

# Catalytic Performance by Kinetics Evaluation of Novel KOH-Modified Zinc Oxide in the Heterogeneous Transesterification of Rice Bran Oil to Biodiesel

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**Abstract.** Biodiesel is one of the promising biofuel today, the transesterification process to obtain biodiesel however is faced with problems of catalysts formulation and evaluation. In this study, kinetics of heterogeneous transesterification of rice bran oil (RBO) with novel prepared KOH-modified ZnO was explored. The catalyst was prepared by wet impregnation, calcined at 500°C for 6 hours characterized using nitrogen adsorption (BET) surface area analysis and basic sites by back titration method. The product biodiesel prepared was then analyzed by nuclear magnetic resonance spectroscopy (<sup>1</sup>HNMR) while kinetic studies for the reaction was carried out at 30, 40, 50, 60, 70 and 80°C temperature at reaction time of 30, 60, 90, 120, 150 and 180mins respectively. The results showed that the reaction follows first order model with respect to triglyceride, has a reaction constant of 0.0003 s<sup>-1</sup>, activation energy of 59 kJmol<sup>-1</sup> while 15K-ZnO catalyst shows the highest turnover frequency (TOF) of 11.56 hr<sup>-1</sup> with oil to biodiesel conversion of 96.5%. Koros-Nowak Criterion test of 1.01 show that the catalytic performance is independent of transport phenomena which indicates that this novel and very active base catalyst for transesterification reaction is was not affected by mass transfer process.

**Keywords:** Kinetics, catalyst efficiency, turnover frequency, Koros-Nowak criterion, biodiesel.

## 1. Introduction

The continued interest in the research of biofuels is increasing due to increased energy demand resulting in continuous depletion of fossil fuels. Energy is the driving force for the global industrialization and development, therefore its security and sustainability are major concern and so the need to develop its alternative sources. Biodiesel is a methyl or ethyl ester of fatty acids from plant oils or animal fats which have similar properties with diesel. It is usually produced using homogeneous basic and acid catalysts [1], [2]. But these catalysts can corrode the reaction vessels and the process is sensitive to water and FFA, soap is easily formed and there is the difficulty of phase and product separation with release of large amount of waste water and organic contaminants [3], [4]. Therefore, those problems causes significant rise in biodiesel cost and pose a major environmental concern. The use of heterogeneous catalysts can prevent some of the above problems, but they require more time, energy and are prone to emulsification and decreased activity. In view of this, various modified catalysts from different techniques are being used in order to improve the catalytic properties of heterogeneous catalysts for optimum application in transesterification; Ca-La<sub>2</sub>O<sub>3</sub> [5] K-CaO [6], K-MgO [7], Mo/CaO [8]. In all the above references the modification is generally reported to improve the catalytic activity and biodiesel yield. Zinc oxide has low solubility and so its application in biodiesel production may help to address the problem of leaching. But it has very low activity in transesterification and so its modification with more basic substances and improved performance is reported;

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Cu/ZnO [9], Zn/Al [10]. RBO was used in order to achieve competitive price value with mineral diesel for commercialization and also encourage farmers for more production of staple food. It also highlight the need for using oil substrates from products usually considered as waste in most parts of the world [11]. Chemical kinetics in reactions is a process of measuring reaction rates in comparison with time and temperature. Through kinetics study, we can understand the contribution of the catalyst which will help to assess the catalyst's role and efficiency in the process, this can save time and resources in modification processes by avoiding those properties that have little or no effect in reactions. Kinetics can therefore serve as fast, efficient and economical way of evaluating catalyst performance without undertaking difficult experimentations and analyses. Monitoring the progress of the reaction and estimating the reaction rate and reacting species, it is possible to evaluate processes and mechanisms of the reaction, time and temperature or energy needed in any reaction. 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 and is used to measure the efficiency of a catalyst [4]. Also, the mass transport phenomena causes reduced performance of modified catalysts, however Koros-Novak criterion can be used to evaluate if the modification process is good and whether its performance is sustained or independent of its effect [6]. All this will help especially in the industrial applications where cost and other resources are always taken into consideration. The kinetics of transesterification reactions under different reacting conditions and methods has been extensively reported in the literature [23]. 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.

