CHEMICAL ENGINEERING TRANSACTIONS
VOL. 56, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216
DOI: 10.3303/CET1756255

Production of Biodiesel from Palm Oil using Chemically Treated Fish Bone Catalyst

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The waste food material namely fish bone is screened for biodiesel synthesis by transesterification reaction to achieve the highest biodiesel yield. The fish bone was chemically treated with $Al(NO_3)_3.9H_2O$ to enhance the biodiesel yield. The solid oxide materials were calcined at 900 °C for 2 - 4 h to convert $CaCO_3$ to CaO species. Transesterification was carried out at 65 °C for 4 h with 12 : 1 methanol to oil ratio. The experiment was designed by central composite design with 2^3 factorial and three centre points to determine the optimum CaO (calcined fish bone) loading, calcination time for catalyst and amount of chemically treated fish bone, wt%. The highest yield of 94.30 wt% was achieved at optimal conditions of calcination time (6.11 h), catalyst loading wt% of (4.02 wt%) and CaO (calcined fish bone) loading of (34.49 %).

1. Introduction

In recent years, there has been a massive depletion in the renewable energy resources. The petroleum shortage is the major concern growing among the researchers as it will be completely depleted in the future generations. With the increase in depletion of petroleum along with the increase in prices and major environment pollution created by fossil fuel ignition, researchers have grown keen interest for alternative fuels. Over the past few years, biodiesel has grabbed consciousness as means of alternative fuel, mainly because of its environment friendly features like it is highly degradable, no toxicity, carbon monoxide emission is low, particulate matter and unoxidised hydrocarbons (Al-Zuhair, 2007).

Biodiesel can be developed from vegetable oils, animal fat, and recycled grease which is produced from outlets like homes, restaurants and food industry. Generally the most suitable feedstocks for production of biodiesel are palm oil, sunflower oil, rapeseed oil and soybean oil (Ma and Hanna, 1999). Biodiesel is produced from triglyceride transesterification which is the major constituent of vegetable oils or animal fats in the presence of an alcohol (Jazie et al., 2013).

Utilisation of a homogeneous catalyst for biodiesel production increases the entire cost of the production (Hillion et al., 2003). A process which is mild, environment friendly and also cost-efficient at the same time is required for biodiesel production and glycerol of a high quality (Jazie et al., 2013).

Numerous attempts for production of chemical catalysts have been made, which eventually turned out to be quite costly. Taking in consideration factors like the cost, product quality, and its development, cheaper sources have been explored. Sources of waste have been selected such as chicken bone and shells (oyster, egg, golden apple snail, mud crab, meretrix venus and mollusk) as rich sources of CaO which are wastes and can be utilised as heterogeneous catalyst for production of biodiesel (Jazie et al., 2013). Synthesis of catalysts if done by these waste materials can further eradicate waste and at the same time produces cost effective catalysts. This study is focusing on producing catalyst which is heterogeneous and low toxic by using waste resources. This study also investigates the optimum conditions for maximum yield of biodiesel by reducing the costs and pollution as compared to that of petroleum and diesel.

Please cite this article as: Sulaiman S., Shah B., Jamal P., 2017, Production of biodiesel from palm oil using chemically treated fish bone catalyst, Chemical Engineering Transactions, 56, 1525-1530 DOI:10.3303/CET1756255

2. Materials and methods

2.1 Materials and catalyst preparation

Palm oil was obtained from a local supermarket nearby. The analytical grade methanol (Merck) was used in the trans-esterification process. Fish bones were collected from a nearby food outlet and cleaned with running water. It is left overnight in a hot air oven at 60 °C. The fish bone was crushed to powder form in a pestle and mortar transferred in a crucible and placed in the furnace at 900 °C for 2-4 h to transform $CaCO_3$ to CaO. The catalyst was kept in a desiccator to avoid the reaction with air prior to further usage. Chemical loading was done by adding 9 g of $[Al(NO_3)_3].9H_2O]$ in varied amount of catalyst at 20 w/w%, 30 w/w% and 40 w/w% and 66 mL of deionised water to prepare the required calcined fish bone loading. The solution is mixed vigorously for 1 h and basicity of the solution is adjusted by dropwise addition of NH_4OH to facilitate precipitation of metal precursors, the solution is aged for 24-48 h in hot air oven at 60 °C to remove excess water completely (Chakraborty and Bekari, 2012). The precipitated catalyst is then calcined at 800 °C for 3 - 9 h to prepare fish bone treated with aluminum nitrate. The catalyst optimised by RSM was further validated and analysed for reusability.

