

# Characterization and Kinetics of Biofuel Produced from Waste Cooking Oil

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**Abstract**— Biodiesel in recent times serves as a better alternative to petro-diesel with waste cooking oil as one of its cheapest feedstocks. The catalytic properties of 10 wt. % of mixed metal oxide of TiO<sub>2</sub>-supported-ZnO catalyst for the conversion of modeled waste cooking oil into biodiesel were investigated at 100, 150 and 200°C in the presence of methanol and hexane co-solvents. The conversion was found to increase with reaction time and temperature. A utilization of hexane co-solvent was found to be of positive effect and increases the rate of trans-esterification reaction producing higher biodiesel yields in small times of reaction. The effect of temperature on transesterification reaction allows the estimation of the apparent activation energy that was found to be ca. 22.468±0.975 kJ/mol.

**Keywords** — Biodiesel, waste cooking oil, ZnO/TiO<sub>2</sub>, co-solvent, apparent activation energy, transesterification

## I. INTRODUCTION

Environmental concerns and increase in world crude oil prices have necessitated researchers to identify renewable raw materials which can be processed into liquid fuel as alternatives to keep pace with societal demand for energy supply. All over the world, various alternative energy sources such as sun, water, wind and biomass are topics of research. Plants derived vegetable oils have been used as a substitute in diesel engines but their direct use was restricted due to high viscosity of the vegetable oil leading to poor fuel atomization, incomplete combustion and carbon deposition which usually causes engine fouling [1], hence vegetable oil converted to biodiesel has become the preferred. Biodiesel has received most interest because 90% of the total world energy is consumed by the transportation sector [2]. In order to reduce the overall production cost of biodiesel, waste cooking oil feedstock was used. Complete heterogeneous catalysts were used to promote the transesterification reaction of waste cooking oil (WCO).

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Heterogeneous catalyst has numerous advantages over homogeneous catalyst as they are environmentally benign, noncorrosive and present fewer disposal problems. They are also much easier to separate from liquid products and can be designed to give higher selectivity, activity and longer lifetimes [3, 4]. The use of catalyst support to disperse heterogeneous catalyst helps to minimize the mass transfer resistance likewise is the use of hexane cosolvent. Catalyst supports generally provide higher surface area through the existence of pores where active metal particles can be anchored [5]. In this study, titanium dioxide was used as a catalyst support and the catalytic properties of the heterogeneous catalyst consisting of mixed metal oxide of zinc and titanium in titanium-supported-zinc oxide catalyst (ZnO/TiO<sub>2</sub>) were investigated. In particular, the activation energy for the conversion of waste cooking oil to biodiesel over the catalyst system was also studied.

## II. EXPERIMENTAL

Titanium (IV) oxide powder was dissolved in deionised water in a mass ratio of 1:1. The resulting solution was stirred properly and dried at 100°C for 12 hours and calcined at 600°C for 10 hours. The catalyst support was crushed and sieved to keep particles size between 53 and 106 µm. In order to deposit zinc oxide on the calcined support by impregnation method, 17 g of zinc nitrate hexahydrate was dissolved in 12 ml of deionized water. The nitrate mixture was then poured slowly into a beaker containing 24 g of titanium support. The resulting catalyst mixture (ZnO/TiO<sub>2</sub>) was dried in air for 12 hours at 100°C. It was subsequently calcined in air for 12 hours at 600°C. The resulting catalyst and support was characterized by XRD to understand the structure of active surface zinc oxide species and tested in transesterification for its catalytic properties.

