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MODEL DEVELOPMENT AND OPTIMIZATION IN METHANOLYSIS OF RICE BRAN OIL USING NANOCRYSTALLINE K-ZnO CATALYST: BOX BEHNKEN DESIGN

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ABSTRACT

In this study, nanocrystalline zinc oxide (ZnO) was precipitated and modified with 2.26% (wt.) potassium (K) through wet impregnation and used for Response Surface Methodology Box Behnken Design (RSM-BBD) Optimization in transesterification of rice bran oil (RBO) to form biodiesel. The catalysts were characterized by Field Emission Scanning Electron Microscopy (FESEM), X-Ray powder Diffraction (XRD) and X-Ray Fluorescence analyses, its basic sites determined by back titration. The transesterification product, biodiesel was analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy and RSM-BBD was also used to optimize the reaction variables on the biodiesel yield. The result reveals basic sites basic sites = 7.82mmol/g which is in close agreement with the experimental value of 7.38mmol/g. Also, quadratic model with high regression $R^2 = 0.9988$ was obtained from the ANOVA of transesterification process, optimization at maximum biodiesel yield criterion give optimum transesterification conditions of catalyst loading=3.60 %(wt.), temperature = 65°C,time = 120 minutes, methanol molar ratio = 6 and response biodiesel yield = 89.20 %, also in close agreement with experimental value of 95.23 %. The amount of K in the optimized catalyst was only 2.26%and it was reused three times after initial use before its final deactivation.

Keywords: K-modified-zinc oxide, Box-Behnken Design, transesterification, biodiesel optimization, catalyst reusability

INTRODUCTION

Biodiesel is a combination of fatty acids methyl or ethyl esters obtained from basic or acid catalysed transesterification reaction of triglycerides (Borges *et al.*, 2013). Plant oils or animal fats are among the major energy containing substrates for biofuels production (Galadima and Muraza, 2015). It is among the best alternative energy sources as it can be used without major modifications to current diesel engines. Unfortunately, commercialization of biodiesel is challenged by a number of problems including; availability and cost of feedstock and effective catalyst formulation (Niju *et al.*, 2014). The use of amphoteric substances in transesterification reactions for biodiesel can have the advantage of simultaneous esterification and transesterification; using their acid sites for esterification of free fatty acids present in oil to ester, at the same time when their basic sites are being used for transesterification of glycerides to ester (Baskar and Aiswarya, 2015). This can prevent two-step process of free fatty acid (FFA) removal before transesterification which is needed as pre-treatment for substrates containing higher FFA (Wan *et al.*, 2014).

Zinc oxide has very low toxicity and solubility, which are good properties needed in heterogeneous catalyst as there is less danger of pollution and enable ease of phase separation after product formation (Yan *et al.*, 2010). Alone, it has low activity in transesterification reaction, hence, acid activation is need modified its properties ((Yoo *et al.*, 2010; Wan *et al.*, 2014; Baskar and Aiswarya, 2015; Nambo *et al.*, 2015). This can pose environmental hazard or raise the cost of biodiesel production. However, the use of K supported on some substances for heterogeneous application was also investigated and it was reported to show remarkable improvement on the catalytic activity of supports (Liao and Chung, 2013; Takase *et al.*, 2014). But K has high solubility in methanol, leading to catalyst deactivation. However, under optimum modification conditions, it was used to prepare stable heterogeneous catalysts for biodiesel production (Ilgen and Akin, 2009; (Liao and Chung, 2013; Takase *et al.*, 2014; Kaur and Ali, 2015). Information from the available literature showed no detailed work was carried out on the use of zinc oxide nanoparticles in the transesterification even though that may help to reduce the amount of K used in the modification which is always the problem leading to leaching and eventual catalyst deactivation.

The use of rice bran oil can be used as good substrate for biodiesel due to its availability (Patil *et al.*, 2009; Gunawan *et al.*, 2011; Sun *et al.*, 2014) but it remain largely unexploited especially in Africa. Its use can as biofuel source will boost the economic value of rice, encouraging its production for food and utilizing the bran for alternative energy generation. Since ZnO does not dissolve in biodiesel (Yan *et al.*, 2010), then its modification with more active substance to prepare a stable modified catalyst will help to produce non-leaching, recyclable catalyst that can be used for commercial biodiesel production.

An equally important aspect of biodiesel production is the optimization of the process to achieve minimum reagent and energy cost for competitive commercialization of the product. Many studies were reported using various mathematical models and tools to optimize reaction conditions for biodiesel production using modified heterogeneous catalysts (Liao and Chung, 2013; Mahdavi and Monajemi, 2014; Sánchez *et al.*, 2014; Veiga *et al.*, 2014). However. RSM-BBD design is reported to be an efficient tool for optimization in biodiesel production (Samart *et al.*, 2015).

The use of zinc oxide nanoparticles modified with potassium at optimum conditions may provide a stable catalyst for use in transesterification at lower reaction condition is reported in our previous works (Kabo *et al.*, 2016, Kabo *et al.*, 2018).

However, this research aimed at developing model for optimization of biodiesel from rice bran oil using K-ZnO nanoparticles as catalyst. It is expected that zinc oxide nanoparticles will use minimum amount of potassium at optimum conditions to form a stable catalyst for transesterification at lower conditions. In addition, the model parameters were used to check potassium leaching and catalyst reusability was also evaluated.

MATERIALS AND METHODS

Materials

The analytical grade reagents used were supplied by QRëC^{TM}; $Zn(CH_3COO)_2$, KOH, NaOH, HCl, and methanol while 99.8% deuterated chloroform for NMR was obtained from Merck, Germany.

