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Influence of Structure and Base Modification of Zinc Oxide Nanostructures on Kinetic Parameters of the Transesterification of Rice Bran Oil to Biodiesel

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ABSTRACT

Biodiesel is an alternative to biofuel that could help to reduce the use of fossil fuels and protect the environment. Evaluation of reaction kinetics provides information on reaction rates and mechanism which is necessary in evaluating catalyst's effectiveness. In this research, zinc oxide (ZnO) nanostructures, nanoparticles, nanoflowers and nanotubes were base-modified with potassium to enhance their active sites and used in the transesterification process for study of kinetic parameters. The nanocatalysts were characterized with FESEM and biodiesel conversion monitored with ^{1}H NMR. The result shows that both structure and base modification have influence on the kinetics parameters. In all the catalysts, activation energy falls within 26-82 $kJmol^{-1}$ indicating that the process was kinetically controlled and nanotubes has the highest rate constant of 0.0287 min^{-1}, lowest activation energy of 59.40 $kJmol^{-1}$ and highest turnover frequency (TOF) of 0.026 s^{-1}. The results show that kinetic parameters of transesterification are not only defendant on catalysts' basic or acid active sites but can also be influenced by structural modification. Therefore, the structural and K-modified ZnO nanoparticles have effect on the kinetic parameters of the tranesterification of rice bran oil (RBO) to biodiel and thus significantly reduce the use of fossil fuels in the environment.

Keywords: *Activation energy; Kinetics; Rate constant; Transesterification, Turnover frequency*

INTRODUCTION

Chemical kinetic is a process of monitoring chemical reactions in relation to reaction rates, effect of various variables, re-arrangement of atoms and formation of intermediates. Chemical kinetics study of a reaction deals with evaluating the reaction order, rate and rate constant, activation energy, turnover frequency and other parameters of interest related it. Kinetics can therefore serve as fast, efficient and economical way of evaluating catalyst performance without undertaking difficult experimentations and analyses. Through kinetics study, we can understand the contribution of the catalyst which will help to assess the catalysts' role and efficiency in the process. Monitoring the progress of the reaction and estimating the reaction rate and reacting species, it is possible to evaluate reaction order and mechanisms, and temperature or energy requirements for any reaction. The kinetics of transesterification reactions under different reacting conditions and methods has been extensibly reported in the literature [1-9]. Nonetheless, with introduction of each catalyst, new and different observations which are unique for the catalyst, method or reaction conditions are reported and so the information will always be useful for research development and commercialization.

Kinetics studies of transesterification were reported with the aim of assessing catalyst reaction rates, activation energy and TOF. But for each new catalyst introduced, there is need to study the kinetics and access its contribution to the reaction rate, activation and efficiency from its turnover frequency for transesterification which is especially related to methanolysis reactions and is largely unreported in the literature. However, both structural and basic modification have significant effect on the kinetics parameters of the transesterification process. This research aims to evaluate kinetics parameters like rate constant, activation energy, and catalyst efficiency associated with the biodiesel production process was evaluated from turnover frequency (TOF) and used to establish relationship between the effect of base and structure modification processes and the studied parameters.

Materials and Methods

Catalysts Preparation

The catalysts used to in the productiom of biodiesel through batch transesterification reaction of RBO with methanol was obtained and subsequently modified with potassium as reported by (Kabo et al., 2016).

Zinc Oxide Surface Modification

Surface modified ZnO was prepared via hydration dehydration of commercial ZnO followed by calcination. Hydration was done by weighing 12.0g of the commercial Zinc oxide sample, mixed with 150 ml distilled water in a 250 ml round bottom flask, and refluxing at 95 ^{o}C for 12 h. The hydrated ZnO obtained after the reflux was vacuum-filtered, dried in oven at 105^{o}C overnight to remove the excess water. The surface modified ZnO labelled as SM-ZnO was then calcined in a furnace at 400 ^{o}C for 2 hrs.