2.2 Transesterification reaction

The transesterification was carried out in a 250 mL conical flask. 50 mL of palm oil with methanol to oil ratio (12 : 1) was taken in the flask. The flasks were then placed in a shaker at 65 °C, 500 rpm for 4 h. Catalyst loading wt% is the amount of treated catalyst added during transesterification. Upon the reaction completion, the catalyst was separated from biodiesel product by centrifugation at 6,000 rpm for 10 min. The biodiesel separated from the catalyst was then transferred into a separator funnel to allow the glycerol to settle down overnight. The settled glycerol was discarded and the upper biodiesel layer was collected. The fatty acid alkyl esters of the biodiesel produced were analysed using GC/MS (Agilent technologies 7890A gas chromatography equipped with 5975C mass spectrometer) to identify the formation of FAME. The operation of GC/MS was run with a split-splitless mode of injection; the capillary column was DB-wax with a length of 30 m, thickness of film was 0.25 µm and 0.25 mm internal diameter.

The carrier gas used in the procedure was helium at a flow rate 30 mL/min, measured at 50 °C; for 35 min. Then the temperature increased to 235 °C at a rate of 4 °C/min and held for 5 min. The sample was then diluted with 4900 µL n-hexane, in 100 µL of biodiesel. 1mL of sample was then transferred in GC vial. The yield of biodiesel produced was then calculated by the Eq(1) (Nasaruddin et al., 2014)

$$Total\ yield\ of\ biodiesel\ (\%w/w\ Palm\ \ oil) = [(weight.of\ biodiesel)/(weight\ of\ palm\ oil\ )]\ \times (100) \qquad (1)$$

2.3 Central composite design

The central composite design was employed to determine the effect of various process conditions. The three variables were calcined fish bone (20 - 40 %), calcination time (3 - 9 h) and catalyst loading (2 - 6 wt%). Each variable has three different levels ranging from low (-1), to medium (0), to high (+1). The yield of biodiesel (%) produced by transesterification of palm oil were used as responses in the RSM. The developed regression model was evaluated by analysing the values of regression co-efficient and analysis of variance (ANOVA) to find the significance of each coefficient. The significance of fit of the quadratic polynomial was determined by the R^2 (coefficient of determination). The correlation between the observed and predicted values, depends on the value of R^2, the closer the value is to 1 the better is the R^2. The central composite design gave 20 runs, for transesterification of palm oil to biodiesel.

3. Results and discussion

3.1 Statistical optimisation of biodiesel production

The RSM optimisation based on central composite design established a complete design matrix, with both the experimental and predicted values obtained for yield response at different points provided by the design are shown in Table 1.

Biodiesel yield obtained ranged from 70.5 % to 95.9 %. The analysis of significant factors was done by identifying the significant factors in the regression model developed by CCD. Design-Expert software suggested quadratic model as the best model which is selected on the basis of sequential model sum of squares, the best model was selected based on the highest order polynomial where the additional terms were significant and the model was not aliased (Hameed et al., 2009). The model equation based on coded values (A, B and C as calcination time, catalyst loading wt% and calcined fish bone) for biodiesel yield was expressed by Eq(2).

$$Biodiesel\ Yield\ (\%) = 92.36 + 0.67A + 0.82B + 3.59C - 2.63A^2 - 6.58B^2 - 3.93C^2 - 0.80AB - 1.05AC - 1.40BC \quad (2)$$

In Eq(2) the positive sign before the terms specifies synergistic effect, whereas negative sign specifies antagonistic effect. The value of correlation coefficient evaluates quality of the model developed (Ahn et al., 2008). The significance of the quadratic model and the interaction of parameters on the responses were determined by statistical analysis of variance (ANOVA).

The significance of each regression coefficient, which also signifies the interaction effect of each cross product is checked by the probability of error value (p-value) (Jazie et al., 2013). The probability value is 0.0002 which indicates that the model is significant. The value of R^2 is 0.9261 which indicates that the model is significant and that there are satisfactory correlations between each of the variables. It is observed that the value of predicted R^2 and adjusted R^2 are in agreement with each other. This signifies that the response fits well with the model. The Table 2 represents ANOVA results for biodiesel yield.

