Feasibility of Using Tabagwang Waste Shells as Catalyst in the Production of Biodiesel from Yellow Grease

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Abstract. Heterogeneous catalytic transesterification of yellow grease, commonly known as used cooking oil, utilizing the calcium oxide derived from waste shells of Jagora asperata, locally known as tabagwang, was carried out to produce biodiesel. Waste tabagwang shells were prepared and calcined at 900°C for 4 hours under static air to obtain CaO. The prepared CaO was used as a catalyst in the transesterification of used cooking oil. Reaction conditions such as temperature (45°C and 60°C), catalyst loading (2% and 10%), and methanol-to-oil molar ratio (6:1 and 9:1) were considered to evaluate the feasibility of the catalyst in terms of percent yield. For the given set of parameters, the largest yield of 4.85 mL biodiesel, corresponding to 9.70%, was obtained at temperature of 45°C, catalyst loading of 2%, and methanol-to-oil ratio of 9:1. Using a two-level factorial design, an optimum yield of 10.06% was calculated with the following conditions: temperature, 47.06°C; catalyst loading, 2.03%; methanol-to-oil molar ratio, 8.93:1.

1. Introduction
The concept of waste-to-energy (WTE) has been a promising solution to obtain viable energy reservoir while reducing the quantity of waste being released to the environment. This notion stems out from the waste management hierarchy wherein the most sustainable choice is the reduction of waste and the least option is disposal [1]. Most WTE technologies include the generation of energy thru incineration; landfill gas; and biofuels, which extends to the utilization of yellow grease to produce biodiesel. Biodiesel is considered as a “green fuel” containing no sulfur and aromatics and has been identified as an ideal complement to conventional liquid fuels [2]. Some of the additional advantages of biodiesel fuel include high cetane number, high flash point, low volatility, and compatibility with other oil when blended. Yellow grease, which is more commonly known as used cooking oil, has been the subject of many transesterification studies. This is because used cooking oil, being a potential waste oil, is a practical and economical feedstock choice as compared to raw vegetable oils [3]. The production of biodiesel from used cooking oil involves transforming an ester into another through interchange of the alkoxy group by the process of transesterification. Triglyceride reacts with an alcohol (usually methanol) to form a mixture of fatty acid alkyl esters (biodiesel) and glycerol, a side-product. This reaction is thermodynamically slow under normal conditions and the use of a combination of heat and catalyst is needed to accelerate the process [4]. Moreover, several factors can affect the reaction yield including...
methanol-to-oil ratio, temperature, amount and type of catalyst used, type of alcohol, and degree of purity of the feedstock.

The use of a suitable catalyst is of great advantage in increasing biodiesel yield. Typically, a homogeneous type of catalyst is used; however, the separation of the catalyst from the reaction mixture is energy-intensive [5]. Heterogeneous catalysts, on the other hand, offer several advantages not only in the ease of separation and product purification but also in catalyst reusability and oil feedstock flexibility [6]. Heterogeneous base-catalyzed transesterifications are found to be more active compared to solid acid catalysts and entail lower reaction time and temperature [7]. Among these heterogeneous base catalysts, calcium oxide (CaO) has become the focus of recent studies because of its low production and high basicity property [8]. Moreover, CaO does not dissolve in methanol, which is ideal in transesterification process. However, some problems encountered in the use of CaO as catalyst are (a) catalyst deactivation due to ambient carbon dioxide and water adsorbed on the basic sites of the catalyst, (b) reactant contamination because of the basic sites that come in contact with water, (c) product contamination due to leaching, (d) small specific surface area, and (e) decrease catalyst activity due to gel formation with methanol when using pure CaO [9]. CaO derived from snail shells was used in the study made by Sani et al. [10] and Birla et al. [11] obtaining 84.14% and 87.28% biodiesel yield, respectively. In the study made by Kaewdaeng et al. [12], a 92.5% biodiesel conversion was observed using CaO from calcined river snail shell ash. Tshizanga et al. [13] obtained 91% fatty acid methyl ester (FAME) yield by using CaO from eggshell ash at optimal operating conditions. Kouzu et al. [14] reported a 93% FAME yield for soybean oil feedstock and 99% yield using CaO derived from limestone at 1 hour and 2 hours reaction time, respectively.

