Sebastian, P. J. (2019). Heterogeneous esterification of waste cooking oil

with sulfated titanium dioxide (STi). *Bioenergy Research*, 12(3): 653-664.

37. Lokman Nolhakim, M. A. H., Shohaimi, N. A. M., Mokhtar, W. N. A. W., Ibrahim, M. L. and Abdullah, R. F. (2021). Immobilization of potassium-based heterogeneous catalyst over alumina beads and powder support in the transesterification of waste cooking oil. *Catalysts*: 11(8): 976.
38. Begum, A.,Hussain. A and Rahman, A. (2012). Effect of deposition temperature on the structural and optical properties of chemically prepared nanocrystalline lead selenide thin films. *Beilstein Journal of Nanotechnology.* 3(1): 438-443.
39. Tauanov, Z., Tsakiridis, P. E., Mikhalovsky, S. V. and Inglezakis, V. J. (2018). Synthetic coal fly ash-derived zeolites doped with silver nanoparticles for mercury (II) removal from water. *Journal of Environmental Management*,. 224: 164-171.
40. Naeem, A., Wali Khan, I., Farooq, Mahmood, T., Ud Din, I., Ali Ghazi, Z. and Saeed, T. (2021). Kinetic and optimization study of sustainable biodiesel production from waste cooking oil using novel heterogeneous solid base catalyst. *Bioresource Technology,* 328: 124831.
41. Visa, M. and Duta, A. (2013). TiO_2/fly ash novel substrate for simultaneous removal of heavy metals and surfactants. *Chemical Engineering Journal*, 223: 860-868.
42. Klubnuan, S., Suwanboon, S. and Amornpitoksuk, P. (2016). Effects of optical band gap energy, band tail energy and particle shape on photocatalytic activities of different ZnO nanostructures prepared by a hydrothermal method. *Optical Materials,* 53: 134-141.
43. Mekonnen, K. D. and Sendekie, Z. B. (2021). NaOH-catalyzed methanolysis optimization of biodiesel synthesis from desert date seed kernel oil. *ACS Omega,* 6(37): 24082-24091.
44. Efavi, J. K. Kanbogtah, D., Apalangya, V., Nyankson, E., Tiburu, E. K., Dodoo Arhin, D., Onwona-Agyeman, B. and Yaya, A. (2018). The effect of NaOH catalyst concentration and extraction time on the yield and properties of Citrullus vulgaris seed oil as a potential biodiesel feed stock. *South African Journal of Chemical Engineering*, 25: 98-102.