Catalyst Preparation

In the preparation of a catalyst required amount of the zinc oxide was measured and transferred into 200ml beaker and 25 ml distilled water added. 10 ml solution of 2% KOH (w) introduced into the beaker containing 10g of ZnO suspended in 50 ml distilled water and the set-up mounted onto hot plate with magnetic stirrer. The mixture was maintained at 90°C stirred with gentle evaporation until the water dried off and then transferred to oven and kept at 105°C for 8 hrs for complete drying. The sample was then transferred to furnace and calcined at required temperature and time. This is the basic sites modified catalyst used in transesterification for biodiesel. All xK-ZnO modified catalysts were prepared in similar way. x is equivalent to 1.5, 3, 4.5, 6, 7.5 and 9% (wt.) K-loading used. The use of KOH on nano-crystalline CaO (Kumar and Ali, 2012) and KOH/MgO (Ilgen and Akin, 2009) prepared by wet impregnation have shown stable catalysts with excellent biodiesel conversion.

Characterization of the Catalyst

The catalyst samples were characterized by Themogravimetric Analysis (TGA), Field Emission Scanning Microscopy (FESEM), X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analyses and basic sites determination was carried-out through basic back titration analysis.

Powder X-ray Diffraction patterns were recorded on a Bruker D8 having Siemens Diffractometer D5000 with Cu-Kα radiation (λ=1.5406Å, 40kV, 40mA). The samples were ground into small particles for smooth surface, pressed into sample holder and scanned at the rate of 0.05s/step and 2θ range of 10 to 70°.

Supra^{TM} 35 VP operating at 10kV was used to capture FESEM micrographs. This process generates imaging from the surface electrons of the samples and so they had to be taken for sputtering and gold coating. The gold coating provides continuous electrical path between the stub surfaces at any of the sample's likely surface that might be exposed to the electron beam. Bio "RAD Polaran Division" SEM sputter coater model system was used. It uses argon and a small electric current. Initially, the samples were placed on an aluminum stub and then taken to the small vacuum chamber of the sputtering coater were their surface was coated with gold.

XRF metals elemental analysis was done using Energy Dispersive X-Ray Fluorescence Spectrometer NEXCG ME65-12 to detect the metals elemental composition of pure ZnO and optimized K-ZnO before the transesterification. Also, the used catalyst was analyzed in order to assess the possibility of leaching. 4 g of the powder sample was weight on powder paper and placed into a sample cell followed by assembling of the sample cell for analysis.

The basic sites of the prepared samples was studied as reported by (Kaur and Ali, 2014) and (Mutreja *et al.*, 2014) using basic back titration method, on the principle that basicity of a base is equivalent to the acidity of the conjugate acid and vice versa. Measurement of the aqueous-soluble basicity was conducted by mixing 0.2 mg of catalyst sample in 10 mL of distilled water and allowed for 24 h. The filtrate obtained was separated by a centrifuge and the resulting solution was neutralized with 10 mL of 0.05 M HCl. Subsequently, the remained acid was titrated with 0.02 M NaOH and phenolphthalein was employed as an indicator. The equivalent concentration of the acid (after its reaction with the catalyst) determined with the NaOH is then subtracted from the original concentration of the acid before reacting with the catalyst and the difference is taken equivalent to be the basic strength of the sample.

Biodiesel Preparation (Transesterification)

The biodiesel was prepared by using 250 ml double necked round bottomed flask is fitted with a condenser and thermometer, then mounted onto retort stand. In one of the reactions, appropriate molar ratio of methanol is measured into the round flask followed by needed weight percent of the catalyst relative to oil. The mixture was then vigorously stirred for 20 min with the aid of magnetic stirrer to form a uniform alkoxide mixture. 22 ml (20g) of rice bran oil was then added and the set up heated in paraffin oil at required temperature under magnetic stirring for the needed time. The product was cooled, allowed to stand overnight and centrifuged. Three layers were distinct. The small upper layer of unreacted methanol was removed while the middle layer of biodiesel was carefully decanted from the lower layer which contains glycerol and the settled solid catalyst.

^{1}HNMR Analysis of the Transesterification Products

The products obtained from the transesterification process were analyzed by ^{1}HNMR spectroscopy for both confirmation of the functional groups and percentage yield determination. The NMR spectra of biodiesel samples were obtained using Bruker 400. Samples were prepared by mixing one to two drops of the biodiesel sample with 0.5ml of 99% deuterated chloroform in 5mm sample tubes. The solution was shaken to achieve homogeneity, appropriately attached to the spinner with the aid of the gauge.

Catalyst Reusability Test

In order to evaluate the reusability of modified K-ZnO, the optimized catalysts were recovered by filtration, washed with methanol and calcined at 200^{o}C for 2 hours to decompose the temporarily adsorbed glycerol and used for transesterification under the same conditions explained earlier.

Catalyst Leaching Test

Leaching is the major cause of catalyst deactivation and also the possibility of homogeneous reaction which can have negative effect on the overall process. In order to screen the possibility of potassium leaching into biodiesel, a simple test as adopted by (Kumar and Ali, 2012) and (Chen *et al.*, 2014). The optimized catalyst and methanol were under mixed in the same experimental conditions as carried out in the transesterification process, but in the absence of RBO oil. The reaction was allowed to proceed for 3 h and the catalyst finally recovered by filtration. The methanol filtrate was used in transesterification reaction of RBO. The reaction was carried out for 2 hr at 65 ^{o}C and only about 4.10% of FAME yield of about was observed.

Design of Experiment for Optimization of Biodiesel Yield

The statistical optimization was performed to evaluate the conditions for optimum biodiesel production. The transesterification, experiments were performed randomly in order to prevent systematic error. Box–Behnken response surface experimental design (BBD) was adopted to evaluate the effects of the variables on the biodiesel yield (Nazwanie *et al.*, 2014; Witek-Krowiak *et al.*, 2014).

