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Reaction Of Waste Cooking Oil With Methanol Using Nano-Mgo/Ac As Catalyst: Optimization Of Relevant Variables By Response Surface Methodology

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Abstract: Optimization of the relevant variables that affect the reaction of waste cooking oil feedstock with the newly developed heterogeneous catalyst (MgO/AC), using a response surface methodology (RSM), was successfully achieved. There were three relevant variables that were optimize, the ratio of methanol to oil, concentration of catalyst and the reaction time. Minitab 17 software was used to design the experiment, one replication was done for randomizes eleven runs. As the two different nano MgO/AC were used as catalyst, (A.10% at 500°C and B. 30% at 400°C) each of them used the same design of the experiment. As the fit linear model shows the interaction, prediction and optimization reported the optimum condition for the reaction using the two catalyst were, methanol to oil ratio 8:1, reaction time 3hrs and the variable that was not significant to the model, concentration of catalyst, for catalyst A. While the optimum condition for the reaction using catalyst B were: methanol to oil ratio 8:1, concentration of catalyst 0.5% and reaction time 1.5hrs. As the validity was done the predicted yield with the given optimum condition, the value of concentration of catalyst used was 1.5% for the reaction using catalyst A and the other factor that remained constant for both model: temperature 65°C and agitation speed at 600 rpm without purification process after the separation period. The yield that obtained from the validation for predicted yield of catalyst A and B were 92.30% and 98.86% respectively. Unfortunately, the product that was produce, the upper layer, from the reaction using the two different nano MgO/AC were not a biodiesel based from the result of FAME content by Gas chromatography (PNS EN 14103:2003).

Keywords: Optimization; Waste Cooking Oil; nano-MgO/AC; Response Surface Methodology

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1. Introduction

Waste cooking oil (WCO) is an environmental problem all over the world due to the improper disposal. Some researcher uses it as raw material to a biomass. Those used oil (waste cooking oil or recycle oil) have a variety of qualities and properties that are differ to clean oil (Leung et al., 2006). Reaction of waste cooking oil to a methanol such as methanolysis, transesterification and esterification are some reaction process to produce a useful product for the community and to solve the pollution problem (Ho et al., 2010, Sheinbaum-Pardo et al., 2013).

Optimization is one of the helpful tools in developing and finding an optimal value when a new process, materials and factors considered. Optimization of production condition is very important in a large-scale production process in order to maximize the yield of product and minimize the production cost (Uzun et al., 2012). Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response (output variables) of interest is influenced by several variables (input variables) and the objective is to optimize this response (Chin et al., 2009, Bradley, 2007, Khuri et al., 2010).

Due to the fact that the Philippines has a growing population, increasing of the food consumption, and there with the production of waste cooking oil (WCO). Researchers have conducted a lot of studies of the possible products that can be produce using waste cooking oil, that are usually useful and helpful to the community and environment as well. Waste cooking oil (WCO) is a potential environmental problem all over the world due to improper disposal. Used oil have different qualities and properties that differ to clean oil.

The aims of this study was to determine the optimum of the methanol to oil ratio, concentration of catalyst and the reaction time for this reaction, while the dependent variables were the reaction temperature and agitation speed using the two set-uo of the newly developed heterogeneous catalyst, nano-MgO/AC, 10% loading calcined at 500˚C (Catalyst A) and 30% loading calcined at 400˚C (Catalyst B). Only one replication was done for each optimization process for the two catalysts.

2. Methodology

2.1 Materials, Reagents and Equipment

Waste cooking oil (WCO) collected by Archdiocese of Manila from different houses and donated by the Integrated Research and Training Center (IRTC) for this study. Pure Methanol (AR), purchased from the BELMAN Company. Heterogeneous catalyst specifically nano-MgO/AC reproduced into two at 500˚C, 10% catalyst loading and 400˚C, 30% catalyst loading produced by Cadavero, L. and Baule, A. (2015).

Vacuum pump (Model: Maruto 1984 Testing Machine Co.) with filter paper was used to filter the waste cooking oil and transferred into clean amber bottle. Reaction process, consisted of hot plate/ temperature bath, reaction flask with Pyrex reflux condenser and rpm controlled mechanical stirrer.