The prepared titanium-supported-zinc oxide catalyst (ZnO/TiO<sub>2</sub>) was tested for transesterification of waste cooking oil in a 300 cm<sup>3</sup> Parr reactor. The required feedstock of waste cooking oil was modeled by mixing 95 g of soybeans oil, 5 g oleic acid, and 61 g of methanol with 3 g of the catalyst. These mixtures were transferred into the reactor and pressurized under an inert-nitrogen gas at pressure of 24 bars that kept all reactants in liquid phase at different reaction temperatures. The reaction was done at different temperatures of 100, 150 and 200°C controlled by a PID controller. Sampling was done at 15, 30, 45 and 60 minutes. After sampling, the products were left to cool to room temperature for phase separation. It was therefore separated into two phases, the bottom glycerol plus the unreacted methanol phase and the top oil plus the methyl esters phase. The methanol was removed by heating the samples in a vacuum dryer at 65°C. When hexane was used as a co-solvent, vacuum pump (v-700) was applied to remove hexane from the samples. Thereafter, the latter was

taken for NMR analysis to determine the waste vegetable to oil conversion. When hexane co-solvent was charged alongside with other feed stocks into the reactor, the hexane co-solvent to oil mole ratio of 1:1 was employed.

### III. RESULTS AND DISCUSSION

#### A. Catalyst Characterization

**XRD Analysis:** The XRD diffraction patterns for the blank TiO<sub>2</sub> support and the catalyst (10 wt. % ZnO/TiO<sub>2</sub>) were generated and plotted as shown in Fig. 1.

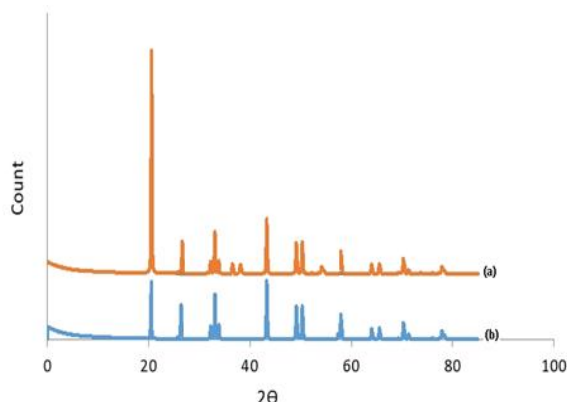


Fig. 1. XRD patterns for (a) blank TiO<sub>2</sub> and (b) TiO<sub>2</sub>-supported-ZnO catalyst

The two patterns look identical and show that the most intense peaks is at 2θ of ca. 20, 32, 43, 48 and 50° with an exception of an additional peaks at 2θ of ca. 34, 36 and 56° that was only detected in the XRD pattern of the catalyst (Fig 1a). This peak can be attributed to ZnO particles stabilized on the titanium support which is in conformity with Hamedani et al. [6] who reported the XRD diffraction peaks for ZnO at scattering angles (2θ) of 31.3670, 34.0270, 35.8596, 47.1635, 56.2572, 62.5384, 67.6356, and 68.7978°. The most intense peak for the catalyst is at Bragg's angle of 36° and this was used to calculate the average ZnO crystallite size (D) using Scherrer equation (i).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (i)$$

Where:  $k$  = shape factor,  $\beta$  = FWHM = line broadening at half the maximum intensity,  $\lambda$  = wavelength of x-rays, and  $\theta$  = Bragg's diffraction angle. The calculated average crystallite size (with  $K = 0.9$  and  $\lambda = 0.15$  nm) was found to be 25.6 nm.

#### B. Catalyst testing

##### Effect of reaction temperature and time on waste vegetable oil conversion

The waste vegetable oil conversion was calculated using NMR analysis data of the biodiesel and unreacted oil phase using equation (ii) [7].

$$C = (2 A_{ME} / 3 A_{\alpha-CH_2}) \times 100\% \quad (ii)$$

Where  $C$  is the percentage conversion of feedstock to FAME,  $A_{ME}$  is area from the integration value of the protons of the methyl esters (the strong singlet peak) and  $A_{\alpha-CH_2}$  is area from the integration value of the methylene protons. Multiplayers 2 and 3 are attributed to the fact that methylene carbon owns two protons and the alcohol (methanol derived) carbon has three attached protons. The <sup>1</sup>H NMR spectrum of

a sample collected after 60 minutes of reaction at 200°C with the addition of hexane co-solvent is shown in Fig. 2.