The biodiesel production was studied with four factors to optimize and investigate the influence of process variable; catalyst loading X_1 (1-6 % (wt)) of oil), reaction temperature X_2, (40–65 ^{o}C), reaction time X_3 (30–180 mins), and methanol to oil molar ratio X_4 (6-21) on the response biodiesel yield. All the factors were used because of the possibility of interaction effect during the transesterification reaction. After selection of process (independent) variables, experiments were established based on a BBD suggested values and the complete design consists of 29 experiments with five centre points.

Statistical Analysis and Model Fitting

Statistical analysis of the data were carried out using the Design Expert software 7.1 and a second order full factorial equation was obtained and used in order to optimize the effect of the parameters on the response. For predicting the optimal point after performing experiments, a second-order polynomial quadratic equation (Equation 1) was fitted to correlate the relationship between independent variables and responses and interactive effect of the process variables. Regression coefficients of the quadratic model was evaluated by analysis of variance (ANOVA). All the terms in the model were tested by student's F-test and significance of the F-values at probability levels ($p \leq 0.05$) were analysed. The developed mathematical models were used for the construction of three dimensional (3D) response surface plots in order to predict the relationships between independent and dependent variables. The experimental data were evaluated with determination coefficient (R^2), adjusted determination of coefficient (R^2 adj.), predicted determination of coefficient (R^2 pred.). Verification experiments were performed under the optimal conditions and the value of the experiments was compared with the predicted values of the developed model equations

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \mathcal{E} \qquad (1)$$

Where, Y is the response factor (molar yield of ''biodiesel'' reaction); x_i the *i*th independent factor; β_0 the intercept; β_i the first order coefficient of the model; β_{ii} the quadratic coefficient of *i* factor; β_{ij} the linear coefficients of the model for interaction between *i* and *j* factors; and $\mathcal{E}$ the experimental error (Thirugnanasambandham *et al.*, 2014).

RESULTS AND DISCUSSION

Characteristization of catalyst

The surface characteristics of the K-ZnO nanoparticle catalyst was carried out using FESEM as shown in Fig. 1. It was observed that there was no crystal growth during the precipitation process, hence, Zn^{2+} ions where immediately precipitated and so no nucleation took place in production of the nanoparticles as presented in Fig. 1.

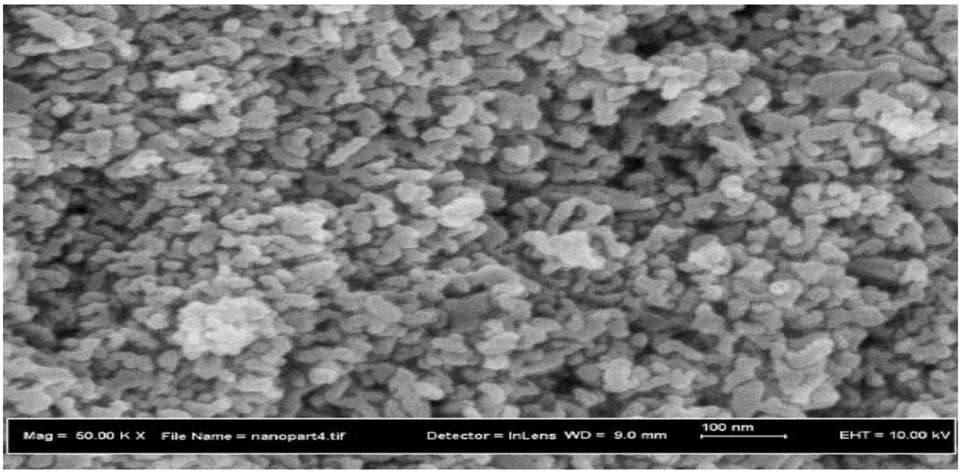


Fig.1: FESEM micrograph of the Nano-crystalline ZnO prepared

Ray Powder Diffraction (XRD) Analysis

The XRD analysis was carried out to investigate the presence of K_2O in the ZnO crystal phase. The spectra in Fig.2 .The diffraction pattern of NP-ZnO is matched with that of zincite synthetic, JCPDS pdf card number 01-071-6424 with peaks at 2θ positions of 31.7095, 34.3838, 36.1948, 47.4509, 56.5279, 62.8015, 66.3983, 67.8441 and 69.022 as already observed (Hariharan, 2006). The 3 prominent peaks appeared at 2θ positions of 31.7095, 34.3838 and 36.1948. Average crystallite size was calculated as 59.94 nm which is much higher than observed in FESEM. This is because the FESEM micrograph indicates particle size, which could contain aggregate of much smaller crystallites. The growth of ZnO nanoparticles was favored along 101 planes which was used in calculating its average size.

The K_2O peaks could be observed at $2\theta = 28, 31, 33$, and 51^o (Kumar and Ali, 2012; Mutreja *et al.*, 2014; Takase *et al.*, 2014). The XRD spectra obtained from 2% KOH modified was the same with that of pure ZnO due to low amount or instrumental resolution, but from 4% K upward, the presence of K_2O could be observed. The intensity of K_2O peaks is weak due to low concentration of K on the surface and does not increase with the amount of K used, suggesting fine deposition onto ZnO crystals. This will enable interaction between K and Zn which may weaken the Zn^{2+}-O^{2-} bond thereby enabling better interaction with methanol and thus increasing its catalytic activity and yield (Spivey, 1997). In all the K-modified ZnO catalysts, ZnO peak intensities remain approximately the same indicating that there was no increase in crystallite size due to the adsorption of K on to the ZnO and that K was properly dispersed on the ZnO nano-structures (Mutreja *et al.*, 2014).