In this study, CaO was obtained from waste shells of *Jagora asperata*, a freshwater snail abundant in the Philippines. Fig. 1 shows the freshwater snail, locally known as tabagwang or susong pilipit in the Philippines.

\[
\text{CaCO}_3(s) \xrightarrow{\Delta} \text{CaO}(s) + \text{CO}_2(g)
\]

Fig. 1. *Jagora asperata*, locally known as tabagwang or susong pilipit in the Philippines.

2. Materials and methods

2.1. Catalyst preparation

Waste tabagwang shells were washed several times with deionized water to remove impurities. The washed shells were air-dried for about 8 hours. The dried shells were crushed and pulverized using porcelain mortar. Calcination of the pulverized shells was performed using a muffle furnace at 900°C.
for 4 hours under static air to eliminate any form of carbon and to obtain complete conversion of CaCO$_3$ to CaO. The prepared CaO catalyst was stored in a sealed vial to avoid reaction with air.

2.2. Transesterification experiment
Transesterification experiments were carried out in a 250 mL Florence flask under conventional heating method using a magnetic hotplate at atmospheric pressure. Reaction parameters were varied: (a) temperature at 45°C and 60°C, (b) catalyst loading of 2% and 10%, and (c) methanol-to-oil molar ratio of 6:1 and 9:1.

The used cooking oil was subjected to pre-treatment by heating it at 60°C for 1 hour. 50 mL of the preheated oil was added to the reactor and the desired amount of catalyst and methanol were added. The reaction duration was set to 3 hours at constant stirring.

After the reaction, the mixture was cooled at room temperature and the CaO solid catalyst was removed by vacuum filtration. The filtrate, which contains FAME, glycerol, and unreacted methanol was subjected to heat at 80°C to evaporate the alcohol. The biodiesel was isolated by centrifugation and quantified in terms of percent yield (2). The transesterification experiments were done in duplicates.

\[
\text{Yield (\%) = } \frac{\text{Volume of biodiesel}}{\text{Volume of used cooking oil}} \times 100
\]  

(2)

2.3. Process optimization
A two-level factorial design using Design Expert 9 (Stat-Ease) was employed to optimize the reaction parameters within the given range of values. This will be the basis of future investigation in varying different parameters to obtain a desirable, economical biodiesel yield.

Table 1 gives the summary of the design. There were eight (8) runs generated by the software. A logit transformation was used which is a recommended transformation bounded data or response pertaining to percent yield. Equation (3) is the logit transformation equation as given by the Design Expert 9.

\[
\text{logit (Y)} = \log_e \left[ \frac{Y - \text{lower limit}}{\text{upper limit} - Y} \right]
\]  

(3)

where \(Y\) is the actual response (percent yield). The lower and upper limit used in the study is 0% and 100%, respectively.

| Factor | Name (Unit)                  | Type   | Minimum | Maximum | Mean  | Std. Dev. |
|--------|------------------------------|--------|---------|---------|-------|-----------|
| A      | Temperature (°C)             | Numeric| 45      | 60      | 52.5  | 8.01784   |
| B      | Catalyst Loading (%)         | Numeric| 2       | 10      | 6     | 4.27618   |
| C      | Methanol-to-oil molar ratio  | Numeric| 6:1     | 9:1     | 7.5   | 1.60357   |

3. Results
3.1. Transesterification experiments
The result of the transesterification experiments is summarized in Table 2. The highest biodiesel yield in terms of volume is 4.85 mL, corresponding to a 9.7% yield. The reaction parameters for this run are temperature at 45°C, 2% catalyst loading, and 9:1 methanol-to-oil molar ratio.

