BBD Optimization of K-ZnO Catalyst Modification Process for Heterogeneous Transesterification of Rice Bran Oil to Biodiesel

K S Kabo¹, A R Yacob¹, W A W A Bakar¹, N A Buang¹, A M Bello¹ and A Ruskam¹
¹Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

E-mail: kamalskabo@yahoo.com

Abstract. Environmentally benign zinc oxide (ZnO) was modified with 0-15% (wt.) potassium through wet impregnation and used in transesterification of rice bran oil (RBO) to form biodiesel. The catalyst was characterized by X-Ray powder Diffraction (XRD), its basic sites determined by back titration and Response Surface Methodology (RSM) Box-Behnken Design (BBD) was used to optimize the modification process variables on the basic sites of the catalyst. The transesterification product, biodiesel was analyzed by Nuclear Magnetic Resonance (NMR) spectroscopy. The result reveals K-modified ZnO with highly increased basic sites. Quadratic model with high regression $R^2 = 0.9995$ was obtained from the ANOVA of modification process, optimization at maximum basic sites criterion gave optimum modification conditions of K-loading $= 8.5$ % (wt.), calcination temperature $= 480$ °C and time $= 4$ hours with response and basic sites $= 8.14$ mmol/g which is in close agreement with the experimental value of 7.64 mmol/g. The catalyst was used and a value of 95.53 % biodiesel conversion was obtained and effect of potassium leaching was not significant in the process.

Keywords: K-modified-zinc oxide, basic sites optimization, biodiesel, catalyst leaching.

1. Introduction

There is increasing concern for environmental safety and need for sustainable energy resources for use as green transportation fuels. Biodiesel is among the best alternative energy sources as doesn’t increase carbon to the atmosphere and can be used in its pure form without major modifications to current diesel engines. It is obtained from renewable sources and so becomes part of the solution to the global energy crisis due to increased consumption, leading to rapid depletion of existing fossil fuel reserves, high cost and increased greenhouse emissions [1]. Unfortunately, commercialization of biodiesel is challenged by a number of problems including availability and cost of feedstock and effective catalyst formulation.

Zinc oxide has very low toxicity and solubility limits which are good properties needed in heterogeneous catalyst as there is less danger of pollution and enable ease of phase separation after product formation [2]. Alone, it has low activity in transesterification reaction and so in order to use it at lower temperature, its properties need to be modified [2,3,4,5]. But the catalysts preparation in the reported literature involves the use of solvent for co-precipitation or harsher reaction conditions are used during the transesterification, both of which can pose environmental hazard or raise the cost of...
biodiesel production. Potassium hydroxid (KOH) alone is very good homogeneous catalyst with excellent yield in transesterification reactions for biodiesel, but there are so many problems of phase, catalyst and glycerol separation associated with homogeneous catalysts. The use of KOH supported on some substances for heterogeneous application was also investigated and it was reported to show remarkable improvement on the catalytic activity of substances used [6,7]. RBO oil is reported to be a good substrate for biodiesel due to the availability [8,9,10] but it is largely wasted and remain unexploited especially in Africa. This idea can be used to prevent wastage, boost economic value of rice, improving its production for food and utilizing the bran for alternative energy generation. Since ZnO does not dissolve in biodiesel [2], then its modification with more active substance to prepare a 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 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 [6, 11,12,13]. However, optimization of modification process of heterogeneous catalysts prior to application is not reported in the previous studies and that can help in the reduction of excessive use of active substances (main cause of leaching), high energy and time used in calcination all of which are important in cost and environmental saving. Response surface experimental Box–Behnken Design (BBD) was used because it covers entire design space at minimum number of experimental runs [14,15].

In this research, zinc oxide was modified with K to prepare active catalyst with high biodiesel yield at atmospheric pressure, low catalyst loading, temperature and methanol to oil ratio. BBD was used to optimize the effect of K-loading, calcination temperature and time on the basic sites response. The best catalyst prepared was then used for the transesterification of rice bran oil to biodiesel. The potassium leaching was also evaluated.

2. Materials and methods

2.1 Materials
The analytical grade reagents used were supplied by QRëCTM; ZnO, KOH, NaOH, HCl, and methanol while 99.8% deuterated chloroform for NMR was obtained from Merck, Germany.