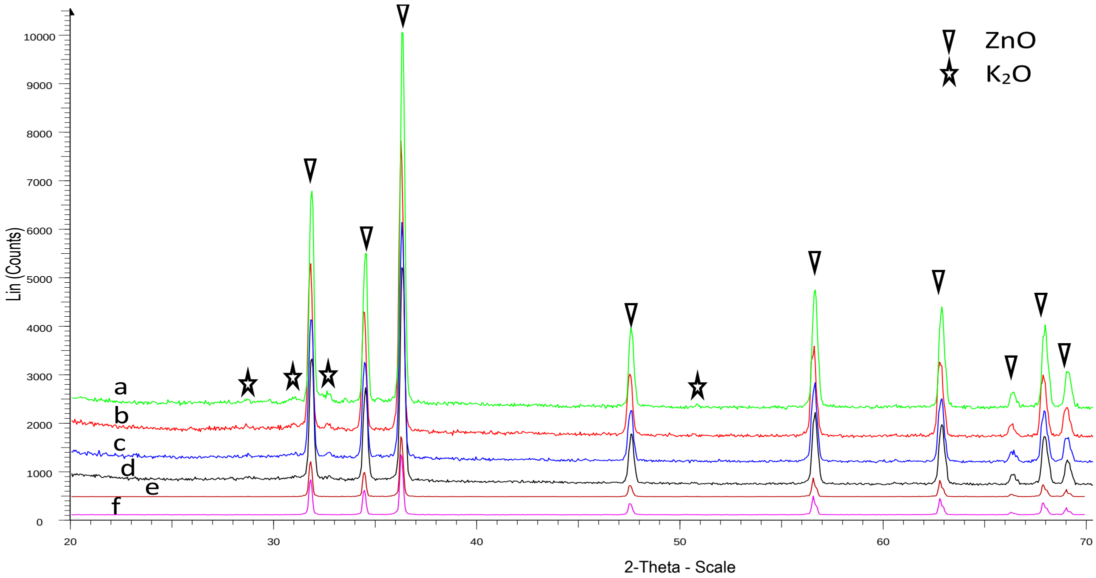
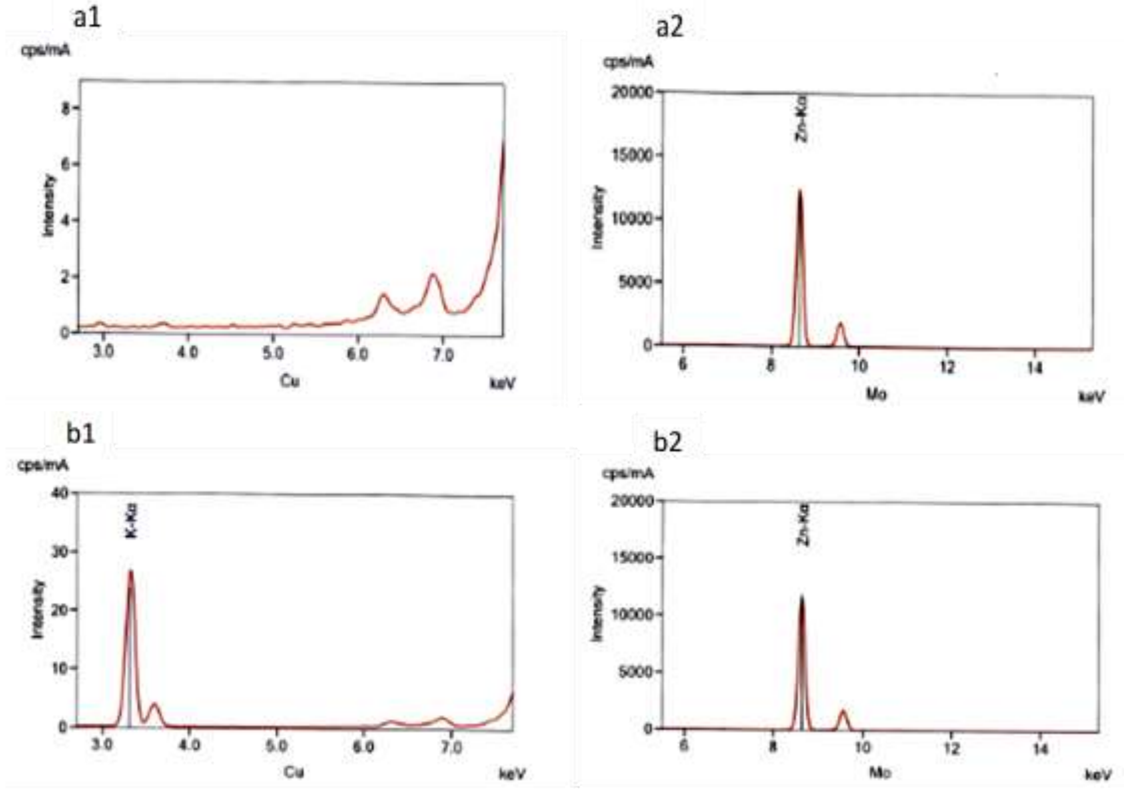


Fig.2: XRD diffraction patterns of (a) ZnO-10K, (b) ZnO-8K, (c) ZnO-6K, (d) ZnO-4K, (e) ZnO-2K and (f) ZnO-0K modified zinc oxide catalysts calcined at 520ºC for 4 hrs 30mins.

X-Ray Fluorescence (XRF) Analysis

XRF analysis for metal elements as shown in Fig. 3, indicate that for pure ZnO, no peak K was observed (Fig 3a1). Zn peak could be observed at 8.3 eV. (Fig. 3a2).However, upon modification, the XRF spectra of 5K-ZnO shows the presence of peak of K at 3.3eV (Fig. 3b1) and Zn peak at 8.3 eV. (Fig. 3b2).