It was observed that as the temperature is increased from 45°C to 60°C, where other parameters are held constant, the reaction yield decreases. A previous study reported that temperature has an important effect in the transesterification reaction [16]. An increase in biodiesel yield should be expected when temperature is increased since an increase in temperature brings forth higher molecular kinetic energy. This increases the collision probability of the reactant molecules which will result in higher conversion rate. However, as seen in the study, higher temperature of 60°C lowers the percent yield. This can be explained by the fact that the boiling point of methanol is 65°C. A reaction temperature close to 65°C
without proper monitoring control in the incremental increase of temperature will allow the methanol to vaporize and exist in the vapor phase, decreasing the amount available in the liquid phase to react with the oil.

Moreover, a decrease in methanol-to-oil ratio while temperature and catalyst loading are fixed leads to a decrease in reaction yield. A study shows that excess amount of methanol is used to favor the forward reaction and reduce any possibility of a backward reaction where the FAME and glycerol reacts to form the triglyceride [17]. For the effect of catalyst loading, it was observed that generally an increase in catalyst loading from 2% to 10% leads to a slight decrease in biodiesel yield. This result is the same with the work of Hsiao et al. [18] where a decrease in the conversion rate was observed upon increasing the catalyst amount from 3% to 4%. They attributed this observation to the saponification reaction initiated by too much catalyst used in the reaction.

### 3.2. Optimization of reaction parameters

The degrees of freedom used for evaluation is summarized in Table 3. A good design provides at least three lack of fit and four pure error degrees of freedom. Furthermore, the standard error (Std. Err.), variance inflation factor (VIF) and coefficient of determination ($R^2$) is given in Table 4.

**Table 2.** Amount of biodiesel produced by varying reaction parameters.

| Run | Temperature (°C) | Catalyst Loading (%) | Methanol-to-oil Molar Ratio | Replicate Runs | Volume of Biodiesel Produced (mL) | Percent Yield (%) |
|-----|------------------|---------------------|-----------------------------|----------------|-----------------------------------|-------------------|
| 1   | 45               | 2                   | 6:1                         | 0.5            | 0.4                              | 0.45              |
| 2   | 45               | 2                   | 9:1                         | 5.2            | 4.5                              | 0.85              |
| 3   | 45               | 10                  | 6:1                         | 1.0            | 0.8                              | 0.90              |
| 4   | 45               | 10                  | 9:1                         | 5.5            | 4.0                              | 0.85              |
| 5   | 60               | 2                   | 6:1                         | 0.3            | 0.4                              | 0.35              |
| 6   | 60               | 2                   | 9:1                         | 4.4            | 4.5                              | 0.45              |
| 7   | 60               | 10                  | 6:1                         | 0.0            | 0.5                              | 0.25              |
| 8   | 60               | 10                  | 9:1                         | 4.0            | 2.2                              | 3.10              |

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**Table 3.** Degrees of freedom.

| Degree of freedom |  |
|-------------------|---|
| Model             | 3 |
| Residuals         | 4 |
| Lack of fit       | 4 |
| Pure error        | 0 |
| Corr Total        | 7 |

**Table 4.** Standard errors, variance inflation factor and coefficient of determination.

| Factor | Std. Err. | VIF | $R^2$ | 0.5 Std. Dev. | 1 Std. Dev. | 2 Std. Dev. |
|--------|-----------|-----|-------|---------------|-------------|-------------|
| A      | 0.35      | 1.00| 0.0   | 8.6%          | 19.5%       | 57.2%       |
| B      | 0.35      | 1.00| 0.0   | 8.6%          | 19.5%       | 57.2%       |
| C      | 0.35      | 1.00| 0.0   | 8.6%          | 19.5%       | 57.2%       |

The VIF is a measure of how much the variance of the model coefficient increases due to the lack of orthogonality in the design. The ideal VIF is 1.0. Similar standard error, Std. Err. = 0.35, was observed within the type of coefficient. VIF was 1.00 which indicates that the predictor is not correlated with other variables, meaning that the coefficients are not poorly estimated due to multicollinearity. The
observed $R_i^2 = 0.0$ is also ideal because high $R_i^2$ values indicate that the terms are correlated with each other, possibly leading to poor model. $R_i^2$ was calculated by regressing the factor in question on all other factors and having $R_i^2 = 0$ indicates that the design is orthogonal.