2.2 Catalyst Preparation
Basic Sites Modification of the Catalyst was carried out in order to improve its basic sites through wet impregnation method. In the preparation of a catalyst, 10g of zinc oxide was measured and transferred into 200 ml beaker and 25 ml distilled water added. 3% KOH (w) accurately measured into the beaker 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 hours 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 ZnO-XK modified catalysts were prepared in similar way. X is equivalent to 3, 6, 9, 12 and 15% (wt.) KOH used. The use of KOH on nano-crystalline CaO prepared by wet impregnation as reported by [16] have shown an excellent biodiesel conversion and recyclable catalyst without any significant potassium leaching.

2.3 Characterization of the Catalyst
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 65°C temperature under magnetic stirring for 3 hours. The product was cooled, allowed to stand overnight and centrifuged and three layers were distinctly observed. 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. The transesterification reaction is given in Scheme 1.

\[
\begin{align*}
\text{Triglyceride(Oil)} & \rightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{OH} + \text{CH}_3\text{OH} \\
\text{Methanol} & \rightarrow \text{catalyst} \rightarrow \text{CH}_2\text{COOR}_1 + \text{CH}_2\text{COOR}_2 + \text{CH}_2\text{COOR}_3 \\
\text{Glycerol} & \rightarrow \text{Methyl esters}
\end{align*}
\]

**Scheme 1.** Transesterification reaction.

2.4 **NMR Analysis of the Transesterification Products**

The substances obtained after the transesterification 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.

2.5 **Design of Experiment**

Optimization was performed to evaluate the optimum conditions needed to prepare the catalyst with high amount of basic sites needed. In the modification process, experiments were performed randomly in order to prevent systematic error. Response Surface Methodology Box–Behnken Design (RSM-BBD) was used to study the effects of the variables on response because it covers entire design space at minimum number of experimental runs [14,15].

The amount of basic sites was evaluated to analyze the effect of three variables; potassium loading, X1 (0-15 % (wt)), calcination temperature, X2 (300-800 °C) and time, X3 (3-6 hours) at three numeric factors levels on the response, basic sites. Based on the design, a total number of 17 experiments with 5 center points were obtained. The experiments were then carried-out at random and the yield was compared against the predicted.

2.6 **Statistical Analysis and Model Fitting**

Statistical software Design Expert 7.1 was used. Second order full factorial equation was 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 were 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 ≤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.

\[
Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon
\]  

(1)

Where,

- \(Y\) is the response factor (molar yield of ‘‘biodiesel’’ reaction),
- \(x_i\) the \(i\)th independent factor,
\[ \beta_o \] the intercept;
\[ \beta_i \] the first order coefficient of the model;
\[ \beta_{ii} \] the quadratic coefficient of \( i \) factor;
\[ \beta_{ij} \] the linear coefficients of the model for interaction between \( i \) and \( j \) factors; and
\[ \epsilon \] the experimental error [24].

3. Results and Discussions
In this research, zinc oxide was modified with KOH by wet impregnation, the catalysts prepared were characterized by XRD and basic back titration method. BBD experimental design was used to evaluate the effect of catalyst modification process variables on the response basic sites. The transesterification was carried out and the results are presented as follows.

3.1 Basic Strength Sites Back Titration 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 metal oxides [17]. All KOH-modified ZnO sample have higher basic sites compared to the pure calcined ZnO samples. The combination of KOH with calcination temperature increases the basic strength of the catalysts. This occurs as a result of interaction of potassium with zinc oxide at high temperature which became adsorbed to form K-ZnO single phase and improve its basic strength. In contrast, calcination at low temperatures does not significantly improve the basic sites due to inability of the potassium to strongly adsorb on ZnO surfaces. The result also showed that, at optimum conditions, the use of KOH above 9 % did not cause significant increase in basic sites. This indicates that, the basic sites came from the modified catalyst and not from the KOH itself. This is in agreement with the results of KOH modified CaO [16] and K/MgO [18], which reported neither increased basic sites nor catalytic performance and higher amount of KOH and better K-Mg surface interactions 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. The summary of basic sites result is given in Table 1.