Preparation of Zinc Oxide Nanoflowers

Zinc oxide nanoflowers were synthesized via solvothermal method. 0.25 M Zinc acetate solution and Sodium hydroxide solution were prepared in de-ionized water at room temperature. Zinc acetate solution was gently heated to 80 ^{o}C, the NaOH soluttion was slowly added under vigorous stirring until the pH reached 11 with formation of white precipitate. The precipitate was poured into a Teflon lined sealed stainless steel autoclave and heated at 120 ^{o}C for 4 hrs, After which the autoclave is allowed to cool down to the room temperature. The precipitate was centrifuged, washed several times with distilled water and then dried at 60 ^{o}C for 12 hrs. The Zinc oxide nanoflower obtained was labelled as NF-ZnO.

Preparation of Zinc Oxide Nanotubes

ZnO nanotubes was prepared using solvothermal method as reported by Ethanolic solutions of 0.25 M Zinc acetate and 0.5 M NaOH were appropriately prepared. The NaOH solution was slowly introduced into the zinc acetate solution under magnetic stirring at 60 ^{o}C for 30 mins. Excess NaOH solution was used until a pH of 11 was reached and a suspension was obtained. The suspensions were allowed to cool and transferred to Teflon linen stainless steel autoclave, placed in a furnace at 140 ^{o}C for 8 hrs. The precipitate was collected, washed with methanol and dried at 60 ^{o}C in air for 12 hrs. This sample was labelled NT-ZnO.

The modified catalysts were characterised by FESEM. The samples were named as; Surface modified commercial ZnO sample SMK-ZnO, Nanoparticles, Nanotubes NTK and Nanoflowers NFK.

Biodiesel Preparation and Analysis

A temperature range different methanol to oil ratios, catalyst loading and reaction time were be covered to obtain the necessary data needed for process optimization and kinetics studies. ^{1}H NMR technique was used in the analysis of the products [10, 11].The data used in the kinetics measurement was obtained from the methanolysis product by varying the reaction conditions. Optimum catalyst loading of 3.7 % (wt.) and 1:9 MOR ratio were maintained. However, reaction time and temperature were varied accordingly. A temperature range of 45, 50, 55, 60 and 65 and time range of 30, 60, 90 and 120 mins, except for nanotubes due to lower reaction time; 45, 60, 75 and were used. During the NMR analysis to obtain biodiesel concentrations, sampling was done by taking about 5 ml of sample under required time and temperature, then immediately stored in ice to quench the reaction. After cooling, samples were centrifuged and to obtain the product for the ^{1}H NMR analysis [11]. Data obtained from the analysis of products under various conditions stated were used for the kinetics study and calculations.

Order of the Reaction

Order of the reaction is term used to describe the relationship between the concentration of the reacting species and rate of the reaction. It is and indicator of reaction mechanism pathway and is numerically determined as the number to which concentration term in the rate law equation is raised. In general, most reactions are classified as first or second order, however, zero and pseudo-first order reactions are also frequently reported depending on the nature of the relationship observed.

Transesterification reaction involves the use of various reacting species under different experimental conditions. Thus, different reaction order were reported depending on the reactants and reaction conditions. Kusdiana and Saka [12] described the first step of transesterification under super critical conditions reactions as pseudo second order while the subsequent steps take first or zero order pathways. Stavarache *et al* [13] reported that the kinetics of this reaction is quite complicated and may involve up to twelve equilibrium reactions. Similarly, Glisic and Orlovi [14] explained that the overall reaction occurs as a sequence of three steps, parallel with respect to alcohol and consecutive with respect to triglyceride. Triglyceride (TG) reacts with an alcohol (ROH) in the first reaction and forms diglyceride (DG) and fatty acid methyl ester

(FAME). Monoglycerides (MG) and fatty acid methyl esters (FAME) are formed in the second reaction from diglyceride (DG) and methanol. The third and final reaction with products, appearing as glycerol (GL) and again fatty acid methyl esters (FAME) and so they proposed reaction to be second order.

However, general observation from the literature on the kinetics of heterogeneously catalysed biodiesel is pseudo-first order. This due to use of excess methanol to oil ratio above the stoichiometric molar ratio of 3:1, thus the excess methanol concentration is considered as constant and so pseudo-first order reaction pathway is adopted [15-19], the rate law equation can be expressed as in Eq. 1.

$$-\ln(1-x) = kt \text{ ....1}$$

Where x is the concentration from biodiesel conversion, k is the reaction rate constant and t is the time of reaction as reported elsewhere [20].