Figures 3: XRF spectra for the elemental analysis: a1 and a2 for the pure and ab1 and b2 for 5K-modified ZnO

The data summary in Table 1 showed that pure ZnO sample composed of 100% Zn and no K was detected. But, 5K-ZnO contains actual 97.70% Zn and 2.26% K as summarized in Table 1. This indicates that the actual amount of K 5% KOH-modified catalyst was only 2.26%,this indicate that a very low quantity of K was dispersed on the catalyst during the modification process.

Table 1: Summary of XRF elemental composition of pure and K-modified ZnO catalyst

Sample	%Zn	%K
ZnO	100	Nd
5K-ZnO	97.7	2.26

Basic Sites Strength Analysis

The results of basic sites analysis obtained from back titration showed moderate basic sites compared to modified catalysts using the same method, 9.80 mmol/g from was obtained from Na-modified mixed-metal oxides (Singh and Fernando, 2009), a basicity of 7.2-9.3 is enough for good catalytic activity (Islam *et al.*, 2012). Modified K-ZnO sample have higher basic sites compared to the pure calcined ZnO samples because combination of K-loading with calcination temperature increases the basic strength of the catalysts. This occurs due to interaction of potassium with ZnO at high temperature which became adsorbed and improved its basic strength (Querini *et al.*, 1999). In contrast, calcination at low temperatures does not significantly improve the basic sites due to inability of the K to strongly adsorb on ZnO surfaces. The result also showed that, at optimum conditions, the use of K-load above 6 % did not cause significant increase in basic sites. This indicated that, the basic sites came from the modified catalyst and not from the K itself. This is in agreement with the results of K-modified CaO (Kumar and Ali, 2012) and K/MgO (Querini *et al.*, 1999), they found neither increased basic sites nor catalytic performance at higher K-loading while better K-Mg surface interactions occur at optimum conditions respectively. Also, at temperatures above 600°C, decomposition of K_2O takes place and this leads to the deterioration of the resultant basic sites in the catalysts as shown in the experimental design results. The summary of basic sites result is presented in Table 2.

Table 2: Basic sites of K-ZnO catalysts prepared under optimized calcination temperature and time

Catalyst	ZnO-0K	ZnO-3K	ZnO-6K	ZnO-9K	ZnO-12K	ZnO-15K
Basic Sites (mmol/g)	3.61	4.37	6.74	7.93	8.05	8.13

^{1}HNMR Results of Biodiesel Analysis

Biodiesel was prepared from ZnO and K-modified ZnO under various reaction conditions. The samples were characterized by ^{1}HMR for both qualitative and quantitative analysis. The disappearance of methoxy triglyceride protons peak at δ = 4.3 ppm and formation of fatty acid ester methoxy protons peak at δ = 3.67 ppm as shown in Fig.5 indicated the formation of biodiesel while the ratio of the δ = 3.67 ppm methoxy protons of biodiesel with δ = 2.3 ppm methylinic protons of oil is used for quantitative determination. The spectra obtained were analyzed with the Bruker TOPSPIN 2.1 software and the yield was calculated using Equation 3 from ratio of the peak area of methylene protons of the triglycerides (A_1) which appears at δ =2.3 ppm with that of methoxy protons present in the fatty acid methyl esters of the biodiesel which appears at δ = 3.67ppm (A_2) (Guzmán-vargas *et al.*, 2015; Kaur and Ali, 2015). The result of biodiesel yield calculated is presented in Table 5.

$$\%\,Yied = \frac{A_1/_3}{A_2/_2} \times 100\% \qquad (3)$$

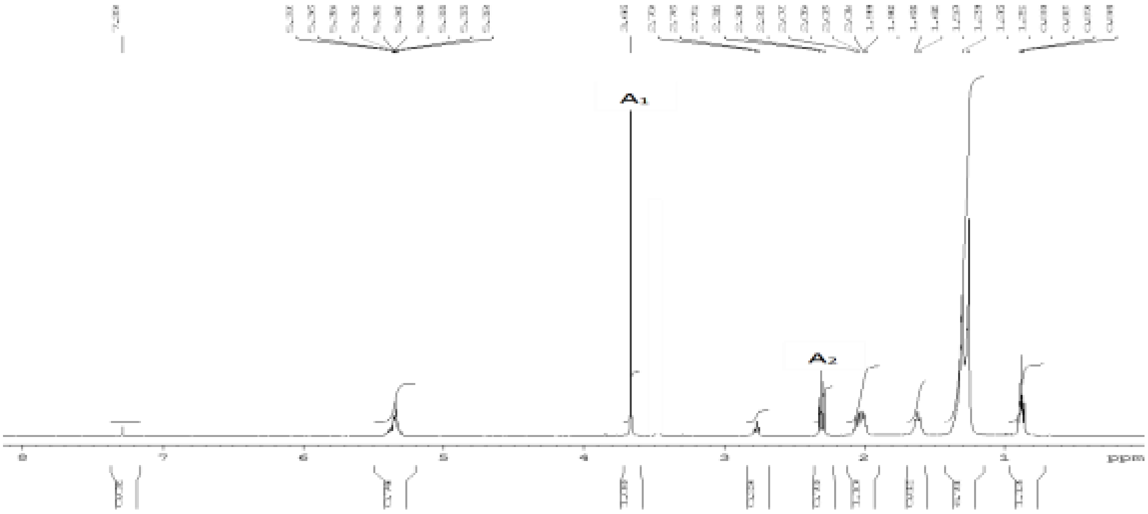


Fig.5: NMR Spectra of 95.53% biodiesel prepared under optimized conditions of catalyst loading=3.60, temperature = 65 °C,X_3 = 120 mins and MOR = 6.

