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PHOTOCHEMICAL AND PHOTOCATALYTIC ESTERIFICATION OF WASTE COOKING OIL UNDER VISIBLE LIGHT IRRADIATION USING MECHANOCHEMICALLY SYNTHESIZED ZnO/SILICA

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Abstract: *Production of biodiesel from waste cooking oils via alkali catalyzed transesterification reaction is hampered by the unacceptably high amount of free fatty acids (FFA) present in waste cooking oils. Therefore, catalytic esterification of waste cooking oil with small alcohols is performed before the transesterification reaction. Herein, ZnO/silica composite was synthesized via mechanochemical route and characterized using x-ray diffraction, x-ray fluorescence spectroscopy and scanning electron microscopy. Photochemical and photocatalytic esterification of free fatty acids in a sample of waste cooking oil with methanol was performed under visible light irradiation. The efficiency of photochemical esterification was found to be strongly dependent on the power of the light used. Significant increase in the efficiency of the photochemical esterification was observed when synthesized ZnO/silica composite was used as the photocatalyst. The photocatalytic activity of the ZnO/silica composite under visible light irradiation is attributed to the impurities present in the silica support. Photocatalytic esterification using ZnO/silica composite is a promising method to reduce the FFA content of waste cooking oil under ambient conditions.*

Keywords: *Biodiesel, Waste Cooking Oil, Esterification, Photocatalyst, ZnO/silica composite.*

1. Introduction

Biodiesel is a clean biofuel produced from renewable feedstock, mainly vegetable oils, green algae and animal fats. Biodiesel is a renewable alternative to petroleum based diesel that can be used in compression-ignition engines with little or no modification [1]. Biodiesel is mostly produced via catalytic transesterification of triglycerides contained in fats and oils with methanol [2]. Utilization of waste cooking oil for biodiesel production will add value to it, and reduce environmental pollution. Production of biodiesel from waste cooking oil via alkali catalyzed transesterification reaction is hampered by the unacceptably high amount of free fatty acids present in waste cooking oil with may cause soap formation [3,4]. Soap formation reduces the yield of biodiesel, and also leads to increase in catalyst consumption [5]. This results in high production cost of biodiesel. Therefore, fats and oils containing high level of free fatty acids must undergo esterification of their free fatty acids with small alcohols before the actual transesterification process is performed.

Esterification of free fatty acids to yield alky esters in the presence of an acidic catalyst is the conventional route to reduce free fatty acids of oils used in biodiesel production. Esterification is commonly

carried out in a homogeneous phase in the presence of acidic catalysts because of its high conversion efficiency and lower cost. However, the use of the homogenous acidic catalysts has some drawbacks such as effluent disposal problem, corrosion of process equipment, loss of catalysts, high amount of alkali required for neutralization of the effluent, etc. In view of these problems of homogeneous catalysis, heterogeneous catalysis has been considered in order to minimize environmental pollution and reduce production cost of biodiesel. Several heterogeneous catalysts have been developed for esterification of biodiesel feedstock with high free fatty acids [6, 7].

Photocatalysis is a light induced catalytic process that involves oxidization and/or reduction of organic molecules via redox reactions activated through the electron-hole pair generated on the surface of semiconductors upon light irradiation [8-10]. Heterogeneous photocatalysis has many advantages over thermal catalytic processes because photocatalysis can be performed at room temperature and atmospheric pressure using direct solar energy or artificial light sources, thereby reducing operating costs. It is environmentally friendly process and enables reusability of the catalyst which minimizes its consumption [11]. Most research works on photocatalysis focus on treatment of polluted water and air [10, 12, 13] Very few works have been reported on free fatty acids esterification by a heterogeneous photocatalytic process [14, 15].

ZnO is one of the most extensively used heterogeneous photocatalysts for various processes under solar and/or ultraviolent irradiation [16, 17]. Although the free fatty acids could be photocatalytically esterified using ZnO alone, separation of ZnO particles after photocatalytic esterification is a difficult problem. This problem can be solved by anchoring ZnO particles on suitable support materials. Thus, Corro *et al* [15] synthesized ZnO/silica and applied it for photocatalytic esterification of Jatropha curcas oil under UV irradiation. 96 % conversion of free fatty acids was achieved at a fixed methanol to oil ratio of 12:1, photocatalyst dosage of 15 wt% and UV irradiation time of 4 hours [4]. To the best of our knowledge, there is no any published literature report on the photochemical and photocatalytic esterification of waste cooking oil under visible light irradiation. Thus, this paper focuses on photochemical and photocatalytic esterification of free fatty acids in waste cooking oil using ZnO/silica composite under visible light irradiation.