Table 5 gives the ANOVA for the factorial model. The model F-value of 30.90 implies that the model is significant. There is a 0.32% chance that this value could occur due to noise. Moreover, a “Prob > F” value less than 0.0500 indicate significant model terms. In this study, the methanol-to-oil molar ratio (Factor C) is a significant term in the model.

The final equation of the model in terms of the coded factors is given (4) with $R^2 = 0.9586$. This equation can be used to make predictions about the response for given levels of each factor. The predicted $R^2$ is 0.8345 which is in reasonable agreement with the adjusted $R^2$ of 0.9276. The normal plot of residuals and the predicted vs. actual plot is shown in Fig. 2. For the model graphs, both the contour and 3D surface is shown in Fig. 3.

Logit(Percent Yield) = $-3.56 - 0.26A - 0.006246B + 1.18C$

(4)

where A is the reaction temperature, B is the catalyst loading, and C is the methanol-to-oil ratio.

Table 5. Analysis of Variance table.

| Source                  | Sum of Squares | df | Mean Square | F Value | p-value | Comment        |
|-------------------------|----------------|----|-------------|---------|---------|----------------|
| Model                   | 11.65          | 3  | 3.88        | 30.90   | 0.0032  | Significant    |
| A: Temperature          | 0.55           | 1  | 0.55        | 4.41    | 0.1037  |                |
| B: Catalyst Loading     | 3.121E-04      | 1  | 3.121E-04   | 2.484E-03 | 0.9626  |                |
| C: Methanol-to-oil ratio| 11.09          | 1  | 11.09       | 88.29   | 0.0007  | Significant term |
| Residual                | 0.50           | 4  | 0.13        |         |         |                |
| Cor Total               | 12.15          | 7  |             |         |         |                |

Fig. 2. (a) Normal plot of residuals and (b) Plot of predicted vs. actual.
For the numerical optimization, model terms (i.e. temperature, catalyst loading and methanol-to-oil molar ratio) are set with specific goal to optimize the response (percent yield). All three model terms are set in range while the response is to be maximized. An optimum yield of 10.06% was calculated with the following conditions: temperature, 47.06°C; catalyst loading, 2.03%; methanol-to-oil molar ratio, 8.93:1. Comparison of this result to the previously obtained data from Table 2, focusing on the experimental run yielding the highest percent yield of 9.70%, shows that in order to increase the yield, an increase by 2°C in reaction temperature is needed while maintaining a catalyst loading of 2% and methanol-to-oil molar ratio of 9:1.

Fig. 3. Model graphs showing contour plot and 3D surface of the optimization process vs. actual.
4. Conclusion

In this study, calcium oxide was derived from waste tabagwang shells and utilized as a heterogeneous catalyst for the transesterification of used cooking oil. The CaO obtained showed promising results as a heterogeneous catalyst. The problem of separation of catalyst from the reaction mixture was addressed and the possible reusability of the catalyst will be looked into the next phase of the study. Moreover, it might be convenient to impregnate the CaO into a porous material that will act as support and will give better regeneration of the catalyst. Characterization of the prepared catalyst will also be considered to check its purity. Comparison of the catalytic performance of the CaO obtained from tabagwang shells to the commercial CaO should also be considered in future study. Although lower biodiesel yield was obtained, this can be improved by setting wider range values of the parameters being considered. The optimum parameters provided by the two-level factorial design experiment will determine the new low and high boundary values of the next experimental design.

5. References

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