Table 1: Experimental design using RSM for statistical optimisation of process conditions

Run	Input Variables			Experimental biodiesel yield (%)	Predicted biodiesel yield (%)
	A	B	C		
	Calcination time (h)	Catalyst loading wt%	Calcined fish bone (%)		
1	6	4	30	93.2	92.36
2	6	4	30	92	92.36
3	6	4	30	95.9	92.36
4	3	6	40	84.67	83.40
5	9	6	40	82.2	81.06
6	6	4	30	93.5	92.36
7	9	6	20	78.9	78.78
8	6	4	40	88.3	92.02
9	3	2	20	70.5	70.90
10	6	4	30	94	94.60
11	9	2	20	75.4	75.93
12	3	6	20	77	76.94
13	6	4	30	91.5	92.36
14	9	4	30	89	90.41
15	6	2	30	84.6	84.97
16	3	2	40	83.6	82.98
17	6	4	20	85.6	84.85
18	6	6	30	84	86.60
19	3	4	30	87.5	89.06
20	9	2	40	84.5	83.82

Table 2: ANOVA of quadratic model for biodiesel yield

Source	Sum of Squares	F - Value	Prob > F	Remarks
Model	818.3643	18.9311	< 0.0001	significant
A	4.5293	0.9430	0.3544	-
B	6.6749	1.3897	0.2657	-
C	128.6657	26.7876	0.0004	-
A^2	19.0018	3.9561	0.0747	-
B^2	119.0158	24.7785	0.0006	-
C^2	42.4440	8.8366	0.0140	-
AB	5.0721	1.0560	0.3283	-
AC	8.7571	1.8232	0.2067	-
BC	15.7641	3.2820	0.1001	-
Lack of Fit	35.8168	2.9322	0.1314	not significant

R^2 = 0.9446, adjusted R^2 = 0.8947, CV = 2.55, Adequate precision = 13.847, predicted R^2 = 0.7441

3.2 Yield of biodiesel on the basis of independent variables

Figure 1 shows that all the input factors i.e. calcined fish bone loading; catalyst loading wt% and calcination time, providing the highest yield are within range. The highest conversion of palm oil to biodiesel can be observed from the contours and 3D curves. A strong interaction was observed between chemically treated catalyst wt% and calcination time in Figure 1, due to the elliptical shape of the graph. It is observed that with the increase in catalyst wt% with respect to calcination time the yield of biodiesel increased. However, further increase of catalyst resulted in a decrease of yield which can be justified by problems in diffusion during reaction and hence hindering the action of the catalyst. Romero et al. (2011) stated that with further increase in calcination time of 4 h the catalytic activity of the catalyst was inversely suppressed (Romero et al., 2011). The extended treatment process would cause the shrinkage of the catalyst and therefore lowering the size of the particle (Viriya-Empikul et al., 2010). Yield of 94.30 wt% is achieved at optimal conditions of calcination time (6.11 h) and catalyst loading wt% of (4.02 wt%). Figure 2, the interaction between calcined fish bone loading and calcination time indicates a weak interaction between the two parameters. An increase in calcined fish bone loading with respect to calcination time increased the yield of biodiesel. In Figure 3 the most significant interaction was that of chemically treated catalyst wt% and calcined fish bone loading, the yield of biodiesel had an increase with the increase in both the factors, however when the catalyst wt% reached up to 4 wt% approximately, the yield of biodiesel decreased. The result was in compliance with the study done by Asri et al. (2012).

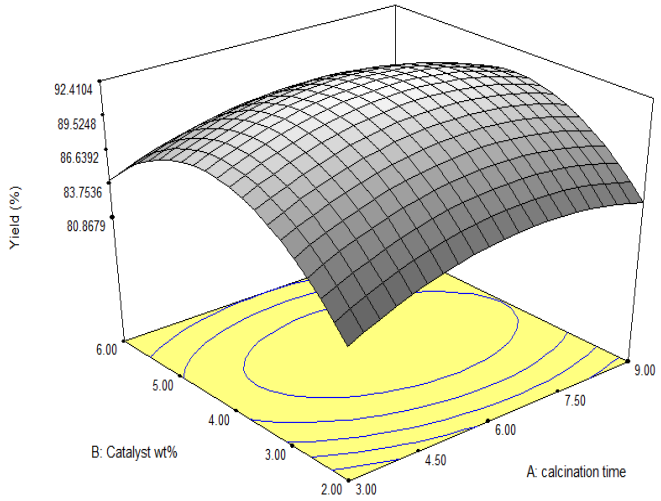

Figure 1: The 3D response surfaces above represent the interaction between catalyst loading wt% and calcination time