2.2 Preparation of Sample

The waste cooking oil sample was filtered first using cheesecloth for about three times and filtered again using vacuum pump (Model: Maruto 1984 Testing Machine Co.) disregarding the impurities present. All pretreated samples were pulled together and from this mixture, samples for specific gravity, acid number, Free Fatty acid and for the reaction were obtained.

2.3 Reaction of Waste Cooking Oil with MeOH

The waste cooking oil was preheated using hot plate until desired temperature of 65˚C was obtained. The methanol and the catalyst were added to the oil. Reaction started along with heating and stirring of the solution. The solution was equipped with reflux condenser to prevent alcohol loss. As the reaction reached the required time, heating and stirring were stopped. The round bottom flask containing the mixture was set aside for twenty-four (24) hours to enhance the

separation. Two distinct liquid phases were formed, the upper layer and the lower layer mixed with some unreacted catalyst and impurities. The separatory funnel was used to remove the upper layer from the lower layer. Obtained products were weighed.

2.4 Design of Experiment (DOE) using Response Surface Methodology (RSM)

Design of Experiment (DOE), Minitab 17 software was used to obtain the Response Surface Methodology (RSM), with three (3) factors, eight (8) runs and three (3) center points with a total runs of eleven. Table 1 shows the three independent variables with its corresponding low and high values, set by the researchers. For methanol to oil ratio the highest value is 8 and 6 for the lowest value. Concentration of catalyst has highest value of 1.50% and 0.50% for its lowest value. Reaction time has the highest value of 3 hours while 1.50 hours for its lowest value.

Table 1. Factor and factor settings

Variables	Low	High
MeOH:Oil	6:1	8:1
Catalyst load (%)	0.50	1.50
Time (hr)	1.50	3.00

Table 2 describes the experimental design, with respect to the upper layer. In this experiment, only one replication was done in each heterogeneous catalyst. The experimental runs were randomized to maximize the observed responses.

2.5. Data Analysis

The results were analyzed using the Design of Experiment in Minitab 17 software where used Response surface methodology (RSM). Using the three parameters to be optimized specifically MeOH:Oil ratio, catalyst concentration (%) and reaction time (hr). Values of the given parameters were inputted at only one replication for each heterogeneous catalyst with a total runs of eleven at a randomized process. At 0.10 confidence level, R^2 value of 88.79% for the catalyst A and 73.03% for catalyst B was determined on the results.

Table 2. The DOE for optimizing MgO/AC transesterification

Std Order	Run Order	MeOH: Oil	Cat Load (%)	Time (hr)
1	1	6:1	0.5	1.5
5	2	6:1	0.5	3
8	3	8:1	1.5	3
3	4	6:1	1.5	1.5
10	5	7:1	1	2.25
7	6	6:1	1.5	3
11	7	7:1	1	2.25
9	8	7:1	1	2.25
6	9	8:1	0.5	3
4	10	8:1	1.5	1.5
2	11	8:1	0.5	1.5

3. Results and Discussion

3.1 Reaction products between WCO and MeOH using the two catalyst

The actual mass of the lower and upper layer were tabulated in Table 4.3 in standard order, for the two catalyst respectively.

3.2 Determination of Relevant Variables affecting the product yield

It can be observed from the plot, figure 1, both non-intersecting (MeOH:oil ratio*catalyst loading and catalyst loading*time) and intersecting (MeOH:oil*time). Non-intersecting lines indicate no effect on the parameter being optimized. Results indicate that of all parameters varied in this study, only MeOH:oil ratio and time has an effect on the yield of upper layer product while catalyst loading has no effect on the yield. This indicates that the catalyst loading only affects the rate of the reaction.