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

3.2 X-Ray Powder Diffraction (XRD) Analysis
The XRD analysis was carried out to investigate the presence of K2O in the ZnO crystal phase. The spectra in Figure 1 indicates hexagonal wurtzite zinc oxide, zincite with reference number 01-075-1526. The three most intense peaks appeared at the \( 2\theta = 36.53 \) (101), 32.07 (100) and 34.46 (002) respectively. Others are \( 2\theta = 47.79 \) (102), 57.16 (110), 63.10 (103), 67.07 (200), 68.49 (112) and 69.77 (201) [19]. The K2O peaks could be observed at \( 2\theta = 28, 31, 33, \) and 51° [7,16,20]. In the XRD spectra obtained from 8.5% K- modified ZnO, the presence of K2O could be observed. The intensity of K2O peaks is weak due to low concentration of K on the surface and does not increase with the amount of KOH used, suggesting fine deposition of K on to the crystalline lattices of the ZnO. It also indicate 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. In all the KOH-modified ZnO catalysts, ZnO peak intensities remain approximately the same indicating that there was no increase in crystallite size when the K is attached to the ZnO crystalline lattice.
3.3 Result of Basic Sites Experimental Design and Statistical Analysis

For basic sites evaluation, three factors at three levels BBD was used in the optimization of the process variable; KOH loading ($X_1$), calcination temperature ($X_2$) and time ($X_3$) on the response basic sites. A total of 17 experiments were randomly performed to avoid systematic error and the experimental results were compared with the predicted responses as presented in Table 2 and Figure 2. The final quadratic Equation 2 that explain the mathematical relation of the independent variables; $X_1$, $X_2$ and $X_3$ with the response, basic sites was obtained as

$$Y = 7.70 + 2.40X_1 - 0.73X_2 + 0.37X_3 - 0.79X_1X_2 - 0.70X_1X_3 + 0.37X_2X_3 - 2.10X_1^2 - 1.94X_2^2 - 1.84X_3^2 \quad (2)$$

### Table 2. BBD with corresponding experimental results for the basic sites.

| Run | KOH Load ($X_1$) | *Calc. Temp ($X_2$) | *Calc. Time ($X_3$) | *Exp. Basic Sites (mmol/g) | *Pred. Basic Sites (mmol/g) |
|-----|------------------|---------------------|---------------------|---------------------------|-----------------------------|
| 1   | 0.00             | 550.00              | 6.00                | 1.66                      | 1.68                        |
| 2   | 0.00             | 550.00              | 3.00                | 1.04                      | 1.03                        |
| 3   | 15.00            | 800.00              | 4.50                | 4.56                      | 4.53                        |
| 4   | 7.50             | 550.00              | 4.50                | 7.57                      | 7.70                        |
| 5   | 7.50             | 300.00              | 6.00                | 3.96                      | 3.90                        |
| 6   | 0.00             | 300.00              | 4.50                | 1.16                      | 1.19                        |
| 7   | 15.00            | 300.00              | 4.50                | 7.53                      | 7.57                        |
| 8   | 7.50             | 550.00              | 4.50                | 7.63                      | 7.70                        |
| 9   | 7.50             | 550.00              | 4.50                | 7.85                      | 7.70                        |
| 10  | 15.00            | 550.00              | 3.00                | 7.24                      | 7.21                        |
| 11  | 7.50             | 550.00              | 4.50                | 7.72                      | 7.70                        |
| 12  | 7.50             | 800.00              | 3.00                | 3.12                      | 3.18                        |
| 13  | 7.50             | 300.00              | 3.00                | 5.40                      | 5.38                        |
| 14  | 15.00            | 550.00              | 6.00                | 5.08                      | 5.09                        |
| 15  | 0.00             | 800.00              | 4.50                | 1.36                      | 1.32                        |
| 16  | 7.50             | 550.00              | 4.50                | 7.73                      | 7.70                        |
| 17  | 7.50             | 800.00              | 6.00                | 3.17                      | 3.19                        |

*Calc.= calcination  *Exp.= experimental  *Pred.= predicted
In order to validate the model, analysis of variance was used and its summary presented in Table 3. The model F-value of 1438.50 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 < 0.001 obtained indicates that all the model terms are significant. The “lack of fit” F-Values of 0.42 also implies that this factor is not significant. The R²-value 0.9995 obtained for the model is very high. There is also a good agreement between the predicted R²-value of 0.9988 and the adjusted R²-value of 0.9973. Thus, the above analysis indicates that this predicted quadratic model is in good agreement with the experimental responses and it can be adopted.