Rate Constants of Transesterification Reaction

This is a constant that relates the rate of a chemical reaction to the concentration of reactant for a unimolecular reaction, or the product of the concentrations of reactants. Rate constant can be easily determine from the rate law when the reaction order is established and be used to determine the rate of a chemical reaction at a certain temperature [21]. Higher value of reaction rate indicates faster reaction and vice versa. Evaluation of rate constant is important because of its use in determining reaction rates, activation energy, turnover frequency, and thermodynamics of reactions. In catalysis, this will help in assessing the contribution of catalysts in kinetics and thermodynamics of reactions. The rate equation for pseudo-first order reactions (Eq. 1) was used to determine the rate constant.

Activation Energy in transesterification Reactions

This is referred to as the minimum amount of energy needed for a reaction to occur. It is the energy barrier to be overcome before a reaction can proceed to form products [5]. Activation is determined from the Arrhenius equation plot using Eq. 2. In catalysis, the role of catalyst is to lower the activation energy of reacting species to enable its molecule achieve effective collisions necessary for the reaction to occur leading to product formation.

$$\ln k = \ln A - \frac{E_a}{RT} \quad \ldots\ldots\ldots\ldots..2$$

Where k is the rate constant, A is pre-exponential factor, Ea is activation energy, R is universal gas constant and T temperature.

Evaluation of the activation energy can help to determine the contribution of a catalyst in lowering the activation energy in a reaction. The values of activation energy could also be used to determine whether a reaction regime is controlled by kinetics or mass transfer. If the activation energy value falls within the range of 26-82 kJ/mol, the process is controlled by kinetics, otherwise it is controlled by mass transfer effect [16].

Turnover Frequency (TOF) of Catalysts in Transesterification Reactions

The TOF is the number of revolutions of catalytic cycle per unit time or the number of molecules converted per active sites. It is the number of times the reaction takes place per catalytic site per unit time [22, 23]. It is used to measure the efficiency of a catalyst and is calculated from the relationship and can be calculted using the relationshion as reported by [24] in Eq .3.

$$TOF = \frac{moles\ of\ the\ products/m}{f \times t} \quad \ldots\ldots\ldots\ldots\ldots3$$

Many literatures reported the determination of TOF in order to evaluate the efficiency of various catalyst [23, 25].

Results and Discussions

Results of catalysts characterization, biodiesel analysis and kinetics parameters evaluation are presented and discussed as follows;

FESEM Analysis of the Catalysts

FESEM micrographs of the K-modified ZnO structures were recorded and shown in Fig. 1. The image obtained from SMK-ZnO in Fig (a) shows that there was no any significant change in the morphological and particle size before and after the modification. Also, the image recorded form K-modified ZnO nanoparticles shown in Fig (b) indicated the presence of nanoparticles similar to that recorded before modification, showing that no significant morphological change occurred with modification of ZnO nanoparticles. The image of K-modified ZnO nanoflowers in Fig (c) shows no significant changes occurred to the morphology of the ZnO nanoflowers, though, some breakages could be observed as some rods detached from the base of ZnO flowers. The image of K-modified nanotubes in Fig (d) reveals the collapse of the tube structures of ZnO after the K-modification. However, the nanosheets of the collapsed walls from the nanorods could still be observed.

NMR Analysis of the Biodiesel

The proton NMR spectra of biodiesel in Fig. 2, the presence of an intense OCH_3 protons related to fatty acid methyl esters of biodiesel appears at $\delta = 3.68$ ppm could be observed. The degree of conversion can be monitored depending on the signal intensity of methyl protons ester at 3.7 and the appearance or disappearance of CH_2O protons of glyceride signal at $\delta = 4.09$-4.34 ppm which is due the presence of unconverted oil. The percentage conversion of TG to methyl esters was calculated by [26].

Kinetics Analysis

Results of the evaluation of kinetic parameters as obtained from the methods explained above is presented and discussed as follows:

Order of the Reaction

Based on the studied literature, the reaction under our experimental conditions is considered to follow pseudo-first order kinetics model due to use of excess methanol. Therefore, this model is adopted and all our kinetics calculations are based on pseudo-firstorder reactions model.