Table 3. 1 Actual mass of the two layer in standard order

Standard order	Catalyst A		Catalyst B	
	M lower layer (g)	M upper layer(g)	M lower layer (g)	M upper layer (g)
1	94.67	66.70	98.30	58.10
2	90.62	84.69	92.50	92.50
3	94.13	59.31	98.80	56.30
4	91.25	77.84	97.70	86.40
5	88.09	62.00	99.00	59.20
6	88.86	95.20	96.80	89.90
7	101.02	59.41	93.50	88.20
8	92.74	89.92	94.50	56.50
9	94.94	73.15	99.70	82.80
10	95.11	79.94	99.30	81.40
11	90.92	84.00	99.50	82.60

Main effects plot for parameters affecting the yield are graphically shown in Figure 2. Main effects plot describe how the changes on one variable affect the yield. In this study, it can be seen that as MeOH:oil ratio is increased, there is an observed increase in the yield of upper layer up to 90%, while for catalyst loading, as the amount of catalyst is increased, the yield decreases very slightly from 70-73%. On the other hand, as the reaction time is increased the yield increases by 77%.

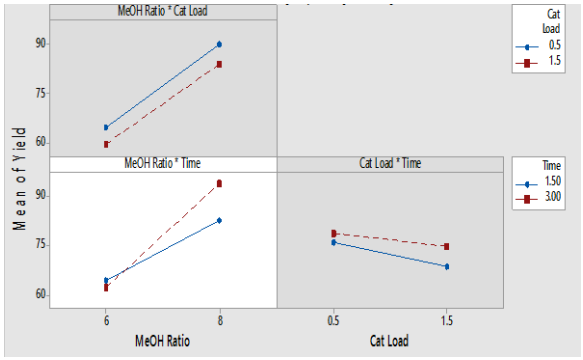

Fig.1 Interaction plots for yield if you change the setting of two factors

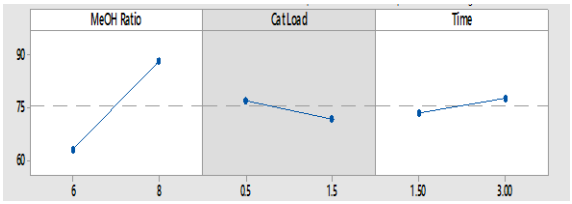

Fig.2 Main affects plots for yield of upper layer

For the catalyst B, figure 3, the plot both intersecting (MeOH:Oil*MeOH:Oil*Time) and non-intersecting (catalyst loading*time). Intersecting lines indicates no effect on the parameter being optimized. Results indicate that of all the parameters varied, both Methanol ratio*Time and Methanol ratio*catalyst loading have an effect on the yield of the product, upper layer, while the catalyst loading and time has no effect on th yield. This indicates that the catalyst loading only affects teh rate of the reaction.

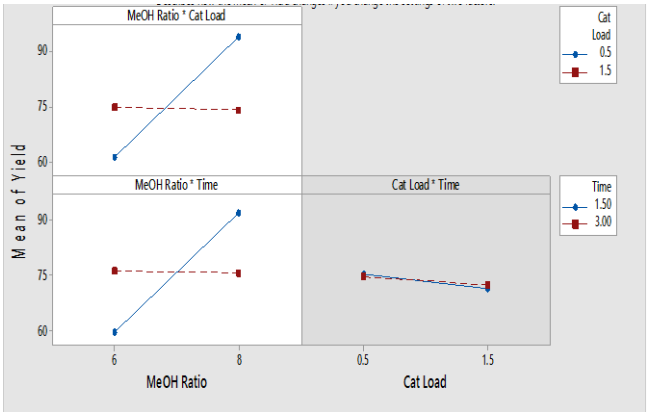

Fig.3 Interaction plots for yield if you change the setting of two factors

Main effects plot for parameters affecting the yield are graphically shown in figure 4. Main effects plot describe how the changes on one variable affect the yield. For this catalyst, MeOH:Oil ratio increased, there is an observed increase in the yield of upper layer up to 87-88%, while the catalyst loading decreased, the yield decrease slightly from 76-74%. On the other hand, as the reaction time is increased, there is no change on the yield of the upper layer.