Table 3. Analysis of variance (ANOVA) for the basic sites modification process.

| Source   | SS   | DF | MS      | F        | P       | Comment     |
|----------|------|----|---------|----------|---------|-------------|
| Model    | 110.92 | 9  | 12.32   | 1438.50  | < 0.0001 | Significant |
| X₁       | 46.03  | 1  | 46.03   | 5372.64  | < 0.0001 | Significant |
| X₂       | 4.26   | 1  | 4.26    | 497.58   | < 0.0001 | Significant |
| X₃       | 1.07   | 1  | 1.07    | 125.25   | < 0.0001 | Significant |
| X₁X₂     | 2.51   | 1  | 2.51    | 293.22   | < 0.0001 | Significant |
| X₁X₃     | 1.93   | 1  | 1.93    | 225.51   | < 0.0001 | Significant |
| X₂X₃     | 0.56   | 1  | 0.56    | 64.78    | < 0.0001 | Significant |
| X₁²      | 18.61  | 1  | 18.61   | 2172.38  | < 0.0001 | Significant |
| X₂²      | 15.93  | 1  | 15.93   | 1859.10  | < 0.0001 | Significant |
| X₃²      | 14.29  | 1  | 14.29   | 1668.32  | < 0.0001 | Significant |
| Residual | 0.060  | 7  | 0.008568|          |          |             |
| Lack of fit | 0.014  | 3  | 0.004792| 0.42     | 0.7488  | Not Significant |
| Pure error | 0.046  | 4  | 0.011   |          |          |             |
| Total    | 110.98 | 16 |         |          |         |             |

SS: sum of squares; DF: degree of freedom; F: f-value; P: p-value

3.4 Effect of KOH loading
KOH loading is the single most important factor in this analysis and it has a positive linear effect on the response basic sites in the modification process as can be observed in Equation 3 and Table 3. From the 3D graphical plot Figures 3 (a and b), it can be seen the KOH loading has slight negative interaction effect with both higher calcination temperature and time. This is due higher temperature and prolonged heating causes aggregation of the particles and decreased surface area and active sites.
It also shows negative intermediate quadratic effect in the general process. In both interactions, the KOH loading leads to higher response, though its increase peaks at about 7.5 % KOH loading at 550°C and 5 hours and starts decreasing as the temperature and time are increased to higher than their mean values. It shows that the optimum amount needed for the modification should not exceed 11.25 %, above which it become waste.

3.5 Effect of Calcination Temperature
Temperature is the second important factor in this modification process as can be observed in Equation 3 and Table 3. The heat is necessary to provide the energy needed to properly adsorb and disperses potassium on the ZnO crystalline structures. From the 3D plot in Figures 3 (b and c), it can be observed that higher temperature has a negative quadratic effect on the modification process. There was increase in the response basic sites as the calcination temperature is raised up to 550°C. Above that, the quadratic effect become negative causing a significant decrease of the response, basic sites. This is due to the decomposition of active substance, K₂O at higher temperatures and possibility of annealing the particles to become large with decreased active sites.

3.6 Effect of Calcination Time
In this modification process, calcination time is the third important factor as can be observed in Equation 3 and Table 3. Adequate time is needed for effective modification, less time does not enable the active substance to adsorb and when time is prolonged there is possibility of its decomposition or annealing to occur. From the 3D plot in Figures 3 (a and c), it can be observed that it has negative interaction with both KOH loading and temperature at higher values. Its quadratic effect on the modification process is also negative. There was increase in the response basic sites as the calcination time is raised up to 4.50 hours. Above that, the quadratic effect become negative causing a significant decrease of the response, basic sites. This is due to the decomposition of active substance, K₂O as calcination time become longer. The residence calcination time can also cause annealing the particles to become larger with decreased active sites.