Rate Constants of the Reaction

Because of the high ratio of methanol to oil in heterogeneous transesterification, its concentration is considered to be constant. So, the rate constants were calculated using the pseudo first order reactions kinetic model as in equation by plotting $-\ln(1-x)$ against t and the slope is calculated as k. Reaction rate constant strongly depends temperature [27], therefore they were measured at 65 ^{o}C.

At 65^{o}C, analysis shows that nanotubes NTK-ZnO has the highest rate constant of 0.00287 followed by nanoparticle NPK-ZnO with 0.00281, followed by nanoflowers NFK-ZnO with 0.00263 and the least was from surface modified commercial with 0.00187 min^{-1}. This analysis is in complete agreement with catalysts properties and biodiesel conversion analyses. It showed that K-modified nanotubes which have the highest basic sites highest biodiesel conversion also have the highest rate, followed by nanoparticles, nanoflowers and finally surface modified commercial ZnO. Rate constants of the catalysts evaluated a summarized in table 1.

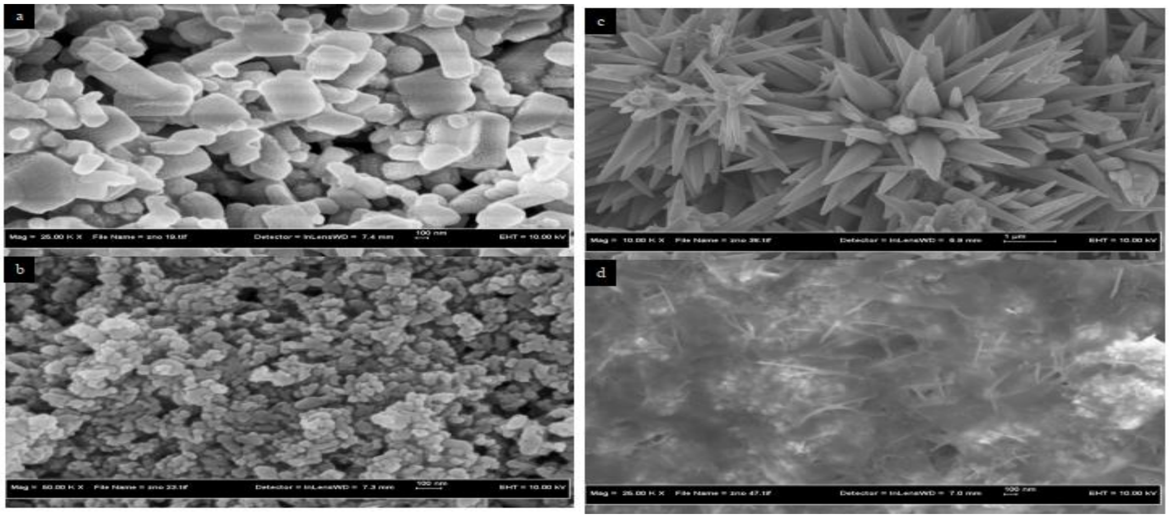

Fig. 1: FESEM micrograph of K-modified ZnO Samples (a) SMK-ZnO (b) NPK-ZnO (c) NFK-ZnO and (d) NTK-ZnO