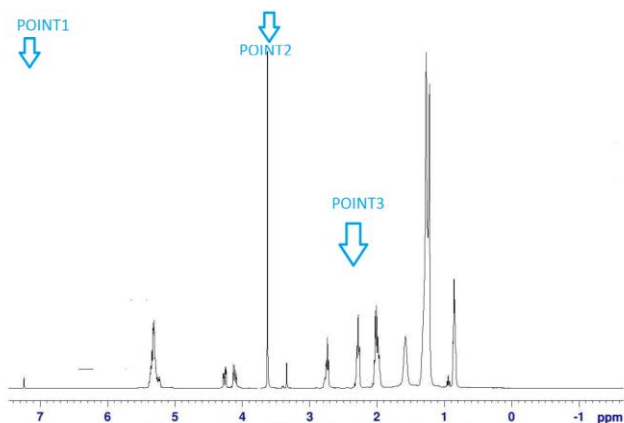


Fig. 2. <sup>1</sup>H NMR spectrum of sample collected after 60 min of reaction at 200°C with hexane as co-solvent.

From the NMR spectra in Fig. 2, point 1, represents the peak for the solvent (CDCl<sub>3</sub>) which is at 7.20 ppm, the peak at 3.6 ppm is for methoxy group of fatty acid methyl ester (FAME) represented by point 2, and point 3 shows the peak for methylene group of the triglyceride at 2.6 ppm. The areas of the peak generated from integration were used for the sample calculation of the percentage conversion of biodiesel. Hence, after 60 minutes of reaction at 200°C with hexane co-solvent using equation (ii) the percentage yield of FAME was 91.3%.

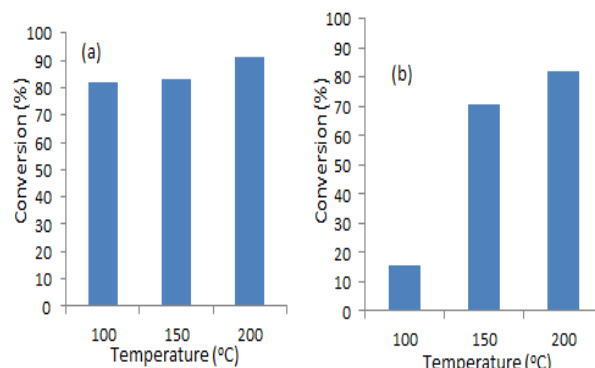


Fig. 3: Effect of temperature on waste oil conversion (a) with hexane co-solvent (b) without hexane co-solvent.

Fig. 3 shows the waste vegetable oil conversion data (alcohol to oil mole ratio of 18:1; hexane to oil mole ratio of 1:1; catalyst amount of 3 wt. % with respect to oil at 60 minutes reaction time) as a function of time and reaction temperature. The waste cooking oil conversion with alcohol to oil mole ratio of 18:1 measured over 10 wt. % of ZnO/TiO<sub>2</sub> catalyst concentration at 100°C is 15.8% after 60 minutes (Fig. 3b). When the reaction temperature was increased to 150°C, there was an increase in waste oil conversions to 70.7% after 60 minutes. The data increased further to 82.1% after 60 minutes when the reaction temperature was increased to 200°C. In comparison to the findings in literatures, a high transesterification conversion of about 98% was observed by Madhuvilakku et al. [8] when they used 200 mg of TiO<sub>2</sub>-ZnO nanocatalyst for 5 hours reaction time at 6:1 methanol to oil molar ratio and 60°C.

However, a similar trend was observed as in the case involving hexane as co-solvent. Oil conversion measured over 10 wt. % of titanium-supported-zinc oxide catalyst with hexane to oil mole ratio of 1:1 at 100°C is 82.1% after 60 minutes (Fig. 3a). Increasing the temperature to 150 and 200°C expectedly produced an increased oil conversion of 83.1 and 91.3% respectively. This result shows that as reaction temperature increases, the waste oil conversion to biodiesel increases over titanium-supported-zinc oxide catalyst (ZnO/TiO<sub>2</sub>). In conclusion, the effect of reaction time and reaction temperature shows that as the temperature increases, the viscosity of waste vegetable oil decreases thereby improving the mass transfer of reactants to the active sites in the catalyst. That is to say, as more energy was added to the system, the effective collision increased which helped to overcome the activation energy barrier. In the same vein, more waste vegetable oil eventually dissolved in methanol to improve the methanol-oil immiscibility which also improved the mass transfer in the catalyst.