3.7 Optimization of Basic Sites Modification
Optimal values of the modification variables were obtained by solving the quadratic equation at maximum basic sites criterion. Considering these parameters (X₁ = 8.68, X₂ = 479.71, X₃ = 4.23 and Basic sites = 8.14) repeated experiments were performed under similar conditions. Experimental value of 7.64 mmol/g was obtained which in good agreement with the predicted value of 8.14 mmol/g and this KOH modified ZnO catalyst chosen in the of transesterification process.
3.8 Results of HNMR Biodiesel Analysis

Biodiesel was prepared from ZnO and KOH-modified ZnO at 65°C, 3 hrs and 9:1 methanol to oil ratio. The samples were characterized by $^1$HMR for both qualitative and quantitative analysis. The disappearance of methoxy triglyceride protons peak at $\delta = 4.3$ ppm and formation of fatty acid ester methoxy protons peak at $\delta = 3.67$ ppm as shown in Figure 4 indicated the formation of biodiesel while the ratio of the $\delta = 3.67$ ppm methoxy protons of biodiesel with $\delta = 2.3$ 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 $\delta = 2.3$ ppm with that of methoxy protons present in the fatty acid methyl esters of the biodiesel which appears at $\delta = 3.67$ppm ($A_2$) [21,22]. A percent conversion of 95.53 % was observed, which shows a very good conversion compared to other heterogeneous catalysts.

\[
\%Yield = \frac{A_1}{A_2} \times 100\% \tag{3}
\]
Figure 4. NMR Spectra of 95.53% biodiesel prepared under optimized conditions of catalyst loading = 5%, temperature = 65 °C, time = 3 hrs mins and MOR = 9.

3.9 Catalyst Leaching
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 [16,23]. The optimized catalyst and methanol were 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 3 hours at 65 °C and only about 4.30% of FAME yield of about was observed. This is showing 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-ZnO catalyst.

4. Conclusion
In order to conserve energy and improve sustainability, a model was developed for optimum conditions of catalyst modification process which provided stable catalyst with improved basic sites. Rice bran oil which is mainly wasted in the farms was used in the transesterification and high conversion to biodiesel was obtained. The catalyst leaching is not significant and so the process is heterogeneously catalyzed and environmental friendly.

References
[1] Khan, T.M.Y., Atabani, A.E., Badruddin, I.A., Badarudin, A., Khayoon, M.S., and Triwahyono, S. (2014) Recent scenario and technologies to utilize non-edible oils for biodiesel production. Renewable and Sustainable Energy Reviews, 37, 840–851. Elsevier.
[2] Yan, S., Mohan, S., Dimaggio, C., Kim, M., Ng, K.Y.S., and Salley, S.O. (2010) Long term activity of modified ZnO nanoparticles for transesterification. Fuel, 89, 2844–2852. Elsevier Ltd.
[3] Yoo, S.J., Lee, H.-S., Veriansyah, B., Kim, J., Kim, J.-D., and Lee, Y.-W. (2010) Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts. Bioresource technology, 101, 8686–9. Elsevier Ltd.

[4] Wan, L., Liu, H., and Skala, D. (2014) Environmental Biodiesel production from soybean oil in subcritical methanol using MnCO3/ZnO as catalyst. “Applied Catalysis B, Environmental,” 152-153, 352–359. Elsevier B.V.

[5] Baskar, G. and Aiswarya, R. (2015) Biodiesel production from waste cooking oil using copper doped zinc oxide nanocomposite as heterogeneous catalyst. BIORESOURCE TECHNOLOGY. Elsevier Ltd.

[6] Liao, C.-C. and Chung, T.-W. (2013) Optimization of process conditions using response surface methodology for the microwave-assisted transesterification of Jatropha oil with KOH impregnated CaO as catalyst. Chemical Engineering Research and Design, 91, 2457–2464. Institution of Chemical Engineers.

[7] Takase, M., Zhang, M., Feng, W., Chen, Y., Zhao, T., Cobbina, S.J., Yang, L., and Wu, X. (2014) Application of zirconia modified with KOH as heterogeneous solid base catalyst to new non-edible oil for biodiesel. ENERGY CONVERSION AND MANAGEMENT, 80, 117–125. Elsevier Ltd.

[8] Patil, P.D., Gude, V.G., and Deng, S. (2009) Biodiesel Production from Jatropha Curcas, Waste Cooking, and Camelina Sativa Oils. Industrial & Engineering Chemistry Research, 48, 10850–10856.