This paper aims to study the kinetics of transesterification of rice bran oil with methanol in the presence of newly introduced KOH-modified ZnO catalyst. The results obtained will be used to evaluate the reaction rate, activation energy, catalysts efficiency from the turnover frequency and Koros-Novak criterion to the determine effect of transport phenomena on the catalyst activity.

## **2. Materials and Method**

The analytical grade reagents used were supplied by QR<sup>ac</sup><sup>TM</sup>; ZnO, KOH, NaOH, HCl, and methanol while 99.8% deuterated chloroform for NMR was obtained from Merck, Germany.

### **2.1. Catalyst Preparation**

The basicity of zinc oxide was modified by wet impregnation method using KOH to prepare XK-ZnO (X is the molar percent of KOH used). In the preparation of 5% (molar) KOH-modified ZnO, 0.1403 g of KOH was accurately measured and dissolved in 50 ml of distilled water followed by addition of 4.0685g ZnO. The mixture was then heated to 100°C under continuous stirring with magnetic stirrer for 1 hr until the water evaporates completely. It was then oven dried at 95°C for 6 hrs and then transferred into crucible and calcined at 500°C for 6 hrs. The use of similar method was reported for CaO and MgO and was found to be good found to be effective in introducing KOH in to the CaO and MgO lattice without the increased activity being affected by transport phenomena or leaching and excellent biodiesel yield [9].

### **2.2. Biodiesel Preparation**

The transesterification was carried out in two necked 250 ml round bottomed flask fitted with refluxing condenser and thermometer for temperature monitoring. The reaction was carried-out with 5 - 25% (molar) KOH-modified-ZnO. 0.5g (5% w/w) of the modified catalyst was mixed with 4.2 ml of methanol (9 times molar equivalent of oil) under reflux with aid of magnetic stirring for 30mins, then 10 g of oil (approximately 11ml) was added, and the reaction monitored for a period of 3 hrs. The mixture was the allowed to stand overnight, centrifuged and the middle biodiesel layer was separated and kept for analysis temperature. For kinetic evaluation the reaction was also conducted at the following temperature 30, 40, 50, 60, 70 and 80°C at time of 30, 60, 90, 120, 150 and 180mins respectively.

### **2.3. Characterization Methods**

The nitrogen adsorption surface area analysis (BET) was done using Micromeritics PulseChemiSorb 2705. The basic back titration test is carried out in order to study the basic strength of the samples analysed

[28]. The biodiesel samples were analysed by  $^1\text{H}$ NMR spectroscopy. Spectra of the samples were obtained using Bruker AB400. NMR analysis in biodiesel for qualitative, quantitative and kinetics studies has been in use for a long time and is still being used due to its simplicity, efficiency and precision [16]–[18].

### 3. Results and Discussion

The results for BET and titration catalyst characterisation,  $^1\text{H}$ NMR biodiesel characterisation and kinetics analysis were presented and discussed below

#### 3.1. Catalyst Characterisation

The BET results are moderate and generally higher than  $2.4\text{m}^2/\text{g}$  for the bulk ZnO indicating increased surface area due to modification. But it can be observed that there is increase from  $5.31\text{m}^2/\text{g}$  for 5%KOH-ZnO to  $8.21\text{m}^2/\text{g}$  for 10K-ZnO and  $9.07\text{m}^2/\text{g}$  for 15K-ZnO. This is due to the increased amount of hydroxyl moieties associated with KOH which is removed after calcination leaving behind its empty cavities in the structure of the modified catalyst. But it rapidly deteriorate to 4.73 for 20K-ZnO and 4.35 for 25K-ZnO suggesting the presence of excessive  $\text{K}_2\text{O}$  which occupying the structural spacings of the modified Catalysts. The results are summarized in table

The results of basic sites analysis obtained from back titration shows that all KOH-modified ZnO sample have higher basic sites compared to  $1.361\text{mmol}/\text{g}$  for the pure calcined ZnO samples. The values of basic sites obtained from modified ZnO for 5K-ZnO; 1.467, 10K-ZnO; 1.480, 15K-ZnO; 1.693, 20K-ZnO; 1.800 and 25K-ZnO; 1.813  $\text{mmol}/\text{g}$ . It could be observed that the basic strength of the modified samples increase as the amount of KOH used in the modification is increased. The highest amount of basic sites was obtained from 25%KOH-modified ZnO. But there was no significant increase in the amount of basic sites between 20K-ZnO and 25K-ZnO. This because, as already confirmed by BET results, the increased  $\text{K}_2\text{O}$  present was not supported on the ZnO and so does not contribute to its basicity. The results are summarized in table 3.1.