### C. Average reaction rate and apparent activation energy

The kinetic modeling used in this study is based on the assumptions given by Sivakumar et al. [9] and Feyzi et al. [10] which are (i) The transesterification chemical reaction was considered to occur in the oil (triglyceride) phase and therefore waste cooking oil was considered as the limiting reactant, (ii) The production of intermediate species was neglected and the overall transesterification reaction was assumed to be a one-step shunt and (iii) The rate constant (k) should be considered not to depend on methanol concentration because it is in excess, the reaction was assumed to be irreversible pseudo-homogeneous, first-order kinetics as a function of the concentration of oil (Triglyceride).

Based on the above assumptions, the transesterification reaction of waste cooking oil conforms to the g kinetic law in equation (iii).

$$\text{Rate (r)} = \frac{-d[\text{TG}]}{dt} = \frac{d[\text{ME}]}{dt} \quad (\text{iii})$$

By rate law, we have an expression which relates the rate of reaction (r), the rate constant (k) and the concentrations of the reactant [TG], hence

$$\text{Rate (r)} = k [\text{TG}] \quad (\text{iv})$$

On combining equations (i) and (ii), we have

$$\text{Rate (r)} = \frac{-d[\text{TG}]}{dt} = \frac{d[\text{ME}]}{dt} = k' [\text{TG}] \quad (\text{v})$$

Therefore,

$$\frac{-d[\text{TG}]}{[\text{TG}]} = k't$$

Integrating both sides by taken initial concentration of [TG] at t = 0 as [TG]<sub>0</sub> and concentration at time t = t as [TG], we have,

$$\ln \frac{[\text{TG}]_c}{[\text{TG}]} = k't \quad (\text{vi})$$

According to mass balance based on mole fraction,

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

Substituting equation (v) into (iv) we obtain equation (viii):

$$-\ln (1 - X_{\text{ME}}) = k't \quad (\text{viii})$$

Where:  $-\ln (1 - X_{\text{ME}}) =$  Triglyceride concentration and  $X_{\text{ME}} =$  Methyl ester concentration.

The concentration of methyl ester without hexane co-solvent (based on mole fraction) at temperatures of 100, 150 and 200°C was calculated. Similar calculation was done to obtain methyl ester concentration using hexane co-solvent at temperatures of 100, 150 and 200°C respectively. The plots of  $-\ln (1 - X)$  versus Time (min) for reaction of waste cooking oil with methanol and hexane co-solvent are shown in Figs. 4 and 5.

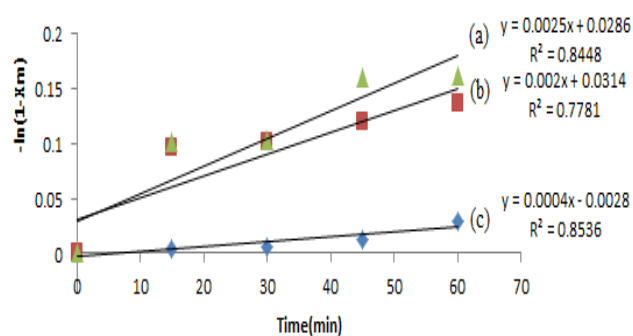


Fig. 4: Plots of  $-\ln (1 - X)$  versus Time (min) for reaction of waste cooking oil with methanol, with hexane co-solvent at (a) 200°C (b) 150°C (c) 100°C