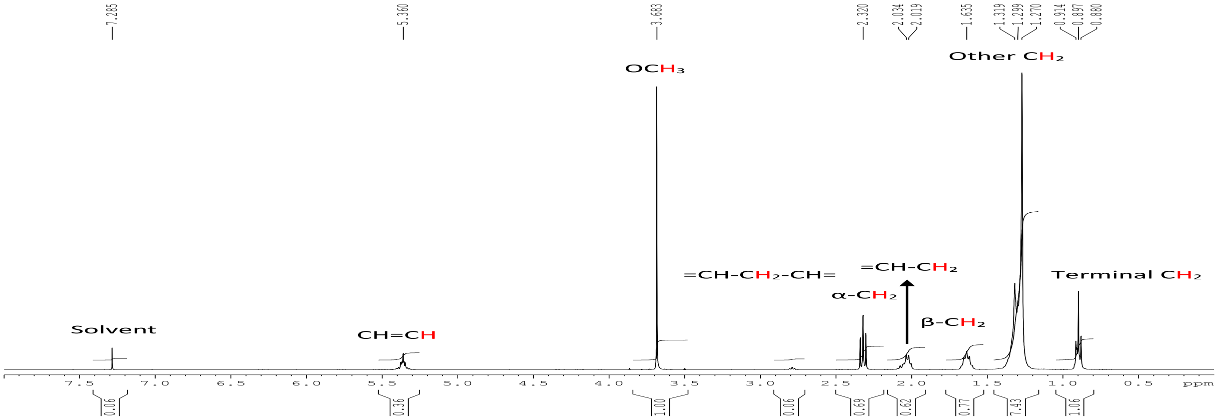

Fig. 2: ^{1}H NMR spectra of 96.24 % fatty acid methyl ester biodiesel

Table 1: Catalysts rate constants with corresponding biodiesel conversion

Catalyst Name	Basic Sites mmol/g	Rate Constant (k) (min^{-1})	Biodiesel Conversion (%)
SMK-ZnO	6.56	0.0187	93.70
NPK-ZnO	8.53	0.0281	95.65
NFK-ZnO	7.15	0.0263	94.70
NTK-ZnO	8.82	0.0287	96.24

K-modified ZnO nanotubes have the highest rate constant among the catalyst, though all the values obtained are than 0.0006 min^{-1} obtained from methanolysis of rice bran oil CaO [28] and is comparable to many rates obtained from other active heterogeneous catalysts reported in the literature [29-34].

Activation Energy

The activation energy Ea was obtained from the Arrhenius equation, for each catalyst, rate constant was obtained at 45, 50, 55, 60 and 65°C by plotting the biodiesel concentration from the conversion against time at each temperature. Then Arrhenius (Eq. 2) plot was used for the determination.

$$\ln k = \ln A - \frac{E_a}{RT} \qquad 2$$

The values of ln*k* were plotted against $\frac{1}{T}$ and it *Ea* was calculated from the slope $\frac{E_a}{R}$.

Where *k* is the rate constant, *A* is pre-exponential factor, *Ea* is the activation energy, *R* is the gas constant = 8.314 and *T* is temperature in kelvin.

Since slope $= -\frac{E_a}{RT}$, then $\mathrm{E_a} = \text{slope} \times \mathrm{R}$, this equation is used in activation energy calculations.

For surface modified commercial K-modified ZnO, SMK-ZnO Plot of ln*k* against $\frac{1}{T}$ in Fig. 3 gives a slope of -7800.181 which gives corresponding Ea value of 64.85 kJmol^{-1}. For nanoparticle K-modified ZnO, NPK-ZnO Plot of ln*k* against $\frac{1}{T}$ in Fig. 4 gives a slope of -7502.725 which gives corresponding *Ea* value of 62.378 kJmol^{-1}.

For nanoflowers K-modified ZnO, NPK-ZnO Plot of ln*k* against $\frac{1}{T}$ in Fig. 5 gives a slope of -7695.895 which gives corresponding *Ea* value of 63.984 kJmol^{-1}.

For nanotubes K-modified ZnO, NPK-ZnO Plot of ln*k* against $\frac{1}{T}$ in Fig. 6 gives a slope of -7145.134 which gives corresponding lowest *Ea* value of 59.404 kJmol^{-1}. The values of activation energy determined were summarized in the Table 2 below.

All the calculated values of the activation energy determined falls within the range of activation energy for heterogeneous transesterification reactions (26-82 kJ/mol). Also, the values obtained being higher than 25 kJ/mol indicates that the reaction is chemically rather than mass transfer controlled [15].