#### 3.2. Biodiesel Analysis

The spectra of biodiesel obtained in Fig. 1 is similar to that of biodiesel. The percentage conversion of oil triglyceride (TG) to methyl esters was calculated by taking the ratio of peak area of methoxy protons from methyl esters which appears at 3.7 ppm and that of methylene proton from glycerides which appears at 2.3 ppm [16] as expressed in Equation 1. The result indicates direct relationship between the KOH concentrations used and conversion up to 15%KOH. But increase of conversion above 15% is not significant, suggesting this as the optimum amount needed in the modification, further addition does not significantly affect the process and therefore is a waste. The relationship between catalyst surface area, basic sites and yield was also given in Table 1.

$$\% \text{Yield} = \frac{A_1/3}{A_2/2} \times 100\% \quad (1)$$

where  $A_1$  = peak area of methoxy protons from methyl esters which appears at 3.7 ppm and  $A_2$ = peak area of methylene protons from glycerides which appears at 2.3 ppm.

Table 1: Summary of the BET surface area, basic sites and biodiesel yield results

Catalyst	Surface area ( $\text{m}^2\text{g}^{-1}$ )	Basic sites( $\text{mmolg}^{-1}$ )	% Yield (%)
ZnO	2.40	1.361	14.17
5K-ZnO	5.31	1.467	55.60
10K-ZnO	8.21	1.480	63.31
15K-ZnO	9.07	1.693	96.24
20K-ZnO	4.73	1.800	96.43
25K-ZnO	4.35	1.813	96.51

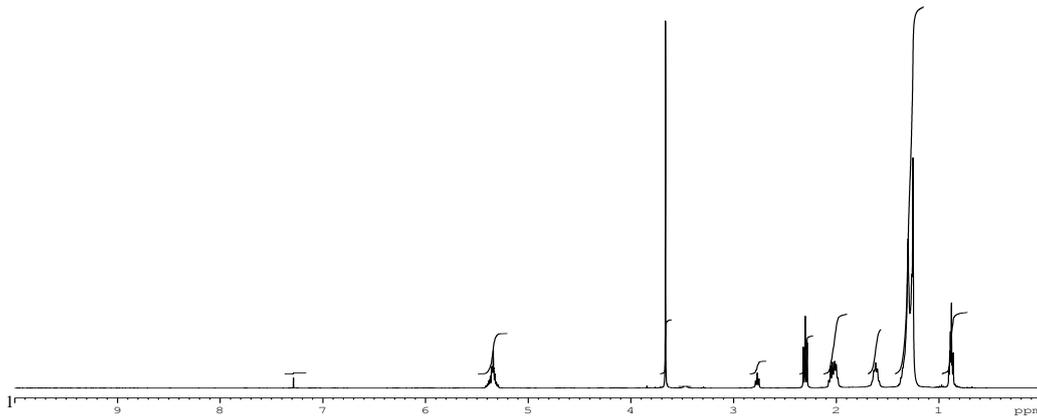


Fig. 1: NMR Spectra of 96% biodiesel

### 3.3. Kinetics Evaluation

The kinetics of heterogeneous transesterification is well reported in the literature. On this newly introduced catalyst, it is studied to evaluate the reaction rate order, activation energy and turnover frequency for efficiency. The best performing catalyst, 15K-ZnO was chosen. In order to determine the effect of transport phenomena on the catalyst, Koros-Novak criterion was adopted and 5 – 25% KOH modified catalyst samples were used.