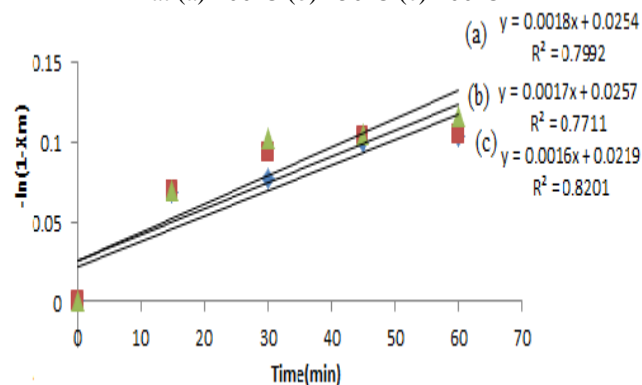


Fig 5: Plots of  $-\ln (1 - X)$  versus Time (min) for reaction of waste cooking oil with methanol, without hexane co-solvent at (a) 200°C (b) 150°C (c) 100°C

The data in Table I were extracted from Figs 4 and 5, which shows the apparent rate constants and their R<sup>2</sup> values. Further observations from Figs. 4 and 5, show an increase in average reaction rate as the temperature increased. For example an average rate of ca. 0.0016 mol/min was measured after 100°C of reaction temperature which increased to 0.0017 mol/min at 150°C and 0.0018 mol/min at 200°C respectively as shown in Fig 5 without the use of hexane co-solvent. The average rate followed a similar trend when hexane was used as co-solvent. At reaction temperature of 100°C, an average rate of 0.0004 mol/min was measured and this increased to 0.0020 mol/min at 150°C and 0.0025 mol/min at 200°C.

TABLE I  
 TEMPERATURES AND RATE CONSTANTS FOR  
 TRANSESTERIFICATION OF WASTE COOKING OIL WITH  
 METHANOL

Without hexane cosolvent			With hexane cosolvent		
Temp, T (°C)	Rate constant s, k (mol min <sup>-1</sup> )	R <sup>2</sup>	Temp, T (°C)	Rate constant s, k (mol min <sup>-1</sup> )	R <sup>2</sup> Value
100	0.0016	0.8201	100	0.0004	0.8536
150	0.0017	0.7711	150	0.0020	0.7781
200	0.0018	0.7992	200	0.0025	0.8448

In explaining this, one may suggest that as the temperature increases, the relative speeds of molecules with respect to one another increases, leading to an increase in collision frequency. The rate constant with respect to temperature was used to determine apparent activation energy through Arrhenius equation as shown by equation (ix).

$$K = A e^{-Ea/RT} \quad (ix)$$

Taking the logarithms of both sides and separating the exponential and pre-exponential terms, we obtain (x).

$$\ln k = \ln A - \frac{Ea}{RT} \quad (x)$$

where; k is the reaction constant, A is the pre-exponential factor; Ea is the activation energy; R is the universal gas constant = 8.314 J mol<sup>-1</sup> K<sup>-1</sup> and T is the absolute temperature in Kelvin.

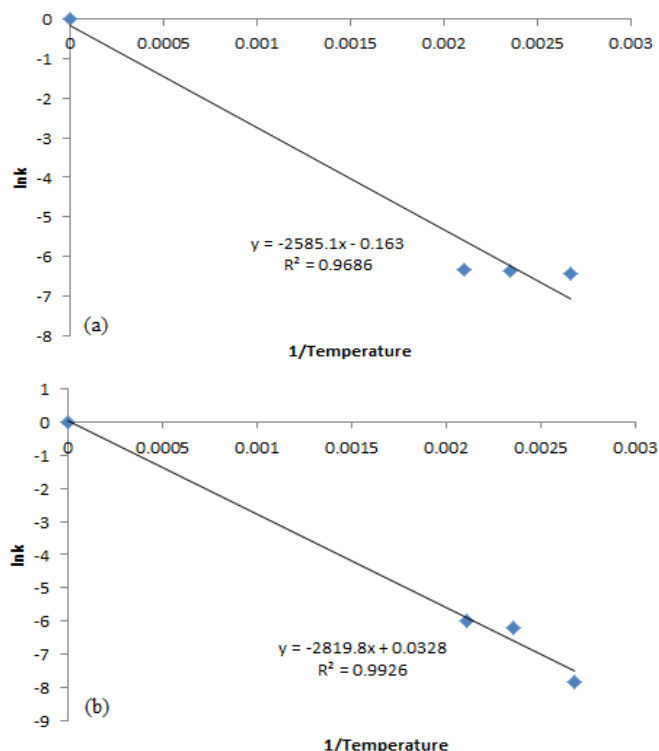


Fig. 6. Arrhenius plot of  $\ln k$  versus  $1/T$  for reaction of waste cooking oil with methanol (a) without hexane co-solvent (b) with hexane co-solvent