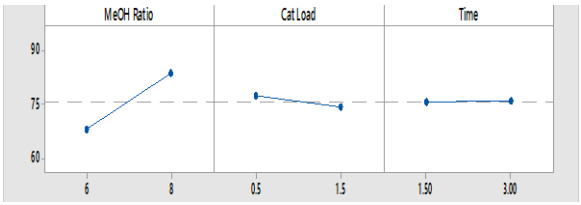

Fig.4 Main affects plots for yield of upper layer

3.3 Determination of Optimal Values

Using RSM in Mnitab 17, optimal values of MeOH:Oil ratio, catalyst loading and reaction time were determined for each catalyst used. The optimal value of catalyst A were: MeOH to oil ratio (8:1) and reaction time is 3hrs, the predicted yield of the upper layer for this is 93.8318% at α=0.05 level of significance. The black line shows the predicted Y(yield) at different settings and the blue lines shows the optimal value. Optimal value were applied and done by three trials using MgO and 10% loading as catalyst A. The value used for the concentration of catalyst was 1.5%, shown in figure 5.

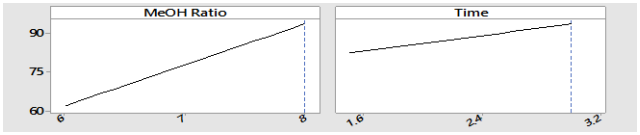

Fig.5 Settings and sensitivity for optimal solution

The optimal value for catalyst B were: MeOH to oil ratio (8:1), concentration of catalyst (0.5%) and the reaction time is 1.5 hrs, the predicted yield was 101.75% at α=0.05 level of significance. The black lines shows the predicted Y (yield) at catalyst B at different settings, and the blue lines indicate the optimal value, shown in figure 6.

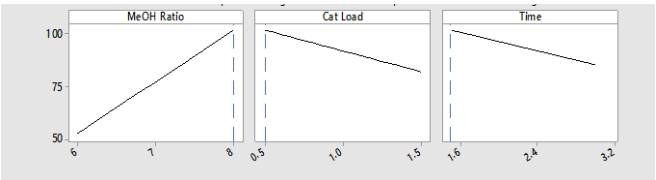

Fig. 6 Settings and sensitivity for optimal solution

4. Conclusion

Reaction of the WCO with MgO/AC (A.10% at 500°C and B. 30% at 400°C) as heterogeneous catalyst was optimized using response surface methodology (RSM). The two heterogeneous catalysts were compared, which of the two was better in optimized the relevant variables affect in the Reaction of waste cooking oil to methanol with heterogenous catalyst. As the study proceed the catalyst B was way better in the two catalysts due to the results of the response surface methodology. The obtained optimal value for catalyst A were: methanol-to-oil ratio (8:1) and reaction time (3hrs), while the third parameter, concentration of the catalyst, was omitted by the model because it was not statistically significant. Based on the optimum setting the yield was reached up to 92%. For catalyst B, the obtained optimal values were: methanol-to-oil ratio (8:1), concentration of catalyst (0.5%) and reaction time (1.5hrs). The yield that was obtained from the optimum setting was reached up to 98%. Despite of the success of the optimization, the result of the FAME content by gas chromatography were no peak for the both catalysts.

Some of the reason why does the catalyst didnt work is due to the amount of impregnated MgO in the Activated Carbon was very small. The loading of the precursors ($Mg(NO_3) \circ 6H_2O$) was according to percent weight with respect to the weight of activated carbon. The formed MgO was based on the loading of the precursors from 10-30% that gives high possibility that the majority the oil reacts with activated carbon. The higher temperature can remove the presence of water, oxygen and carbon dioxide on the surface of basis sites in MgO that handled in air. But there is no inert atmosphere causing the act to decompose.

For further study of this research, the researchers recommend some points that can help to develop and improve this research. One of the thing that the researchers doesn't able to do was to conduct an reaction of the waste cooking with magnesium oxide and test it if the product was really a biodiesel just to confirm that this chemical can really use to produce a biodiesel. In the new develop catalyst, the nano MgO/AC, the researcher

recommend to use a high loading concentration of the magnesium nitrate hexahydrate to impregnation process. Lastly, to identify the content of the upper layer product.

5. ACKNOWLEDGMENT

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