The rate of the reaction was determined as 0.008mol/s. Data fitting was done on the different the reaction models but our results best fit the first order with respect to the triglyceride as indicated in Fig. 2. The rate constant was calculated from the plot of first order reactions model using Equation 2. Logarithm of concentration [A] was plotted against time and the rate constant is obtained from the slope as  $3.0 \times 10^{-4} \text{s}^{-1}$ .

$$\ln[A] = kt + \ln[A_0] \quad (2)$$

where, [A] = concentration [A<sub>0</sub>] = initial concentration, t = time of the reaction and k = rate constant.

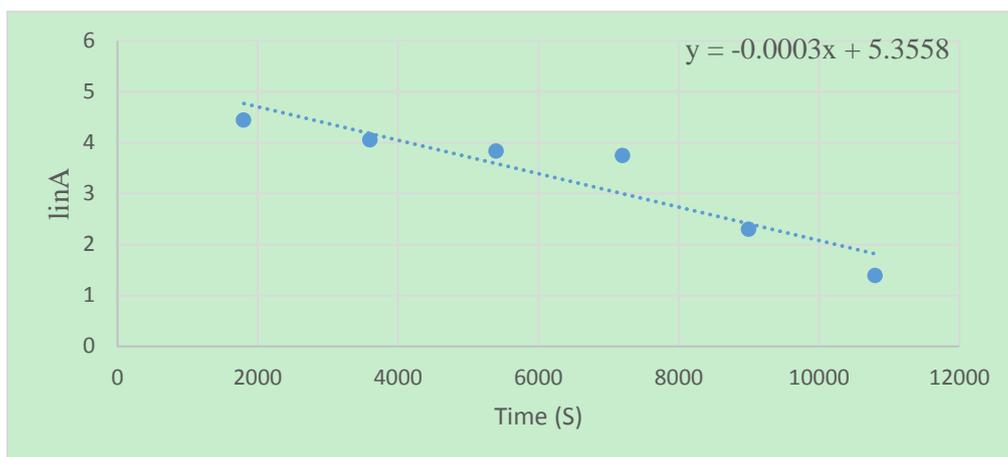


Fig. 2: First order reaction plot for rate constant determination

The activation energy  $E_a$  was obtained from the Arrhenius equation from the plot of  $\ln k$  versus  $\frac{1}{T}$  (Fig. 3). It is calculated as 59.41 kJ/mol which fall within the range of activation energy (26-82 kJ/mol) for heterogeneous transesterification reactions. The value obtained being higher than 25kJ/mol indicates that the reaction is chemically rather than mass transfer controlled [8].

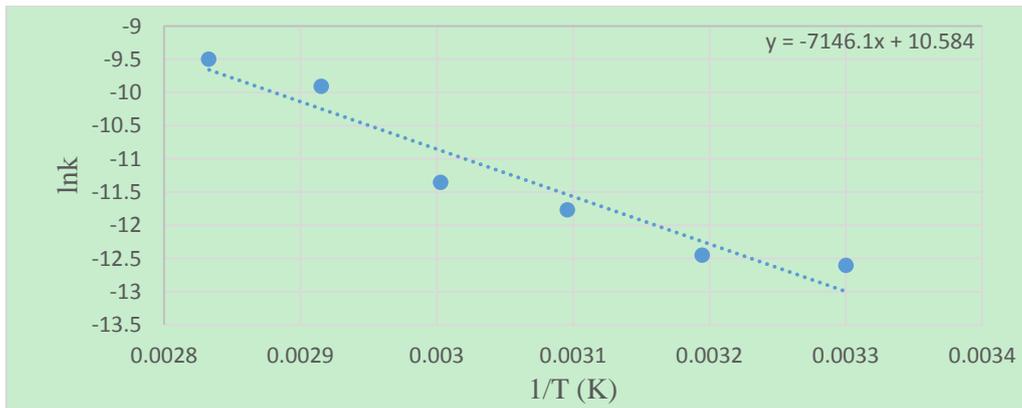


Fig. 3: Arrhenius equation plot for activation energy determination

In order to evaluate the catalyst efficiency Turnover Frequency (TOF) is calculated using relationship in Equation 3;

$$TOF = \frac{\text{number of molecules of the product}}{\text{number of catalyst active site} \times \text{time}} \quad (3)$$

The TOF results for 5% is 7.61, 10%; 8.59, 15%; 11.50, 20%; 10.76 and 25%; 10.69 hr<sup>-1</sup>. This result indicate an increase in the TOF for the catalyst. But the highest TOF was obtained for the 15%. It shows a direct relationship between the increased surface area, KOH used in the modification and the biodiesel yield for all samples. It also shows direct relationship between the TOF and the yield as compared in Table 2. But there was in consistent relationship between TOF and the basic sites. This means that at higher amount KOH, not all the basic sites were made available for the reaction as can be seen in the reduction of surface area due blockage of the structural pores of the catalyst.