[9] Gunawan, S., Maulana, S., Anwar, K., and Widjaja, T. (2011) Rice bran, a potential source of biodiesel production in Indonesia. Industrial Crops and Products, 33, 624–628. Elsevier B.V.

[10] Sun, Y., Ponnusamy, S., Muppaneni, T., Reddy, H.K., Patil, P.D., Li, C., Jiang, L., and Deng, S. (2014) Optimization of high-energy density biodiesel production from camelina sativa oil under supercritical 1-butanol conditions. Fuel, 135, 522–529. Elsevier Ltd.

[11] Mahdavi, V. and Monajemi, A. (2014) Optimization of operational conditions for biodiesel production from cottonseed oil on CaO–MgO/Al2O3 solid base catalysts. Journal of the Taiwan Institute of Chemical Engineers, 45, 2286–2292. Taiwan Institute of Chemical Engineers.

[12] Sánchez, M., Navas, M., Ruggera, J.F., Casella, M.L., Aracil, J., and Martínez, M. (2014) Biodiesel production optimization using γAl2O3 based catalysts. Energy, 73, 661–669.

[13] Veiga, P.M., Luna, A.S., de Figueiredo Portilho, M., de Oliveira Veloso, C., and Henriques, C.A. (2014) Zn,Al-catalysts for heterogeneous biodiesel production: Basicity and process optimization. Energy, 75, 453–462.

[14] Nazwanie, W., Abdullah, W., Azelee, W., Abu, W., Wan Abdullah, W.N., Wan Abu Bakar, W.A., Ali, R., and Embong, Z. (2014) Oxidative desulfurization of commercial diesel catalyzed by tert-butyl hydroperoxide polymolybdate on alumina: optimization by Box-Behnken design. Clean Technologies and Environmental Policy, 433–441.

[15] Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A., and Pokomeda, K. (2014) Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. Bioresource technology, 160, 150–60. Elsevier Ltd.

[16] Kumar, D. and Ali, A. (2012) Nanocrystalline K–CaO for the transesterification of a variety of feedstocks: Structure, kinetics and catalytic properties. Biomass and Bioenergy, 46, 459–468. Elsevier Ltd.

[17] Singh, A.K. and Fernando, S.D. (2009) Preparation and Reaction Kinetics Studies of Na-based Mixed Metal Oxide for Transesterification. Energy & Fuels, 9, 5160–5164.
[18] Querini, C., Cornaglia, L., Ulla, M., and Miró, E. (1999) Catalytic combustion of diesel soot on Co,K/MgO catalysts. Effect of the potassium loading on activity and stability. Applied Catalysis B: Environmental, 20, 165–177.

[19] Hariharan, C. (2006) Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited. Applied Catalysis A: General, 304, 55–61.

[20] Mutreja, V., Singh, S., and Ali, A. (2014) Potassium impregnated nanocrystalline mixed oxides of La and Mg as heterogeneous catalysts for transesterification. Renewable Energy, 62, 226–233. Elsevier Ltd.

[21] Guzmán-vargas, A., Santos-gutiérrez, T., Lima, E., Flores-moreno, J.L., Oliver-tolentino, M.A., and Martínez-ortiz, M.D.J. (2015) Efficient KF loaded on MgCaAl hydrotalcite-like compounds in the transesterification of Jatropha curcas oil. Journal of Alloys and Compounds, 1–6.

[22] Kaur, N. and Ali, A. (2015) Lithium zirconate as solid catalyst for simultaneous esterification and transesterification of low quality triglycerides. “Applied Catalysis A, General,” 489, 193–202. Elsevier B.V.

[23] Chen, J., Jia, L., Guo, X., Xiang, L., and Lou, S. (2014) Production of novel biodiesel from transesterification over KF-modified Ca–Al hydrotalcite catalyst. RSC Adv., 4, 60025–60033.

[24] Thirugnanasambandham, K., Sivakumar, V., Maran, J.P., and Kandasamy, S. (2014) Chitosan based grey wastewater treatment — A statistical design approach. Carbohydrate Polymers, 99, 593–600. Elsevier Ltd.