2. Materials and methods

Materials

The waste cooking oil was obtained from a restaurant in Zaria, Kaduna state, Nigeria. The waste cooking oil was filtered to remove impurities. The oil was analyzed following standard methods [18]. The saponification value of the waste cooking oil was determined according to titremetric method described by Pearson [18]. The acid value (A) of the raw oil before and after the photoesterification reaction was determined according to equation (1):

$$A = \frac{56.1 \times V \times C}{m} \qquad (1)$$

Where V is the volume (ml) of standard volumetric potassium hydroxide (KOH) solution used, C is the concentration (mol/dm^3) of the standard volumetric KOH solution used, m is the mass (g) of the oil sample and 56.1 is the molecular mass of KOH. The molecular weight (M) of the oil was determined from saponification value (SV) and acid value (A) according to equation (2):

$$M = \frac{56.1 \times 1000 \times 3}{SV - A} \qquad (2)$$

The amorphous silica used was obtained via dealumination of Kankara Kaolin [19]. The procedure for mechanochemical synthesis of ZnO has been described elsewhere in details [20]. Briefly, a mixture of $ZnCl_2$, Na_2CO_3 and NaCl were mixed and milled using a high energy ball milling machine (Kera BV) for 8 hours (The molar ratio of NaCl to $ZnCl_2$ was 8:1). NaCl was used as inert diluent to prevent agglomeration of the nanoparticles being formed. After the milling step, the products obtained were then calcined in an electric furnace (Nabertherm GmbH) at 800 ^oC for 4 hours to yield ZnO. The product was thoroughly washed with de-ionized water and dried. Silica supported ZnO was prepared by solid state dispersion method. Thus, the required amount of ZnO was thoroughly mixed with the required amount of silica in absolute ethanol at 40 ^0C. Ethanol was then evaporated. The ZnO/silica powder was heated in an electric furnace at 300 ^0C for 4 hours.

The phase composition of the synthesized ZnO/silica composite was examined using a powder x-ray diffractometer (PANalytical) employing Cu Kα radiation (λ=0.154nm). The morphology of the ZnO/silica composite was investigated using Phenom Pro-X scanning electron microscope (SEM). The chemical composition of the ZnO/silica composite was obtained via x-ray fluorescence (XRF) spectroscopy using Minipal-4 x-ray fluorescence spectrometer.

Photocatalytic and photochemical esterification experiments

A 500-W halogen lamp was used in the experiments because it simulates solar radiation [21, 22]. All experiments were carried out at room temperature (30 ± 5 $^{\circ}C$) and atmospheric pressure. Photoesterification of the waste cooking oil was performed in a 500 ml conical flask. A mixture of waste cooking oil, ZnO/silica composite and methanol was poured into the flask. The waste cooking oil:methanol ratio was 12:1. The mixture was stirred with a magnetic stirrer under visible light irradiation provided by the 500W halogen lamp for 4 hours. Samples were taken at 1 hour interval. The analytical samples were filtered to remove the particles of the ZnO/silica composite photocatalyst. The clear esterified waste cooking oils were then analyzed for free fatty acids. Photochemical experiments were performed under similar conditions without the use of ZnO/silica composite. To study the effect of the power of the incident visible light on the photochemical esterification process, three lamps with different power ratings (100W, 200W and 500W) were used. The conversion of free fatty acids (% $C_{\text{free fatty acids}}$) was obtained using equation (3):

$$\%C_{free\ fatty\ acids} = \frac{A_i - A_t}{A_i} \times 100\% \quad (3)$$

Where A_i is the acid value of the raw waste cooking oil and A_t is the acid value of the waste cooking oil after photocatalytic or photochemical esterification over a given irradiation time.

3. Results and discussion

Properties of the waste cooking oil

The acid value of the waste cooking oil used in this study is 11.22 mgKOH/g which corresponds to a free fatty acid value of 5.64 %. The waste cooking oil has saponification value and molecular weight of 180.29 mgKOH/g oil and 995.45 g/mol, respectively. It has been reported that the content of free fatty acids in oils and fats for base catalysed transesterification reactions shall not exceed 1% [23]. Therefore, it is necessary to perform a pre-treatment process (esterification) on such lipids prior to biodiesel production via base catalysed transesterification.

Characterization of the synthesized ZnO/silica catalysts

Table 1 shows the chemical composition of the synthesized ZnO/silica. The main constituents are SiO_2 (49.6 wt%) and ZnO (45.22 wt%). Apart from ZnO and SiO_2, that were predominant, the catalyst also contained lower amounts of other metal oxides (K_2O, CaO, TiO_2, MnO, Fe_2O_3 etc). These impurities may alter the bandgap of ZnO thereby extending its activity into the visible region of the electromagnetic spectrum [24, 25].