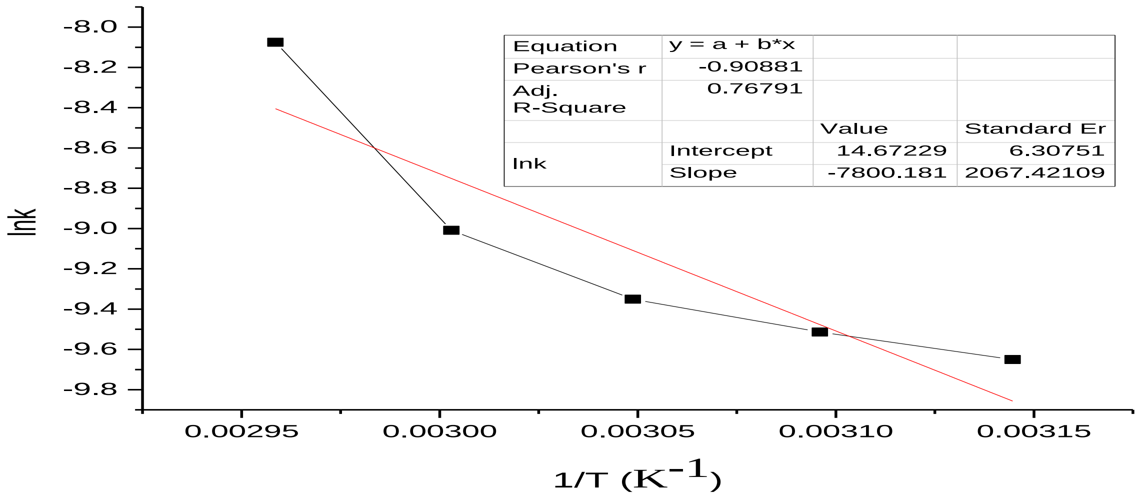

Fig. 3: Arrhenius plot for activation energy determination plot of SMK-ZnO

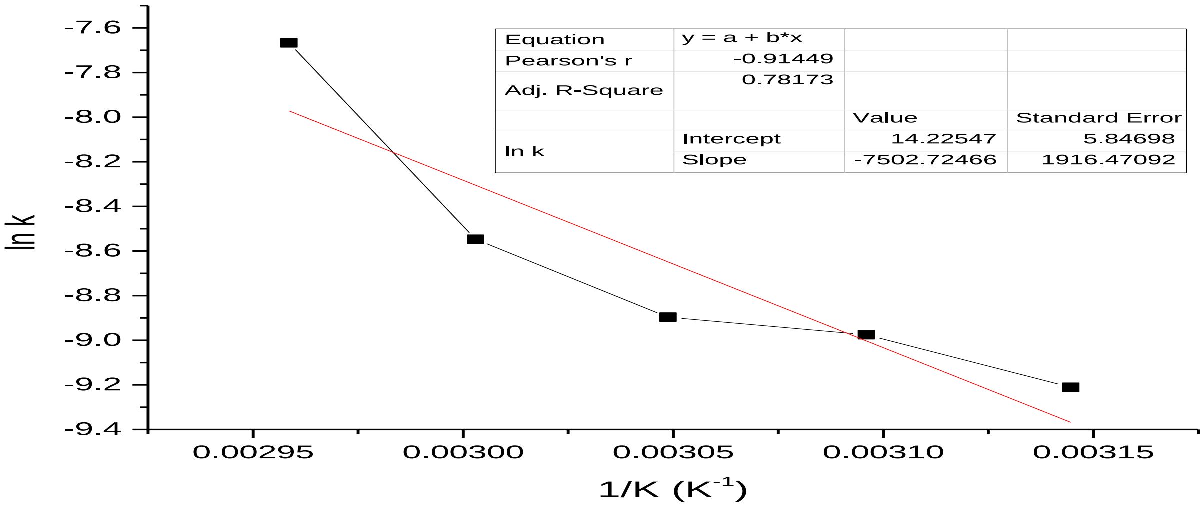

Fig. 4: Arrhenius plot for activation energy determination plot of NPK-ZnO

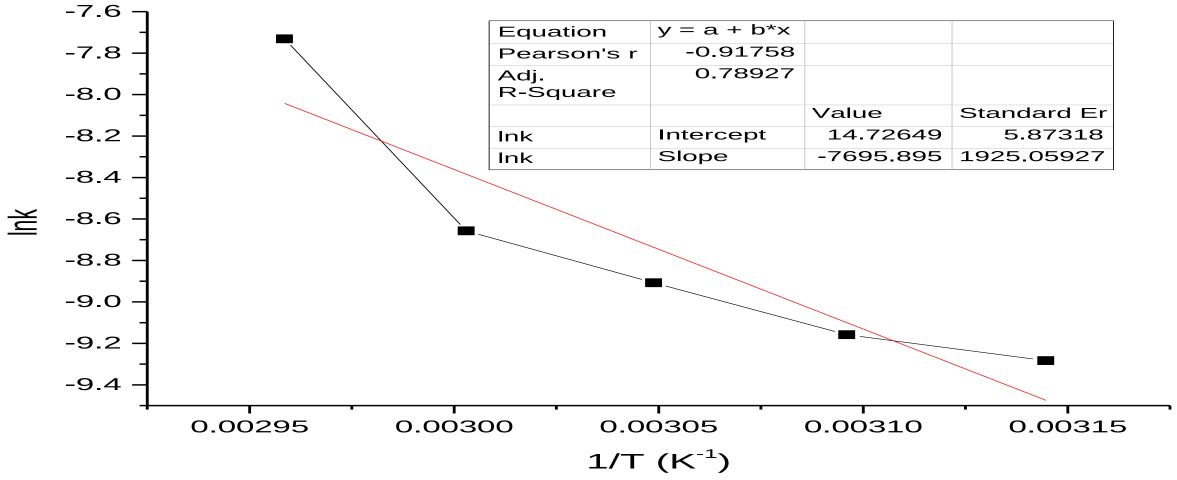

Fig. 5: Arrhenius plot for activation energy determination plot of NFK-ZnO

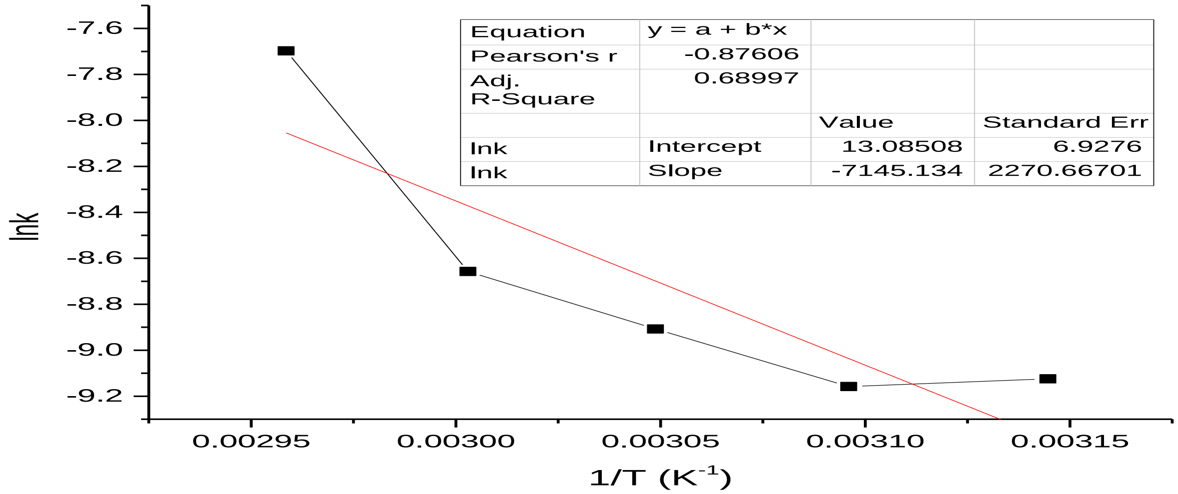

Fig. 6: Arrhenius plot for activation energy determination plot of NTK-ZnO

Table 2: Comparison of catalysts basic sites, activation energy and biodiesel conversion

Catalyst Name	Basic Sites mmol/g	Activation Energy	Biodiesel Conversion
SMK-ZnO	6.56	64.85	93.70
NPK-ZnO	8.53	62.37	95.65
NFK-ZnO	7.15	63.98	94.70
NTK-ZnO	8.82	59.40	96.24

The analysis is in agreement with other results whereby nanotubes have lowered the activation energy most, enabling greater number of reacting species to overcome the energy barrier. This result in the faster rate of reaction and product conversion. The trend follows the regular pattern of nanotubes followed by nanoparticles followed be nanoflowers and finally commercial.