Experimental Design and Statistical Analysis

The results of experimental design and statistical analysis are presented in Table 5 and Fig. 6. The final quadratic equation 2 that explain the mathematical relation of the independent variables; X_1, X_2X_3 and X_4 with the response, biodiesel yield was obtained as

$$Y = 47.16 + 14.82X_1 + 30.49X_2 + 12.12X_3 + 3.24X_4 + 5.86X_1X_2 + 4.60X_1X_3 + 3.99X_1X_4 + 10.57X_2X_3 - 6.05X_2X_4 - 0.24X_3X_4 - 6.97X_1^2 + 8.20X_2^2 - 8.59X_3^2 - 4.16X_4^2 \qquad (2)$$

Table 5: Experimental with corresponding BBD predicted results for the biodiesel yield

Run	Cat.Load; X_1 (%)	Rxn. Temp.;X_2 (°C)	Rxn. Time; X_3 (min)	MOR (mol)	Experimental Yield (%)	Predicted Yield (%)
1	3.50	52.50	180.00	6.00	43.15	43.54
2	3.50	52.50	105.00	13.50	45.72	47.16
3	1.00	52.50	30.00	8.50	8.51	7.75
4	3.50	40.00	105.00	21.00	28.41	30.00
5	3.50	65.00	105.00	21.00	79.85	78.88
6	6.00	52.50	30.00	13.50	29.72	29.70
7	3.50	40.00	180.00	13.50	18.31	17.84
8	3.50	52.00	105.00	13.50	47.44	47.16
9	3.50	65.00	180.00	13.50	98.18	99.96
10	3.50	65.00	30.00	13.50	53.72	54.59

11	1.00	40.00	105.00	13.50	8.79	8.93
12	3.50	52.50	105.00	13.50	47.35	47.16
13	3.50	52.50	105.00	6.00	21.07	21.96
14	3.50	52.50	30.00	21.00	25.88	25.77
15	3.50	40.00	30.00	13.50	16.11	14.73
16	3.50	52.50	180.00	21.00	50.15	49.53
17	1.00	52.50	180.00	13.50	25.21	24.30
18	6.00	40.00	105.00	13.50	26.87	26.87
19	3.50	40.00	105.00	6.00	11.30	11.42
20	3.50	65.00	105.00	6.00	86.95	84.52
21	6.00	65.00	105.00	13.50	99.26	99.56
22	1.00	65.00	105.00	13.50	57.76	58.21
23	3.50	52.50	30.00	6.00	17.42	18.82
24	6.00	52.50	105.00	21.00	58.24	58.08
25	6.00	52.50	180.00	13.50	63.31	63.14
26	6.00	52.50	105.00	6.00	43.58	43.63
27	3.50	52.50	105.00	13.50	48.06	47.16
28	3.50	52.50	105.00	13.50	47.42	47.16
29	1.00	52.50	105.00	21.00	20.27	20.45

Cat. = catalyst, Rxn. = reaction, MOR = methanol to oil ratio

In order to validate the model, analysis of variance was used and its summary was presented in Table 6. The model F-value of 770.58 implies that the model is significant and that there is only a 0.01% chance that a Model F-Value this value could occur due to noise. The P-values of < 0.05 obtained indicates that model terms are significant. The "lack of fit" F-Values of 2.69 also implies that this factor is not significant. The R^2-value 0.9988 obtained for the model is very high. There is also a good agreement between the predicted R^2-value of 0.9974 and the adjusted R^2-value of 0.9933. Thus, the above analysis indicates that this predicted quadratic model is in good agreement with the experimental responses and therefore it can be adopted.

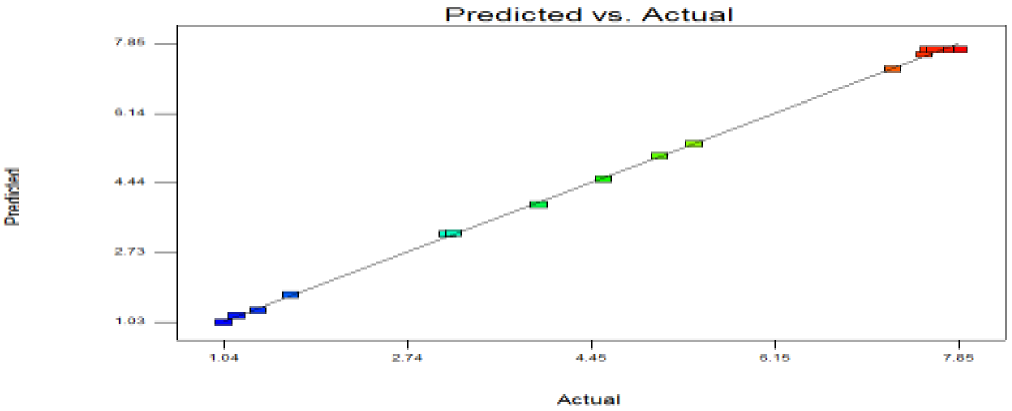


Fig.6: Diagnostic plot of comparison between experimental and predicted biodiesel yield

Table 6: Analysis of variance (ANOVA) for the biodiesel yield

Source	SS	DF	MS	F	P	Comment
Model	18192.03	14	1299.43	770.58	< 0.0001	Significant
X_1	2578.92	1	2578.92	1529.33	< 0.0001	Significant
X_2	11158.73	1	11158.92	6617.26	< 0.0001	Significant
X_3	1724.47	1	1724.47	1022.63	< 0.0001	Significant
X_4	127.43	1	127.43	75.57	< 0.0001	Significant
X_1X_2	137.12	1	137.12	81.32	< 0.0001	Significant