Table 1. Chemical Composition of the synthesized ZnO/silica composite

Component	Concentration, wt%	Component	Concentration, wt %
SiO_2	49.600	ZnO	45.220
SO_3	0.400	Cr_2O_3	0.019
CaO	0.404	TI_2O	0.870
TiO_2	0.071	Er_2O_3	0.038
K_2O	0.601	Nd_2O_3	0.087
MnO	0.023	BaO	0.100
Fe_2O_3	0.293	Ag_2O	1.980
SeO_2	0.220	CuO	0.017

The XRD pattern depicted in Fig. 1 was employed to determine phase composition and crystallite size of the synthesized ZnO/silica composite. The peaks at $2\theta = 31.77^0$, 34.42^0, 36.24^0, 47.52^0, 56.57^0, 62.84^0, 66.35^0, 67.91^0, 69.08^0, and 74.48^0 are in good agreement with the Powder Diffraction Standard data (JCPDS No. 36-1451), corresponding to the hexagonal wurtzite structure of ZnO. The strong and sharp diffraction peaks indicate that the synthesized ZnO via mechanochemical method is of high crystallinity. A crystalline peak with low intensity appeared at Bragg's angle of 26.65^0 due to crystalline silica, which also known as quartz [19]. The other peaks observed were rough background peaks due to the presence of amorphous silica. Thus, the XRD pattern of the ZnO/silica composite is dominated by the characteristics peaks of the wurtzite phase of ZnO; this shows that the amouphous silica does not alter the crystalline structure of ZnO. The same observation was also reported by other researchers [26]. The highest intensity peaks in the XRD pattern (Fig. 1) were used for computing the crystallite size (D) of the prepared ZnO/silica composite using the Debye-Scherrer formula given by equation (4):

$$D = 0.9\lambda / \beta Cos\theta \quad (4)$$

where λ is the wavelength of Cu Kα radiations (0.1542nm), β is the width at half maximum in radians and θ the angle obtained from 2θ value of the reference peak in the XRD pattern. The computed crystallite size of the synthesized ZnO/silica composite was found to be 20.92 nm.

The scanning electron microscopic (SEM) image presented in Fig. 2 reveals deposition of ZnO particles on the silica. ZnO forms small crystallites on the external surface of the silica.

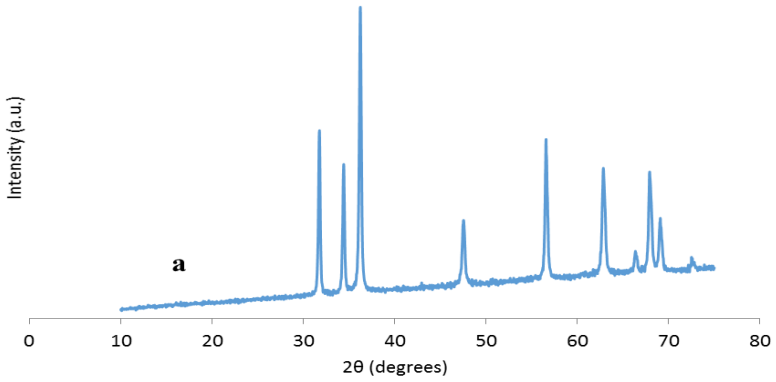

Fig. 1. XRD patterns of the synthesized ZnO/silica composite

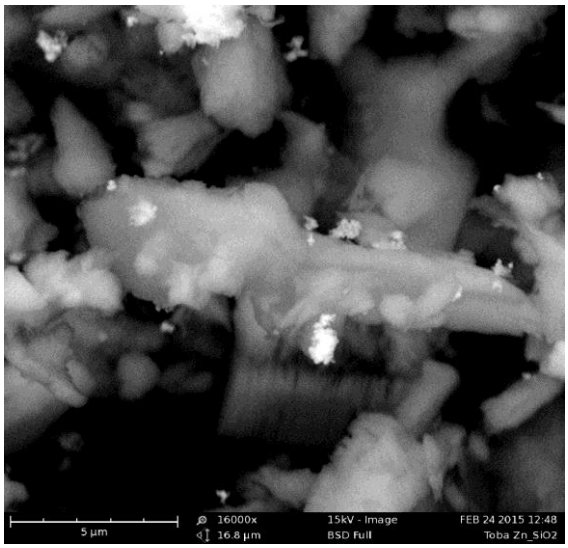

Fig. 2. Scanning electron micrographs of the synthesized ZnO/silica composite

Photochemical esterification of the waste cooking oil

The results of photochemical esterification of waste cooking oil are depicted in Fig. 3, from where it can be seen that the conversion of free fatty acids increases with increase in irradiation time in the absence of a photocatalyst. It has been reported that esterification of carboxylic acids with various alcohols in carbon tetrachloride can be accomplished efficiently by exposure of the solution to UV light [27]. In this work, light power for the photochemical esterification process was varied between 100W and 500W. As apparent in Fig. 3, conversion of free fatty acids increases with increase in lamp power. These results indicate that reduction of free fatty acids in waste cooking oil could be achieved without a photocatalyst. However, photochemical esterification of waste cooking oil strongly depends on the light power.