Turnover Frequency (TOF)

The TOF is the number of revolutions of catalytic cycle per unit time [22], or the number of molecules converted per active sites. It is the number of times the reaction takes place per catalytic site per unit time and is used to measure the efficiency of a catalyst [35]. It can be calculated as reported by [24] using the relationship in Eq. 4. All TOF values repoted were obtained at the optimum conditions

$$TOF = \frac{Acual\ amount\ of\ total\ FAME}{f \times m_{cat} \times t} \quad 4$$

Where m_{cat} is the mass of catalyst used, *f* is catalyst's surface basic sites in mol/g and *t* is the reaction time.

Eq. 5 can be reaaranged and TOF can now be calculated with equation 5 below

$$TOF = \frac{Rate\ of\ catalyst}{f_W \times m_{cat}} \quad 5$$

Using the above relationship, TOF of all the catalysts used in the transesterification under their optimum conditions was calculated as summarized in Table 3.

Table 3: Comparison of catalysts basic sites, TOFs and biodiesel conversion

Catalyst Name	Basic Sites mmol/g	TOF (s^{-1})	Biodiesel Conversion (%)
SMK-ZnO	6.56	0.0120	93.70
NPK-ZnO	8.53	0.0142	95.65
NFK-ZnO	7.15	0.0157	94.70
NTK-ZnO	8.82	0.0260	96.24

From the analysis of the above, the results concur with catalyst basic sites, biodiesel conversion, rate constant and activation energy analyses. The trend follows the order that nanotubes have the highest TOF, however, nanoflowers show higher TOF than nanoparticles due to its relatively lower basic sites, then finally surface modified commercial. Here also ZnO nanotubes have the highest catalyst efficiency from its turnover frequency, consistent with all the previous results. The TOF values obtained are higher compared to the values obtained from K-modified hydrotalcite [36], with K-modified ZnO nanotubes showing highest result.

Kinetics evaluation of the catalysts as summarized in Table 3 shows that even though basic sites concentration was the main factor influencing the reactions kinetics. However, it was also influenced by the catalyst structure. Notably, nanotubes have the highest influence followed by nanoparticles, nanoflowers and finally commercial ZnO. The summary of kinetics parameters is presented in Table 4.

Table 4: Summary of kinetics parameters evaluated

Catalyst Name	Basic Sites mmol/g	Rate Constant (*k*) (mol/s)	Activation Energy	TOF (s^{-1})	Biodiesel Conversion (%)
SMK-ZnO	6.56	0.000311	64.85	0.0120	93.70
NPK-ZnO	8.53	0.000468	62.38	0.0142	95.65
NFK-ZnO	7.15	0.000439	63.98	0.0157	94.70
NTK-ZnO	8.82	0.000479	59.40	0.0260	96.24

Based on the above information, it could be concluded that structural modification of catalysts can significantly affect the kinetics of a process. In particular, methanolysis of rice bran oil was highly influenced by the use of ZnO nanotubes and nanoparticles. Kinetics of the methanolysis of RBO with K-modified ZnO commercial and nanostructures were determined and it was established that structucral and base modification have effect on the kinetics of transesterification process. It was observed that structural modification could significantly affect the kinetics of transesterification process. K-modified ZnO nanotubes have the fastest rate, lowest activation energy and highest TOF, followed by nanoparticles and finally by nanoflowers. K-modified ZnO nanotubes have the fastest rate, lowest activation energy and highest TOF, followed by nanoparticles and finally by nanoflowers. and thus significantly used for kinetic

CONCLUSION

Zinc oxide (ZnO) nanocatalysts were modified with base potassium to enhance their active sites and used to studied the kinetic parameters of the transesterification of Rice Brain Oil (RBO) to biodiel. The results revealed that the activation energy (Ea) fall within 26-82kJmol^{-1} indicating the process was kinetically controlled and the nanotubes has the highest rate constant of 0.0287min, lowest of 59.40kJmol^{-1} and higest turn over frequency (TOF) of 0.026s^{-1}. The results also show that the kinetic parameters of transesterification are not only dependent on catalysts, basic, and active sites but also be influence by the structural modification. Therefore this work was significantly used for the study of kinetics of the methanolysis of RBO and also used to reduce the use fossil fuels in the environment.

Conflict of Interest

The authors declare that the was no conflict of interest in this study.

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