X_1X_3	79.29	1	79.29	47.02	< 0.0001	Significant
X_1X_4	66.56	1	66.56	39.47	< 0.0001	Significant
X_2X_3	446.48	1	446.48	264.77	< 0.0001	Significant
X_2X_4	146.53	1	146.53	86.89	< 0.0001	Significant
X_3X_4	0.24	1	0.24	0.14	0.7127	Not significant
X_1^2	315.84	1	315.84	187.30	< 0.0001	Significant
X_2^2	432.58	1	432.58	256.52	< 0.0001	Significant
X_3^2	479.02	1	479.02	284.08	< 0.0001	Significant
X_4^2	109.54	1	109.54	64.96	< 0.0001	Significant
Residual	23.61	14	1.69			
Lack of fit	20.55	10	2.05	2.69	0.1766	Not significant
Pure error	3.06	4	0.76			
Total	18215.63	28				

SS= sum of squares, DF= degree of freedom, F= f-value, P= p-value

Effect of Catalyst Loading

This factor has a good linear effect on the response yield Figures 7 (a, b and d), it also have positive interaction effect with temperature, MOR and reaction time. However, it has overall negative quadratic effect because at high catalyst concentration, emulsification occurs and the adsorption with the methanol to form alkoxide intermediate is affected. The use of optimum catalyst helps in overcoming mass transport limitation and positively influences the transesterification reaction.

Effect of Reaction Temperature

In this study, reaction temperature is the highest contributing factor on the transesterification process. Within this experimental temperature range, the model shows strong continuous positive linear effect on the response biodiesel yield. This is true because the reaction is kinetically driven and energy in form of heat is needed overcome the activation energy barrier and drive the reaction forward to the products side. It also shows positive interaction effect with the other variables especially the reaction time, indicating that enough time is needed to under optimum temperature to complete the reaction Figures 7 (a, c and c).

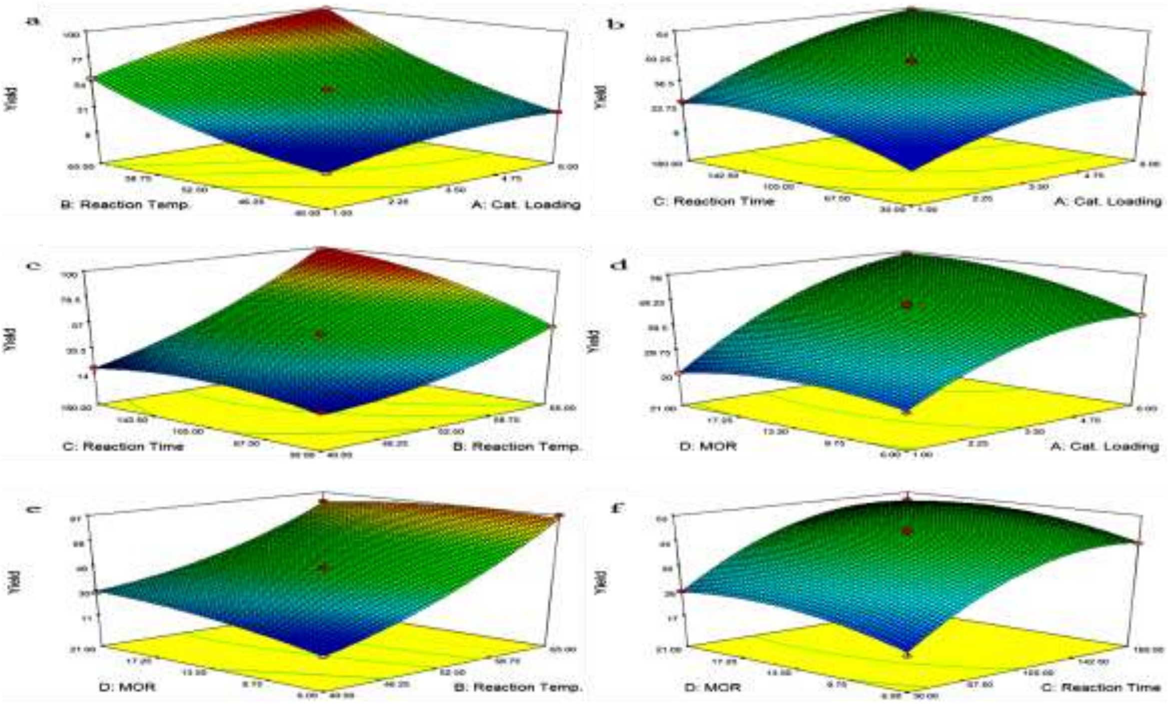


Fig.7: 3D plots of basic sites as a function of (a) reaction temperature and catalyst loading, (b) reaction time and catalyst loading, (c) reaction temperature and time, (d) MOR and catalyst loading, (e) MOR and reaction temperature and (f) MOR and reaction time.

Effect of Reaction Time

This factor has moderate linear effect on the yield. In has negative effect on the response biodiesel yield at low reaction value due to the mass transfer effect of the three-phase system (oil-methanol-catalyst). Immiscibility of oil and methanol leads to the diffusion limitation and thus lowering the rate of reaction. However, this limitation is removed as the time increases to high level. But at higher of reaction time 120 mins, mount of catalyst 3.5 %wt., temperature 52.50 °C and MOR 13.50, decrease in biodiesel yield was observed. This is due the effect of Le Chatelier's principle, after reaching the equilibrium, further proceed of the transesterification may lead to the reverse of reaction to the reactant side and hence decreased biodiesel yield Figures 7 (b, c and f).

Effect of Methanol to Oil Ratio (MOR)

This reaction variable shows the lowest linear effect on the response. A minimum methanol to oil molar ratio 3 should be used to balance the reaction. But more methanol is needed to drive the equilibrium position forward for product formation. For this reason this factor shows low effect because the minimum required ratio is used in all the experimental runs. However, higher methanol ratio shows negative quadratic effect on the response yield Figures 7 (d, e and f). More increment of the methanol to oil molar ratio from 15 to 21 leads to the drop of response biodiesel yield, because excess methanol in the reaction mixture causes increased solubility of the glycerol, promoting glycerolysis reaction, thus, glycerol reacts with the biodiesel to form back monoglyceride and diglyceride reaction intermediates, hence decreased yield.