Table 2: Comparison of biodiesel yield with turnover frequencies of the catalysts

Catalyst	% Yield (%)	TOF (hr <sup>-1</sup> )
ZnO	14.17	4.56
5K-ZnO	55.60	7.61
10K-ZnO	63.31	8.59
15K-ZnO	96.24	11.50
20K-ZnO	96.43	10.76
25K-ZnO	96.51	10.69

Koros-Nowak (KN) Criterion is the test carried out to determine the influence of transport phenomena on the measured catalytic activity [6]. It is calculated using the relationship in equation 4 as;

$$KN \text{ ratio} = \frac{\ln r(\text{molh}^{-1}\text{g}^{-1} \text{catalyst})}{\ln f_w(\text{g}^{-1})} \quad (4)$$

where r = reaction rate and f<sub>w</sub> = mass fraction of K<sup>+</sup> per gram of the catalyst

The plot of the experimental data for KN criterion, from Fig.4, it can be observed that a gradient of 1.01 was obtained. When the gradient of unity is obtained from the KN plot, the catalytic performance is said to be independent of transport phenomena. This implies that presence of K<sup>+</sup> in the modified catalyst was only used to improve its basic strength and catalytic activity but was not affected by the mass transfer of the reacting species and so its catalytic performance is not affected by transport phenomena [19]. Therefore, the modification of ZnO by wet impregnation, could produce a catalyst with very good yield and consistent performance for transesterification process.

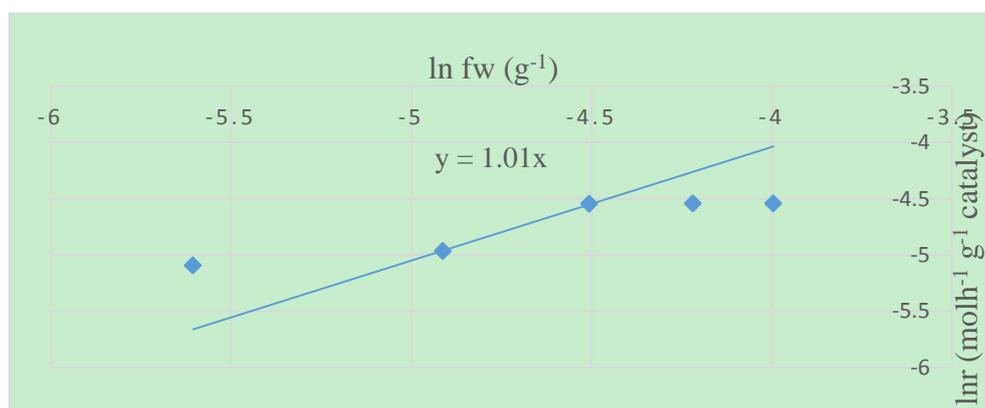


Fig. 4: Koros-Nowak plot for the assessment of transport phenomena on the catalyst

## 4. Conclusion

The results presented of the kinetic evaluation of KOH-modified ZnO. It shows that through simple wet impregnation method, a catalyst for efficient transesterification was prepared. Under the reaction conditions used in the research, high reaction rate is obtained, the process proceed via first order with respect to glyceride. The amount activation of energy obtained indicate that using this catalyst, the transesterification proceed via chemically controlled regime not by mass transfer. The turnover frequency of the various catalyst prepared shows that 15% molar KOH modified ZnO has the highest turnover frequency which is in complete agreement with BET, basic sites, and the NMR results. The data fitting in the Koros-Novak criterion shows the gradient near unity which means performance of the KOH modified catalyst is not affected by any transport phenomena.

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## 6. References

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