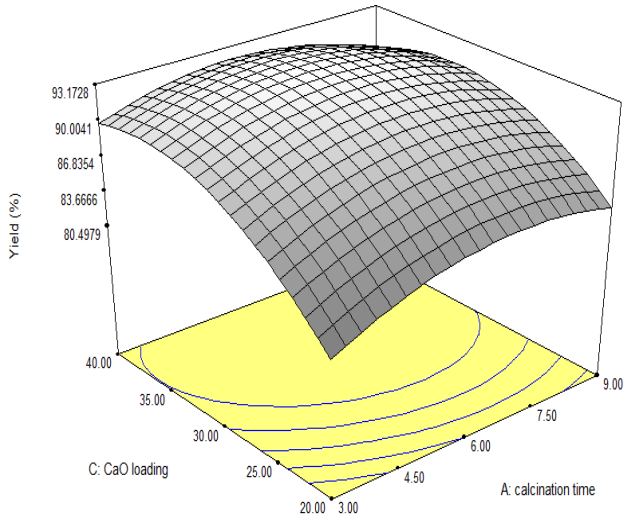

Figure 2: The 3D response surfaces above represent the interaction between CaO loading (calcined fish bone) and calcination time

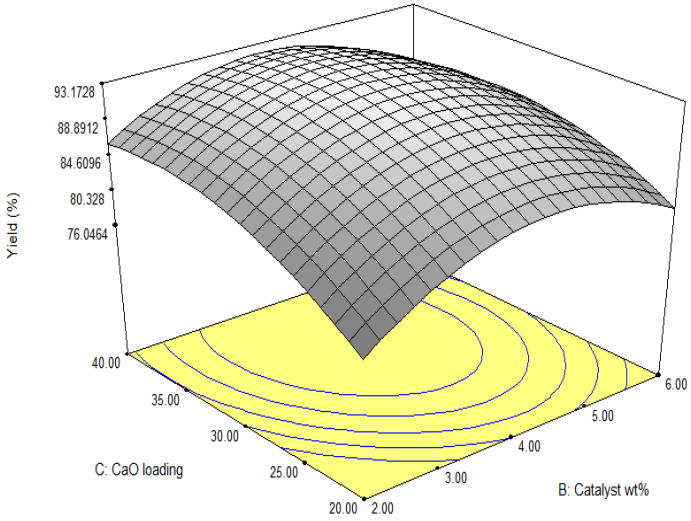

Figure 3: The 3D response surfaces above represent the interaction between CaO loading (calcined fish bone) and catalyst loading wt%

3.3 Validation of biodiesel

The optimum process conditions as suggested by the RSM model were then applied for validation and were performed in triplicate. It was observed that the percentage errors between the predicted responses, 93.18 % and the experimental responses, 94.10 % are quite small, 1.2 %. The optimal conditions for the chemically treated fish bone were calcination time of 6.11, catalyst loading wt% of 4.02 wt% and CaO (calcined fish bone) loading of 34.49 % where 94.30 % of biodiesel were achieved. Aworanti et al. (2013), also observed an experimental value of biodiesel yield of 94.10 %, from pure CaO and a predicted yield value of 94.15 % (Aworanti et al., 2013). The model is reliable and applicable for optimisation of high yield conversion of biodiesel.

4. Conclusions

This study concluded that highly active solid catalysts were obtained by calcining fish bone. Fish bone as a source of CaO has opened up new roads for employing heterogeneous basic catalyst in biodiesel production. There was also a slight increase from 87.2 % to 95.9 % in the yield of biodiesel by chemically treating the calcined catalysts. The optimal conditions for the chemically treated catalysts by calcining fish bone were calcination time of 6.11, catalyst loading wt% of 4.02 wt% and CaO (calcined fish bone) loading of 34.49 %.
This study concluded that highly active solid catalysts were obtained by calcining waste food materials. Fish bone as a source of CaO has opened up new roads for employing heterogeneous basic catalyst in biodiesel production. There was also a sharp increase from 87.2 % to 95.9 % in the yield of biodiesel by chemically treating the calcined catalysts. The optimal conditions for the chemically treated catalysts by calcining fish bone were calcination time of 6.11, catalyst wt% of 4.02 wt% and CaO (calcined fish bone) loading of 34.49%.

Acknowledgments

This research is funded by FRGS grant (FRGS 13-079-0320) and RAGS (RAGS 12-047-0047) grants from Government of Malaysia.

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