Optimization of Biodiesel Yield

Optimal values of the transesterification reaction variables were obtained by solving the quadratic equation at maximum biodiesel yield. Considering these, parameters (X_1 =3.60, X_2 = 65,X_3 = 118.94, X_4 = 8.97 and biodiesel yield = 89.20%) repeated experiments were performed under similar conditions. Experimental value of 95.23 % was obtained which is in good agreement with the predicted value of 89.20%.

Catalyst Reusability Test

Catalyst reusability is an important factor for industrial of heterogeneous catalysts for biodiesel commercialization. During the repeated regeneration and use, the observed biodiesel of optimized K-ZnO catalyst was of 95.32 followed by 93.80%, 90.60%,68.66% for first, second and third consecutive recycled reactions, respectively (Fig. 8). After which its activity dropped to 19.59% in the fourth run of the used catalyst. This reduced catalytic activity is likely caused by gradual K leaching and possibility of carbon covering the catalyst surface after repeated transesterification and calcination processes (Kaur and Ali, 2014).

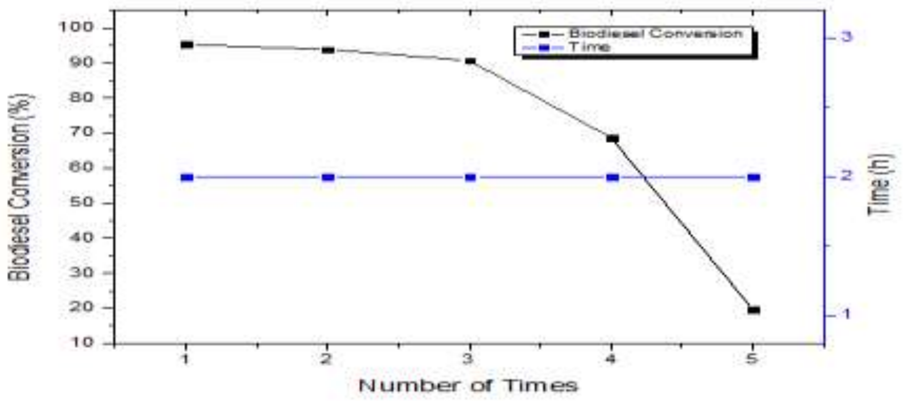


Fig.8: Catalyst Reusability plot

Catalyst Leaching Test

XRF for metal elements analysis of the catalyst after the first use (Fig.9) showed the presence of both K (Fig. 9a1) and Zn (Fig. 9a2) metals. The percent K was detected to be 2.01% which was very close to the initial 2.26% K (Fig. 3) detected on the catalyst before use.

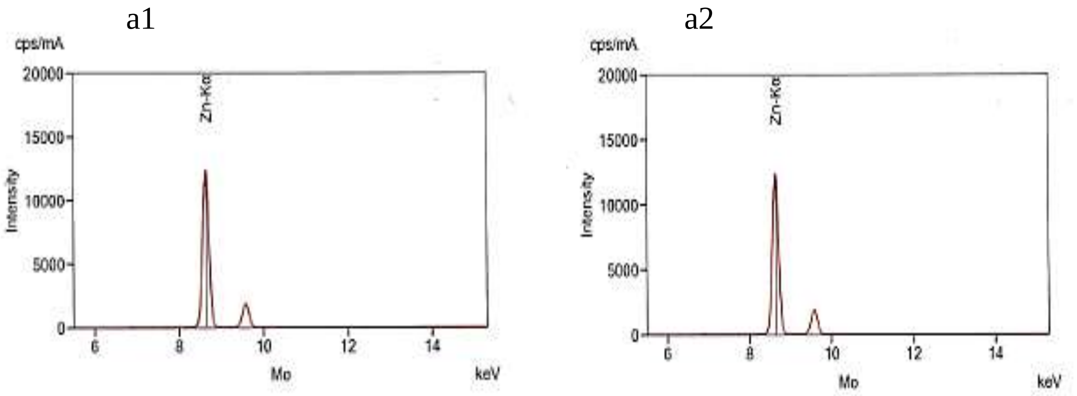


Fig.9: XRF spectra of the used catalyst

Therefore, with reference to the above leaching test, it can be observed that the catalyst leaching only slightly contributed in the process and the reaction was generally catalysed by the modified catalyst, supporting XRD result that the modification process produced a highly dispersed K on ZnO to form stable K-ZnO catalyst, and recyclable catalyst for use in transesterification

CONCLUSION

ZnO was modified through simple wet impregnation method to obtain catalysts with high basic sites, RSM analysis was used and the model obtained can save time and reduce cost. Optimization of the modification variables give 5.06 % K-loading at 520 ^{o}C for 4 hrs 30 mins. Transesterification was carried out and a high biodiesel yield was achieved at relatively lower reaction conditions. RSM-BBD optimization of the process gives a model equation with predicted optimum parameters as 3.60% catalyst loading, 65^{o}C and 120 mins. With the help of the model, high experimental biodiesel yield of 95.23% was obtained using the model parameters. Leaching test showed that the catalyst was stable and can be reused three times after the initial use. The reaction can be said to be heterogeneously catalysed, considering 20 g of oil which used optimum 3.60 % (0.72g) catalyst loading, containing 5.06% K which is equivalent to 0.18% of the oil used. This amount is well below the range of 0.5-2 % catalyst loading needed in the homogeneous transesterification. There was no significant contribution of the leached catalyst in the process and the catalyst was recycled three times after the initial use before it finally deactivate.

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