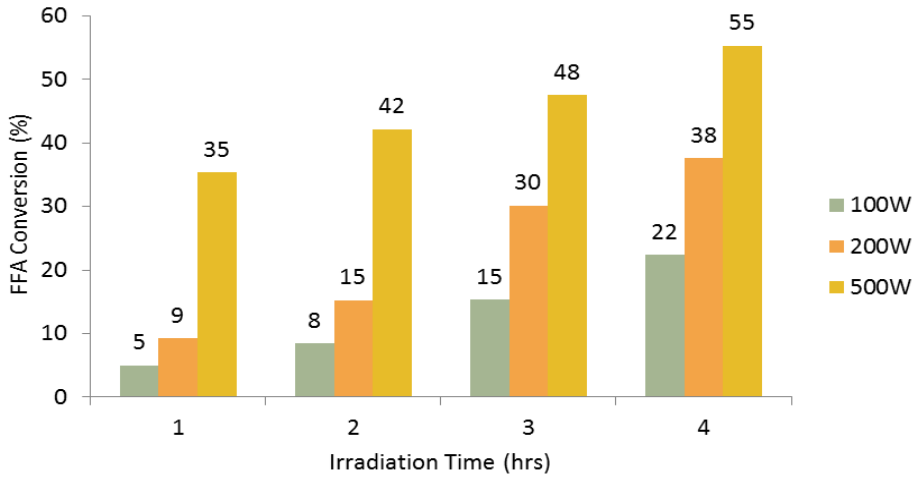

Fig. 3. Effect of irradiation time and lamp power on photochemical esterification of the waste cooking oil in the absence of a photocatalyst

Photocatalytic esterification of the waste cooking oil using the synthesized ZnO/silica composite

Fig. 4 shows the results of photocatalytic esterification of waste cooking oil using ZnO/silica composite. Compared to the results presented in Fig. 3, there is a significant enhancement of conversion of the free fatty acids by the ZnO/silica photocatalyst. For example, after one hour of irradiation with the 500 W halogen lamp, the conversion of free fatty acids achieved via photochemical esterification and photocatalytic esterification are 35 % and 87 %, respectively. Therefore, photocatalytic esterification using ZnO/silica is by far more efficient than photochemical esterification. The conversion of free fatty acids increases with increase in irradiation time. The reaction was very fast during the first one hour due to the high driving force. At irradiation time of 4 hours, 94 %conversion of free fatty acids of the waste cooking oil was achieved. This illustrates the positive role of ZnO/silica in photocatalysing the esterification reaction. Therefore, the use of ZnO/silica will reduce the cost of photocatalytic esterification process.

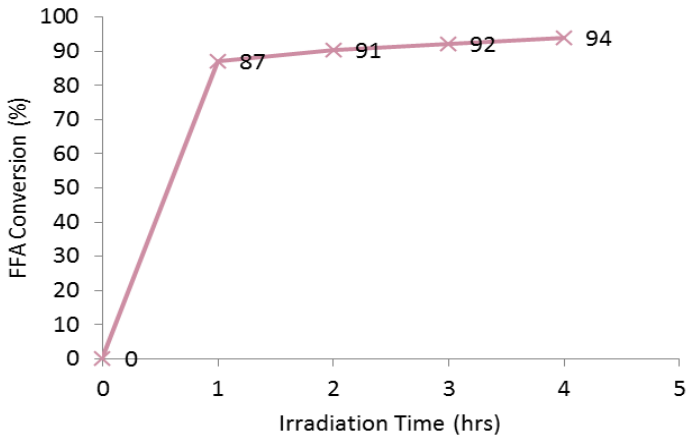

Fig.4. Effect of irradiation time on photocatalytic esterification of waste cooking oil using ZnO/silica composite and 500 W lamp

4. Conclusion

The reduction of free fatty acids in the waste cooking oil via photochemical esterification is possible, but the photochemical esterification process is less efficient than the photocatalytic esterification. The efficiency of photochemical esterification is strongly dependent on the intensity of light. Photocatalytic esterification is a promising process to reduce the FFA content of waste cooking oil under visible light irradiation at room temperature and atmospheric pressure.

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