Equation (x) is a linear equation and a plot of  $\ln k$  versus  $1/T$ , as shown in Fig. 6 validates the first order of the reaction. The activation energy (Ea) has been calculated using the data plotted in Fig. 6, which gives 21.49252

kJ/mol for transesterification reaction without hexane co-solvent and 23.443.82 kJ/mol when hexane was used as co-solvent.

#### IV. CONCLUSIONS

In this study, titanium-supported-zinc oxide (ZnO/TiO<sub>2</sub>) catalyst was prepared by impregnation of titanium support with zinc nitrate followed by drying and calcination at a higher temperature of 600°C. The catalyst was tested in the trans-esterification of modeled waste cooking oil with methanol into biodiesel at 100, 150 and 200°C for a reaction time of 1 hour under an inert-nitrogen gas pressure of 24 bars. The conversion was found to increase with the reaction time and temperature. A utilization of hexane co-solvent was found to be of positive effect and increased the rate of trans-esterification reaction producing higher biodiesel yields in small times of reaction. The apparent activation energy for the reaction over ZnO/TiO<sub>2</sub> catalyst system was estimated as 22.468±0.975 kJ/mol.

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#### REFERENCES

- [1] Y.C. Sharma, B. Singh and S.N. Upadhyay, "Advancements in development and characterization of biodiesel: A review" *Fuel*, vol. 87, 2008, pp. 2355-2373.
- [2] G. Knothe and J. Krahl, "The biodiesel handbook" United States of America AOCs Press (2005).
- [3] A. Anitha, "Transesterification of used cooking oils catalyzed by CsTPA/SBA15 catalyst system in biodiesel production" *IACSIT International Journal of Engineering and Technology*, Vol. 4, No. 1, 2012.
- [4] M.A. Olutoye and B.H. Hameed, "K<sub>2</sub>Mg<sub>1-x</sub>Zn<sub>1+x</sub>O<sub>3</sub> as a heterogeneous catalyst in the transesterification of palm oil to fatty acid methyl esters" *Applied Catalysis A: Vol. 371*, Issues 1-2, 2009, pp. 191-198.
- [5] M. Zabeti, W.M.A. Wan Daud and M. K. Aroua, "Activity of solid catalysts for biodiesel production: A review" *Fuel process. Technol.*, Vol. 90, 2009, pp.770-777.
- [6] N.F. Hamedani and F. Farzaneh, "Synthesis of ZnONanocrystals with hexagonal (Wurtzite) structure in water using microwave irradiation" *J. Sci.*, Vol. 17(3), 2006, pp. 231-234.
- [7] Y.C. Sharma, B. Singh, D. Madhu, Y. Liu and Z. Yaakob, "Fast synthesis of high quality biodiesel from 'waste fish oil' by single step transesterification" *Biofuel Research Journal* Vol. 3, 2014, pp. 78-80.
- [8] R. Madhuvilakku and S. Piraman, Biodiesel synthesis by TiO<sub>2</sub>-ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process, *Bioresource Technology* Vol. 150 2013, pp. 55-59.
- [9] P. Sivakumar, S. Sankaranarayanan, S. Renganathan and P. Sivakumar, "Studies on sono-chemical biodiesel production using smoke deposited nano MgO catalyst" *Bulletin of Chemical Reaction Engineering & Catalysis*, 8 (2), 2013, pp. 89 - 96.
- [10] Feyzi, M., Norouzi, L. and Rafiee, H.R., "Kinetic Study on the Cs<sub>x</sub>H<sub>3-x</sub> PW<sub>12</sub>O<sub>40</sub>/Fe-SiO<sub>2</sub> Nanocatalyst for Biodiesel Production" *The ScientificWorld Journal*, Vol. 2013, Article ID 612712, p. 2